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APPLICATION TRANSMITTAL

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Sir:

Transmitted herewith for filing under 37 C.F.R. § 1.53(b) is the patent application of
INVENTOR(S): Jason K. Stowers, Alan J. Telecky, Douglas A. Keszler and Andrew Grenville
FOR: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

Enclosed are:

[X] Specification and Abstract - 41 pages.
[X] Drawings - 8 sheets (Figs. 1-18).
[ ] Declaration.
[ ] Power of Attorney.
[ ] Certificate Under 37 C.F.R. §3.73(b).
[ ] Information Disclosure Statement.
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[X] This application claims the benefit of U.S. Provisional Application No. 61/350,103, filed June 1, 2010.

Respectfully submitted,

/Peter S. Dardi/

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Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

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PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to copending U.S. provisional patent application serial number 61/350,103 to Stowers et al., entitled "Photopatternable Inorganic Hardmask," incorporated herein by reference.

STATEMENT AS TO GOVERNMENT RIGHTS

Development of the inventions described herein was at least partially funded with government support through U.S. National Science Foundation grants DGE-0549503 and IIP-0912921, and the U.S. government has certain rights in the inventions.

FIELD OF THE INVENTION

The invention relates to patterned inorganic layers that can be used to form elements of devices and/or as a resist for facilitating the patterning of other materials. The invention further relates to radiation based methods for the performance of the patterning and to precursor solutions that can be deposited to form a coating that can be patterned with very high resolution with radiation.

BACKGROUND OF THE INVENTION

For the formation of semiconductor-based devices as well as other electronic devices, the materials are generally patterned to integrate the structure. Thus, the structures are generally formed through an iterative process of sequential deposition and etching steps through which a pattern is formed of the various materials. In this way, a large number of devices can be formed into a small area. Some advances in the art can involve that reduction of the footprint for devices, which can be desirable to enhance performance.

Organic compositions can be used as radiation patterned resists so that a radiation pattern is used to alter the chemical structure of the organic compositions corresponding with the pattern. For example, processes for the patterning of semiconductor wafers can

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entail lithographic transfer of a desired image from a thin film of organic radiation-sensitive material. The patterning of the resist generally involves several steps including exposing the resist to a selected energy source, such as through a mask, to record a latent image and then developing and removing selected regions of the resist. For a positive-tone resist, the exposed regions are transformed to make such regions selectively removable, while for negative-tone resist, the unexposed regions are more readily removable.

Generally, the pattern can be developed with radiation, a reactive gas or liquid solution to remove the selectively sensitive portion of the resist while the other portions of the resist act as a protective etch resistant layer. However, liquid developers can be used effectively to develop the image. The substrate can be selectively etched through the windows or gaps in the remaining areas of the protective resist layer. Alternatively, desired materials can be deposited into the exposed regions of the underlying substrate through the developed windows or gaps in the remaining areas of the protective resist layer. Ultimately, the protective resist layer is removed. The process can be repeated to form additional layers of patterned material. The functional inorganic materials can be deposited using chemical vapor deposition, physical vapor deposition or other desired approaches. Additional processing steps can be used, such as the deposition of conductive materials or implantation of dopants. In the fields of micro- and nanofabrication, feature sizes in integrated circuits have become very small to achieve high-integration densities and improve circuit function.

SUMMARY OF THE INVENTION

In a first aspect, the invention pertains to an aqueous inorganic patterning precursor solution comprising a mixture of water, metal suboxide cations, polyatomic inorganic anions and ligands comprising peroxide groups, wherein the composition has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the resist composition is stable with respect to phase separation for at least about 2 hours without additional mixing.

In a further aspect, the invention pertains to a method for formation of a radiation sensitive inorganic coating precursor solution, the method comprising combining a first

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aqueous solution comprising metal suboxide cations, a complexing solution comprising a ligand having a peroxide group and a composition comprising a polyatomic inorganic anion to form the coating precursor solution. In some embodiments, the molar concentration ratio of ligands to metal suboxide cations is at least about 2.

In another aspect, the invention pertains to a method for patterning an inorganic material on a substrate, the method comprising forming a layer of a radiation patternable coating material to form a coated substrate, heating the coated substrate to remove at least a portion of the solvent, exposing the coated substrate to a pattern of radiation and heating the coated substrate after irradiation. Generally, the patterned coating material comprises metal suboxide cations, ligands comprising a peroxide group and inorganic polyatomic anions. The irradiation of the coated substrate can condense the coating at the irradiated locations. The heating of the coated substrate after irradiation can be to a temperature of at least about 45°C prior to contacting the coating with a developer.

In other aspects, the invention pertains to a patterned structure comprising a substrate and a patterned inorganic material on a surface of the substrate. The patterned inorganic material can comprise a patterned semiconductor material or a patterned dielectric material, and the patterned inorganic material can have edges with an average line-width roughness no more than about 2.25 nm at a pitch of no more than about 60 nm or for individual features having an average width of no more than about 30 nm.

In additional aspects, the invention pertains to a method for forming a patterned structure comprising a suhstrate and a patterned inorganic material on a surface of the substrate. The method can comprise irradiating a layer of coating material with extreme ultraviolet light at a dose of no more than about 100 mJ/cm^2 or an electron beam at a dose equivalent to no more than about 300 $\mu C/cm^2$ at 30 kV, and contacting the irradiated layer with a developing composition to dissolve un-irradiated material to form the patterned inorganic material. In some embodiments, the patterned inorganic material has an average pitch of no more than about 60 nm or for individual features having an average width of no more than about 30 nm.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic drawing depicting a metal cation bonded to a ligand, where M represents a metal atom and O represents an oxygen atom, undergoing a condensation reaction triggered by energy absorption from radiation.

Fig. 2 is a schematic perspective view of a radiation patterned structure with a latent image.

Fig. 3 is a side plan view of the structure of Fig. 2.

Fig. 4 is a schematic perspective view of the structure of Fig. 2 after development of the latent image to remove un-irradiated coating material to form a patterned structure.

Fig. 5 is a side view of the patterned structure of Fig. 4.

Fig. 6 is a side plan view of the patterned structure of Figs. 4 and 5 following etching of the underlayer.

Fig. 7 is a side plan view of the structure of Fig. 6 following etching to remove the patterned, condensed coating material.

Fig. 8 is a side plan view of a "thermal freeze" double patterning process flow. The process shown in Figs. 2-4 is repeated after a bake that renders the first layer insoluble to the second layer.

Fig. 9 is a scanning electron micrograph of step coverage over a metal gate line with a step of about 100nm in height with Hf-based coating material.

Fig. 10 is a scanning electron micrograph of 120-nm pitch lines in Zr-based coating material patterned via 193-mn wavelength interference lithography at a dose level of 20 mJ/cm^2.

Fig. 11 is a scanning electron micrograph of 36-nm pitch lines in Hf-based coating material patterned via electron-beam lithography.

Fig. 12 is an expanded view of a portion of the pattern shown in Fig. 11.

Fig. 13A is a scanning electron micrograph of 36 nm pitch posts patterned by e-beam developed in 2.38% TMAH.

Fig. 13B is a scanning electron micrograph of 36 nm pitch posts patterned by e-beam developed in 25% TMAH.

Fig. 14 is a scanning electron micrograph of a portion of a developed pattern having a line with roughness from 1.6-1.8 nm.

Fig. 15 is a scanning electron micrograph of a double patterned structure formed using e-beam lithography with a coating material as described herein.

Fig. 16 is an expanded view of a portion of the pattern shown in Fig. 15.

Fig. 17 is a scanning electron micrograph of etched silicon nanopillars of width 40 nm. The pillars were fabricated via ion-etching through a hard mask formed with a Hf-based coating material.

Figs. 18A-D are scanning electron micrographs of EUV lithography performed with the Hf-based coating materials described herein and developed in 25% TMAH. In each case, the figure shows lines and spaces of a given pitch, comprised of lines with widths approximately half the stated pitch: A) 32-nm pitch lines and spaces, B) 30-nm pitch lines and spaces, C) 28-nm pitch lines and spaces, D) 26-nm pitch lines and spaces.

DETAILED DESCRIPTION OF THE INVENTION

Significant improvements in inorganic precursor solutions provide for superior direct patterning results for inorganic oxide materials comprising polyatomic ions. The precursor solutions can be used to deposit an inorganic coating material that is radiation sensitive. In embodiments of particular interest, exposure to the radiation converts the irradiated coating material into a condensed material that is resistant to removal with a developer composition. Selective removal of at least a portion of the un-irradiated coating material leaves a pattern including regions of the condensed coating material and regions where the un-irradiated coating material has been removed to expose the underlying substrate. The coating materials can be designed to be sensitive to selected radiation, such as ultraviolet light and/or electron beams. Furthermore, the precursor solutions can be formulated to be stable with an appropriate shelf life for commercial distribution.

The compositional changes to form the improved precursor solutions also provide for improved development of the image. In particular, the irradiated coating material can result in a stable inorganic material with a high level of resistance to the developer, e.g., a suitable liquid to dissolve un-irradiated coating material. Thus, the coating layers can be made thin without removing the condensed coating material during development. Compared to conventional organic resists, the inorganic materials described herein have

extremely high resistance to many etch chemistries for commercially relevant functional layers. This enables process simplification through avoidance of intermediate sacrificial inorganic pattern transfer layers that would otherwise be used to supplement the patterned organic resists with respect to the mask function. Also, the coating material provides for convenient double patterning. Specifically, following a thermal treatment, condensed portions of the coating material that have been irradiated are stable with respect to contact with many composition including further precursor solutions. Thus, multiple patterning can be performed without removing previously deposited hard-mask coating materials.

The patterned inorganic coating material can be subsequently removed after the patterned material is used as a mask to pattern desired functional materials. Alternatively, the resulting patterned inorganic material can be incorporated into the structure as a component of the device(s). If the patterned inorganic coating material is incorporated into the structure, many steps of the processing procedure can be eliminated through the use of a direct patterning of the material with radiation. Alternatively, it has been found that very high resolution structures can be formed using thin inorganic coating materials exposed using short wavelength electromagnetic radiation and/or electron beams, and that line-width roughness can be reduced to very low levels for the formation of improved patterned structures.

The formation of integrated electronic devices and the like involves the patterning of the materials to form individual elements or components within the structures. Generally, this patterning involves different compositions covering portions of layers that interface with each other to induce desired functionality. The various materials can comprise semiconductors, which can have selected dopants, dielectrics, electrical conductors and/or other types of materials. To form high resolution patterns, radiation sensitive organic compositions can be used to introduce patterns, and the compositions can be referred to as resists since portions of the composition are processed to be resistant to development/etching such that selective material removal can be used to introduce a selected pattern. Radiation with the selected pattern or the negative of the pattern can be used to expose the resist and to form a pattern or latent image with developer resistant regions and developer dissolvable regions. The radiation sensitive inorganic compositions described herein can be used for the direct formation of desired inorganic

material structures within the device and/or as a radiation patternable inorganic resist that is a replacement for an organic resist. In either case, significant processing improvements can be exploited, and the structure of the patterned material can be also improved.

To form the coating material, a precursor solution is applied to a surface of a substrate, such as a wafer or the like. In some embodiments, the inorganic precursor solution can have a relatively low concentration of metal ions such that the rheology of the coating composition, e.g., the viscosity, allows the formation of a thin coating on the substrate. The use of a thinner coating is consistent with the formation of higher resolution structures upon exposure to radiation and development of the pattern. The relatively high density and small spatial dimensions of the independently processable chemical moieties of the coating material can be exploited for the formation of structures with reduced line-width roughness, small feature sizes and/or extremely high resolution.

The coating materials described herein can be designed for use with particular radiation types, and the precursor solution can be correspondingly formulated to provide the desired coating material composition. In particular, the coating materials can be engineered to have a desired absorption of a selected radiation, and use of a coating material with a greater absorption cross section of the radiation allows for the corresponding use of a lower radiation dose. With appropriate selection of the composition, the patterning composition can be sensitive to, for example, ultraviolet light, x-rays or electron beams, as well as a particular wavelength or range of wavelengths within each radiation type. These particular radiation types are desirable due to the ability to form small patterns based on short radiation wavelengths. Thus, using the coating materials described herein, small patterns can be effectively formed with corresponding low line-width roughness that can enhance device formation abilities. Also, since the radiation patterned coating material is thin and has a high contrast with respect to sensitivity to appropriate developers, following removal of the un-irradiated coating material, the structures can have a small pitch between adjacent structures.

The precursor solution comprises an aqueous solution with metal suboxide cations, radiation sensitive ligands comprising peroxide groups, and polyatomic anions. Metal suboxide cations are polyatomic cations with a metal element and covalently bonded

oxygen atoms. Aqueous solutions of metal suboxide or metal hydroxides can tend to be unstable with respect to gelling and/or precipitation. In particular, the solutions are unstable upon solvent removal and can form oxo-hydroxide networks with the metal cations. The precipitated materials though can have useful properties, as described below. The precursor solutions have been formulated with improved stability and control of the precipitation so that radiation can be used to induce a change in the material. In particular, peroxide-based ligands stabilize the precursor solutions while also providing control over the processing of the materials.

Specifically, the precursor solution can comprise sufficient radiation sensitive ligands such that the solution has a molar concentration ratio of radiation sensitive ligands to metal suboxide cations of at least about 2 and in some embodiments at least about 5. In particular, the higher peroxide-based ligand concentrations provide for a surprisingly large improvement in the precursor stability. While not wanting to be limited by theory, the increase in the radiation sensitive ligand concentration evidently reduces agglomeration of the metal cations to stabilize the solution. Thus, the precursor solution can be stable relative to settling of solids without further stirring for at least two hours and possibly for significantly longer periods of time, such as greater than a month. Due to the long stability times, the improved precursors have increased versatility with respect to potential commercial uses. Hydrogen peroxide provides a desirable radiation sensitive ligand, although other inorganic peroxides can be suitable. In some embodiments, an organic peroxide can be used, but generally the organic components should be removed thoroughly for the formation of the final product at least for some electronics applications.

Furthermore, it has been discovered that materials formed with metal suboxide cations and polyatomic anions can provide useful material properties, which make the materials suitable for components of electronic devices and the like. Additional metal cations and anions can be incorporated into the materials to adjust the properties. These general precursor solutions are described further in published PCT application WO 2009/120169 to Keszler et al., entitled "Solution Processed Thin Films and Laminates, Devices Comprising Such Thin Films and Laminates, and Methods for the Use and Manufacture," incorporated herein by reference (hereinafter "Keszler PCT application").

As described herein, significant improvements in the precursor solutions have been accomplished through the use of significantly higher radiation sensitive ligand concentrations. Even more surprisingly, significantly increasing the radiation sensitive ligand concentration in the precursor solutions results in a coating material that has greater contrast following radiation exposure so that there are surprising added benefits where precursor solution stabilization further accomplishes improved patterning and shorter development times.

The metal suboxide cations can be selected to achieve the desired radiation absorption. In particular, ZrO^{+2} based coating materials exhibit good absorption of far ultraviolet light at a 193 nm wavelength. HfO^{+2} based coating materials exhibit good absorption of x-ray radiation and electron beam radiation and can also contribute desirable properties to the coating material, such as density and smoothness. Some precursor solutions effectively incorporate a blend of ZrO^{+2} and HfO^{+2} cations to provide for desirable overall properties of the coating materials. The precursor solutions can comprise additional metal cations to increase the absorption of some radiation wavelengths of significance for lithography. The metal cations can have various degrees of hydrolysis from interactions with water, and the state of hydrolysis with water generally is significantly pH dependent. The metal ion concentration can be selected to provide desired properties for the precursor solution, with more dilute solutions generally consistent with the formation of thinner coating materials.

Sulfate anions can be desirable polyatomic anions for incorporation in the precursor solutions, although other polyatomic anions can be desirable alternatives or additions to the sulfate anions. The concentration of polyatomic anions has been found to correlate with the sensitivity of the coating material to various developer compositions. Some polyatomic anions comprise metal atoms with covalent bonds with oxygen atoms and/or hydroxide groups, and anion structure can also be pH dependent.

Refined precursor solutions with greater stability also provide for a coating material having the potential of a greater contrast between the radiation exposed and unexposed portions of the substrate. Specifically, the un-irradiated coating material can be relatively more easily dissolved by suitable developer compositions while the exposed coating material can remain appropriately resistant to the developer composition. Since

the un-irradiated coating material can be relatively more easily dissolvable with a developer in comparison with the irradiated coating material, the contact time with the developer can be reduced while still maintaining desired removal of the coating composition. Specifically, with the improved compositions and corresponding materials, line-width roughness has been reduced to surprisingly low levels. Correspondingly, the pitch can be made very small between adjacent elements with appropriate isolation, generally electrical isolation, between the adjacent elements. The irradiated coating composition can be very resistant to the development/etching process so that the coating composition can be made very thin without compromising the efficacy of the development process with respect to clean removal of the un-irradiated coating composition while leaving appropriate portions of the irradiated patterning composition on the surface of the substrate. The ability to shorten the exposure time to the developer further is consistent with the use of thin coatings without damaging the exposed portions of the coating.

To perform the patterning, the precursor solution is generally applied to the entire surface of the substrate or a selected portion thereof. The precursor composition can be deposited onto a substrate, for example, using conventional coating approaches. Prior to the application of the coating material, the substrate surface can be prepared using a hydrophilic surface treatment to increase the hydrophilic nature of the surface for improved wetting with the aqueous precursor solution. For example, precursor solutions can be coated onto wafers or other substrates using spin coating, although other coating approaches can be used, such as spray coating, knife edge coating or other appropriate techniques. Printing techniques, such as screen printing, inkjet printing and the like, can be used for applying the precursor solution. However, the fine patterning generally is performed with radiation based patterning rather than using printing. The removal of at least a portion of the solvent can stabilize the coating material for further processing. Solvent can be removed in part during the coating process itself. Also, the substrate with the coating material can be heated to contribute to the removal of solvent. Following the removal of sufficient solvent, the coating material is generally relatively stable to allow for the patterning and can be further processed for patterning.

The coating material generally is radiation sensitive such that exposure to radiation modifies the composition of the coating material at irradiated regions as a latent image. The radiation pattern can be introduced through the passage or reflection of the radiation through a physical mask and suitable optics can be used to deliver the patterned radiation to the coating material. Additionally or alternatively, a beam of radiation can he scanned across the coating material to form a pattern in the coating material as a latent image based on exposure to the radiation. The radiation absorption results in the condensation of the irradiated portion of the coating material. In other words, the energy from radiation absorption results in agglomeration of the metal ions to change the character of the irradiated material.

While not wanting to be limited by theory, it is believed that upon absorption of the radiation, the peroxide functional groups are fragmented, and the composition correspondingly condenses through the formation of bridging metal-oxygen bonds. Through the condensation reaction, the radiation pattern is transferred to a pattern in the coating material. Specifically, there is a pattern of irradiated, and correspondingly condensed, coating material and of un-irradiated coating material, which is substantially unchanged from its composition prior to patterned irradiation of the coating material.

It has been discovered that the contrast in material properties can be increased between the condensed coating composition and the un-irradiated coating composition through the heating of the material following irradiation. In particular, the heating process is found to increase the condensation of the irradiated coating composition. The heating does not significantly change the ability to remove the un-irradiated material in a development step.

The patterned coating composition can be exposed to a developer liquid, such as 2.38 weight percent tetramethyl ammonium hydroxide (the standard developer in semiconductor lithography), that removes the un-irradiated portion of the coating material. The development can be performed in a short period of time hased on the appropriate selection of the developer composition. Furthermore, due to the stabilization of the condensed, irradiated coating material, the condensed coating material can be very stable against the developer. The condensed coating material forms a very hard masking material.

Following the patterning of the coating material, additional layers of material can be applied over the pattern and/or additional etching can be performed through the windows created by removing un-irradiated coating material to selectively remove substrate material based on the latent image in the patterned coating material. In this way, the patterned coating material can be used to assemble a structure with further complementary patterning of various compositions. Ions may also be selectively implanted into the substrate through the windows of the patterned coating material for control of electrical properties. The dense nature of the patterned inorganic coating provides a higher implantation resistance relative to a conventional organic patterned coating. Since the patterned coating material is itself an inorganic material that can incorporate desirable properties to a structure, the patterned coating material can be directly incorporated into a device. For embodiments in which the coating material is incorporated directly into the structure, distinct steps that just accomplish the patterning and removal of a resist are avoided such that very significant processing advantages can be achieved. These uses are elaborated on in the following discussion.

As noted above, the radiation sensitive coating materials described herein can be used as a negative resist. After developing the patterned coating material to remove the un-irradiated coating material, the pattern can be used for additional processing steps. In particular, the substrate may be etched through the gaps in the patterned coating. Furthermore, additional materials can be deposited with the additional materials penetrating through the gaps in the patterned coating material to reach the underlying substrate. In some embodiments, combinations of etching and/or deposition can be based on the pattern in the coating material. After the additional processing is performed based on the patterned coating material, the inorganic coating material, i.e., inorganic resist, can be removed using a suitable etching composition or other etching process. For example, the irradiated coating material can be removed with a dry BCl_3 plasma etch or an aqueous HF wet etch. The use of similar compositions as a negative resist as well as some embodiments of a positive resist is described in the Keszler PCT application, which has been incorporated herein by reference. Relative to organic resists, the inorganic coating

material provides distinct advantages with respect to absorption of selected radiation as well as high contrast between exposed and non-exposed regions such that high resolution can be achieved with moderate radiation doses.

The direct use of a patterned radiation-sensitive inorganic coating material provides the ability to form a patterned inorganic layer without the separate use of an organic resist. The large contrast in properties between the irradiated and non-irradiated regions of the inorganic coating material provides for the ability to form thin patterned layers in which the non-irradiated portion can be cleanly removed without significantly damaging the resistant condensed portions of the coating material during the development process. Due to the density and general etch resistance of the patterned inorganic coating material, the thin patterned coating material can be effectively used for further processing of the structure including, for example, etching and ion implantation, that is guided by the patterned inorganic coating material as a mask. In some embodiments, the condensed inorganic coating material can be designed with an appropriate thickness and physical properties to be directly incorporated into the device as a functional element. For example, the product metal suboxide compositions can be used as dielectrics, as described in published U.S. patent application 2005/0242330A to Herman et al., entitled "Dielectric Material," incorporated herein by reference. Also, some embodiments of the metal suboxide compositions exhibit semiconducting properties as described in published U.S. patent application 2010/0044698A to Herman et al., entitled "Semiconductor Film Composition," incorporated herein by reference. Thus, the coating materials can be selected to have appropriate functionality.

The general uses of lithographic procedures are well known in the electronics art. See, for example, U.S. patent 7,208,341 to Lee et al., entitled "Method for Manufacturing Printed Circuit Board," Harry J. Levinson, "Principles of Lithography," 2nd Edition, SPIE Press, Monograph Vol. PM146 (2005), and Chris Mack, "Fundamental Principles of Optical Lithography, The Science of Microfabrication," Willey-Interscience (2007), all three of which are incorporated herein by reference. Generally, the substrate is a single crystal silicon wafer, which may include other layers, although other substrates, such as polymers, can be used. In particular, the processing temperatures for the inorganic coating materials described herein are relatively low, so that the formation of patterned

inorganic materials as described herein can be performed with very high resolution on substrates that may not be able to be processed without damage at higher temperatures, such as above 600°C. Suitable devices in which elements can be patterned using the inorganic coating materials described herein include, for example, integrated electronic circuits, solar cells, electronic displays and the like.

Precursor Solutions

The precursor solutions have been formulated to achieve very high levels of stability such that the precursor solutions have appropriate shelf lives for commercial products. Also, it has been discovered that the formulation of the precursor solutions can be designed to achieve desired levels of radiation absorption for a selected radiation based on the selection of the metal cations. The precursor solutions are based on metal oxide chemistry and aqueous solutions of metal cations with polyatomic anions. The precursor solutions are designed to form a coating composition upon at least partial solvent removal and ultimately an inorganic solid with metal oxides and polyatomic anions. The control of the precursor solution is based on high concentrations of radiation sensitive ligands to the metal cations, specifically peroxide-based ligands. In particular, if the mole ratio of peroxide groups to the metal cations is at least 2, more stable solutions can be formed. The more stable precursor solutions provide an added advantage of greater contrast between the ultimate irradiated coating material and un-irradiated coating material.

The aqueous precursor solutions generally comprise one or more metal cations. In aqueous solutions, metal cations are hydrated due to interactions with the water molecules. The nature of the interactions is generally pH dependent. Specifically, hydrolysis can take place to bond oxygen atoms to the metal ion to form hydroxide ligands or oxo bonds with the corresponding release of hydrogen ions. As additional hydrolysis takes place, the solutions can become unstable with respect to precipitation of the metal oxide or with respect to gelation. Ultimately, it is desirable to form the oxide material, but this progression to the oxide is controlled as part of the procedure for processing the solution first to a coating material and then to the ultimate metal oxide composition with polyatomic anions. Solvent removal can contribute to the formation of

the oxide, but this approach does not provide significant control of the process without the use of the peroxide-based ligands as described herein. As described below, peroxide-based ligands can be used to provide significant control to the processing of the solution.

Thus, the aqueous solutions of the metal cations are poised for further processing. In particular, it can be desirous to use as an added component of the precursor solution, a metal suboxide cation that can poise the solution further toward a metal oxide composition. In general, the precursor solution comprises from about 0.01M to about 1.4M metal suboxide cation, in further embodiments from about 0.05M to about 1.2M, and in additional embodiments from about 0.1M to about 1.0M. A person of ordinary skill in the art will recognize that additional ranges of metal suboxide cations within the explicit ranges above are contemplated and are within the present disclosure. The metal suboxides can be added as suitable salts, such as halides salts, e.g., chlorides, fluorides, bromides, iodides or combinations thereof. Based on the use of the metal suboxide ions in the precursor solutions, relatively low levels of heating can be used to form the oxides while maintaining good control of the solutions based on the use of the radiation sensitive ligands.

Various metal ions can be provided as metal suboxide cations, such as VO^{+2}, SbO^{+}, ReO_3^{+}, TiO^{+2}, TaO^{+3}, TaO_2^{+}, YO^{+}, NbO^{+2}, MoO^{+2}, WO^{+4}, WO_2^{+2}, AlO^{+}, GaO^{+}, CrO^{+}, FeO^{+}, BiO^{+},LaO^{+}, CeO^{+}, PrO^{+}, NdO^{+}, PmO^{+}, SmO^{+}, EuO^{+}, GdO^{+}, TbO^{+}, DyO^{+}, HoO^{+}, ErO^{+}, TmO^{+}, YbO^{+}, LuO^{+}, $TiO_y(OH)_z^{(4-2y-z)+}$, $TaO_y(OH)_z^{(5-2y-z)+}$, $YO_y(OH)_z^{(3-2y-z)+}$, $NbO_y(OH)_z^{(4-2y-z)+}$, $MoO_y(OH)_z^{(4-2y-z)+}$, $WO_y(OH)_z^{(6-2y-z)+}$, $AlO_y(OH)_z^{(3-2y-z)+}$, $GaO_y(OH)_z^{(3-2y-z)+}$, $Zn(OH)^{+}$, $CrO_y(OH)_z^{(3-2y-z)+}$, $FeO_y(OH)_z^{(3-2y-z)+}$, $BiO_y(OH)_z^{(3-2y-z)+}$, $LaO_y(OH)_z^{(3-2y-z)+}$, $CeO_y(OH)_z^{(3-2y-z)+}$, $PrO_y(OH)_z^{(3-2y-z)+}$, $NbO_y(OH)_z^{(3-2y-z)+}$, $PmO_y(OH)_z^{(3-2y-z)+}$, $SmO_y(OH)_z^{(3-2y-z)+}$, $EuO_y(OH)_z^{(3-2y-z)+}$, $GdO_y(OH)_z^{(3-2y-z)+}$, $TbO_y(OH)_z^{(3-2y-z)+}$, $DyO_y(OH)_z^{(3-2y-z)+}$, $HoO_y(OH)_z^{(3-2y-z)+}$, $ErO_y(OH)_z^{(3-2y-z)+}$, $TmO_y(OH)_z^{(3-2y-z)+}$, $YbO_y(OH)_z^{(3-2y-z)+}$, $LuO_y(OH)_z^{(3-2y-z)+}$, or combinations thereof. The y and z parameters can be selected such that the ions have a positive charge based on the particular oxidation state of the metal atom. Metal suboxide cations of particular interest include, for example, ZrO^{+2}, $ZrOOH^{+}$, $Zr(OH)_2^{+2}$, $Zr(OH)_3^{+}$, HfO^{+2}, $HfOOH^{+}$, $Hf(OH)_2^{+2}$, $Hf(OH)_3^{+}$ combinations thereof and/or combinations with other metal suboxide cations. Furthermore, the solution can comprise additional metal cations, such as cations of

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hafnium (Hf^{+4}), titanium (Ti^{+4}), zirconium (Zr^{+4}), cerium (Ce^{+4}), tin (Sn^{+4}), tantalum (Ta^{+5}), niobium (Nb^{+4}), yttrium (Y^{+3}), molybdenum (Mo^{+6}), tungsten (W^{+6}), aluminum (Al^{+3}), gallium (Ga^{+3}), zinc (Zn^{+2}), chromium (Cr^{+3}), iron (Fe^{+3}), bismuth (Bi^{+3}), scandium (Sc^{+3}), vanadium (V^{+4}), manganese (Mn^{+2}, Mn^{+3}, Mn^{+4}), cobalt (Co^{+2}, Co^{+3}), nickel (Ni^{+2}, Ni^{+3}), indium (In^{+3}), antimony (Sb^{+5}), iridium (Ir^{+3}, Ir^{+4}), platinum (Pt^{+2}, Pt^{+4}), lanthanum (La^{+3}), praseodymium (Pr^{+3}), neodymium (Nd^{+3}), promethium (Pm^{+3}), samarium (Sm^{+3}), europium (Eu^{+3}), gadolinium (Gd^{+3}), terbium (Tb^{+3}), dysprosium (Dy^{+3}), holmium (Ho^{+3}), erbium (Eb^{+3}), thulium (Tm^{+3}), ytterbium (Yb^{+3}), lutetium (Lu^{+3}) or combinations thereof. As noted above, the state of the cations in solution is pH dependent, such that the initial state of oxygen coordination can change in solution, but the trend is toward hydrolysis leading to oxide formation. It has been found that peroxide-based ligands can hinder the formation of a metal-oxygen network that leads to gelation and ultimately precipitation. Thus, the peroxide can be used to form a stable state that can be quickly condensed upon rupture of the peroxide bonds.

The metal cations generally significantly influence the absorption of radiation. Therefore, the metal cations can be selected based on the desired radiation and absorption cross section. It has been found that ZrO^{+2} provides good absorption of ultraviolet light at 193 nm wavelength and other far ultraviolet radiation. HfO^{+2} provides good absorption of electron beam material and extreme UV radiation. Further tuning of the composition for radiation absorption can be adjusted based on the addition of other metal ions. For example, one or more ions (cations or anions) comprising titanium, zinc, calcium, indium, tin, antimony, bismuth or combinations thereof can be added to the precursor solution to form a coating material with an absorption edge moved to longer wavelengths, to provide, for example, sensitivity to 248 nm wavelength ultraviolet light. Also, one or more ions (cations or anions) comprising magnesium, boron, calcium, aluminum, silicon, phosphorous or combinations thereof can be used to increase the absorption cross section at shorter wavelengths. The energy absorbed is transferred to the peroxide ligand which can result in the rupturing of the peroxide bond, which provides desired control over the material properties.

The precursor solutions can also comprise polyatomic anions, which are generally oxygen based. Through the formation of an ultimate inorganic oxide, oxygen-based

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polyatomic anions can carry over into the oxide within an ultimate solid material. As with the cations, the nature of the anions can be pH dependent. Suitable oxygen-based polyatomic anions include, for example, SO_4^{-2}, BO_3^{-3}, AsO_4^{-3}, MoO_4^{-2}, PO_4^{-3}, WO_4^{-2}, SeO_4^{-2}, SiO_4^{-4}, their protonated forms, and combinations thereof. Generally, the precursor solution comprises a polyatomic anion concentration from about 0.5 to about 2.0 times the metal suboxide cation concentration, in other embodiments from about 0.75 to about 1.5 times the metal suboxide cation concentration, and in further embodiments from about 0.8 to about 1.3 times the metal suboxide cation concentration. A person of ordinary skill in the art will recognize that additional ranges of anion concentrations within the explicit ranges above are contemplated and are within the present disclosure. The polyatomic anions can be added as an acid if the pH adjustment is suitable, and/or the polyatomic anions can be added along with a desired metal cation. The precursor solution can generally be prepared with additional anions, such as halide anions, which may be added with the metal suboxide cations. Halide anions may react with the peroxide ligands to form halogen molecules, such as Cl_2, Br_2 or I_2. The reaction with halide ions reduces the peroxide concentrations a modest amount relative to the added amounts of peroxide.

The peroxide-based ligands stabilize the composition with respect to condensation. In particular, at high relative concentration of peroxide-based ligands, significant amounts of water can be removed from the composition without forming a condensed metal oxide or metal hydroxide. Based on the discovery of this stabilization property, solutions can be formed with high concentrations of radiation sensitive ligands that have good shelf stability while retaining convenient processing to form coatings. Radiation sensitive ligands of particular interest have a peroxide group, -O-O-. As noted above in the context of Fig. 1, energy from absorbed radiation can break the oxygen-oxygen bond. As the peroxide groups are broken, the corresponding stabilization is lost, as the composition condenses with the formation of M-O-M bonds, where M represents a metal atom. Thus, the condensation can be controlled with radiation. Compositions with high radiation sensitive ligand concentrations can be highly stable with respect to the avoidance of spontaneous condensation.

The chemically simplest ligand composition would be hydrogen peroxide, H_2O_2, which is soluble in water. Additional peroxide-based ligands include, for example, organic compositions and/or inorganic compositions. In some embodiments, inorganic peroxide-based ligands can he desirable since carbon can be disadvantageous for many devices. If an inorganic peroxide is used as a radiation sensitive ligand, the risk of carbon contamination from the radiation sensitive ligand is avoided. Suitable inorganic peroxide ligands include, for example, peroxysulfate (SO_5H^-), peroxydisulfate ($S_2O_8^{-2}$), peroxychlorates (ClO_5H^-), or the like or combinations thereof. The precursor composition generally comprises a ligand concentration of at least a factor of about 2 times the metal cation concentration, in further embodiments at least a factor of about 3, in other embodiments at least a factor of about 4 and in additional embodiments a factor from about 5 to about 25 times the metal cation concentration.

In general, the desired compounds are dissolved to form an aqueous solution. After the components of the solution are dissolved and combined, the character of the species may change as a result of hydration and peroxide-based ligand binding. When the composition of the solution is referenced herein, the reference is to the components as added to the solution since the nature of the species in solution may not be well known.

In some embodiments, it may be desirable to form separate solutions that can be combined to form the precursor solution from the combination. Specifically, separate solutions can be formed comprising one or more of the following: the metal suboxide cations, any additional metal cations, the peroxide-based ligands and the polyatomic anions. If multiple metal cations are introduced, the multiple metal cations can be introduced into the same solution and/or in separate solutions. Generally, the separate solutions can be well mixed. In some embodiments, the metal cation solution is then mixed with the peroxide-based ligand solution such that the peroxide-based ligand can conjugate with the metal cations. The resulting solution can be referred to as a stabilized metal cation solution. In some embodiments, the stabilized metal cation solution is allowed to stabilize for at least about five minutes and in further embodiments at least about 15 minutes prior to further processing. The polymeric anion solution can be added to the stabilized metal cation solution to form the stabilized precursor solution. This order of combining the solutions can lead to more desirable results in some embodiments

of the precursor solution. The solutions can be combined under appropriate mixing conditions and at appropriate rates to achieve good mixing.

The concentrations of the species in the precursor solutions can be selected to achieve desired properties of the solution. In particular, lower concentrations overall can result in a desirable properties of the solution for certain coating approaches, such as spin coating, can achieve thinner coatings using reasonable coating parameters. In general, the concentration can be selected to be appropriate for the selected coating approach. As noted above, a relatively large ratio of peroxide-based ligand relative to the metal cations can be used to greatly stabilize the precursor solutions. Stability of the precursor solutions can be evaluated with respect to changes relative to the initial solution. Specifically, a solution has lost stability if a phase separation occurs with the production of large sol particles. Based on the improved stabilization approaches described herein, the solutions can be stable for at least about 2 hours without additional mixing, in further embodiments at least about 1 day, in other embodiments at least about 5 days and in additional embodiments at least about 25 days. A person of ordinary skill in the art will recognize that additional ranges of stabilization times are contemplated and are within the present disclosure. The solutions can be formulated with sufficient stabilization times that the solutions can be commercially distributed with appropriate shelf lives.

Coating Material

A coating material is formed through the deposition of the precursor solution onto a selected substrate. A substrate generally presents a surface onto which the coating material can be deposited, and the substrate may comprise a plurality of layers in which the surface relates to an upper most layer. The substrate surface can be treated to prepare the surface for adhesion of the coating material. Prior to preparation of the surface, the surface can be cleaned and/or smoothed as appropriate. Suitable substrate surfaces can comprise any reasonable material. Some substrates of particular interest include, for example, silicon wafers, silica substrates, other inorganic materials, polymer substrates, such as organic polymers, composites thereof and combinations thereof across a surface and/or in layers of the substrate. Wafers, such as relatively thin cylindrical structures, can be convenient, although any reasonable shaped structure can be used. Polymer

substrates or substrates with polymer layers on non-polymer structures can be desirable for certain applications based on their low cost and flexibility, and suitable polymers can be selected based on the relatively low processing temperatures that can be used for the processing of the patternable inorganic materials described herein. Suitable polymers can include, for example, polycarbonates, polyimides, polyesters, polyalkenes, copolymers thereof and mixtures thereof. In general, it is desirable for the substrate to have a flat surface, especially for high resolution applications.

Traditional organic resists are soluble in nonpolar solvents and are deposited onto hydrophobic surfaces. The surfaces can be treated with compounds, such as hexamethyldisilazane (HMDS), to render the surfaces hydrophobic and to promote adhesion of polymer resists. In contrast, the inorganic patternable coating materials described herein are based on aqueous solutions, which suggests that it may be desirable to apply the solution to a hydrophilic surface for application to the substrate surface. Suitable methods can be used for particular substrate compositions to render the substrate hydrophilic, if the surface is not initially hydrophilic to a desired degree. For silicon substrates, a variety of methods can be used to render the surface hydrophilic including, but not limited to, soak in a basic detergent, oxygen plasma treatment, UV ozone treatment, soaking in a piranha etchant (3:1 mixture of concentrated H_2SO_4(aq) and 30% by weight H_2O_2(aq)), and treating with dimethylsulfoxide (DMSO) followed by heating at about 225°C to about 275°C for up to about 5 minutes.

In general, any suitable coating process can be used to deliver the precursor solution to a substrate. Suitable coating approaches can include, for example, spin coating, spray coating, dip coating, knife edge coating, printing approaches, such as inkjet printing and screen printing, and the like. Some of these coating approaches form patterns of coating material during the coating process, although the resolution available currently from printing or the like has a significantly lower level of resolution than available from radiation based patterning as described herein. The coating material can be applied in multiple coating steps to provide greater control over the coating process. For example, multiple spin coatings can be performed to yield an ultimate coating thickness desired. The heat processing described below can be applied after each coating step or after a plurality of coating steps.

If patterning is performed using radiation, spin coating can be a desirable approach to cover the substrate relatively uniformly, although there can be edge effects. In some embodiments, a wafer can be spun at rates from about 500 rpm to about 10,000 rpm, in further embodiments from about 1000 rpm to about 7500 rpm and in additional embodiments from about 2000 rpm to about 6000 rpm. The spinning speed can be adjusted to obtain a desired coating thickness. The spin coating can be performed for times from about 5 seconds to about 5 minutes and in further embodiments from about 15 seconds to about 2 minutes. An initial low speed spin, e.g. at 50 rpm to 250 rpm, can be used to perform an initial bulk spreading of the composition across the substrate. A back side rinse, edge beam removal step or the like can be performed with water or other suitable rinse to remove any edge bead. A person or ordinary skill in the art will recognize that additional ranges of spin coating parameters within the explicit ranges above are contemplated and are within the present disclosure.

The thickness of the coating generally can be a function of the precursor solution concentration, viscosity and the spin speed. For other coating processes, the thickness can generally also be adjusted through the selection of the coating parameters. In some embodiments, it can be desirable to use a thin coating to facilitate formation of small and highly resolved features. In some embodiments, the coating materials can have an average thickness of no more than about 1 micron, in further embodiments no more than about 250 nanometers (nm), in additional embodiments from about 1 nanometers (nm) to about 50 nm, in other embodiments from about 1 nm to about 40 nm and in some embodiments from about 1 nm to about 25 nm. A person of ordinary skill in the art will recognize that additional ranges of thicknesses within the explicit ranges above are contemplated and are within the present disclosure. The thickness can be evaluated using non-contact methods of x-ray reflectivity and/or ellipsometry based on the optical properties of the film.

The coating process itself can result in the evaporation of a portion of the solvent since many coating processes form droplets or other forms of the coating material with larger surface areas and/or movement of the solution that stimulates evaporation. The loss of solvent tends to increase the viscosity of the coating material as the concentration of the species in the material increases. In general, the coating material can be heated

prior to radiation exposure to further drive off solvent and promote densification of the coating material. As a result of the heat treatment and densification of the coating material, the coating material can exhibit an increase in index of refraction and in absorption of radiation without significant loss of contrast as a result of thermal decomposition of the peroxide groups.

An objective during the coating process can be to remove sufficient solvent to stabilize the coating material for further processing. The solvent removal process may not be quantitatively controlled with respect to specific amounts of solvent remaining in the coating material, and empirical evaluation of the resulting coating material properties generally can be performed to select processing conditions that are effective for the patterning process. While heating is not needed for successful application of the process, it can be desirable to heat the coated substrate to speed the processing and/or to increase the reproducibility of the process. In embodiments in which heat is applied to remove solvent, the coating material can be heated to temperatures from about 45°C to about 150°C, in further embodiments from about 50°C to about 130°C and in other embodiments from about 60°C to about 110°C. The heating for solvent removal can generally be performed for at least about 0.1 minute, in further embodiments from about 0.5 minutes to about 30 minutes and in additional embodiments from about 0.75 minutes to about 10 minutes. A person of ordinary skill in the art will recognize that additional ranges of heating temperature and times within the explicit ranges above are contemplated and are within the present disclosure.

Patterned Exposure And Patterned Coating Material

The coating material can be finely patterned using radiation. As noted above, the composition of the precursor solution and thereby the corresponding coating material can be designed for sufficient absorption of a desired form of radiation. The absorption of the radiation results in transfer of energy that breaks the peroxide -O-O- bonds so that at least some of the peroxide-based ligands are no longer available to stabilize the material. With the absorption of a sufficient amount of radiation, the exposed coating material condenses. The radiation generally can be delivered according to a selected pattern. The radiation pattern is transferred to a corresponding pattern or latent image in the coating material

with irradiated areas and un-irradiated areas. The irradiated areas comprise condensed coating material, and the un-irradiated areas comprise generally the as-formed coating material. As noted below, very sharp edges can be formed upon development of the coating material with the removal of the un-irradiated coating material.

Radiation generally can be directed to the coated substrate through a mask or a radiation beam can be controllably scanned across the substrate. In general, the radiation can comprise electromagnetic radiation, an electron beam (beta radiation), or other suitable radiation. In general, electromagnetic radiation can have a desired wavelength or range of wavelengths, such as visible radiation, ultraviolet radiation or x-ray radiation. The resolution achievable for the radiation pattern is generally dependent on the radiation wavelength, and a higher resolution pattern generally can be achieved with shorter wavelength radiation. Thus, it can he desirable to use ultraviolet light, x-ray radiation or an electron beam to achieve particularly high resolution patterns.

Following International Standard ISO 21348 (2007) incorporated herein by reference, ultraviolet light extends between wavelengths of greater than or equal 100 nm and less than 400 nm. A krypton fluoride laser can bc used as a source for 248 nm ultraviolet light. The ultraviolet range can be subdivided in several ways under accepted Standards, such as extreme ultraviolet (EUV) from greater than or equal 10 nm to less than 121 nm and far ultraviolet (FUV) from greater than or equal to 122 nm to less than 200 nm. A 193 nm line from an argon fluoride laser can be used as a radiation source in the FUV. EUV light has been used for lithography at 13.5 nm, and this light is generated from a Xe or Sn plasma source excited using high energy lasers or discharge pulses. Soft x-rays can be defined from greater than or equal 0.1 nm to less than 10 nm.

The amount of electromagnetic radiation can be characterized by a fluence or dose which is obtained by the integrated radiative flux over the exposure time. Suitable radiation fluences can be from about 1 mJ/cm^2 to about 150 mJ/cm^2, in further embodiments from about 2 mJ/cm^2 to about 100 mJ/cm^2 and in further embodiments from about 3 mJ/cm^2 to about 50 mJ/cm^2. A person of ordinary skill in the art will recognize that additional ranges of radiation fluences within the explicit ranges above are contemplated and are within the present disclosure.

With electron beam lithography, the electron beam generally induces secondary electrons which generally modify the irradiated material. The resolution can be a function at least in part of the range of the secondary electrons in the material in which a higher resolution is generally believed to result from a shorter range of the secondary electrons. Based on high resolution achievable with electron lithography using the inorganic coating materials described herein, the range of the secondary electrons in the inorganic material is limited. Electron beams can be characterized by the energy of the beam, and suitable energies can range from about 5 eV to about 200 keV and in further embodiments from about 7.5 eV to about 100 keV. Proximity-corrected beam doses at 30 keV can range from about 0.1microcoulombs per centimeter squared ($\mu C/cm^2$) to about 5 millicoulombs per centimeter squared (mC/cm^2), in further embodiments from about 0.5 $\mu C/cm^2$ to about 1 mC/cm^2 and in other embodiments from about 1 $\mu C/cm^2$ to about 100 $\mu C/cm^2$. A person of ordinary skill in the art can compute corresponding doses at other beam energies based on the teachings herein and will recognize that additional ranges of electron beam properties within the explicit ranges above are contemplated and are within the present disclosure.

Following exposure with radiation, the coating material is patterned with irradiated regions and un-irradiated regions. Referring to Figs. 2 and 3, a patterned structure 100 is shown comprising a substrate 102, a thin film 103 and patterned coating material 104. Patterned coating material 104 comprises condensed regions 110, 112, 114, 116 of irradiated coating material and regions and uncondensed regions 118, 120 of un-irradiated coating material. The patterned formed by condensed regions 110, 112, 114, 116 and uncondensed regions 118, 120 represent a latent image in to the coating material.

Based on the design of the inorganic coating material, there is a large contrast of material properties between the irradiated regions that have condensed coating material and the un-irradiated, uncondensed coating material. It has been surprisingly found that the contrast can be improved with a post-irradiation heat treatment, although satisfactory results can be achieved in some embodiments without post-irradiation heat treatment. The post-exposure heat treatment seems to anneal the irradiated coating material to improve its condensation without significantly condensing the un-irradiated regions of coating material based on thermal decomposition of the peroxide. For embodiments in

which the heat treatment is used, the post-irradiation heat treatment can be performed at temperatures from about 45°C to about 150°C, in additional embodiments from about 50°C to about 130°C and in further embodiments from about 60°C to about 110°C. The heating for solvent removal can generally be performed for at least about 0.1 minute, in further embodiments from about 0.5 minutes to about 30 minutes and in additional embodiments from about 0.75 minutes to about 10 minutes. A person of ordinary skill in the art will recognize that additional ranges of post-irradiation heating temperature and times within the explicit ranges above are contemplated and are within the present disclosure. This high contrast in material properties further facilitates the formation of sharp lines in the pattern following development as described in the following section.

Development and Patterned Structure

Development of the image involves the contact of the patterned coating material including the latent image to a developer composition to remove the un-irradiated coating material. Referring to Figs. 4 and 5, the latent image of the structure shown in Figs. 2 and 3 has been developed through contact with a developer to form patterned structure 130. After development of the image, substrate 102 is exposed along the top surface through openings 132, 134. Openings 132, 134 are located at the positions of uncondensed regions 118, 120, respectively.

In general, the developer can be aqueous acids or bases. Generally, aqueous bases can be used to obtain sharper images. To reduce contamination from the developer, it can be desirable to use a developer that does not have metal atoms. Thus, quaternary ammonium hydroxide compositions, such as tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide or combinations thereof, are desirable as developers. In general, the quaternary ammonium hydroxides of particular interest can be represented with the formula R_4NOH, where R = a methyl group, an ethyl group, a propyl group, a butyl group, or combinations thereof. The inorganic coating materials generally can be developed with the same developer commonly used presently for polymer resists, specifically tetramethyl ammonium hydroxide (TMAH). Commercial TMAH is available at 2.38 weight percent, and this concentration can be used for the processing described herein. However, in some

embodiments for the development of the inorganic materials, the developer can be delivered at higher concentrations relative to the concentrations generally used for the development of organic resists, such as 25% by weight TMAH. Furthermore, mixed quaternary tetraalkyl- ammonium hydroxides can be selected to provide improved line edge profiles based on empirical evaluation. In general, the developer can comprise from about 2 to about 40 weight percent, in further embodiments from about 3 to about 35 weight percent and in other embodiments from about 4 to about 30 weight percent tetra-alkylammonium hydroxide. A person of ordinary skill in the art will recognize that additional ranges of developer concentrations within the explicit ranges above are contemplated and are within the present disclosure.

In addition to the primary developer composition, the developer can comprise additional compositions to facilitate the development process. Suitable additives include, for example, dissolved salts with cations selected from the group consisting of ammonium, d-block metal cations (hafnium, zirconium, lanthanum, or the like), f-block metal cations (cerium, lutetium or the like), p-block metal cations (aluminum, tin, or the like), alkali metals (lithium, sodium, potassium or the like), and combinations thereof, and with anions selected from the group consisting of fluoride, chloride, bromide, iodide, nitrate, sulfate, phosphate, silicate, borate, peroxide, butoxide, formate, ethylenediamine-tetraacetic acid (EDTA), tungstate, molybdate, or the like and combinations thereof. If the optional additives are present, the developer can comprise no more than about 10 weight percent additive and in further embodiments no more than about 5 weight percent additive. A person of ordinary skill in the art will recognize that additional ranges of additive concentrations within the explicit ranges above are contemplated and are within the present disclosure. The additives can be selected to improve contrast, sensitivity and line width roughness. The additives in the developer can also inhibit formation and precipitation of HfO_2/ZrO_2 particles.

With a weaker developer, e.g., lower concentration developer, a higher temperature development process can be used to increase the rate of the process. With a stronger developer, the temperature of the development process can be lower to reduce the rate and/or control the kinetics of the development. In general, the temperature of the

development can be adjusted between the appropriate values of an aqueous solvent. Additionally, developer with dissolved inorganic coating material near the developer-coating interface can be dispersed with ultrasonication during development.

The developer can be applied to the patterned coating material using any reasonable approach. For example, the developer can be sprayed onto the patterned coating material. Also, spin coating can be used. For automated processing, a puddle method can be used involving the pouring of the developer onto the coating material in a stationary format. If desired spin rinsing and/or drying can be used to complete the development process. Suitable rinsing solutions include, for example, ultrapure water, methyl alcohol, ethyl alcohol, propyl alcohol and combinations thereof. After the image is developed, the coating material is disposed on the substrate as a pattern.

After completion of the development step, the coating materials can be heat treated to further condense the material and to further dehydrate the material. This heat treatment can be particularly desirable for embodiments in which the inorganic coating material is incorporated into the ultimate device, although it may be desirable to perform the heat treatment for some embodiments in which the inorganic coating material is used as a resist and ultimately removed if the stabilization of the coating material is desirable to facilitate further patterning. In particular, the bake of the patterned coating material can be performed under conditions in which the patterned coating material exhibits desired levels of etch selectivity. In some embodiments, the patterned coating material can be heated to a temperature from about 150°C to about 600°C, in further embodiments from about 175°C to about 500°C and in additional embodiments from about 200°C to about 400°C. The heating can be performed for at least about 1 minute, in other embodiment for about 2 minutes to about 1 hour, in further embodiments from about 2.5 minutes to about 25 minutes. A person of ordinary skill in the art will recognize that additional ranges of temperatures and time for the heat treatment within the explicit ranges above are contemplated and are within the present disclosure.

With organic resists, structures are susceptible to pattern collapse if the aspect ratio, height divided by width, of a structure becomes too large. Pattern collapse can be associated with mechanical instability of a high aspect ratio structure such that forces, e.g., surface tension, associated with the processing steps distort the structural elements.

Low aspect ratio structures are more stable with respect to potential distorting forces. With the patternable inorganic materials described herein, due to the ability to process effectively the structures with thinner layers of coating material, improved patterning can be accomplished without the need for high aspect ratio patterned coating material. Thus, very high resolution features have been formed without resorting to high aspect ratio features in the patterned coating material.

The resulting structures can have sharp edges with very low line-width roughness. In particular, in addition to the ability to reduce line-width roughness, the high contrast also allows for the formation of small features and spaces between features as well as the ability to form very well resolved two-dimensional patterns (e.g., sharp corners). Thus, in some embodiments, adjacent linear segments of neighboring structures can have an average pitch of no more than about 60 nm, in some embodiments no more than about 50 nm and in further embodiments no more than about 40 nm. Pitch can be evaluated by design and confirmed with scanning electron microscopy (SEM), such as with a top-down image. As used herein, pitch refers to the spatial period, or the center-to-center distances of repeating structural elements. Feature dimensions of a pattern can also be described with respect to the average width of the feature, which is generally evaluated away from corners or the like. Also, features can refer to gaps between material elements and/or to material elements. In some embodiments, average widths can be no more than about 30 nm, in further embodiments no more than about 25 nm, and in additional embodiments no more than about 20 nm. Average line-width roughness can be no more than about 2.25 nm, and in further embodiments from about 1.2 nm to about 2.0 nm. Evaluating line-width roughness is performed by analysis of top-down SEM images to derive a 3σ deviation from the mean line-width. The mean contains both high-frequency and low-frequency roughness, i.e., short correlation lengths and long correlation lengths, respectively. The line-width roughness of organic resists is characterized primarily by long correlation lengths, while the present inorganic coating materials exhibit significantly shorter correlation lengths. In a pattern transfer process, short correlation roughness can be smoothed during the etching process, producing a much higher fidelity

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pattern. A person of ordinary skill in the art will recognize that additional ranges of pitch, average widths and line-width roughness within the explicit ranges above are contemplated and are within the present disclosure.

Further Processing of Patterned Coating Material

After forming a patterned coating material, the coating material can be further processed to facilitate formation of the selected devices. Furthermore, further material deposition and/or patterning generally can be performed to complete structures. The coating material may or may not ultimately be removed. The quality of the patterned coating material can in any case be carried forward for the formation of improved devices, such as devices with smaller foot prints and the like.

The patterned coating material forms openings to the underlying substrate, as shown for example in Figs. 4 and 5. As with conventional resists, the patterned coating material forms an etch mask which can be used to transfer the pattern to selectively remove an underlying thin film. Referring to Fig. 6, underlying thin film 103 is patterned leaving features 152, 154, 156 respectively under condensed regions 110, 112, 114. Compared with conventional polymer resists, the materials described herein can provide significantly greater etch resistance.

Alternatively or additionally, the deposition of a further material can alter the properties of the underlying structure and/or provide contact to the underlying structure. The further coating material can be selected based on the desired properties of the material. In addition, ions can be selectively implanted into the underlying structure, as the density of the patterned inorganic coating material can provide a high implant resistance. In some embodiments, the further deposited material can be a dielectric, a semiconductor, a conductor or other suitable material. The further deposited material can be deposited using suitable approaches, such as solution based approaches, chemical vapor deposition (CVD), sputtering, physical vapor deposition (PVD), or other suitable approach.

In general, a plurality of additional layers can be deposited. In conjunction with the deposition of a plurality of layers, additional patterning can be performed. Any

additional patterning, if performed, can be performed with additional quantities of the coating materials described herein, with polymer-based resists, with other patterning approaches or a combination thereof.

As noted above, a layer of coating material following patterning may or may not be removed. If the layer is not removed, the patterned coating material is incorporated into the structure. For embodiments in which the patterned coating material is incorporated into the structure, the properties of the coating material can be selected to provide for desired patterning properties as well as also for the properties of the material within the structure.

If it is desired to remove the patterned coating material, the coating material functions as a resist. The patterned coating material is used to pattern a subsequently deposited material prior to the removal of the resist/coating material and/or to selectively etch the substrate through the spaces in the condensed coating material. The coating material can be removed using a suitable etching process. Specifically, to remove the condensed coating material, a dry etch can be performed, for example, with a BCl_3 plasma, Cl_2 plasma, HBr plasma, Ar plasma or plasmas with other appropriate process gases. Alternatively or additionally, a wet etch with, for example, HF(aq) or buffered HF(aq)/NH_4F can be used to remove the patterned coating material. Referring to Fig. 7, the structure of Fig. 6 is shown after removal of the coating material. Etched structure 150 comprises substrate 102 and features 152, 154, 156.

The coating materials are particularly convenient for performing multiple patterning using a thermal freeze process, as described generally with conventional resists in P. Zimmerman, J. Photopolym. Sci. Technol., Vol. 22, No. 5, 2009, p. 625. A double patterning process with a "thermal freeze" is outlined in Fig. 8. In the first step, the coating material is formed into a pattern 160 on substrate 162 using a lithographic process and development as described with respect to Figs. 4 and 5. A heating step 164 is performed to dehydrate the coating material. This heating step is equivalent to the post-development heating step described in the Development section above. This "thermal freeze" process makes the coating material insoluble to a subsequent deposition of a second layer of the coating material. A second lithographic and development step 166 is performed to form a double patterned structure 168 on substrate 162. After an etch

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step 170, the product double patterned structure 172 is formed. Note that it is straightforward to extend this process to multiple coat and pattern steps, and such extensions are contemplated and are within the present disclosure. With respect to multiple patterning, a significant difference between the inorganic coating materials described herein and conventional organic resists is that organic resists remain soluble in conventional resist casting solvents even after a thermal bake. The resist materials described herein can be dehydrated with a thermal bake such that they are not water soluble and subsequent coating layers can be applied.

EXAMPLES

Example 1: Preparation of Precursor Solutions

This example describes a method that has been used to prepare precursor solutions comprising metal suboxide cations based on hafnium (Hf) and/or zirconium (Zr).

Separate aqueous solutions were prepared for the components of the precursor solution. For convenience of notation, the respective solutions can be referred to as Part A for the metal suboxide cations, Part B for the peroxide-based ligand solution and Part C for the solution comprising polyatomic anions. A solution Part A1 was prepared by filtering a solution of 0.5 mol $ZrOCl_2 \cdot 8H_2O$ (161.125, Alfa Aesar 99.9%) combined with 500 mL of ultrapure water (18-MΩ·cm electrical resistance). A solution Part A2 was prepared by filtering a solution of 0.5 mol $HfOCl_2 \cdot 8H_2O$ (204.76g, Alfa Aesar 98%) combined with 500 mL of ultrapure water. As described below, Part A1 was used to form precursor solutions for 193-nm lithography patterning, and Part A2 was used to form precursor solutions for 13-nm (also known as extreme UV or EUV) or electron-beam lithography patterning. Solution Part B was prepared by diluting H_2O_2(aq) (30% w/w, Mallinckrodt Baker) with ultrapure water to yield a 6-8% w/w H_2O_2(aq) solution. Solution Part C comprised 2-5 M H_2SO_4(aq) either obtained in certified concentrations (Fischer Scientific, 10 N) or diluted from concentrated solutions (98% H_2SO_4, Mallinckrodt Baker) with ultrapure water.

For 193-nm lithography patterning, a Zr based precursor solution was prepared. For EUV or electron-beam lithography patterning, an Hf based precursor solution was

prepared. The method used to prepare either precursor solution was the same except that a Zr based precursor solution was prepared with Part A1 and an Hf based precursor solution was prepared with Part A2. Selected ratios of component solutions Part A1 or Part A2, Part B, and Part C were measured into individual pre-cleaned polyethylene bottles. A sufficient quantity of ultrapure water to obtain the targeted final metal concentration was added to the Part C component solution. The components in the bottles were then combined by pouring Part A1 or Part A2 component solution into Part B component solution, waiting 5 minutes, then pouring Part C into the combined Part A1 or Part A2 and Part B and waiting another 5 minutes. This particular mixing sequence has been found to limit particle growth.

Using the method described above, a 30 mL formulation of a Zr based precursor solution with a final zirconium concentration of 0.16 M was obtained by combining 4.8 mL of solution Part A1 (Zr), 1.8 mL of solution Part B (H_2O_2), 2.16 mL of solution Part C (H_2SO_4(aq)), and 21.24 mL of ultrapure water. Using the method described above, a 30 mL formulation of an Hf based precursor solution with a final hafnium concentration of 0.15 M was obtained by combining 4.5 mL of solution Part A2 (Hf), 16.875 mL of solution Part B (H_2O_2), 1.8 mL of solution Part C (H_2SO_4(aq)), and 6.825 mL of ultrapure water.

Example 2: Preparation and Deposition of Coating Material

This example describes preparation of substrate surfaces and deposition of patternable coating materials using the precursors solutions made according to Example 1.

Five inch silicon wafers were used for substrates. The surfaces of the silicon wafers were pretreated with a basic detergent, an acidic detergent, O_2 plasma, ultraviolet ozone, piranha etch solution or DMSO with a subsequent heating to a temperature between 225°C and 275°C to render the surfaces hydrophilic. The selected precursor solution was coated on a standard lithography spin coating track. A wafer was loaded onto a spin coater, and the precursor solution was dispensed onto the center of the wafer. The amount of precursor solution dispensed was selected based on the desired coating thickness and on the size of the wafer. The spin coater was spun at 100 RPM for 5

seconds to spread the resist across the wafer and then at 3000 RPM for 30-60 seconds to cast the resist film. The wafer was subjected to a pre-exposure bake at 40-200°C for 0.1-5 minutes.

This method has also been used to coat wafers with steps. Fig. 9 shows coverage of a Hf based coating material over a wafer with an approximately 100 nm step for a thin film transistor (TFT) gate dielectric application. The coating was created from five sequentially deposited layers to demonstrate that step coverage is possible. Appropriate coverage on sharper steps has been observed.

Example 3: 193-nm Lithographic Patterning of a Zr Based Coating Material

This example describes a method that has been used to pattern a Zr suboxide based coating material.

The coating material was produced according to the method of Example 2 with a ZrO^{+2}-based coating composition. The coating material was deposited at a thickness form 10-50 nm. The Zr-based coating material was irradiated with patterned 193-nm (deep UV) ligbt using a lithographic processing system having an ArF laser source with a mask or generated interference pattern. After irradiation, the wafer was passed back to the wafer track and subjected to a post-exposure bake at 40°C to 200°C for 1-5 minutes. The exposure with the 193 nm UV light resulted in a patterned coating material. The patterned coating material was developed with 2.38 weight percent TMAH using a puddle development process. The TMAH was contacted with the coating material for 20 seconds, and then the substrate was rinsed with water and dried. Referring to Fig. 10, highly resolved patterns were produced using the developer. Fig. 10 is a pattern of 120-nm pitch lines (approximately 60nm lines and spaces) in a Zr-based coating material produced by 193-nm lithography at a dose level of 20 mJ/cm^2.

Example 4: Electron-Beam and EUV Lithographic Patterning of an Hf Based Coating Material

This example describes a method that has been used to pattern an Hf suboxide based coating material.

The coating material was produced and deposited according to the method of Example 2 with an HfO^{+2} based coating composition. In one embodiment, an Hf-based coating composition was exposed with an electron-beam at 30 keV and about 78 $\mu C/cm^2$. The resulting patterned coating material was developed with 2.38 to 25 weight percent TMAH using a dip method. The developer was contacted with the wafer for 20 seconds. Then, the wafer was rinsed with water and dried. Contact with the developer results in the pattern as shown in Figs. 11, 12, 13A, and 13B. Highly resolved patterns were produced. Fig. 11 shows 36-nm pitch lines in Hf-based coating material. Another pattern with a pitch of 36-nm is shown in Fig. 12. This pattern was generated with an e-beam dose of 244 $\mu C/cm^2$.

Figs. 13A and 13B show 36-nm pitch posts in Hf-based coating material patterned by electron beam radiation. The sample shown in Fig. 13A was developed with a 2.38 weight percent TMAH concentration, while the sample shown in Fig. 13B was developed with a 25 weight percent TMAH concentration. A 25 weight percent TMAH concentration development resulted in more accurately defined posts, but these samples involved about 8 x higher electron beam dose. A pattern with a 1.6 to 1.8 nm line width roughness is shown in Fig. 14 for a pattern with a 21 nm linewidth on a 60 nm pitch.

A double patterned structure is shown in Figs. 15 and 16. The patterning was performed with a 30 keV electron beam with a dose of 500 $\mu C/cm^2$. After the first layer was patterned, the coating was baked at 220C before the second coating was applied. A higher magnification view is shown in Fig. 16. Well resolved and uniform 30-nm contact holes are visible in Fig. 16.

Ion etching was performed through a hard mask formed with a Hf-based coating material as described in this example after developing. The coating material functioned as a mask for the ion etching. A scanning electron micrograph of silicon nanopillars is shown in Fig. 17. The patterned structure after ion etching had a pillar width of 40 nm. The mask exhibited excellent resistance to the ion etch.

The EUV images were obtained using projection lithography with a numerical aperture of 0.25 operating at 13nm. The resist was applied with a thickness of 20nm by spin coating on a silicon wafer, followed by a post-apply bake of 50°C. After exposure at approximately 80mJ/cm^2, a post-exposure bake of 75°C was used prior to development in

25% TMAH. The developed patterns are shown in Figs. 18A-D. The patterns shown in Fig. 18 have pitches of A) 32-nm, B) 30-nm, C) 28-nm and D) 26-nm.

The embodiments above are intended to be illustrative and not limiting. Additional embodiments are within the claims. In addition, although the present invention has been described with reference to particular embodiments, those skilled in the art will recognize that changes can be made in form and detail without departing from the spirit and scope of the invention. Any incorporation by reference of documents above is limited such that no subject matter is incorporated that is contrary to the explicit disclosure herein.

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What we claim is:

1. An aqueous inorganic patterning precursor solution comprising a mixture of water, metal suboxide cations, polyatomic inorganic anions and radiation sensitive ligands comprising peroxide groups, wherein the composition has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours without additional mixing.

2. The aqueous inorganic patterning composition of claim 1 having a metal suboxide cation concentration from about 0.01 M to about 1.4 M.

3. The aqueous inorganic patterning composition of claim 2 having a polyatomic anion concentration from about 0.75 to about 1.5 times the metal suboxide cation concentration.

4. The aqueous inorganic patterning composition of claim 1 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof.

5. The aqueous inorganic patterning composition of claim 1 wherein the polyatomic anions comprise sulfate.

6. The aqueous inorganic patterning composition of claim 1 wherein the polyatomic anions comprise borate, phosphate, tungstate, silicate or combinations thereof.

7. The aqueous inorganic patterning composition of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

8. The aqueous inorganic patterning composition of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 7.

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9. The aqueous inorganic patterning composition of claim 1 having a stability of at least 24 hours without additional mixing.

10. The aqueous inorganic patterning composition of claim 1 comprising Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or a combination thereof within an appropriate oxygenated ion.

11. A method for formation of a radiation sensitive inorganic coating precursor solution, the method comprising:

combining a first aqueous solution comprising metal suboxide cations, a complexing solution comprising a ligand having a peroxide group and a composition comprising a polyatomic inorganic anion to form the coating precursor solution, wherein the molar concentration ratio of ligands to metal suboxide cations is at least about 2.

12. The method of claim 11 wherein the first aqueous solution is mixed with the complexing solution to form a ligand-cation mixture solution prior to introduction of the inorganic anions.

13. The method of claim 12 wherein the ligand-cation mixture solution is aged at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion.

14. A method for patterning an inorganic material on a substrate, the method comprising:

forming a layer of a radiation patternable coating material comprising a solvent, metal suboxide cations, ligands comprising a peroxide group and inorganic polyatomic anions to form a coated substrate;

heating the coated substrate to remove at least a portion of the solvent;

irradiating the coated substrate to a pattern of radiation to condense the coating at the irradiated locations; and

heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the coating with a developer.

15. The method of claim 14 wherein the radiation is ultraviolet light.

16. The method of claim 14 wherein the radiation is light having a wavelength of about 193 nm.

17. The method of claim 14 wherein the radiation is extreme ultraviolet light.

18. The method of claim 14 wherein the radiation comprises an electron beam.

19. The method of claim 14 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof and wherein the polyatomic anions comprise sulfate anions.

20. The method of claim 14 wherein the coating material comprises a molar concentration ratio of ligands to metal suboxide eations of at least about 5.

21. The method of claim 14 wherein the formation of the coating is performed using spin coating, spray coating, dip coating or knife edge coating.

22. The method of claim 14 wherein the layer of coating material has an average thickness from about 1 nm to about 40 nm.

23. The method of claim 14 wherein the radiation is directed through a mask to expose selected portions of the coated substrate.

24. The method of claim 14 wherein a laser beam or an electron beam is scanned over the coated substrate to expose selected portions of the coated substrate.

25. The method of claim 14 further comprising exposing the coated substrate with a developing composition to at least partially remove the coating composition at unexposed locations.

26. The method of claim 25 wherein the developing composition is contacted with the coated substrate for no more than about 75 seconds.

27. The method of claim 25 wherein the developing composition comprises tetramethyl ammonium hydroxide.

28. The method of claim 27 wherein the developing composition has a concentration of tetramethyl ammonium hydroxide of about 2.38 weight percent.

29. The method of claim 14 wherein the substrate is treated along a surface with a hydrophilic surface treatment prior to the forming of the radiation patternable coating material.

30. The method of claim 14 wherein the forming of the radiation patternable coating material comprises a plurality of coating steps to form a coating material of a selected thickness.

31. A structure comprising a substrate and a patterned inorganic material on a surface of the substrate, wherein the patterned inorganic material has edges with an average line-width roughness no more than about 2.25 nm at a pitch of no more than about 60 nm or for individual features having an average width of no more than about 30 nm.

32. The structure of claim 31 wherein the patterned inorganic material comprises a metal suboxide composition.

33. The structure of claim 31 wherein the patterned inorganic material comprises a patterned semiconductor material or a patterned dielectric material.

34. The structure of claim 31 wherein the average line-width roughness is from about 1.2 nm to about 2.0 nm.

35. A method for forming a patterned structure comprising a substrate and a patterned inorganic material on a surface of the substrate, the method comprising:

irradiating a layer of coating material with extreme ultraviolet light at a dose of no more than about 100 mJ/cm^2 or with an electron beam at a dose equivalent to no more than about 300 $\mu C/cm^2$ at 30 kV; and

contacting the irradiated layer with a developing composition to dissolve un-irradiated material to form a patterned inorganic material, wherein the patterned inorganic material has an average pitch of no more than about 60 nm or for individual features having an average width of no more than about 30 nm.

36. The method of claim 35 wherein the patterned inorganic material comprises a metal suboxide composition.

37. The method of claim 35 wherein the patterned inorganic material has an average pitch of no more than about 40 nm or for individual features having an average width of no more than about 20 nm.

38. The method of claim 35 wherein the patterned inorganic material comprises a patterned semiconductor material or a patterned dielectric material.

Abstract

Stabilized precursor solutions can be used to form radiation inorganic coating materials. The precursor solutions generally comprise metal suboxide cations, peroxide-based ligands and polyatomic anions. Design of the precursor solutions can be performed to achieve a high level of stability of the precursor solutions. The resulting coating materials can be designed for patterning with a selected radiation, such as ultraviolet light, x-ray radiation or electron beam radiation. The radiation patterned coating material can have a high contrast with respect to material properties, such that development of a latent image can be successful to form lines with very low line-width roughness and adjacent structures with a very small pitch.

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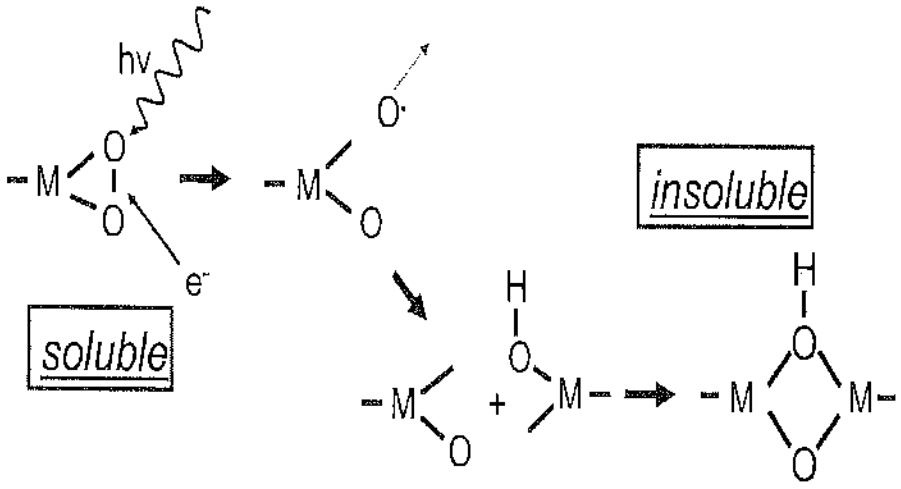


Fig. 1

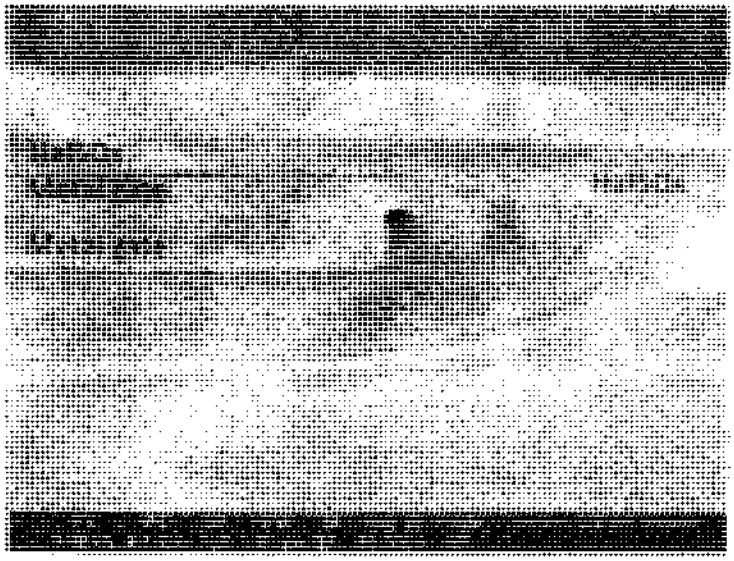


Fig. 9

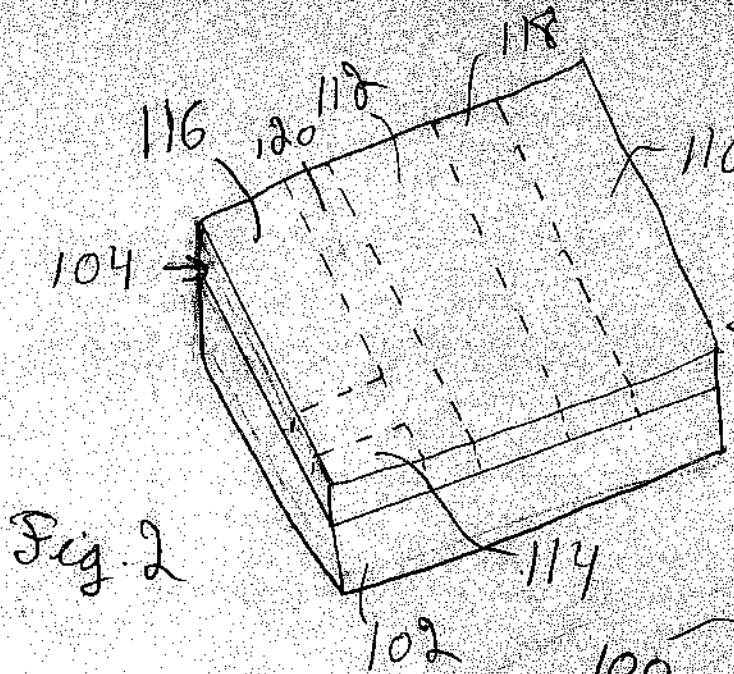


Fig. 2

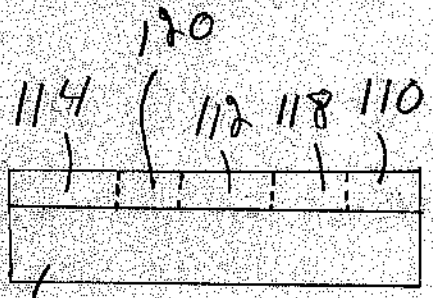


Fig. 3

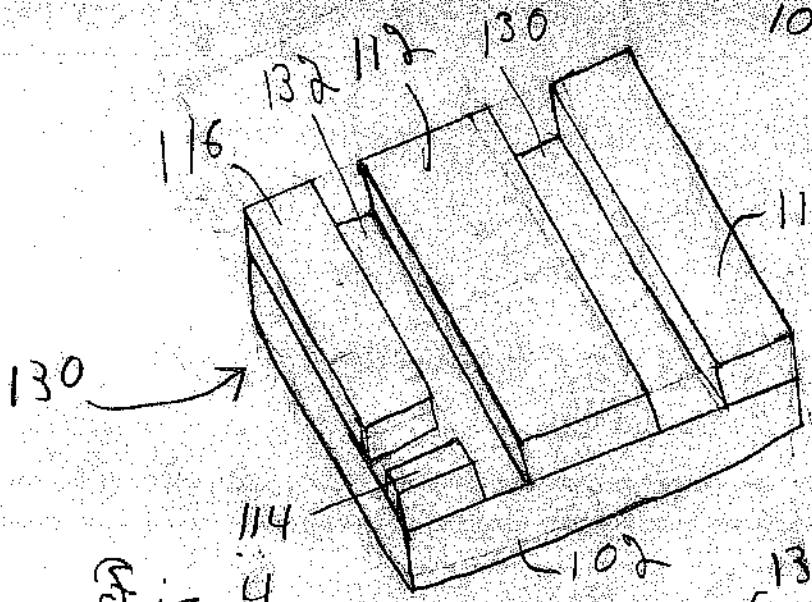


Fig. 4

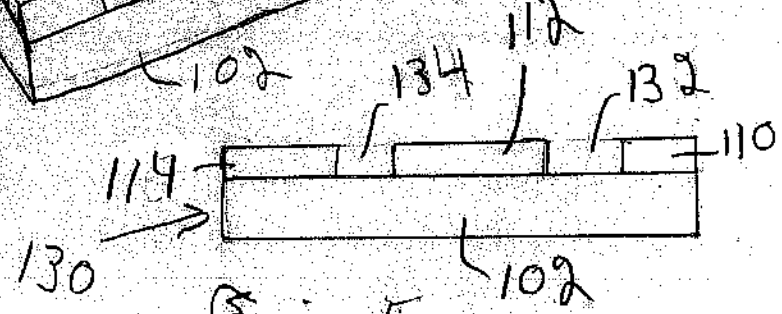


Fig. 5

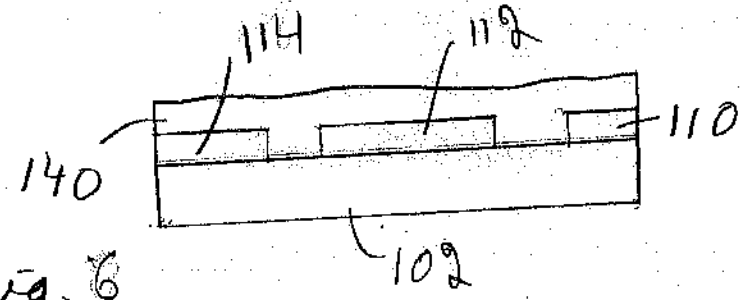


Fig. 6

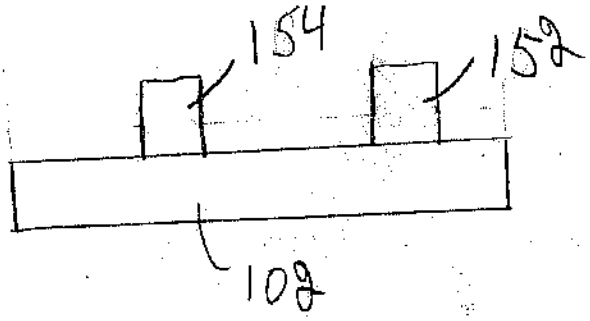


Fig. 7

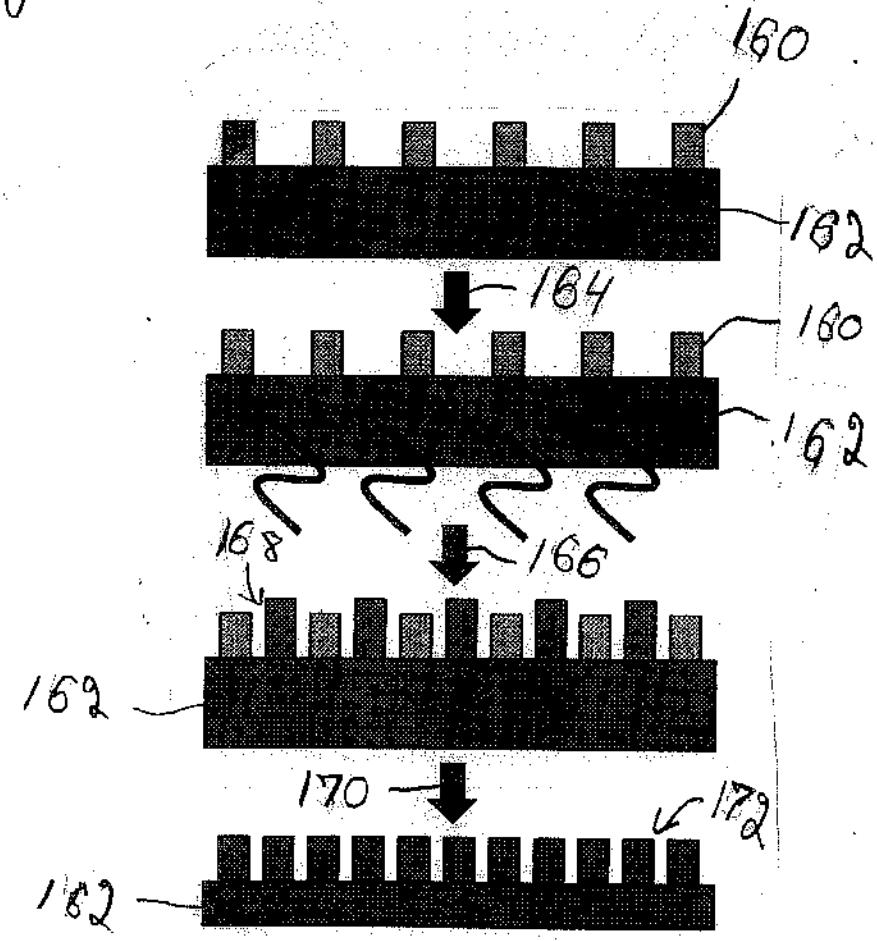


Fig. 8

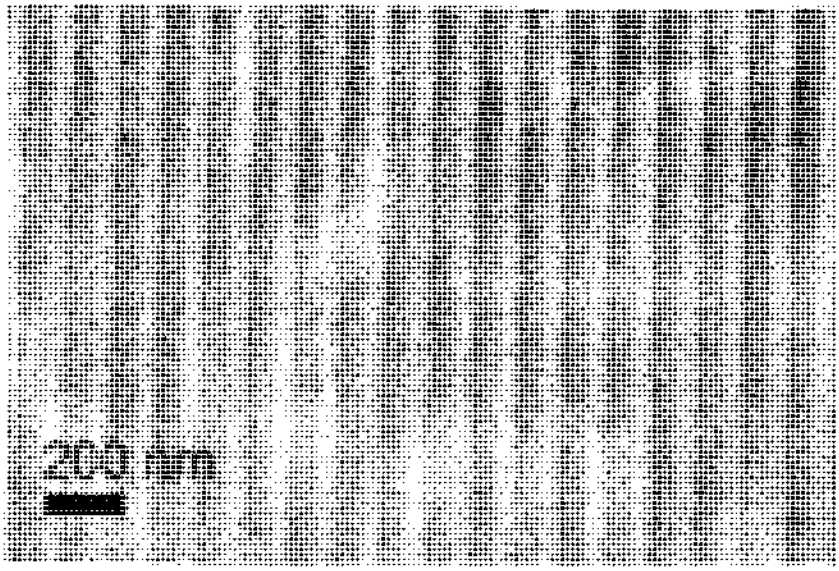


Fig. 10

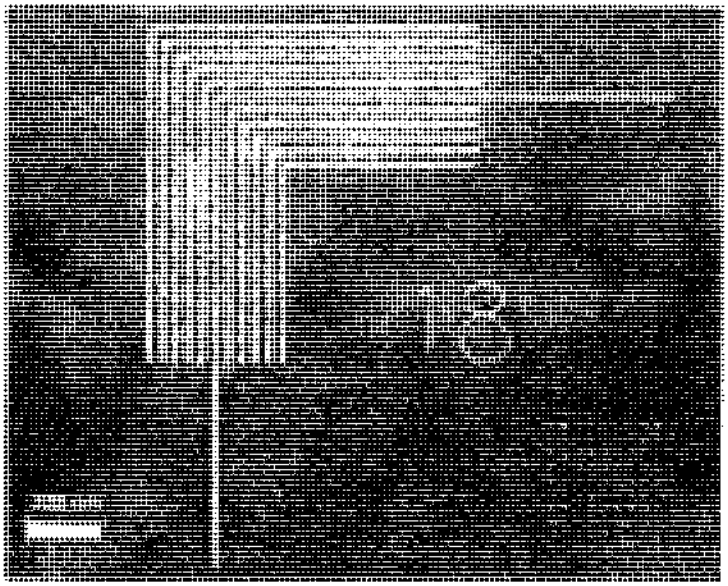


Fig. 11

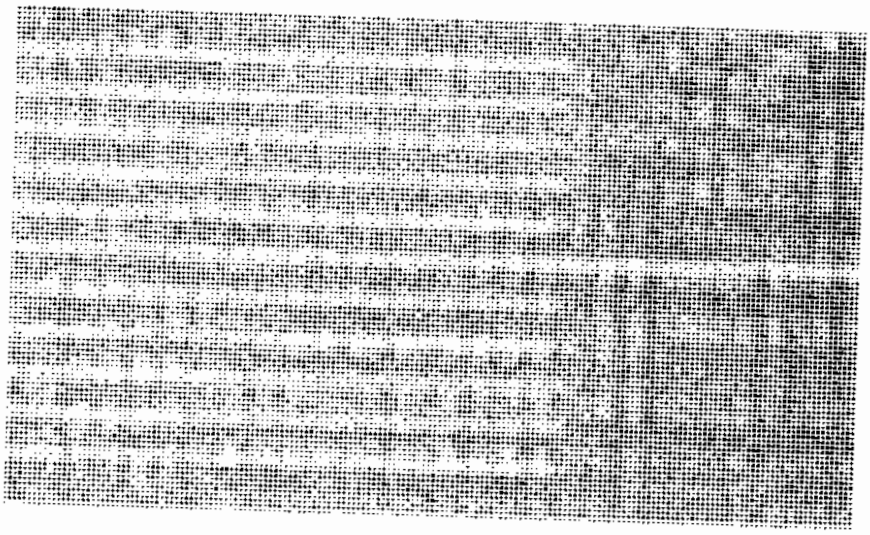


Fig. 12

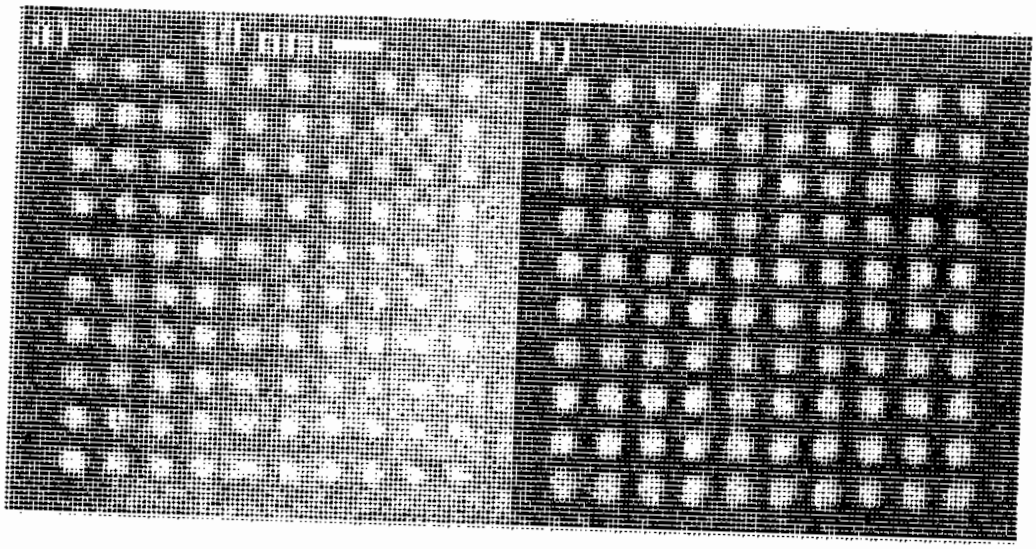


Fig. 13A

Fig. 13B

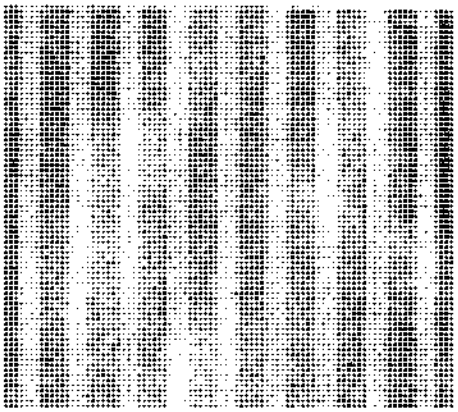


Fig. 14

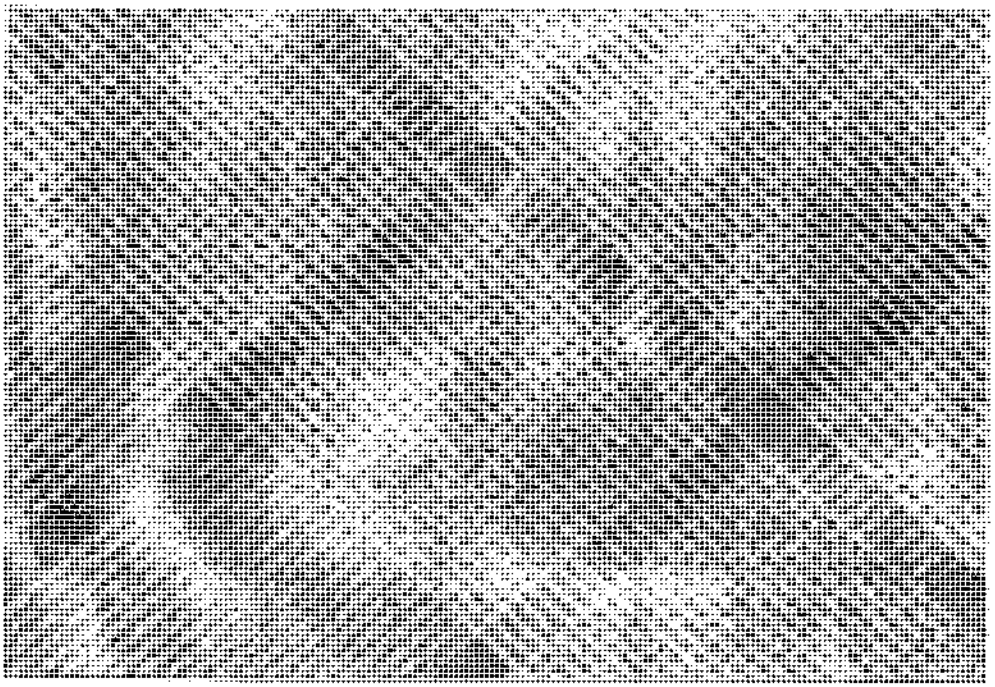


Fig. 15

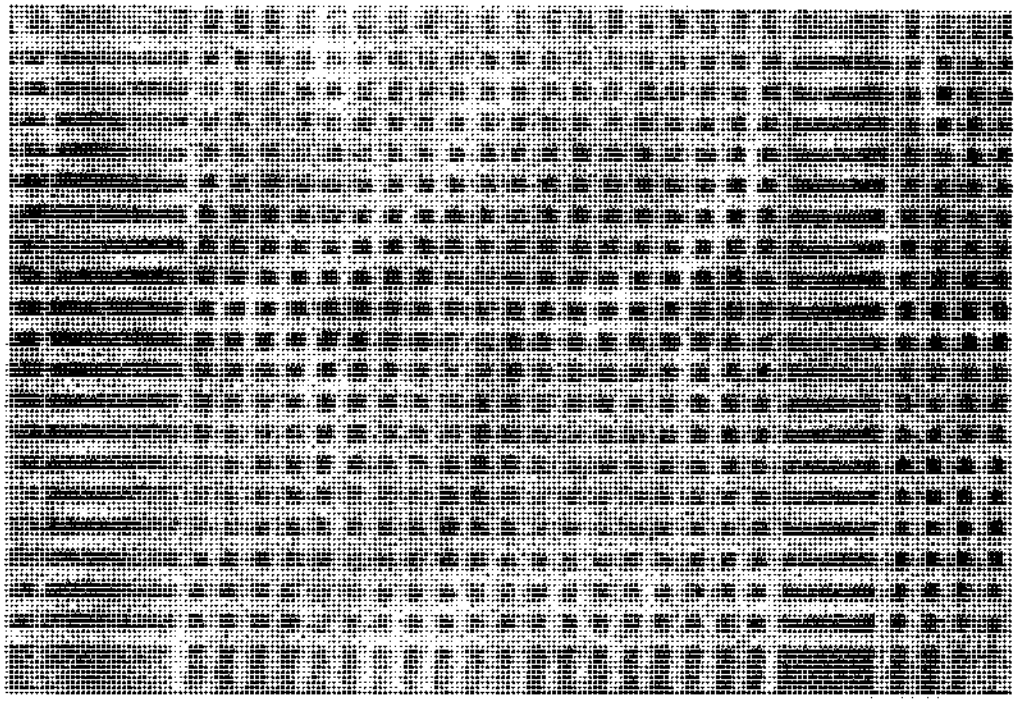


Fig. 16

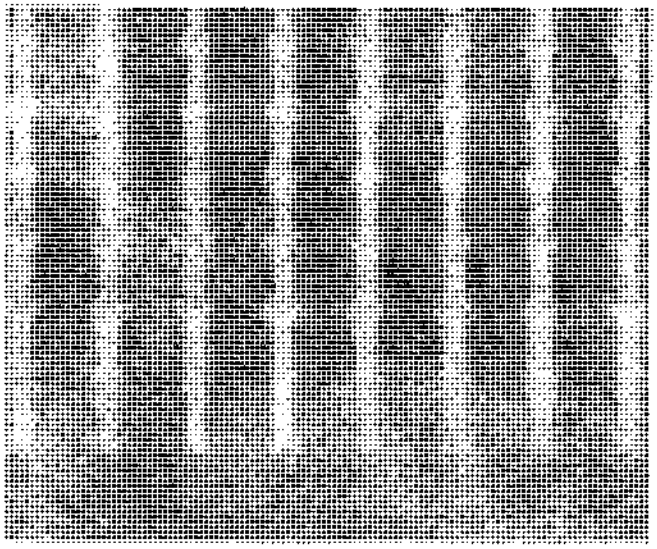


Fig. 17

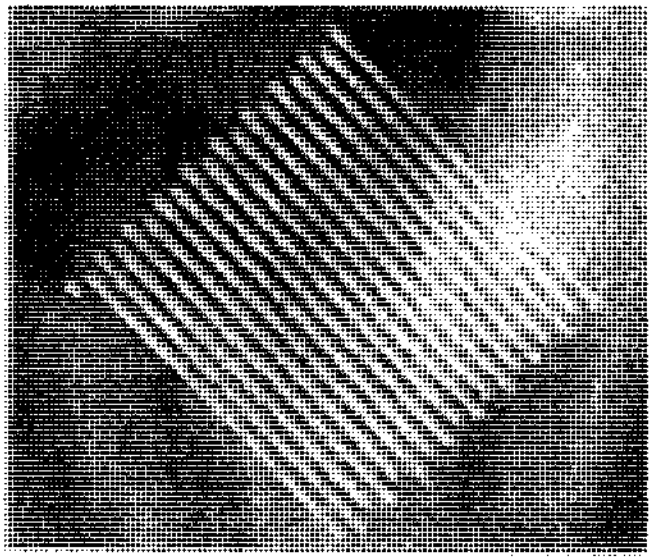


Fig. 18A

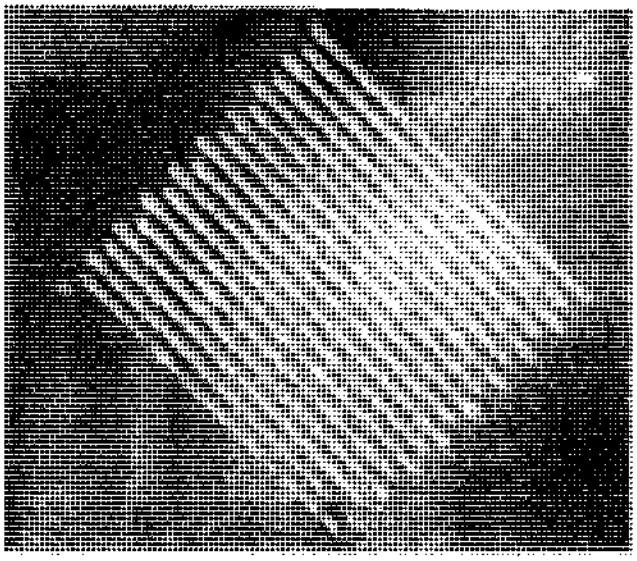


Fig. 18B

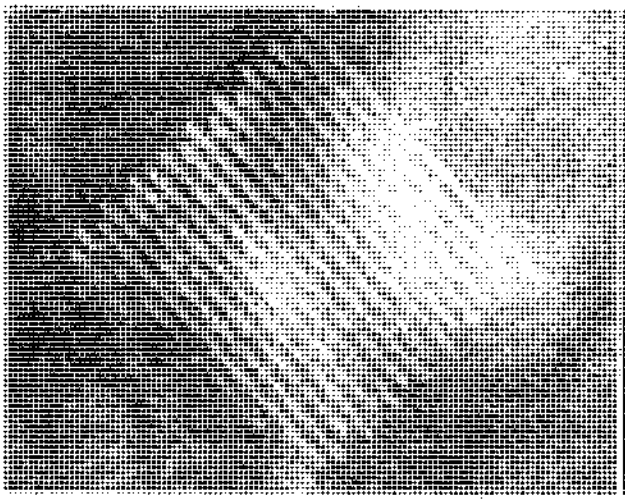


Fig. 18C

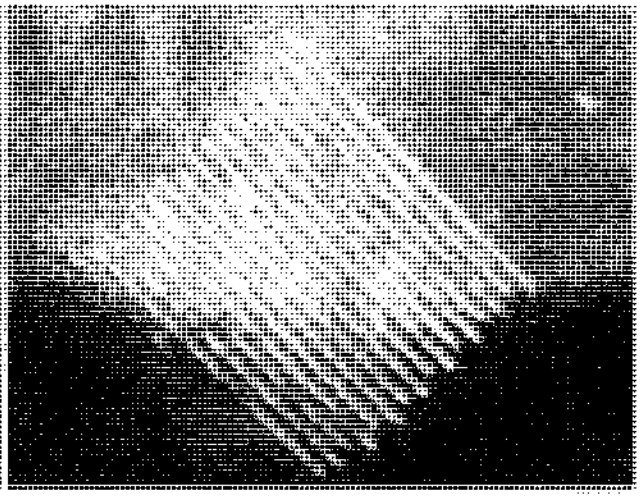


Fig. 18D

Electronic Acknowledgement Receipt

EFS ID:	8161066
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	05-AUG-2010
Filing Date:	
Time Stamp:	13:54:36
Application Type:	Utility under 35 USC 111(a)

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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal of New Application	Transmittal.pdf	70126 3fcd6bc8ac780a97bf9d6636a25e7130885579de	no	2

Warnings:	
Information:	

2	Specification	Specification.pdf	2172960 3311856861a75d6ea071e747803fb3162a42348c	no	35
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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (12-04)

Date: 08/05/2010

Approved for use through 7/31/2006. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: **12/850,867**

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE ($)	SMALL ENTITY FEE ($)	OR	LARGE ENTITY RATE ($)	LARGE ENTITY FEE ($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	82		N/A	
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	270		N/A	
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	110		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	38	18	X$ 26	468	OR	2X$52	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	5 minus 3 =	2	X$110	220		1X$220	
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $270 ($135 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR						
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))			195			390	
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	1150		TOTAL	

APPLICATION AS AMENDED – PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE ($)	SMALL ENTITY ADDITIONAL FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE ($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))					N/A		OR	N/A	
						TOTAL ADD'T FEE		OR	TOTAL ADD'T FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)	OR	RATE ($)	ADDITIONAL FEE ($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))					N/A		OR	N/A	
						TOTAL ADD'T FEE		OR	TOTAL ADD'T FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
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Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
12/850,867	08/05/2010	1795	0.00	5063.02US02	38	5

CONFIRMATION NO. 1662

62274
DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

FILING RECEIPT

OC000000043377431

Date Mailed: 09/10/2010

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Applicant(s)

Jason K. Stowers, Residence Not Provided;
Alan J. Telecky, Residence Not Provided;
Douglas A. Keszler, Residence Not Provided;
Andrew Grenville, Residence Not Provided;

Power of Attorney: None

Domestic Priority data as claimed by applicant

This appln claims benefit of 61/350,103 06/01/2010

Foreign Applications

If Required, Foreign Filing License Granted: 09/07/2010

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 12/850,867**

Projected Publication Date: To Be Determined - pending completion of Missing Parts

Non-Publication Request: No

Early Publication Request: No
**** SMALL ENTITY ****

Title

PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

Preliminary Class

430

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4158).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where

the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02

CONFIRMATION NO. 1662

62274
DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

FORMALITIES LETTER

OC000000043377432

Date Mailed: 09/10/2010

NOTICE TO FILE MISSING PARTS OF NONPROVISIONAL APPLICATION

FILED UNDER 37 CFR 1.53(b)

Filing Date Granted

Items Required To Avoid Abandonment:

An application number and filing date have been accorded to this application. The item(s) indicated below, however, are missing. Applicant is given **TWO MONTHS** from the date of this Notice within which to file all required items and pay any fees required below to avoid abandonment. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(a).

- The statutory basic filing fee is missing.
  *Applicant must submit $**82** to complete the basic filing fee for a small entity.*
- The oath or declaration is missing.
  A properly signed oath or declaration in compliance with 37 CFR 1.63, identifying the application by the above Application Number and Filing Date, is required.
  Note: If a petition under 37 CFR 1.47 is being filed, an oath or declaration in compliance with 37 CFR 1.63 signed by all available joint inventors, or if no inventor is available by a party with sufficient proprietary interest, is required.

The application is informal since it does not comply with the regulations for the reason(s) indicated below.

The required item(s) identified below must be timely submitted to avoid abandonment:

- Replacement drawings in compliance with 37 CFR 1.84 and 37 CFR 1.121(d) are required. The drawings submitted are not acceptable because:
  - The drawings must be reasonably free from erasures and must be free from alterations, overwriting, interlineations, folds, and copy marks. See Figure(s) 2-8.

Applicant is cautioned that correction of the above items may cause the specification and drawings page count to exceed 100 pages. If the specification and drawings exceed 100 pages, applicant will need to submit the required application size fee.

The applicant needs to satisfy supplemental fees problems indicated below.

The required item(s) identified below must be timely submitted to avoid abandonment:

- Additional claim fees of $**688** as a small entity, including any required multiple dependent claim fee, are required. Applicant must submit the additional claim fees or cancel the additional claims for which fees are due.
- To avoid abandonment, a surcharge (for late submission of filing fee, search fee, examination fee or oath or declaration) as set forth in 37 CFR 1.16(f) of $**65** for a small entity in compliance with 37 CFR 1.27, must be submitted with the missing items identified in this notice.

SUMMARY OF FEES DUE:

Total additional fee(s) required for this application is $**1215** for a small entity
- $**82** Statutory basic filing fee.
- $**65** Surcharge.
- The application search fee has not been paid. Applicant must submit $**270** to complete the search fee.
- The application examination fee has not been paid. Applicant must submit $**110** to complete the examination fee for a small entity in compliance with 37 CFR 1.27.
- Total additional claim fee(s) for this application is $**688**
  - $**220** for **2** independent claims over 3.
  - $**468** for **18** total claims over 20.

Replies should be mailed to:

Mail Stop Missing Parts
Commissioner for Patents
P.O. Box 1450
Alexandria VA 22313-1450

Registered users of EFS-Web may alternatively submit their reply to this notice via EFS-Web.
https://sportal.uspto.gov/authenticate/AuthenticateUserLocalEPF.html

For more information about EFS-Web please call the USPTO Electronic Business Center at **1-866-217-9197** or visit our website at http://www.uspto.gov/ebc.

If you are not using EFS-Web to submit your reply, you must include a copy of this notice.

/anguyen/

Office of Data Management, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US02

Jason K. Stowers Confirmation No.: 1662

Application No.: 12/850,867

Filed: August 5, 2010 Group Art Unit: 1795

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

RESPONSE TO NOTICE TO FILE MISSING PARTS OF NONPROVISIONAL APPLICATION

Mail Stop Missing Parts
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In response to the Notice to File Missing Parts of Application - Filing Date Granted mailed September 10, 2010, submitted herewith are an executed Declaration, Preliminary Amendment and 2 (two) sheets of corrected drawings (Figures 2-8).

The filing fee has been calculated as shown below:

Application filed on or after December 8, 2004:					
	No. Filed	No. Extra	Small Entity Rate	OR	Large Entity Rate
Basic Filing Fee			$82	OR	$330
Utility Search Fee			$270	OR	$540
Utility Examination Fee			$110	OR	$220
Total Claims	38 - 20	=18	x 26 = $468	OR	x 52 = $
Independent Claims	5 - 3	= 2	x 110 = $220	OR	x 220 = $
Presence of Multiple Dependent Claim			+ 195	OR	+ 390
Surcharge - Late filing fee or oath or declaration			+ 65	OR	+ 130
Utility Application Size Fee - per each additional 50 sheets that exceeds 100 sheets:			x 135 = $	OR	x 270 = $
		TOTAL	**$1,215.00**	**TOTAL**	**$**
**If the difference is less than zero, enter "0". Total # of sheets = (Spec and Abst pgs)+Dwg Sheets					

Applicant(s) is/are entitled to small entity status in accordance with 37 CFR 1.27. The Commissioner is hereby authorized to charge a credit card in the amount of $1,215.00. The Commissioner is hereby authorized to grant any extensions of time and to charge any fees under 37 C.F.R. §§ 1.16 and 1.17 that may be required during the entire pendency of this application to Deposit Account No. 50-3863.

Entry of these documents should complete all of the filing formalities and fully satisfy all requirements of the Notice to File Missing Parts. Accordingly, examination and allowance of this application in due course are respectfully solicited.

The Commissioner is hereby authorized to charge any underpayment or credit any overpayment to Deposit Account No. 50-3863.

Respectfully submitted,

/Peter S. Dardi/

Peter S. Dardi, Ph.D., Reg. #39,650

Customer No. 62274
Dardi & Herbert, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432
Telephone: (404) 949-5730

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

November 10, 2010
Date

/Peter S. Dardi/
Peter S. Dardi, Ph.D., Reg. #39,650

Lam Research Ex. 1004 - Page 61 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

DECLARATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS the specification of which is attached hereto unless the following is checked:

[X] The specification was filed on August 5, 2010 as United States Application Number or PCT International Application Number 12/850,867 and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)			Priority Claimed
(Number)	(Country)	(Day/Month/Year Filed)	(Yes/No)
(Number)	(Country)	(Day/Month/Year Filed)	(Yes/No)

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

61/350,103	June 1, 2010
(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application(s) in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)
(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Jason K. Stowers
Full name of sole or first inventor (given name, family name)

Jason K Stowers — 11-5-10
Inventor's signature — Date

Corvallis, Oregon — U.S.
Residence (City and either State or Foreign Country) — Citizenship

805 NW Witham Drive
~~737 NW 31st Street~~, Corvallis, Oregon 97330
Mailing Address

Alan J. Telecky
Full name of second joint inventor, if any (given name, family name)

Alan J Telecky — 11-8-10
Second Inventor's signature — Date

Corvallis, Oregon — U.S.
Residence (City and either State or Foreign Country) — Citizenship

720 SW 55th Street, Corvallis, Oregon 97333
Mailing Address

Douglas A. Keszler
Full name of third joint inventor, if any (given name, family name)

Douglas A Keszler — 3 NOV 10
Third Inventor's signature — Date

Corvallis, Oregon — U.S.
Residence (City and either State or Foreign Country) — Citizenship

8927 NW Lorri Place, Corvallis, Oregon 97330
Mailing Address

Andrew Grenville
Full name of fourth joint inventor, if any (given name, family name)

[signature] — 11/3/2010
Fourth Inventor's signature — Date

Eugene, Oregon — U.S.
Residence (City and either State or Foreign Country) — Citizenship

1925 Fairmount Boulevard Eugene, OR 97403
Mailing Address

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US02

Jason K. Stowers Confirmation No.: 1662

Application No.: 12/850,867

Filed: August 5, 2010 Group Art Unit: 1795

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

PRELIMINARY AMENDMENT

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

Prior to examining the present application, please enter the following amendments and consider the following remarks. This document includes the following sections:

A. Amendments to the Drawings

B. Remarks

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

November 10, 2010
Date

/Peter S. Dardi
Peter S. Dardi, Ph.D., Reg. #39,650

AMENDMENTS TO THE DRAWINGS

Figures 2-7 have been corrected to conform to the corresponding discussion in the specification. In particular, underlying thin film 103 has been added to the Figures as discussed at page 24, line 17-20 and page 29, lines 15-16. Reference numbers 130, 132 have been corrected to read 132, 134 in Figures 4 and 5. Also, elements 152, 154, 156 have been corrected in Fig. 6 and 7 to correspond with the discussion on page 29, line 12-18 and page 30, lines 18-20.

Lam Research Ex. 1004 - Page 66 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

REMARKS

By this Amendment, the figures have been corrected to correspond with the corresponding discussion in the specification. The specific corrections are noted in the Amendments to the drawings noted above. The correction of the drawings is supported by the discussion in the specification. No new matter is introduced.

Favorable consideration and prompt allowance of the application are respectfully requested. The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,

/Peter S. Dardi/

Peter S. Dardi, Ph.D., Registration #39,650

Customer No. 62274
Dardi & Herbert, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432
Telephone: (404) 949-5730

Lam Research Ex. 1004 - Page 67 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

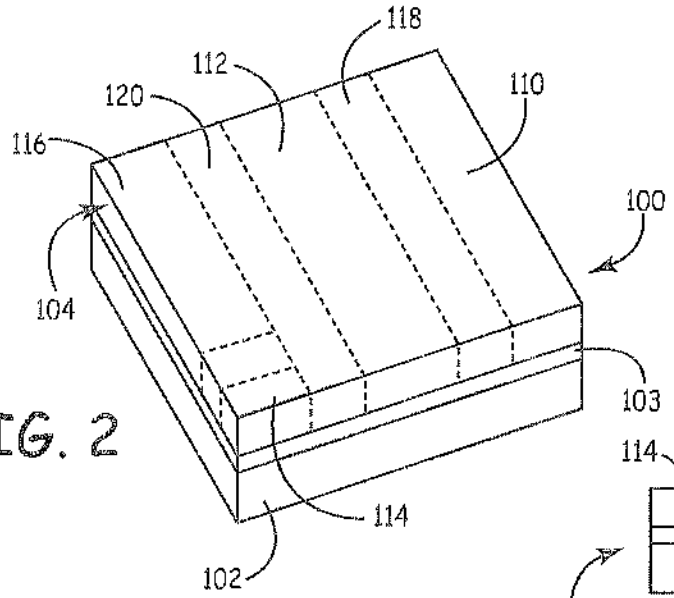


FIG. 2

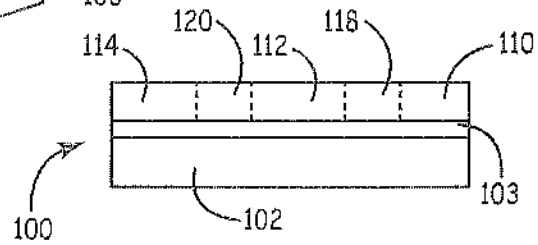


FIG. 3

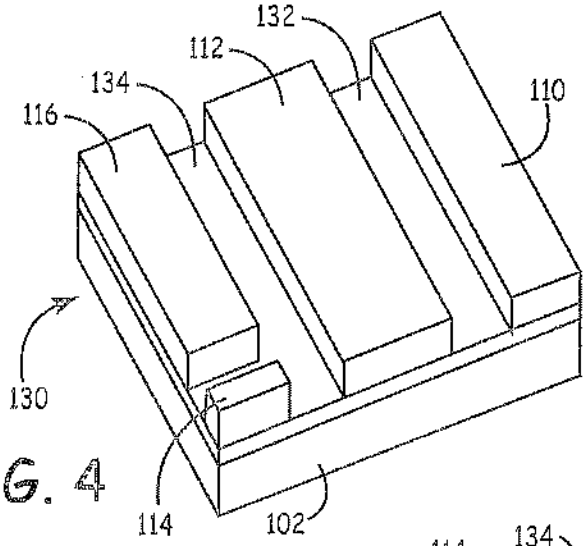


FIG. 4

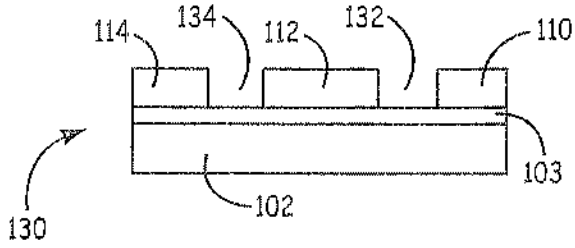


FIG. 5

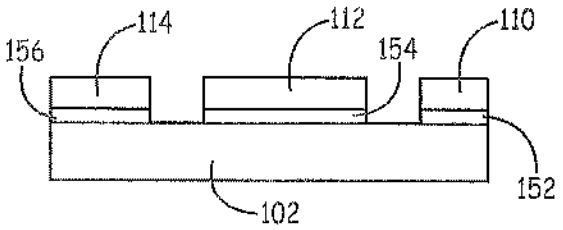


FIG. 6

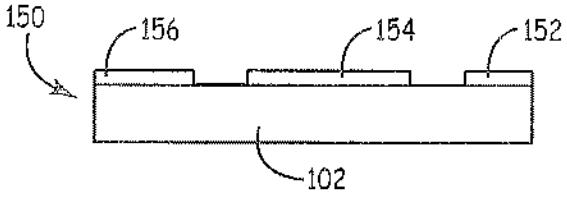


FIG. 7

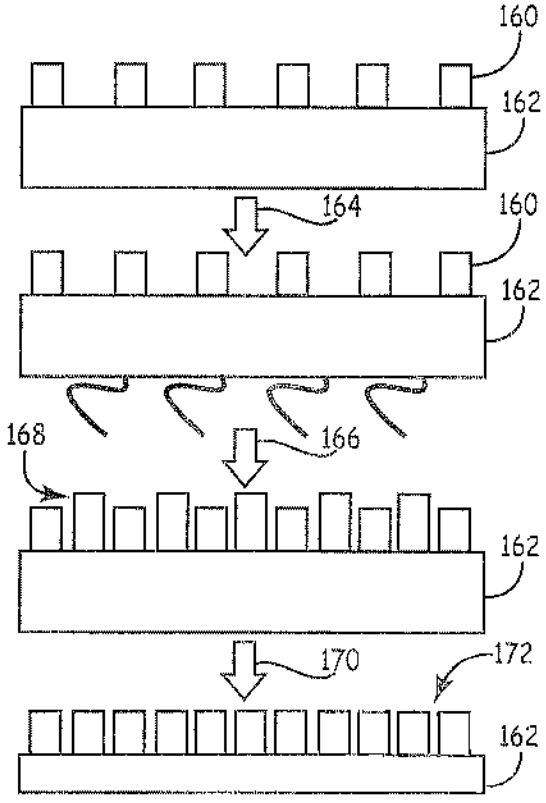


FIG. 8

Electronic Patent Application Fee Transmittal

Application Number:	12850867
Filing Date:	05-Aug-2010
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Peter S. Dardi
Attorney Docket Number:	5063.02US02

Filed as Small Entity

Utility under 35 USC 111(a) Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Utility filing Fee (Electronic filing)	4011	1	82	82
Utility Search Fee	2111	1	270	270
Utility Examination Fee	2311	1	110	110
Pages:				
Claims:				
Claims in excess of 20	2202	18	26	468
Independent claims in excess of 3	2201	2	110	220
Miscellaneous-Filing:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Late filing fee for oath or declaration	2051	1	65	65
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**1215**

Electronic Acknowledgement Receipt

EFS ID:	8805644
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	10-NOV-2010
Filing Date:	05-AUG-2010
Time Stamp:	11:00:24
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$1215
RAM confirmation Number	8326
Deposit Account	503863
Authorized User	DARDI,PETER S.

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

Charge any Additional Fees required under 37 C.F.R. Section 1.16 (National application filing, search, and examination fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.17 (Patent application and reexamination processing fees)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Applicant Response to Pre-Exam Formalities Notice	Response.pdf	85230 df9da7c6e7bfa8783c99ab19ebcd46a4272a6ad5	no	2
Warnings:					
Information:					
2	Oath or Declaration filed	Declaration.pdf	120631 f7cba98f1522461655b17e6b60fd9dc1ad48c06d	no	3
Warnings:					
Information:					
3	Preliminary Amendment	Pre_Amend.pdf	31674 abb11f9588de3e4f988ec73e12c10c99a10e62b0	no	1
Warnings:					
Information:					
4	Miscellaneous Incoming Letter	Pre_Draw.pdf	18656 d7a074849f4efad01d7dccde09c1b8059756109a	no	1
Warnings:					
Information:					
5	Applicant Arguments/Remarks Made in an Amendment	Remarks.pdf	25660 97e9c4fc81592e8b69bff0152930160d1ed66f02	no	1
Warnings:					
Information:					
6	Drawings-only black and white line drawings	Drawings_2-8.pdf	373486 58e128aedb8ae1657f590ce85cff79482b344b29	no	2
Warnings:					
Information:					
7	Fee Worksheet (PTO-875)	fee-info.pdf	40089 0f36c31393ce1d5be2da5d776194a8b26aebb867	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	695426		

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
12/850,867	08/05/2010	1795	1215	5063.02US02	38	5

CONFIRMATION NO. 1662

UPDATED FILING RECEIPT

62274
DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

OC000000044553042

Date Mailed: 11/22/2010

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Applicant(s)

Jason K. Stowers, Corvallis, OR;
Alan J. Telecky, Corvallis, OR;
Douglas A. Keszler, Corvallis, OR;
Andrew Grenville, Eugene, OR;

Power of Attorney: None

Domestic Priority data as claimed by applicant

This appln claims benefit of 61/350,103 06/01/2010

Foreign Applications

If Required, Foreign Filing License Granted: 09/07/2010

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 12/850,867**

Projected Publication Date: 12/01/2011

Non-Publication Request: No

Early Publication Request: No
**** SMALL ENTITY ****

Title

PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

Preliminary Class

430

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4158).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where

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NOT GRANTED

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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US02

Jason K. Stowers Confirmation No. 1662

Application No.: 12/850,867

Filed: August 5, 2010

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

POWER OF ATTORNEY AND CORRESPONDENCE ADDRESS INDICATION FORM

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I hereby appoint the practitioners associated with **Customer Number 62274** to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

Address all telephone calls to: Peter S. Dardi, Ph.D. at telephone number (404) 949-5730.

Address all correspondence to:

Customer Number 62274
Dardi & Herbert, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

Jan 17, 2011
Date

Peter S. Dardi, Ph.D., Reg. #39,650

Additionally, please charge any future fees to Deposit Account No. 50-3863.

All previous powers of attorney granted in this case are hereby revoked.

Inpria Corporation, Assignee

Date: 17 DEC 2010

DOUGLAS A KESZLER
Signature

Douglas A. Keszler
Name Printed or Typed

Chief Scientist
Title

ANDREW GRENVILLE

CEO

Electronic Acknowledgement Receipt

EFS ID:	9242624
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	17-JAN-2011
Filing Date:	05-AUG-2010
Time Stamp:	12:34:05
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Assignee showing of ownership per 37 CFR 3.73(b).	Certificate.pdf	211646 bf61b273e56bb7e271a0ea9e71f40cbad5366dbf	no	5

Warnings:	
Information:	

2	Power of Attorney	POA.pdf	58946 e3e40f22c854a3dd208b676619646a5782128a0b	no	2

Warnings:	
Information:	
Total Files Size (in bytes):	270592

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New Applications Under 35 U.S.C. 111

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National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US02

Jason K. Stowers Confirmation No. 1662

Application No.: 12/850,867

Filed: August 5, 2010

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

CERTIFICATE UNDER 37 C.F.R. § 3.73(b)

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Inpria Corporation, a corporation, states that it is the assignee of the entire right, title and interest in the patent application identified above by virtue of either:

A. [X] An assignment from the inventor(s) of the patent application identified above. The assignment was recorded in the Patent and Trademark Office at Reel _____, Frame _____, or for which a copy thereof is attached.

OR

B. [ ] A chain of title from the inventor(s), of the patent application identified above, to the current assignee as shown below:

1. From _____ to _____

The document was recorded in the Patent and Trademark Office at Reel _____, Frame _____ or for which a copy thereof is attached.

2. From _____ to _____

The document was recorded in the Patent and Trademark Office at Reel _____, Frame _____ or for which a copy thereof is attached.

3. From _____ to _____

The document was recorded in the Patent and Trademark Office at Reel _____, Frame _____ or for which a copy thereof is attached.

[ ] Additional documents in the chain of title are listed on a supplemental sheet.

[ ] Copies of assignments or other documents in the chain of title are attached.

The undersigned (whose title is supplied below) is empowered to sign this statement on behalf of the assignee.

Date: 17 DEC 2010

Douglas A Keszler
Signature

Douglas A. Keszler
Name Printed or Typed

Chief Scientist
Title

Lam Research Ex. 1004 - Page 83 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

ASSIGNMENT

WHEREAS, we, Jason K. Stowers of Corvallis, Oregon, Alan J. Telecky of Corvallis, Oregon, Douglas A. Keszler of Corvallis, Oregon and Andrew Grenville of Eugene, Oregon, have invented certain new and useful improvements in PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS, for which an application for Letters Patent of the United States has been made, and which may be identified in the United States Patent Office by Application No. 12/850,867, filed August 5, 2010.

WHEREAS, Inpria Corporation, ("Assignee"), having its principal offices at 2001 NW Monroe Ave, Suite 203, Corvallis, Oregon 97330, is desirous of acquiring the entire right, title and interest in and to said invention, said application and in, to and under any and all Letters Patent to be obtained therefor;

NOW, THEREFORE, for and in consideration of One Dollar ($1.00) and other good and valuable consideration to us in hand paid by said Assignee, the receipt of which is hereby acknowledged, we have sold, assigned and transferred, and by these presents do hereby sell, assign and transfer unto the said Assignee, its successors and assigns, our entire right, title and interest in and to said invention, said application, all applications claiming priority to said application including all divisions, continuations or renewals thereof, and the Letters Patent, both foreign and domestic, that may or shall issue, therefrom including all reissues or extensions of such patents including all of our rights under the International Convention, and we do hereby authorize and request the Commissioner of Patents to issue said Letters Patent to the above mentioned Assignee in accordance herewith.

We hereby authorize the above mentioned Assignee, its successors and assigns, or anyone it may properly designate, to insert in this instrument the date of execution and/or filing date and application number of said application when ascertained.

We further authorize said Assignee, its successors and assigns, or anyone it may properly designate, to apply for Letters Patent, in its own name if desired, in any and all foreign countries, and additionally to claim the filing date of said United States application and/or otherwise take advantage of the provisions of the International Convention.

Upon said consideration we do hereby covenant and agree with the said Assignee, its successors and assigns, that we will not execute in writing or do any act whatsoever conflicting with these presents, and that we or our executors or administrators will at any time upon request, without further or additional consideration, but at the expense of the said Assignee, its successors and assigns, execute such additional writings and do such additional acts as said Assignee, its successors and assigns, may deem necessary or desirable to perfect the Assignee's enjoyment of this grant, and render all necessary assistance in making application for and obtaining original, divisional, reissued or extended Letters Patent of the United States, or of any and all foreign countries on said invention, and in enforcing any rights occurring as a result of such applications

or patents, by giving testimony in any proceedings or transactions involving such applications or patents.

IN WITNESS WHEREOF, we have hereunto set our hands and affixed our seal as dated below.

Date: 1-7-11

Jason K. Stowers

Subscribed and sworn to before me
this 7th day of January, ~~2010~~ 2011

Jane Gutter
Notary Public

[Notary Seal]

OFFICIAL SEAL
JANE GUTTER
NOTARY PUBLIC-OREGON
COMMISSION NO 415773
MY COMMISSION EXPIRES APRIL 01, 2011

Date: 1/7/2011

Alan J. Telecky

Subscribed and sworn to before me
this 7th day of January, ~~2010~~ 2011

Jane Gutter
Notary Public

[Notary Seal]

OFFICIAL SEAL
JANE GUTTER
NOTARY PUBLIC-OREGON
COMMISSION NO 415773
MY COMMISSION EXPIRES APRIL 01, 2011

Date: 7 JAN 2011

Douglas A Keszler

Douglas A. Keszler

Subscribed and sworn to before me
this 7th day of January, ~~2010~~ 2011

Jane Gutter

Notary Public

[Notary Seal]

OFFICIAL SEAL
JANE GUTTER
NOTARY PUBLIC-OREGON
COMMISSION NO 415773
MY COMMISSION EXPIRES APRIL 01, 2011

Date: JANUARY 7, 2011

Andrew Grenville

Subscribed and sworn to before me
this 7th day of January, ~~2010~~ 2011

Jane Gutter

Notary Public

[Notary Seal]

OFFICIAL SEAL
JANE GUTTER
NOTARY PUBLIC-OREGON
COMMISSION NO 415773
MY COMMISSION EXPIRES APRIL 01, 2011

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02

CONFIRMATION NO. 1662

62274
DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

POA ACCEPTANCE LETTER

OC000000045612879

Date Mailed: 01/26/2011

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 01/17/2011.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

/sleutchit/

Office of Data Management, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

Doc Code: PD.TO.AUTH
Document Description: Authorization to access Appl. by Trilateral Office

PTO/SB/39 (07-09)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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AUTHORIZATION TO PERMIT ACCESS TO APPLICATION BY PARTICIPATING OFFICES

Send completed form to: Commissioner for Patents
P.O. Box 1450, Alexandria, VA 22313-1450

COMPLETE IF KNOWN	
Application Number	12/850,867
Filing Date	August 5, 2010
First Named Inventor	STOWERS et al.
Attorney Docket Number	5063.02US02
Title (Required)	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

The undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the World Intellectual Property Office (WIPO), and any other intellectual property offices in which a foreign application claiming priority to the above-identified patent application is filed access to the above-identified patent application. See 37 CFR 1.14(c) and (h).

In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the above-identified application with respect to: 1) the above-identified patent application-as-filed; 2) any foreign application to which the above-identified patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the above-identified patent application; and 3) any U.S. application-as-filed from which benefit is sought in the above-identified patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date of filing the Authorization to Permit Access to Application by Participating Offices.

This written authorization should be submitted prior to the filing of a subsequent foreign application, in which priority is claimed to the above-identified patent application, with any intellectual property office (e.g., the EPO, JPO, KIPO, or DAS Accessing Office). However, if applicant does not wish the EPO, JPO, KIPO, WIPO, or other intellectual property office in which a foreign application claiming priority to the above-identified patent application is filed to have access to the above-identified patent application, this written authorization should not be filed.

No fee will be charged under 37 CFR 1.19(b)(1) for providing a participating intellectual property office with an electronic copy of the above-identified patent application.

This form must be signed by an authorized party in accordance with 37 CFR 1.14(c).

/Peter S. Dardi/	May 13, 2011
Signature	Date
Peter S. Dardi	404-949-5730
Printed or Typed Name	Telephone Number
Attorney	39,650
Title	Registration Number, if applicable

This collection of information is required by 37 CFR 1.14(h). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process an application). Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 6 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Electronic Acknowledgement Receipt

EFS ID:	10084882
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	13-MAY-2011
Filing Date:	05-AUG-2010
Time Stamp:	14:17:26
Application Type:	Utility under 35 USC 111(a)

Payment information:

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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Authorization to access Appl. by Trilateral Office	Authorization_To_Permit_Access.pdf	105035 226bb30a22613d6dff98229fa31b5ab870fe42a9	no	1

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If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
12/850,867	08/05/2010	1783	1215	5063.02US02	38	5

CONFIRMATION NO. 1662

REPLACEMENT FILING RECEIPT

62274
DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

OC000000047680997

Date Mailed: 05/17/2011

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Applicant(s)

Jason K. Stowers, Corvallis, OR;
Alan J. Telecky, Corvallis, OR;
Douglas A. Keszler, Corvallis, OR;
Andrew Grenville, Eugene, OR;

Power of Attorney: The patent practitioners associated with Customer Number 62274

Domestic Priority data as claimed by applicant

This appln claims benefit of 61/350,103 06/01/2010

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The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 12/850,867**

Projected Publication Date: 12/01/2011

Non-Publication Request: No

Early Publication Request: No
**** SMALL ENTITY ****

Title

PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

Preliminary Class

428

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(Not for submission under 37 CFR 1.99)

Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1783
Examiner Name	Gugliotta, Nicole T.
Attorney Docket Number	5063.02US02

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	3385915		1968-05-28	Hamling	
	2	5025094		1991-06-18	King	
	3	6183716	B1	2001-02-06	Sleight et al.	
	4	6197896	B1	2001-03-06	Aviram et al.	
	5	6583071	B1	2003-06-24	Weidman et al.	
	6	6844604	B2	2005-01-18	Lee et al.	
	7	6927108	B2	2005-08-09	Weng et al.	
	8	6946677	B2	2005-09-20	Ostergard	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
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	Art Unit	1783
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	Attorney Docket Number	5063.02US02

	9	7208341	B2	2007-04-24	Lee et al.	
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	2	20060088962	A1	2006-04-27	Herman et al.	
	3	20080286683	A1	2008-11-20	Brodsky et al.	
	4	20100044698	A1	2010-02-25	Herman et al.	
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	Art Unit	1783
	Examiner Name	Gugliotta, Nicole T.
	Attorney Docket Number	5063.02US02

	1	2008/082448	WO	A1	2008-07-10	Keszler et al.		☐
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	1	AHMED ET AL., "Synthesis and Characterization of Zirconium and Hafnium Sulfates, Hydroxide Sulfates and Oxide Sulfates", Acta Chemica Scandinavica, 53:24-33 (1999).	☐
	2	International Standard ISO 21348 "Space Environment (natural and artificial) - Process for determining solar irradiances", First Edition 2007, Reference number: ISO 21348:2007(E) (20 pages).	☐
	3	STOWERS, "Direct Patterning of Solution Deposited Metal Oxides", A Dissertation to Oregon State University, August 14, 2008 (149 pages).	☐
	4	STOWERS ET AL., "High resolution, high sensitivity inorganic resists", Microelectronic Engineering, 86:730-733 (2009).	☐
	5	ZHANG ET AL., "Stabilization of Cubic ZrO2 with Rh(III) and/or La(III), Journal of Solid State Chemistry, 72:131-136 (1988).	☐
	6	ZIMMERMAN, "Extension Options for 193nm Immersion Lithography", Journal of Photopolymer Science and Technology, 22(5):625-634 (2009) (Abstract), for full article please see http://www.jstage.jst.go.jp/article/photopolymer/22/5/625/_pdf.	☐

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	Filing Date	2010-08-05
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	Examiner Name	Gugliotta, Nicole T.
	Attorney Docket Number	5063.02US02

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(Not for submission under 37 CFR 1.99)

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Filing Date	2010-08-05
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Art Unit	1783
Examiner Name	Gugliotta, Nicole T.
Attorney Docket Number	5063.02US02

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☐ Fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

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Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	MengMeng Anne Fahrni
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	15-AUG-2011
Filing Date:	05-AUG-2010
Time Stamp:	11:02:41
Application Type:	Utility under 35 USC 111(a)

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2	Foreign Reference	WO2009120169A1.pdf	3302660 84299058addb3a8d903a25674eaf4accf2c31a73	no	74
Warnings:					
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3	Non Patent Literature	AHMED_ET_AL.pdf	1293068 e01766c87f1bf562a8732b821b0a0e5f7b5ddf66	no	10
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7	Non Patent Literature	ZHANG_ET_AL.pdf	438702 e85ed1aaf75ee94303ff93ab8877aa58f4dee6d4	no	6
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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 July 2008 (10.07.2008)

PCT

(10) International Publication Number
WO 2008/082448 A1

(51) International Patent Classification:
C08F 10/00 (2006.01) *H01L 21/00* (2006.01)

(21) International Application Number:
PCT/US2007/023084

(22) International Filing Date: 31 October 2007 (31.10.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/856,070 1 November 2006 (01.11.2006) US

(71) Applicant *(for all designated States except US)*: **STATE OF OREGON ACTING BY AND THROUGH THE STATE BOARD OF HIGHER EDUCATION ON BEHALF OF OREGON STATE UNIVERSITY** [US/US]; Office Of Technology Transfer, 312 Kerr Administrative Building, Corvallis, OR 97331-2140 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **KESZLER, Douglas, A.** [US/US]; 8927 Nw Lorri Place, Corvallis, OR 97330 (US). **ANDERSON, Jeremy** [US/US]; 4882 Sw Aster Street, Corvallis, OR 97333 (US). **HERSH, Peter, A.** [US/US]; 2027 Nw Arthur Place, Corvallis, OR 97330 (US). **STOWERS, Jason, K.** [US/US]; 962 Sw Adams Avenue, Corvallis, OR 97331 (US). **MEYERS, Stephen, T.** [US/US]; 153 Gilbert Hall, Corvallis, OR 97331 (US).

(74) Agent: **SLATER, Stacey, C.**; Klarquist Sparkman, Llp, One World Trade Center, Suite 1600, 121 Sw Salmon Street, Portland, OR 97204 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

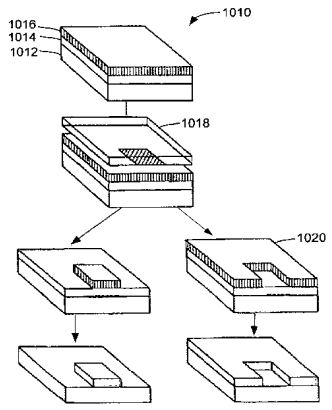
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— *with international search report*

[Continued on next page]

(54) Title: SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THEIR USE AND MANUFACTURE



(57) Abstract: Devices having a thin film or laminate structure comprising hafnium and/or zirconium oxy hydroxy compounds, and methods for making such devices, are disclosed. The hafnium and zirconium compounds can be doped, typically with other metals, such as lanthanum. Examples of electronic devices or components that can be made include, without limitation, insulators, transistors and capacitors. A method for patterning a device using a positive or negative resist also is described. For example, a master plate for imprint lithography can be made. An embodiment of a method for making a device having a corrosion barrier also is described. Embodiments of an optical device comprising an optical substrate and coating also are described. Embodiments of a physical ruler also are disclosed, such as for accurately measuring dimensions using an electron microscope.

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SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THEIR USE AND MANUFACTURE

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of the earlier filing date of U.S. provisional application No. 60/856,070, filed November 1, 2006, which is incorporated in its entirety herein by reference.

FIELD

The present disclosure concerns embodiments of features and devices comprising inorganic metal oxide materials useful for creating spatially-defined structures for purposes including electronic and optical applications, and embodiments of methods for their manufacture and use.

ACKNOWLEDGMENT OF GOVERNMENT SUPPORT

Embodiments of the present disclosure have been developed using federal funding under DARPA grant number HR0011-06-0045. The United States government has certain rights in the invention.

BACKGROUND

Electronic devices currently are made using iterative process steps, such as sequential deposition and etching of materials. For devices comprising inorganic materials, metal-organic precursors have been used extensively for solution-based deposition of inorganic oxides. The presence of the organic moiety necessitates a high-temperature burnout step to remove the organic material. This step can cause significant volume change, crystallization and the phenomenon of "mud cracking." The associated defects inhibit the performance of these materials as coatings and within devices.

Methods for solution processing materials for electronic device applications have been patented. For example, Ostergard, U.S. Patent No. 6,946,677, entitled "Pre-Patterned Substrate for Organic Thin Film Transistor Structures and Circuits and Related Method for Making Same," describes forming a desired circuit

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configuration in the surface of a substrate, thereby pre-patterning the area to receive material useful for forming an organic thin film transistor (OTFT) structure and interconnecting conductive paths. According to the '677 patent, OTFT material is deposited in the pre-patterned area using printing techniques such as inkjet printing.

Weng *et al.*, U.S. Patent No. 6,927,108, describes solution processing thin-film materials to form transistors. The '108 patent describes forming "conductive solution-processed thin film material contacts, semiconductor solution-processed thin film material active regions, and dielectric solution-processed thin film material isolations in a sequence and organization to form a solution-processed thin film structure capable of transistor operation."

U.S. Patent Publication No. 2005/0242330 A1, which is incorporated herein by reference, concerns hafnium and zirconium compounds useful for electronic applications. U.S. Patent Publication No. 2005/0242330 A1 names Dr. Douglas Keszler as an inventor, who also is an inventor of embodiments disclosed herein.

SUMMARY

U.S. Patent Publication No. 2005/0242330 A1 discloses compounds and solution deposition of inorganic compounds in a manner that addresses deficiencies of prior technologies. For example, solution deposition according to the present invention avoids using organic materials required for metal-organic deposition techniques, and hence also avoids organic burnout and tbe cracking problems associated with burnout.

One embodiment of the present invention concerns devices, such as electronic devices, having a thin film or laminate structure comprising at least one hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, hafnium and/or zirconium oxy hydroxy phosphate ($HfO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable. X may have any value in a range of from about 0.1 to about 3.5/(polyatomic ion charge). For example, x may be any value within the

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range of from about 0.1 to about 1.75 for a polyatomic ion with a charge of 2, such as the oxy hydroxy sulfate compounds. Z may have any value range of from 0.0 to about 3.8.

Particular embodiments concern thin films or laminates comprising a hafnium or zirconium oxy hydroxy sulfate compound having a formula $(MO_{2-x-z/2}(OH)_z(SO_4)_x)$, wherein M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 1.75, and any value for z in a range of from 0.0 to about 3.8. These compounds also are referred to as HafSOx and ZircSOx. The hafnium and zirconium compounds also can be doped, typically with other metals, such as calcium, cerium, lanthanum, or combinations thereof. Certain embodiments have used lanthanum as a dopant to produce compounds having a formula $M_{1-x}La_yO_{2-x-z/2-y/z}(OH)_z(SO_4)_x$ (MSOx:La), where the composition and stoichiometry are as stated above. A particular example of a lanthanum-doped compound is $Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$. Additional exemplary compounds include HafSOx:La, ZircSOx:La, HafSOx:Ce, or ZircSOx:Ca. In certain embodiments, sulfate is subsequently removed via ion exchange with an aqueous base, resulting in $M(OH)_x$ or MO_x films. Suitable aqueous hases include group I metal hydroxides, group II metal hydroxides, group III metal hydroxides, lanthanide hydroxides, ammonium hydroxide, and/or aqueous tertiary amines, among others.

Certain embodiments concern thin oxide films or laminates comprising complex compositions with two or more metals. At least one of the metal cations has a charge greater than 3^+, and the total concentration of cations with charge greater than 3^+ exceeds 50 mol% of the metal cations in the target oxide. A non-aqueous solution comprising dissolved salts and an amount of water is prepared. The amount of water is less than 20 mol% relative to the non-aqueous solvent. The pH of the solution is increased relative to the starting solution by adding a base or by reaction of free protons via oxidation-reduction mechanisms. The final solution pH depends upon the metal cations used, but will typically be in the range of about 2-9. The increased pH results in hydrolysis of water molecules bound to the cations and condensation of these resulting hydroxo-cations. The solvent is evaporated, and the resulting solid is dissolved or dispersed in water and subsequently applied to a

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substrate as a liquid film. The liquid film is then thermally cured at a temperature between about 100 °C and 600 °C for about 5-240 minutes.

Examples of electronic devices, or components of devices, that can be made according to this invention include, without limitation, insulators, such as a gate insulator in a field effect transistor, transistors, such as a field effect transistor, and capacitors, such as a MIM capacitor. Thin films and laminates made according to this embodiment had a permittivity value within the range of from about 9 to about 12, a breakdown field from at least 3 MV cm^{-1} up to about 6 MV cm^{-1}, and a leakage current near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}. Devices made using ZircSOx:Ca had a breakdown field of about 3.6 MV cm^{-1}, a leakage current of less than about 50 nA cm^{-2}, more typically less than about 10 nA cm^{-2}.

Field effect transistors can be made using HafSOx:La and/or ZircSOx:La as gate dielectric materials. Certain disclosed embodiments used zinc indium oxide and/or zinc tin oxide as channels. Particular field effect transistors had an on-to-off ratio of greater than 10^6, and nA cm^{-2} gate leakage currents.

Another embodiment of the present invention concerns a method for patterning a device using a photoresist. A particular embodiment of the method comprises first providing a structure to be patterned. The structure typically comprises: a substrate, such as a semiconductor material, a metal, glass, a polymeric material, or combinations thereof; a material layer for patterning, such as silica; and a resist layer. The resist layer typically includes disclosed hafnium and/or zirconium oxy hydroxy compounds. The structure is exposed to an energy source, such as an electron beam or light, with particular examples using ultraviolet light. Thereafter, material is removed to pattern the device, or it is retained as an active, patterned component of the device.

The resist may be a positive resist or a negative resist. For example, the method can include exposing the resist layer to an energy source to convert the resist layer material into a developer-soluble material. The developer-soluble material is then removed using a developer. Suitable developers may includes acids, bases, and/or ultrasonic agitation, among others. Again by way of example, the method can comprise removing resist layer material exposed to the energy source. Without limiting the invention to a particular theory of operation, at least for certain

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embodiments, exposure to the energy source may cause the resist layer to polymerize, making it relatively less soluble in a developer than prior to exposure to the energy source.

One embodiment of a positive resist comprises a bilayer. A first layer of the bilayer comprises a copper formate film deposited on a hafnium oxide sulfate (HafSOx) film. The copper formate film is soluble in acid and the undoped HafSOx film is insoluble in acid. Exposing the bilayer to light through a mask or to a focused electron beam causes the two films to interdiffuse in exposed areas, thereby rendering the previously undoped HafSOx film soluble.

Another embodiment of a bilayer process for making a resist comprises depositing a first layer of a solid acid or base, where the acid or base contains one or more metal atoms, onto a substrate. A liquid suspension containing an oxide precursor, such as copper formate, is applied in a desired pattern onto the first layer. Under heated conditions, the precursor decomposes to an oxide. The oxide subsequently reacts and interdiffuses with the first layer, forming a product that can be etched to reveal a pattern. An alternate embodiment comprises depositing oxide particles onto the first layer, with or without heating, resulting in a direct reaction to form a product that can be etched. A further embodiment comprises depositing a thin layer of the oxide precursor onto the first layer. A pattern of activated precursor is then formed by light exposure through a photomask or direct writing with a focused laser or electron beam.

Another embodiment of the present invention concerns a master plate for imprint lithography. The master plate comprises a substrate, such as a flexible or glass substrate, and at least one layer of a thin film or laminate structure comprising at least one disclosed hafnium and/or zirconium oxy hydroxy compound. A particular embodiment of a master plate includes a layer of HafSOx deposited onto the substrate, and a second layer, such as a ZircSOx:Cu layer. The master plate may be patterned by exposure to an energy source, such as exposure to light or an electron beam through a mask to cause the two films to interdiffuse in exposed areas. This renders previously undoped HafSOx film soluble, which is removed to at least partially define printing features of the master plate.

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In another embodiment, masks or templates can be fabricated using the films of the present invention in a single layer process. A thin film of an inorganic precursor, such as a solid acid or base, is deposited onto a substrate in combination with a peroxide or similar anion. The film is heated to produce a structurally rigid film. It is then exposed through a photomask or via a laser or electron beam to induce condensation/crosslinking in exposed areas. The solubility of the exposed areas decreases relative to the unexposed areas. The unexposed areas can then be selectively etched, producing a negative-tone image in the film. Positive-tone images also can be formed by preheating the film to higher temperatures before exposure. In some embodiments, an $M(OH)_x/H_2O_2$ film is formed by treating a film such as HafSOx with a mixture of sodium hydroxide and hydrogen peroxide. The resulting film is then patterned by exposure to light or an electron beam.

A method for forming a device also is described, comprising providing a structure to be patterned comprising a substrate, a material layer for patterning, and a metal oxide layer comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The structure is patterned and then exposed to an energy source to form a durable material having a desired pattern produced by patterning the structure. One embodiment of a device made according to the method can include a channel array, such as a micro- or nano-channel array. For such embodiments, the method for making the device can include stamping unit features of a desired size scale into a semi-solid hafnium or zirconium compound to form a stamped layer.

An embodiment of a method for making a device having a corrosion barrier also is described. Disclosed embodiments of the method comprise providing a device, and forming at least one corrosion barrier on the device. The corrosion barrier typically comprises a metal oxide layer comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The method also can include exposing the compound to an energy source to form the corrosion barrier. Examples of such devices include metal and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal and ceramic-based systems, fibers for

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composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, and catalyst supports.

An embodiment of a method for forming fibers also is disclosed. A solution is formed comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The solution is then drawn into fibers. The fibers may be converted into solid, stable forms by any suitable process, such as hydrolysis, annealing, air pyrolysis, and combinations thereof.

Embodiments of an optical device also are described. Particular disclosed embodiments of the device comprise an optical substrate, and a substrate coating comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The layer may be an antireflective coating. The optical substrate and coating may define, for example, a dielectric mirror, an X-ray mirror, an interference filter, a diffractive grating, and/or a waveguide. The optical device also may include a layer that is transparent, such as visibly transparent or transparent to ultraviolet light. The layer may be selectively doped to provide a doped layer having luminescent ions selected from Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof. Doping the layer can be used to produce a light-emitting layer.

Embodiments of a method for making a physical ruler also are disclosed. Certain embodiments comprise forming at least one acid-soluble layer by solution deposition of disclosed hafnium and/or zirconium oxy hydroxy compounds. At least one acid-insoluble layer is formed adjacent to the acid-soluble layer, the acid-insoluble layer being formed by solution deposition of disclosed hafnium and/or zirconium oxy hydroxy compounds. Repeating these steps produces alternating layers, and the method includes accurately determining widths of alternating acid-insoluble and acid-soluble layers. Width determination can be accomplished using any suitable method, such as X-ray reflectivity. Moreover, at least one layer is etched to define a digitated secondary reference pattern for measuring objects. Certain embodiments of such a device are useful for accurately measuring dimensions using an electron microscope.

The foregoing and other objects, features, and advantages of the invention will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 provides thermogravimetric analysis (relative moisture versus temperature) (TGA) for HafSOx (x = 0.70) with various pretreatments and with samples heated under flowing $N_2(g)$ at a rate of 10 °C minute^{-1}.

FIG. 2 is an XRD pattern for HafSOx powders after heating at stated temperatures in air for 1 hour, except as noted.

FIG. 3 is an XRD pattern for HafSOx:32% La powders after heating at stated temperatures for 1 hour, except as noted.

FIG. 4 is an XRD pattern for HafSOx films after heating at given temperatures in air for 5 minutes, where the very small features at 31.8° and 45.6° are attributed to the substrate.

FIG. 5 is an XRD pattern for HafSOx:24% La thin films after heating at stated temperatures in air for 5 minutes.

FIG. 6 illustrates dielectric breakdown characteristics for HafSOx film.

FIG. 7 is an SEM showing one embodiment of HafSOx deposited on tantalum (Ta) metal on a silicon dioxide substrate.

FIG. 8 is an SEM for HafSOx:24% La deposited on Ta.

FIG. 9 is an XRR pattern for HafSOx/ZircSOx multilayer thin-film comprising 14 alternating layers (7 bilayers) having a bilayer thickness of 17.6 nm.

FIG. 10 is a schematic diagram illustrating positive or negative photoresist procedures.

FIG. 11 is a schematic diagram illustrating a positive resist using a bilayer system, the illustrated embodiment comprising a Cu-doped zirconium oxide sulfate (Cu:ZircSOx) film deposited on a hafnium oxide sulfate (HafSOx) film.

FIG. 12 is a schematic diagram illustrating a bilayer process for producing a patterned oxide on a substrate.

FIG. 13 is a schematic diagram illustrating a bilayer process for producing a patterned oxide on a substrate.

FIG. 14 is a schematic diagram illustrating a single layer process for producing a patterned film on a substrate.

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FIG. 15 is a graph of thickness versus etch time for a thermally pre-treated, single-layer film.

FIG. 16 is a film patterned by an electron beam.

FIG. 17 is a schematic diagram illustrating hot embossing lithography for use with semi-solid forms of compounds disclosed herein having much higher mechanical strength, chemical stability, and unique electrical and optical properties relative to organic polymers.

FIG. 18 is a schematic diagram illustrating one method for making a physical ruler for use in standardizing measurements in applications, such as electron microscopy.

FIG. 19 is an AFM image of an unexchanged HafSOx film deposited on silica.

FIG. 20 is a TEM image of HfO_2 following ion exchange of HafSOx and thermal treatment at 850 °C.

FIG. 21 is an AFM image of a HfO_2 film deposited on silica and formed from HafSOx thermal decomposition after heating above 700 °C.

FIG. 22 is an AFM image of a HafSOx film deposited on silica, treated with 0.1M NaOH, and heated to 450 °C for 10 minutes.

FIG. 23 is an AFM image of a HfO_2 film deposited on silica, treated with 0.1M NaOH and heated to 850 °C for 10 minutes.

FIG. 24 provides XRD plots of untreated hafnia films.

FIG. 25 provides XRD plots of treated hafnia films.

FIG. 26 provides XRD plots of untreated zirconia films.

FIG. 27 provides XRD plots of treated zirconia films.

FIG. 28 is an SEM image of an indium gallium zinc oxide semiconductor film deposited on silica.

FIG. 29 is a line pattern produced via ink-jet printing and inorganic diffusion-reaction.

FIG. 30 is a pattern produced by exposing a bilayer film to UV light.

FIG. 31 is a film patterned by electron-beam writing.

FIG. 32 is a film patterned by electron-beam writing.

FIG. 33 is a film patterned photographically.

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FIG. 34 is a film patterned photographically.

FIG. 35 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

FIG. 36 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

FIG. 37 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

DETAILED DESCRIPTION

Disclosed embodiments of the present invention concern devices, including electronic devices or components of electronic devices, which can be made by solution deposition of inorganic materials. Throughout this disclosure, the singular terms "a," "an," and "the" include plural referents unless the context clearly indicates otherwise. Similarly, the word "or" is intended to include "and" unless the context clearly indicates otherwise. The term "includes" means "comprises." All percentages recited herein are atomic percentages unless indicated otherwise. All patents and publications mentioned herein are incorporated by reference in their entirety, unless otherwise indicated. In case of conflict, the present specification, including explanations of terms, will control. The materials, methods, and examples recited herein are illustrative only and are not intended to be limiting.

I. Metal Oxide Sulfate Materials Generally and U.S. Patent Publication No. 2005/0242330 A1

The present disclosure concerns embodiments of a method for solution deposition of inorganic materials, typically solution deposition of metal oxide sulfate inorganic materials that are useful for electronic applications. Embodiments of these materials are described in U.S. Patent Publication No. 2005/0242330 A1. Certain portions of that puhlished application, from paragraph 009 through paragraph 014, are paraphrased below. References to figures in this paraphrased text refer to the figures as published with the '330 publication.

> FIG. 1 illustrates one embodiment of a process for manufacturing a dielectric precursor material. Process 10 generally comprises providing a first reactant 12, such as a metal-containing cation, providing a second reactant 14, such as a polyatomic anion, and then reacting the polyatomic anion and the metal-containing cation. The metal-containing cation and the polyatomic anion may be in solution, such as an aqueous solution, when reacted together. In one embodiment, the metal-containing cation may be provided using an aqucous solution of a hafnium oxy halide, such as hafnium

oxy chloride ($HfOCl_2$(aq)). The polyatomic anion, such as sulfate (SO_4^{2-}), may be provided using an aqueous solution of sulfuric acid (H_2SO_4(aq)). These two reactants may be mixed together using processes and relative amounts suitable for making desired materials. The mixture may be heated.

The reaction may produce a precursor solution 16. Precursor solution 16 may be immediately used as desired, such as by being applied to a substrate. Optionally, precursor solution 16 may be at least partially dehydrated and then applied. In the example given above, the precursor solution may then form hafnium oxy-hydroxy sulfate ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$). With reference to the variables in this formula, x and z may be fixed or variable, and may have any value. For example, the value of x typically is from about 0.1 to about 1.9, and a value for z is from 0.0 to about 2.0. For one embodiment the values were x=0.5 and z=0. Hydroxyl groups may be a part of the metal-containing cation, and the compound may comprise hafnium oxy-hydroxy sulfate ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$).

In other embodiments, the polyatomic anion may include one or more of sulfate (SO_4^{2-}), borate (BO_3^{3-}), phosphate (PO_4^{3-}), tungstate (WO_4^{2-}) and silicate (SiO_4^{4-}). The metal-containing cation may comprise a metal suboxide, and may include one or more of hafnium (Hf^{4+}), titanium (Ti^{4+}), zirconium (Zr^{4+}), cerium (Ce^{4+}), tin (Sn^{4+}), tantalum (Ta^{5+}), niobium (Nb^{4+}), yttrium (Y^{3+}), molybdenum (Mo^{4+}), tungsten (W^{6+}), aluminum (Al^{3+}), gallium (Ga^{3+}), zinc (Zn^{2+}), chromium (Cr^{3+}), iron (Fe^{3+}), bismuth (Bi^{3+}), lanthanides, hafnium oxy-hydroxide ($HfO_y(OH)_z^{(4-2y-z)+}$), zirconium oxy-hydroxide ($ZrO_y(OH)_z^{(4-2y-z)+}$), titanium oxy-hydroxide ($TiO_y(OH)_z^{(4-2y-z)+}$), tantalum oxy-hydroxide ($TaO_y(OH)_z^{(5-2y-z)+}$), yttrium oxy-hydroxide ($YO_y(OH)_z^{(3-2y-z)+}$), niobium oxy-hydroxide ($NbO_y(OH)z^{(4-2y-z)+}$), molybdenum oxy-hydroxide ($MoO_y(OH)_z^{(4-2y-z)+}$), tungsten oxy-hydroxide ($WO_y(OH)_z^{(6-2y-z)+}$), aluminum oxy-hydroxide ($AlO_y(OH)_z^{(3-2y-z)+}$), gallium oxy-hydroxide ($GaO_y(OH)_z^{(3-2y-z)+}$), zinc oxy-hydroxide ($ZnO_y(OH)_z^{(2-2y-z)+}$), chromium oxy-hydroxide ($CrO_y(OH)_z^{(3-2y-z)+}$), iron oxy-hydroxide ($FeO_y(OH)_z^{(3-2y-z)+}$), bismuth oxy-hydroxide ($BiO_y(OH)_z^{(3-2y-z)+}$), and oxy-hydroxides of the lanthanide series. The value of y is related to the charge on the metal cation and the amount of hydroxide and other polyatomic anion that is bound to the metal cation.

Embodiments of the method using polyatomic anions and metal-containing cations disclosed herein may result in the formation of a dielectric precursor material that does not require using organics for forming complexes, i.e., the sources of the anion and the cation do not contain organics. However, organic materials can be used, if desired or necessary for certain embodiments. For example, a non-complexing organic, such as ethanol, may be used as a partial solvent in the precursor solution. If complexing organics are not included in the precursor material, the precursor solution typically does not have to be heated or annealed at temperatures as high as 400 °C or higher, to decompose/combust any organic materials once the precursor solution is applied to a substrate. Polymerization of the

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precursor solution upon heating and/or drying results in the formation of amorphous films and not polycrystalline materials, thereby allowing solutions-hased-application of the dielectric material on a substrate.

In general, disclosed embodiments of the present process may be conducted at ambient conditions, such as atmospheric pressure in air. Accordingly, vacuum processing is not required, but may be utilized if desired. The process may be conducted at a temperature above ambient, such as in a range of from about 80 °C to about 850 °C, typically in a temperature range of from about 80 °C to at most 350 °C, and often at a temperature of at most 100 °C. These low pressure and low temperature processing steps may reduce the energy requirements for disclosed processes. Due to the low temperatures useful for processing the dielectric films, the films may be processed on or applied as a solution to low-temperature substrates, such as plastic substrates. The amorphous, non-crystalline dielectric precursor solution produced allows even, conformal coverage of the precursor solution on a substrate, such as on a wafer. The solution also may be applied in a predetermined, specific pattern, such as by using inkjet printing, so that no masking or etching steps are used. Accordingly, the process of the present disclosure may eliminate or reduce the usage of hazardous or toxic materials that may be used for the formation and removal of materials during photolithography processing on substrates. Thus the present process is time efficient and environmentally "green" relative to known processes. Moreover, the hafnium oxide and sulfate materials utilized in one example embodiment of the present disclosure may not be toxic materials.

Examples of materials used in the process of the present disclosure include compounds belonging to the family of compounds including hafnium oxy hydroxy sulfates ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$), hafnium oxy hydroxy tungstates ($HfO_{2-x-z/2}(OH)_z(WO_4)_x$), hafnium oxy hydroxy borates ($HfO_{2-x-z/2}(OH)_z(BO_3)_x$), hafnium oxy hydroxy phosphates ($HfO_{2-x-z/2}OH_z(PO_4)_x$), and hafnium oxy hydroxy silicates ($HfO_{2-x-z/2}OH_z(SiO_4)_x$). These materials may be polymerized at temperatures as low as 80 °C and may remain amorphous up to approximately 740 °C, and even as high as 1,200 °C. Material polymerization may be controlled by adjusting the heating rate, by using co-solvents, by other suitable methods, and by any and all combinations of such methods. Amorphous films of the present disclosure may reduce defect formation at grain boundaries and may reduce crack formation upon an amorphous-to-crystalline transition. Moreover, the dielectric films of the present disclosure may have a reasonably high dielectric constant, i.e., a dielectric constant higher than the dielectric constant of organic compounds. The ability to form high quality dielectrics by solution-based processing, such as inkjet printing applications, allows formation of low cost electronic components, such as field effect transistors or capacitors.

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FIG. 2 schematically illustrates one embodiment of a process for applying precursor solution 16 to form a dielectric material. Precursor solution 16, such as hafnium oxy sulfate, may be applied to a substrate 18, such as a wafer, by an applicator 20. In one embodiment, applicator 20 may comprise an inkjet printer having nozzles 22. The aqueous precursor solution 16 is ejected through nozzles 22 of the inkjet printer. In other embodiments, applicator 20 may comprise a spin-coater, a dip-coater, or a spray-coater such that the method of applying the precursor solution may comprise, respectively, spin-coating, dip-coating, or spray-coating. Due to the amorphous, solution-based properties of precursor solution 16, precursor solution 16 may allow good conformal coverage when applied. Once applied to the substrate surface, or to a film or films deposited on the substrate, the precursor solution may be dehydrated, such as by heating with a heater 24, or by other dehydration devices, to remove or reduce the amount of water in the precursor solution. This dehydration step may cause precipitation of an amorphous dielectric material 26, such as a hafnium oxy sulfate thin film, on wafer 18.

FIG. 3 is a graph showing possible solution concentrations for differing precursor concentrations for one embodiment of dielectric material precursor solutions 16 (see FIG. 1), in particular, for the reaction of sulfuric acid (H_2SO_4) with hafnium oxy chloride ($HfOCl_2$). More particularly, FIG. 3 shows a graph of total sulfate concentration (molarity (M)) versus total hafnium concentration (M). Region 28 represents a clear solution, i.e., a solution with no visually detectable precipitate therein, wherein region 28 is a region of excess sulfuric acid (H_2SO_4). Region 30 represents a clear solution, i.e., a solution with no visually detectable precipitate therein. Region 30 is a region of excess hafnium oxy chloride ($HfOCl_2$). Line 32 represents a stoichiometric line wherein sulfuric acid and hafnium oxy chloride are each present in a one-to-one ratio (1:1 stoichiometric ratio). Region 34 represents a precipitation area, i.e., a solution having a visually detectable precipitate therein. Region 34, or portions thereof, therefore, may represent solutions that are not best suited for forming smooth substantially defect free films by inkjet printing applications, but its use is not foreclosed. Accordingly, when precursor solution 16 (see FIG. 2) is applied through an inkjet printer application device 20 (see FIG. 2), it may be desirable that the concentration of the first and second reactants fall within either of regions 28 or 30, but not within solids region 34. Solids present in the solutions of region 34 may occlude nozzles 22, may form an unsmooth film, or may otherwise result in unfavorable precursor solution application. In other words, the solutions of regions 28 and 30 may represent possible precursor solution "inks" that may be applied through an inkjet printhead or by a dropper method.

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II. General Discussion

New thin-film dielectrics and nanolaminates have been developed using solution deposition, typically aqueous solution deposition, of smooth, dense films. Solution deposition techniques include spin coating and inkjet printing. Solution deposition may be followed by modest thermal treatment ($T < 325$ °C).

A variety of analytical techniques have been used to define the chemistry of the materials made according to the present disclosure, both as powders and films. The quality and functionality of the films have been assessed by X-ray reflectivity, electronic microscopy, and performance in electronic devices. Dielectric characteristics have been determined for working embodiments, and include permittivity values covering the range of from about 9 to about 12; breakdown fields up to at least 6 MV cm^{-1}; and leakage currents near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}. The surface smoothness and pore-free nature of the films facilitate the production of unique nanolaminated structures having individual layers at least as thin as about 2 nanometers. Relatively high permittivity films can be realized using disclosed embodiments of the present invention, while also providing high-breakdown strengths and low-leakage currents in thin-film metal-insulator-metal (MIM) capacitors and thin-film transistors (TFTs). The exceptional characteristics of the insulating films also have allowed fabrication of unique nanolaminated structures.

Amorphous materials are desirable for use as thin-film dielectrics; they do not have grain boundaries, and hence are not susceptible to roughness and charge conduction associated with crystallites. Numerous oxides of hafnium and zirconium, e.g., the simple binaries, silicates, and aluminates, have been examined as candidates for high-permittivity dielectric applications. In multiple-component materials, crystallization can be inhibited to produce more robust breakdown characteristics relative to the pure binary oxides, though permittivity may be sacrificed. These dielectric films often are formed using a variety of metal-organic or metal-salt precursors and techniques such as atomic layer deposition (ALD), chemical vapor deposition (CVD), sol-gel processing, or combinations thereof. However, making useful dielectric films by solution deposition methods that are

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both dense and amorphous may require inhibiting crystallization and cracking, both during deposition and subsequent processing.

Certain disclosed embodiments of the present invention concern the development of metal oxide films. Metal oxides are exemplified herein generally by reference to hafnium and zirconium sulfate systems having representative formulas $HfO_{2-x}(SO_4)_x$ and $ZrO_{2-x}(SO_4)_x$, respectively, where $0.1 \leq x \leq 1.5$. These compounds are referred to herein by the acronyms HafSOx and ZircSOx, respectively. To define the chemistry and physical properties of these systems, HafSOx, and doped analogs thereof, such as the La-substituted derivative HafSOx:La, have been made, both as powders and thin films. Thin-film dielectric properties of HafSOx, ZircSOx, and selected derivatives have been assessed by fabricating capacitors and TFTs. These analyses revealed that very high-quality, dense films could be produced. Film thickness and fabrication of mixed HafSOx/ZircSOx nanolaminates can now be controlled by spin-coating processes.

A number of phases and crystal structures have been reported from examination of HfO_2-SO_3-H_2O and ZrO_2-SO_3-H_2O systems. Several structures are characterized as simple hydrates of formulations $Hf(SO_4)_2 \cdot nH_2O$ or $Zr(SO_4)_2 \cdot nH_2O$, exhibiting variations in the degree of hydration and in the structural dimensionality associated with the condensation of the metal atom, sulfate groups, and water. Materials rich in metal relative to sulfate are known, including $Zr_2(OH)_2(SO_4)_3 \cdot 4H_2O$; $Hf(OH)_2SO_4$, $Zr(OH)_2SO_4$, and their hydrates; $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13} \cdot 33H_2O$ and $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$; and $Zr_3O_5SO_4$ and its hydrate. All of these structures (with the possible exception of $Zr_3O_5SO_4$) are likely unstable when subjected to air at both room temperature and under moderate heating, resulting from changes in hydrogen bonding or dehydration. This allows the dehydration and condensation processes to be used to develop amorphous films.

Starting from aqueous solutions with selected fractions of sulfate relative to hafnium (variable x), HafSOx precipitates were induced by heating. FIG. 1 is a thermogravimetric analysis (TGA) of air-dried HafSOx precipitates. TGA is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature. Heating an air-dried HafSOx precipitate leads to mass loss in three domains. Similar characteristics have been observed for other

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HafSOx derivatives as well. The large mass loss below a temperature of about 200 °C is attributed to loss of incorporated water. Mass loss in the temperature range of from about 200 °C to about 700 °C is attributed mainly to elimination of more tightly bound hydroxyl species as water. The sharp mass loss that begins above about 700 °C, is attributed to sulfate decomposition according to $SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$. Assuming dehydrated HafSOx powder is converted completely to HfO_2 between 700 °C and 950 °C, the sulfate fraction can be calculated from the mass loss. Determining mass loss of samples revealed that increasing levels of sulfate in the mother solution yielded increasing levels of sulfate in precipitates. Specifically, the sulfate-to-hafnium ratio varied from about 46% to about 71% for dehydrated formulas of $HfO_{1.54}(SO_4)_{0.46}$ and $HfO_{1.29}(SO_4)_{0.71}$, respectively. The same maximum sulfate composition precipitated whether $H_2SO_4(aq)$ or $(NH_4)_2SO_4(aq)$ was used as the sulfate source; products with sulfate levels < 46% were not examined. The onset of sulfate loss occurred above 720 °C for all samples, though some variations in the thermogravimetric profiles were observed. Peak positions for the derivatives of these heating curves, as definable values, reveal decomposition between 793 °C and 817 °C for samples tested. The highest decomposition temperatures were observed for samples having maximum sulfate content with $H_2SO_4(aq)$ as the sulfate source.

Again with reference to FIG. 1, samples with maximum sulfate content also were heated prior to TGA measurements. Mass losses associated with water were reduced, and calculated sulfate contents were similar for both preheated and regular samples. This sulfate content of 70–71% mimics the compositions of the reported crystals $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$ and $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}\cdot 33H_2O$. From TGA studies, Ahmed, Fjellvåg, and Kjekhus also found that sulfate decomposition for $Hf_{18}O_{23}(SO_4)_{13}$ and $Zr_{18}O_{23}(SO_4)_{13}$ occurs at temperatures higher than those for the Hf and Zr disulfates within their study, and higher than those for the basic sulfates $Hf(OH)_2SO_4\cdot H_2O$ and $Zr_3O_5SO_4$ reported by others. In addition to enhanced thermal stability, a sulfate-to-metal ratio of approximately 13:18 exhibits special stability within this system. As such, this composition may be suitable for purposes where solution processing and heating are required.

The sulfate $La_2O_2SO_4$ has a decomposition temperature of greater than 1,300 °C. Lanthanum (La) was added to the mother HafSOx solution to produce

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additional compounds having modified physical properties, such as modified dehydration properties and thermal characteristics, one example being thermal stability. A mixed-metal system, $Hf_{1-z}La_zO_{2-x-z/2}(SO_4)_x$ (HafSOx:La), exemplifies such compounds. To produce such compounds a solution containing the precursor materials and 23% La (total metal) was heated to form precipitates. Chemical analysis indicated that only 3% La was found in the product. From TGA, a sulfate-to-metal ratio of 71% was established, and the decomposition (as derivative peak) at 820 °C was found to be consistent with maximal sulfate content. Co-precipitation was then induced by adding NH_3(aq) to a salt solution of the constituent species containing 32% La. The chemical composition of the product was analyzed, revealing the same fraction of La as that present in the mother solution. Thermal decomposition for this formula was markedly different from undoped HafSOx. Mass loss attributed to sulfate was apparent above 700 °C, though heating features were less abrupt and no constant mass was achieved with heating to 1,000 °C, even when heating at the slower rate of 2 °C minute^{-1}. For this heating rate, decomposition (as derivative peak) occurs at approximately 870 °C, though this value depends on heating conditions. Complete decomposition to the oxides was accomplished by heating to 1,500 °C, yielding the formula $Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$ for the dried precipitate.

XRD data were collected for precipitated HafSOx powders to establish temperature ranges for crystalline phases. After air drying, a complex diffraction pattern was recorded for samples having maximum sulfate content and H_2SO_4(aq) as the sulfate source; other samples exhibited no or diffuse diffraction. XRD data for HafSOx (x = 0.70) are shown in FIG. 2. After heating air dried samples for 1 hour at temperatures between from about 100 °C to about 700 °C, the material becomes amorphous. Crystalline peaks characteristic of monoclinic HfO_2 are observed after heating at 750 °C and above for 1 hour. As the onset of sulfate loss occurs at 720 °C by TGA, crystallization is found to coincide with sulfate loss. Inclusion of 3% La generates similar diffraction profiles for temperatures up to 1,000 °C.

XRD data for HafSOx:32% La are shown in FIG. 3. Both the precipitated material and that heated to 700 °C are X-ray amorphous. Just as with unsubstituted HafSOx, a detectable crystalline phase forms between 700 °C and 750 °C (1 hour

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heating), which is the temperature interval over which sulfate begins to decompose. Yet with substitution of 32% La, monoclinic HfO_2 is not the detected phase. Rather, the diffraction profile is consistent with cubic (or tetragonal) HfO_2, the phases of HfO_2 often stabilized by lanthanide atom inclusion. High-temperature heating generates $Hf_2La_2O_7$ and monoclinic HfO_2 as predicted from consideration of the appropriate phase diagrams. Intermediate temperature oxide phases are consistent with work on the system ZrO_2-La_2O_3 by Zhang, Kershaw, and Dwight, who found that 10–37% lanthanum stabilizes cubic zirconia at 900 °C, with phase separation occurring at 1,050 °C.

HafSOx and HafSOx:La thin films having thicknesses of from about 200 nanometers to about 300 nanometers were fabricated for materials characterization. Compositions for the films were determined with EMPA, based on relative concentrations of Hf, La, Cl, and S. Oxygen levels are less precise by this method, so dehydrated formulas are expressed. Two representative HafSOx films heated at 325 °C (5 minutes) were determined to be $HfO_{0.985}(SO_4)_{0.67}Cl_{0.69}$ and $HfO_{0.915}(SO_4)_{0.85}Cl_{0.47}$, representing 67% and 85% sulfate relative to hafnium. The 85% sulfate film was further heated to 650 °C (5 minutes) and determined to be $HfO_{1.275}(SO_4)_{0.71}Cl_{0.03}$. Also, the HafSOx:La film heated at 330 °C (5 minutes) was determined to be $Hf_{0.76}La_{0.24}O_{0.73}(SO_4)_{0.96}Cl_{0.38}$. For HafSOx heated to 650 °C, the sulfate ratio was reduced to 71%, which matches the composition for heat precipitated HafSOx powders with maximal sulfate. For HafSOx:La, the measured fraction of La (24%) agrees well with the 23% La concentration in the precursor solution.

Transmission Fourier transform infrared (FTIR) analyses for HafSOx (x ~ 0.67 & 0.85), and HafSOx:La films were collected after heating for 5 minutes at selected temperatures. FTIR spectra were used to detect principally two functional groups. Absorption in the range 3000–3600 cm^{-1} is attributed to hydroxyl groups; and absorption in the range 1000–1200 cm^{-1} is attributed to sulfate groups. With heating, hydroxyl absorption diminishes over the range from about 325 °C to about 600 °C, while sulfate stretches are nearly eliminated between about 650 °C and 700 °C for HafSOx films, and between about 700 °C and 750 °C for the HafSOx:La

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film. (The profiles for sulfate absorption are slightly distorted since SiO_2 from the substrates absorbs at a similar energy, but spectra are qualitatively correct.)

Thin-film XRD data were collected for HafSOx ($x \sim 0.67$ & 0.85) and HafSOx:24% La films after heating at indicated temperatures for 5 minutes each, as shown in FIGS. 4 and 5, respectively. For both HafSOx compositions, films are X-ray amorphous from about 325 °C to about 650 °C. Monoclinic HfO_2 is detected at about 700 °C and above. HafSOx:La films are amorphous from about 330 °C to about 700 °C, while a cubic phase is detected from about 750 °C to about 1000 °C. The cubic phase is apparently unstable at 1,100 °C, as separation into monoclinic HfO_2 and $Hf_2La_2O_7$ phases commences. For HafSOx and HafSOx:La films, loss of sulfate can be directly correlated with oxide crystallization, which is consistent with powder behavior.

Films of HafSOx, ZircSOx, and derivatives thereof, were deposited by spin-coating for use as dielectrics. MIM capacitors were tested to determine the parameters of permittivity and loss tangent at 1 kHz, as well as electric-field breakdown strength. "Breakdown" is defined as the field where current density surpasses 10 $\mu A\ cm^{-2}$. Similar tests were conducted for HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, and ZircSOx:Ca. FIG. 6 illustrates dielectric breakdown characteristics for HafSOx dielectric film where the aluminum dot contacts represent an area of 0.011 cm^2. HafSOx and ZircSOx films had breakdown fields of 4–6 MV cm^{-1}. A breakdown field of 3.6 MV cm^{-1} was found for ZircSOx:Ca. At an applied field of 1 MV cm^{-1}, all six variations exhibited leakage current less than 50 nA cm^{-2}, and leakage currents less than 10 nA cm^{-2} were observed for many compositions. Permittivity values of from about 9 to about 12, and loss tangent < 1% were measured for all variations.

Field-effect transistors (FETs) were fabricated with HafSOx:La or ZircSOx:La as the gate dielectrics and zinc indium oxide or zinc tin oxide as the channels. Current modulation was achieved; drain-to-source current saturated with increasing drain-to-source voltage, providing an on-to-off ratio greater than 10^6; and gate leakage currents are in the range of pA cm^{-2}. These results clearly indicate that HafSOx:La and ZircSOx:La films are sufficiently robust for device integration; the requirement for a quality dielectric/channel interface is also met.

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As a new class of amorphous multi-component oxide dielectric films, HafSOx, ZircSOx, and their derivatives may be compared to other mixed systems, particularly aluminates and silicates, represented as $(MO_2)_{1-x}(Al_2O_3)_x$ and $(MO_2)_{1-x}(SiO_2)_x$ where M = Hf or Zr. Various film compositions for each of these systems have been deposited by conventional vapor phase techniques. In the cases of Hf or Zr aluminates and silicates with 20–50 mol% Al_2O_3 or SiO_2 (as common compositions for dielectric applications), crystallization typically occurs at about 800 °C to about 1,000 °C, in conjunction with phase segregation. For tested HafSOx powders and films, crystallization occurs at approximately 700 °C as sulfate decomposes. As dielectrics, these aluminates and silicates exhibit permittivity values of 10–15, compared to values of 9–12 for HafSOx and ZircSOx. This new class of oxide sulfate materials can be considered amorphous, moderate temperature, medium permittivity dielectrics.

Scanning electron microscopy (SEM) and X-ray reflectivity (XRR) were used to further examine film qualities. SEM images for HafSOx and HafSOx:La films are shown in FIGS. 7 and 8. These images reveal smooth surfaces and dense, uniform cross-sections for films having thicknesses in the range of from about 150 nanometers to about 300 nanometers, as typically used for dielectric testing. FIG. 7 shows a SiO_2 substrate 710 upon which a 506-nm layer of Ta metal 712 and a 160-nm HafSOx film 714 have been deposited. FIG. 8 shows a SiO_2 substrate 810 upon which a 512-nm layer of Ta metal 812 and a 192-nm HafSOx/La film 814 have been deposited.

As a stringent measure of reproducibility for thinner film fabrication, multilayer structures with a HafSOx/ZircSOx repeating motif were deposited and analyzed by XRR. The interference pattern from one XRR scan is shown in FIG. 9. Positions of peak maxima, representative of standing wave harmonics, were used to find the thickness of the repeating bilayer. By systematically varying the thicknesses of HafSOx and ZircSOx independently, the thicknesses of the individual layers were determined. Within a nanolaminate stack, single layers as thin as about 3 nanometers were measured. As high order reflections in the diffraction pattern are observed, each bilayer was deposited with a variability < 0.5, including roughness.

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Shrinking device dimensions have led to the need to replace thin, high leakage-current SiO_2 as a dielectric in Si CMOS technologies. The replacement dielectrics must exhibit a high permittivity, allowing thicker layers to exhibit the same device capacitance with smaller leakage currents. HfO_2 and ZrO_2 have attracted considerable attention as replacement gate dielectrics because of their desirable dielectric properties and thermal properties. One of the challenges for HfO_2 and ZrO_2 dielectrics is making smooth, dense, pinhole-free, ultra-thin films having a thickness less than or equal to 13 nm. Previously ultra-thin films have been formed using atomic layer deposition (ALD). Despite some promising results from ALD, the processing requires using a vacuum with long deposition times (1 Å/min), which leads to high costs and low throughput. This has driven some work on the solution based deposition of HfO_2 and ZrO_2. To date these films have not reached the same uniformity and density of the ALD films.

Using an exchange reaction, ultra-thin $M(OH)_x$ and MO_x films can be fabricated that rival ALD quality and are suitable for use in DRAM (dynamic random access memory) and Si CMOS (complementary metal-oxide semiconductor) technologies. For disclosed embodiments, the films are deposited in a sulfate form via inorganic condensation using spin-coating. For example, a semi-solid film can be formed with the composition $MO_x{\cdot}HCl{\cdot}H_2SO_4$. The sulfate is removed by ion exchange using an aqueous sodium hydroxide solution:

$$MO_x{\cdot}HCl{\cdot}H_2SO_4 + OH^-(aq) \rightarrow M(OH)_{2x} + Cl^-(aq) + SO_4^{2-}(aq)$$

The resulting hydroxo and/or oxide films are smooth, dense, and pinhole free. For example, HfO_2 films with a thickness of about 2 nanometers can fabricated from HafSOx films. Exchanged films are subjected to thermal treatments up to about 800 °C for about 10 seconds to 10 minutes, resulting in a film surface roughness of about 0.1 nanometer. Such film characteristics satisfy requirements for metal-dielectric gates in CMOS and related technologies, while replacing expensive atomic layer deposition processing with low-cost spin-on or misting techniques.

The deposited semi-solid hydrated hydroxo films allow for anion exchange without disruption of the films' morphology. For example, oxoanions such as SO_4^{2-}, WO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-}, VO_4^{3-}, AlO_4^{5-}, GaO_4^{5-}, and their protonated forms, e.g., HPO_4^{2-}, $H_2PO_4^-$, and the halides F^-, Cl^-, Br^-, and I^-, can be selectively exchanged by

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placing the films in a metal salt bath, e.g., Na_2SO_4(aq). This provides opportunities to optimize film performance for electronic applications and other applications, such as ion exchange chromatography and filtration.

For some embodiments of oxide films, it is difficult to produce single-source precursor liquid suspensions that can be directly applied to a substrate to provide a complex composition, e.g., two or more metal atoms. The following methods allow the production of the such liquid suspensions and their use as single-source precursors for deposition of films of suitable quality for device applications.

The following describes a general method for synthesizing an aqueous precursor solution and depositing metal oxide films using the precursor. The aqueous precursor is distinctive in that it comprises polymeric or oligomeric metal-hydroxo compounds condensed via hydrolysis in a non-aqueous polar solvent and subsequently transferred to an aqueous environment for deposition. Advantageous thin-film electrical and optical properties and processing temperatures are achieved by condensing metal hydroxides to dense solid oxides without deleterious organic contaminants. Disclosed embodiments of the synthetic method follow the general procedure: 1) dissolution of metal salt in polar solvent; 2) hydrolysis and condensation; 3) solvent evaporation; 4) dissolution in H_2O; and 5) solution deposition and curing.

One or more soluble salts comprising a metal cation (M^{a+}) and one or more anions (X^{b-}) are dissolved in a non-complexing, non-aqueous polar solvent such as aliphatic alcohols or nitriles, particularly lower (10 carbon atoms or fewer) alkyl alcohols and nitriles, such as methanol, ethanol, acetonitrile, or a mixture thereof. Many solvent systems are possible. Suitable solvents for a particular application can be selected by considering boiling point (typically less than 150 °C), low toxicity, and acid-base and redox properties compatible with intended solution-phase reactions. Metal sources may include simple ionic or molecular salts ($Zn(NO_3)_2$, $SnCl_4$, etc.); oxy or hydroxy salts ($ZrO(NO_3)_2$, ZnOHCl, etc.); or potentially organic salts ($Fc(CH_3CO_2)_2$, $Cu(CHOO)_2$, etc.). At least one of the metal cations must have a formal charge greater than 3^+ and the total concentration of such ions (M^{a+} where $a > 3$) should exceed 50 mol% of the metal cations in the target oxide. Concurrently, an amount of H_2O is introduced into the solution as hydrates of the metal salts

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described above, as a pure liquid, or a basic solution detailed below. The amount of water is determined by the cations chosen; typical amounts of water will not exceed 20 mol% of the non-aqueous polar solvent.

The pH of the solution is then raised relative to the starting pH by adding an appropriate base or by reaction of free protons via oxidation-reduction mechanisms. The increased pH drives hydrolysis of the H_2O ligands bound by the acidic ($a > 3$) cations and condensation of the resulting hydroxo-cations. The final solution pH depends upon the metal cations used, but will typically be in the range of about 2-9. This may be accomplished using one of the following techniques, or any and all combinations thereof:

a) Addition of a basic aqueous solution containing NH_4OH, $(NH_4)_3PO_4$, CsOH, or similar compounds. Specific compounds (NH_4OH) may be chosen to decompose or volatilize during subsequent processing. Other cations (e.g., Cs) or polyatomic anions (e.g., PO_4^{-3}) may be used if they are intended to comprise part of the final oxide film to achieve unique morphological, optical, or electrical properties following dehydration.

b) Addition and dissolution of a small amount of a basic oxide such as CaO or SrO, with a similar goal of inclusion in the final oxide film.

c) Addition of NH_3 or other gaseous compounds, which form a basic solution in H_2O.

d) Addition of electropositive metal reducing agents, such as Zn, Al or Fe, which may consume protons through direct reduction to H_2, or as part of other proton-consuming oxidation-reduction processes such as the reduction of NO_3^-. Resultant cationic species are thereafter incorporated into the final oxide film.

e) Addition of aqueous or gaseous oxidizing or reducing agents such as N_2H_4, H_2CO, or H_2O_2 in liquid form, or as soluble salts, with a similar purpose of consuming protons or decomposing counter ions but without inclusion in the final oxide film.

The solution may be stirred at room temperature, heated, or exposed to solvothermal conditions to promote thermohydrolysis and condensation, depending on the final composition desired. Following a suitable reaction period the solution

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will contain one or more soluble oligomeric or polymeric metal-hydroxo cationic species. These species may be homo or hetero-metallic in nature. The degree of condensation is limited by the restricted molar ratio of H_2O (aquo- and hydroxo-ligands) available, while the decreased polarity and size of the non-aqueous solvent relative to H_2O may prevent additional condensation and precipitation processes through steric effects or altered charge-screening properties.

Soluble metal species are isolated by evaporating the non-aqueous solvent. Isolated metal-hydroxo compounds may form crystalline or amorphous solids or gels depending on certain processing considerations, such as solvent, counterion, and hydrolysis ratio.

Precursor solutions for oxide films are prepared by dissolving or dispersing the isolated solid in H_2O. The resulting sol or solution is homogenous, and may or may not be thermodynamically stable.

Precursor solutions are applied to a substrate using any suitable technique, including printing, spin, spray, or dip-coating to form a patterned or blanket liquid film. Liquid films are thermally cured under atmospheric conditions for about 5-240 minutes at a temperature from about 100 °C to 600 °C. Vacuum or forming gas (e.g., H_2 and flowing N_2 or Ar) anneals may be used to alter oxygen stoichiometry or cation oxidation state as appropriate for the chemical or optoelectronic properties desired.

The smoothness and high atomic density of the films described herein allow fabrication of purely inorganic nanolaminates via solution processing. These films represent a new platform for developing a wide range of applications, as discussed further below.

III. Applications

A person of ordinary skill in the art will appreciate that the HafSOx and ZircSOx compounds, and films comprising such compounds, can be used to make a number of different devices, and can be used to practice a variety of processes utilizing such compounds. Metal-organic precursors have been extensively employed in the solution-based deposition of inorganic oxides. The presence of the organic moiety necessitates a high-temperature burnout step, which leads to

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significant volume change and generally to crystallization and the phenomenon of "mud cracking." These problems are eliminated by using disclosed embodiments of the present invention and suitable inorganic compositions to form amorphous HafSOx and ZircSOx films, where simple dehydration and polymerization lead to film quality preservation. To understand phase stability, representative HafSOx and HafSOx:La powders and films were characterized at various temperatures. Thin-films based on HafSOx and ZircSOx were deposited in multiple configurations in order to examine the quality and utility of the films. Several derivatives have been used to produce capacitor dielectrics. HafSOx:La and ZircSOx:La were used to form gate dielectrics in FET devices. Nanolaminate layers of HafSOx and ZircSOx exhibited remarkable smoothness with reproducibility within a couple atomic layers. Classes of films comprising HafSOx, ZircSOx, and their derivatives are useful, amongst other things, as electrical insulators, protective barriers, optical coatings, and/or as inorganic polymers for photolithography.

A. Patterned films for Resist, Imprint Lithography, and Printing

Photolithography is commonly used to transfer geometric shapes on a mask to the surface of a silicon wafer or other semiconductor. For the past four decades, photolithographic processing has been the driving force for the improvements in resolution and dimensional control of device features in the microelectronics industry. These advances have made possible the high-performance personal computers, cell phones, CD players, and other innumerable advanced electronic products that are now considered to be essential parts of our lives. The photolithographic advances that have made these products possible have largely centered on developing short-wavelength exposure tools and an extraordinary extension in the resolution and feature-size capabilities of polymer resists. As the quest for ever smaller features and device-yield improvements continue, however, the limitations and inefficiencies of polymer-based resist technology are becoming more evident.

The smallest feature sizes realized via lithography have been produced by electron-beam writing of inorganic materials. The beam-dose energies required to

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produce these features, however, have been much too high to receive more than passing interest for use in a manufacturing environment.

During the deposition and processing of the films described herein, it is possible to control the film hydration level, which provides a method for controlling the interdiffusion of stacked films and their resulting physical and chemical properties. This controlled interdiffusion with resulting induced modifications in material solubility, coupled with the high quality of the films, was used to develop a new lithographic patterning method. This methodology involves depositing and reacting two distinct films, and it is designated as bilayer diffusion. In addition, small coordinating species such as peroxide (O_2^{2-}) can be incorporated into aqueous-based inorganic liquid suspensions and films to provide an additional, new lithographic patterning method. In this technique, energy (e.g., light, electron beam, heat) can be applied to films, inducing condensation reactions that alter the solubility of the film, thereby allowing lithographic patterning.

Patterns can be formed using a positive or negative photoresist. This process is illustrated schematically in FIG. 10 with reference to a laminate structure 1010 having a silicon substrate 1012, a silica layer 1014 and a resist layer 1016. For positive resists, the resist layer 1016 is exposed to an energy source, such as UV light, wherever the underlying material is to be removed. In these resists, exposure to the UV light changes the chemical structure of the resist layer 1016 so that it becomes more soluble in the developer. The exposed resist layer 1016 is then removed by the developer solution, leaving areas of the bare underlying material. In other words, "whatever shows, goes." The mask 1018, therefore, contains an exact copy of the pattern which is to remain on the wafer.

Negative resists behave in just the opposite manner. Exposure to the UV light causes the negative resist to polymerize, and it therefore is more difficult to dissolve. As a result, the negative resist 1020 remains on the surface wherever it is exposed, and the developer solution removes only the unexposed portions. Masks used for negative photoresists, therefore, contain the inverse (or photographic "negative") of the pattern to be transferred.

Resist materials in current use for electronics manufacture are organic polymers. These polymers exhibit coiling and morphologies that limit pattern

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resolution. Inorganic thin films of the present invention form the basis for a new resist technology. Here, negative resists can be realized by exposing the inorganic films in semi-solid form to light or electron beams, causing them to lose solvent, particularly water during dehydration. This hardens the films, rendering them insoluble in acid.

One embodiment of a positive resist can be made using a bilayer system. A first layer of the bilayer comprises a copper formate film deposited on a hafnium oxide sulfate (HafSOx) film. The copper formate film is soluble in acid and the undoped HafSOx film is insoluble in acid. Exposing the bilayer to light through a mask or to a focused electron beam causes the two films to interdiffuse in exposed areas, thereby rendering the previously undoped HafSOx film soluble.

One embodiment of this process is illustrated schematically in FIG. 11. With reference to FIG. 11, a laminate structure 1110 is first formed, such as by spin coating or inkjet coating suitable materials, in desired orders and thicknesses as required to define a working device. More specifically, a substrate material 1112 is first selected. A person of ordinary skill in the art will appreciate that any of a number of substrate materials potentially can be used to practice this embodiment of the present invention. Solely by way of example, and without limitation, suitable substrates include semiconductor materials, metals, glass, polymeric materials, and combinations thereof. As such the resist technology can be useful for a variety of applications in semiconductor manufacture. Once a suitable substrate 1112 is selected, a first layer 1114 of HafSOx is solution deposited onto the substrate 1112. Thereafter, a second layer, such as a layer 1116 of Cu:ZircSOx, is solution deposited onto layer 1114. The laminate structure 1110 is then subjected to an energy source, such as an electron beam or light, through a mask. Upon exposure to light or an electron beam through a mask, the two films interdiffuse in the exposed areas to render the previously undoped HafSOx film soluble to produce a laminate structure 1120. The exposed structure 1120 is then developed. The previously undoped HafSOx film is soluble, and hence is removed as indicated in laminate structure 1130.

On a flexible or glass substrate, the pattern illustrated in structure 1130 can be considered the master plate for imprint lithography or for generalized printing

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processes such as gravure printing. Forming a hardened patterned material of HafSOx in this way also provides a means for developing micro- and nano-channel arrays in the fabrication of devices for fluid control and delivery. Such devices could be applied in medical diagnostics, ink delivery, and chemical synthesis.

Another embodiment of a bilayer process is shown in FIG. 12. The process produces a patterned oxide on a selected substrate 1210. The substrate can, for example, be a glass, semiconductor wafer, metal, metal alloy, plastic, or a combination thereof. The first step of the process involves depositing a thin film 1212 (from about 1 nm to about 100 nm) of a solid acid or base, e.g., hydrated sulfate, phosphate, nitrate, silicate, aluminate, borate, or mixtures thereof, containing one or more of the metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu. In addition the solid acid/base can contain one or more of NH_3, OH, F, Cl, Br, I. The solid acid/base is preferably deposited via spin coating or printing; physical and vapor deposition are additional options. As one example, the solid acid can be deposited from an aqueous solution of $HfOCl_2$ and H_2SO_4(aq) via spin coating. The solid acid is heated sufficiently to produce a structurally rigid film 1212, such as by heating at about 50 °C for about 2 minutes. In the printing mode of operation, the substrate 1210 can be placed on a heated platen (about 25 – 300 °C), and an ink containing an oxide precursor 1214, e.g., copper formate, can be applied in a desired pattern by delivery through an ink-jet head or by bringing the substrate 1210 into contact with a template containing the precursor 1214. The template comprises a portion of a microcontact, letterpress, or gravure printer. Under heated conditions (greater than about 250 °C), the precursor 1214 decomposes to an oxide, subsequently reacting and interdiffusing with the solid acid, forming a product 1216 that can readily be washed or etched to reveal a pattern 1218. The oxide precursor also may be replaced by an ink suspension or paste containing fine oxide micro- or nanoparticles. Application of the fine particles with or without heating results in a direct reaction to form a product that can be etched to reveal a pattern.

An alternate embodiment is shown in FIG. 13 for producing a patterned oxide on a selected substrate 1310. The initial step involves depositing a solid acid 1312 or base onto the substrate. The oxide precursor 1314 is then applied as a

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blanket coat via spin coating, printing, chemical vapor, or physical vapor deposition. A pattern of activated precursor 1316 is then formed by exposure to an energy source, such as light, via a photomask. Suitable light sources include an unfiltered deuterium lamp or a light source producing light at 193 nm, among others. Alternatively, a pattern of activated precursor 1316 is formed by directly writing with a focused laser or electron beam. If necessary, the activated and patterned structure 1316 can then be heated to a temperature from about 125 °C to about 350 °C to promote interdiffusion of the two layers. The exposed areas can then be etched to produce the desired pattern 1318. A procedure to improve exposure sensitivity involves using a very thin layer (about 2 nm) of oxide precursor on the solid acid. The precursor layer is then covered with a layer of an oxide that is deposited via any suitable technique, such as chemical or physical vapor deposition or by solution casting of oxide nanoparticles. The layers interdiffuse following exposure of the thin layer of precursor.

The processes described above correlate to a positive resist technology. It is also possible to select solid acids/bases and precursors that will produce insoluble products. These products can be used to produce positive images in at least two ways. In one embodiment, the two layers completely interdiffuse to form a single insoluble layer. Following printing or exposure and development, the soluble portions of the film are then washed or etched to reveal a positive pattern. In an alternative approach, interdiffusion occurs only at the interface between the precursor and the solid acid/base to produce a thin, insoluble barrier layer. This barrier layer is then used to control the etching of the film stack to produce a positive image. The barrier layer is photosensitive. Prior to light exposure, it prevents reaction between the precursor and solid acid/base layers that would otherwise readily interdiffuse on contact. Once the barrier layer is photosensitized, it becomes a reactive oxide. The barrier is "broken," and the top layer can then interdiffuse with the lower layer.

Next-generation patterning, whether based on photo or imprinting, uses masks or templates, typically fabricated by electron-beam lithography. Many of these templates or masks are being fabricated with the hard mask HSQ (hydrogen silsesquioxane). HSQ masks are widely used for fabricating a variety of electronic,

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data storage, and microelectromechanical devices. HSQ is also under development as a hard master/template for imprint lithography.

Masks or templates can be fabricated using the films described herein in a single layer process as shown in FIG. 14. The first step of the process involves depositing a thin film (from about 1 nm to about 100 nm) of an inorganic precursor 1410 onto a substrate 1412. The inorganic precursor1410 may be a solid acid or base, e.g., hydrated sulfate, phosphate, nitrate, silicate, aluminate, borate, or mixtures thereof, containing one or more of the metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu in combination with peroxide or similar coordinating anion. In addition the solid acid/base and peroxide mixture can contain one or more of NH_3, OH, F, Cl, Br, I. The solid acid/base is preferably deposited via spin coating, liquid misting, or printing; physical and vapor deposition are additional options. As one example, the solid acid can be deposited from an aqueous solution of $HfOCl_2$ H_2SO_4(aq), and H_2O_2(aq) via spin coating. The solid acid is heated sufficiently, such as to a temperature of from about 50 °C to about 125 °C, and for a period of time from about 10 seconds to about 10 minutes to produce a structurally rigid film. The film is then exposed through a photomask or via a defined laser or electron beam to induce condensation in the exposed areas. The solubility of exposed areas 1414 decreases relative to unexposed regions, so the unexposed regions can be selectively etched in acid or base. Examples of acids or bases that can be used include hydrochloric acid, sulfuric acid, hydroxgen peroxide, sodium hydroxide, and tetramethyl ammonium hydroxide, among others. Typically, the concentration of the acids or bases used is within the range of about 0.1 M to about 1 M. The film is then developed in aqueous acid or base to etch the unexposed regions following an optional thermal cure at a temperature greater than about 100 °C. This process produces a negative-tone image in the film. By prehcating the applied film to higher temperatures prior to field exposures, differential etching rates can be induced to realizc positive-tone images. FIG. 15 demonstrates differential etching rates for thermally pre-treated, single-layer film. The graph demonstrates that thermal treatment affects etching rates such that exposed regions etch faster than unexposed regions following an initial time.

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In another embodiment, a HafSOx film is treated with a mixture of sodium hydroxide and hydrogen peroxide, resulting in anion exchange and formation of a $M(OH)_x/H_2O_2$ film. Alternatively, a previously prepared $M(OH)_x$ film may be soaked in hydrogen peroxide to form a $M(OH)_x/H_2O_2$ film. The resulting $M(OH)_x/H_2O_2$ film is then patterned by exposure to light or an electron beam. These techniques provide a means for directly patterning simple of complex MO_x films without a polymer resist. For example, HfO_2 films may be directly patterned for use as high k dielectrics in Si CMOS circuits and printed electronics applications. In another example, a patterned TiO_2 film can be produced from a $Ti(OH)_x/H_2O_2$ film formed by solution deposition of $Ti(OH)_4$ in H_2O_2.

These methods substantially eliminate diffusion used in two-layer embodiments, lower exposure doses, and improve line-edge roughness and critical dimensions. FIG. 16 is an AFM (atomic force microscope) image of a HafSOx film patterned via a single-layer, negative tone process with an electron beam at dose levels ranging from greater than 0 $\mu C/cm^2$ to at least 400 $\mu C/cm^2$. The nanometer scale to the right of the image indicates the height of the features etched into the film. As shown in FIG. 16, features have been written via electron-beam exposure at dose levels as low as 2 $\mu C/cm^2$. This dose level is comparable to the best known chemically amplified polymer resists and 1000 times lower than that previously demonstrated for an inorganic resist. Features can be produced with a resolution of less than about 20 nm. In addition, the films demonstrate structural integrity (e.g., smooth, dense, pinhole-free) to less than 3 nm, nearly an order of magnitude smaller than that demonstrated for HSQ.

The film application, heating, and etching steps associated with a polymer resist, as well as the vacuum and high-temperature processing steps of the inorganic material, have been eliminated in the patterning process. The resulting patterned film could be a functional component of an electronic device, a hard mask for subsequent patterning of the underlying substrate, or a template for imprinting. Except for the electron-beam exposure, all processing is conducted in a normal environment in air. Considering the elimination of several processing steps, the disclosed technique provides a new method to improve device production yields and lower fabrication costs. Relying on the exclusive use of aqueous chemistries, the

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process is also environmentally green, and washed products can be completely recovered and recycled. The technique has applications to many advancing technologies. Its use is not restricted only to the systems described herein.

B. Hot Embossing Lithography

Hot embossing lithography is another method for producing patterns in HafSOx, ZircSOx and related materials. This process, illustrated schematically in FIG. 17, most commonly has been applied to creating patterns with organic polymers. The semi-solid form of HafSOx and related compositions provides an opportunity to pattern inorganic materials having much higher mechanical strength, chemical stability, and unique electrical and optical properties relative to organic polymers.

With reference to FIG. 17, HafSOx or related inorganic material, instead of an organic polymer, is solution deposited, such as by spin coating or inkjet printing, on a suitable substrate 1712 to form HafSOx layer 1714. Substrate 1712 and HafSOx layer 1714 define laminate structure 1710. A stamp 1716 with unit features of desired size scale, such as nanometer, micrometer or millimeter size scale, is pressed into the semi-solid HafSOx or related film layer 1714 to form stamped layer 1718. Stamped layer 1718 and substrate 1712 are then heated to harden the HafSOx. The stamp is then removed to define a patterned HafSOx material in patterned laminate structure 1720.

C. Measuring Device

The chemistry developed for the bilayer positive resist technology noted above also can be used to fabricate a physical ruler, as illustrated in FIG. 18, for use in standardizing measurements in suitable fields, such as electron microscopy. In this application, a nanolaminate 1810 of alternating acid-soluble layers 1812 and acid-insoluble layers 1814 is deposited. The acid soluble layers are formed by solution deposition of a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy

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phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8. Typically this layer is doped with copper. The acid-insoluble layers are formed by solution deposition of a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8.

The widths of the layers 1812 and 1814 are accurately determined, such as by using X-ray reflectivity. The acid-soluble layers 1812 are then etched to reveal a finger-type pattern 1820 that can be used as a secondary reference in accurately measuring objects in an electron microscope.

D. Corrosion Barriers

The precursor liquid can be coated onto a suitable substrate, such as a metal or alloy or ceramic, to form a corrosion barrier. In addition, the liquid can be drawn into fibers, placed in a mold, or used alone. The liquid is converted into solid, stable form by any suitable process, including hydrolysis, annealing, or pyrolysis in air. Typically, this requires heating to temperatures, and for a period of time, effective to achieve the desired results, such as a temperature normally above 100 °C for at least a few seconds, more typically at least a few minutes.

Because of the atomically dense nature of the films, potential applications include, but are not limited to, thermal, corrosion and oxidation protection for metals and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based

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ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal and ceramic-based systems, fibers for composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, catalyst supports, as well as many others. The ability to laminate the films provides an opportunity to randomize the location of defects in one layer relative to another, providing enhanced corrosion protection.

E. Optical Coatings

The precursor liquids can be coated as individual layers and in multilayer formats onto suitable optical substrates to produce antireflection coatings, dielectric mirrors, X-ray mirrors, interference filters, waveguides, planar coatings, and scratch-resistant surfaces. Multilayer periodicity is achieved by alternately depositing at least two material compositions. Single layer periodicity can be achieved by etching, as described for photolithography processes. The amorphous nature, sharp interfaces between layers, and abilities to control dielectric constants provides a process for realizing performance near theoretical limits.

In multilayer or single layer configurations, which have been selectively deposited or etched, the periodic structure is appropriate for diffracting applications. Combinations of single or multiple materials and/or voids may define the structures. The use of void space allows for great contrast of physical properties within given structures. Functional characteristics may be enhanced or realized by the use of void space. Optical gratings may be similarly defined.

Because substantially smooth surface films can be deposited according to embodiments of the method disclosed herein, films may be used to planarize substrate layers such as metal, ceramics, and plastics that exhibit greater degrees of roughness.

F. Luminescent Films

A material may absorb energy and emit photons in a number of luminescent processes. The luminescent events may involve only the predominant phase (or host), or also may include added elements. A single material may serve as host for numerous luminescent additives. Many of the disclosed film compositions are

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visibly transparent with transparency potentially extending into the ultraviolet portion of the spectrum. These materials potentially function well as luminescent host materials. These materials can be selectively doped with common luminescent ions, including by way of example, and without limitation, Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof, to yield light-emitting films of interest for lighting and display applications.

G. Printed Electronics

Manufacturers are seeking new, efficient fabrication methods that eliminate the limitations of conventional vapor deposition and lithographic processing. Printing and related maskless techniques are widely regarded as paths forward for realizing advancement in manufacturing efficiencies for back-plane electronics.

The disclosed solution-processed thin films exhibit morphological and device-functional characteristics similar to those achieved by the most advanced vapor-phase processing methods. Solutions of the disclosed compositions can be imprinted, such as with microcontact, gravure, an inkjet printer or other suitable means. The resulting imprinted solutions can be used to fabricate stable inorganic transistor arrays exhibiting device mobilities of about 10 cm^2/Vs with dielectric leakage current densities less than about 20 nA/cm^2. Dielectric and semiconductor inks also can be printed onto glass substrates to produce transistor arrays having mobility of about 1 cm^2/Vs and dielectric leakage currents less than about 100 nA/cm^2. MIM capacitor arrays can be fabricated with relative dielectric constants greater than about 5 and leakage current densities less than about 50 nA/cm^2.

IV. EXAMPLES

The following examples are provided to exemplify particular features of working and/or hypothetical embodiments of the present invention. A person of ordinary skill in the art will appreciate that the scope of the present invention is not limited to the particular features stated in such examples.

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Example 1

This example describes a general method that has been used to prepare solutions as sources for bulk precipitates or for use as thin film precursors. The following reagents were used: $HfOCl_2 \cdot 8H_2O$ (Alfa Aesar, 99+% excluding 1.5%Zr); $ZrOCl_2 \cdot 8H_2O$ (Wah Chang spectrographic grade); $La_2(SO_4)_3$ (Alfa Aesar, 99.9%); $La(NO_3)_3 \cdot 6H_2O$ (Johnson Matthey, 99.9%); $Ce_2(SO_4)_3 \cdot 8H_2O$ (Strem, 99%); CaO (Alfa Aesar, 99.95%); $(NH_4)_2SO_4$ (Mallinkrodt AR); H_2SO_4(aq) (EM Science, GR ACS, 95-98%); and NH_3(aq) (EM Science, GR ACS, 28-30%). All solutions were prepared by combining $HfOCl_2$ or $ZrOCl_2$ with $La_2(SO_4)_3$, $Ce_2(SO_4)_3$, or CaO as necessary for a total metal concentration of about 0.8 M, followed by addition of sulfate solution, for a total metal concentration of about 0.5 M. These solutions were directly used for heat-induced precipitation and spin-coating dielectric films. Additional modifications were made as necessary to serve as precursors for hydroxide precipitation reactions or nanolaminate depositions.

Example 2

This example describes a general method that has been used for bulk precipitation from solutions made according to Example 1. Precipitation was induced by immersing tubes of solution in a boiling water bath for 40 minutes. For hydroxide-induced precipitation, $HfOCl_2$ and $La_2(SO_4)_3$ were mixed as 23% La (metal percent), followed by addition of solutions of $La(NO_3)_3$ and $(NH_4)_2SO_4$ to provide a hafnium concentration ([Hf]) of about 0.39 M, a lanthanum concentration ([La]) of about 0.18 M, and a sulfate ([SO_4]) concentration of about 0.42 M. 1.9 mole equivalents (relative to total metals) of saturated NH_3(aq) were then added quickly and the resulting mixture stirred for 1 minute. All precipitates were separated from the supernatant by paper filtration with suction, including several rinses with de-ionized water. The filtrates were dried at room temperature for 1 day. Samples were subsequently heated in alumina crucibles in ambient air at temperatures from about 100 °C to about 1,500 °C for about 1 to about 4 hours. XRD data was collected with a Siemens D5000 diffractometer, utilizing Cu Kα radiation. Thermogravimetric data were collected with a Shimadzu TGA-50 by heating samples (10–20 mg) in a Pt crucible under flowing N_2(g), typically at a rate

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of 10 °C minute^{-1}, and holding for 15 minutes at the highest temperature. Inductively coupled plasma atomic emission spectroscopy (ICPAES) was conducted with a Jobin Yvon JY2000 analysis setup. Samples were dissolved in digestion bombs at 200 °C for a few hours and diluted to measurable levels.

Example 3

This example describes a general method that has been used for deposition of thins films using solutions made according to Example 1. Thin-films of HafSOx, ZircSOx, and derivatives with added La, Ce, or Ca, were deposited on Si substrates by spin-coating at 3,000 rpm for 30 seconds, followed by immediate hotplate polymerization at 135° C for 1.5–2 minutes (additional heating on a 325 °C oven surface for 15 seconds to about 2 minutes may be required for certain derivatives). This process was repeated until desired deposited film thicknesses were obtained. A final oven anneal at 325 °C for 5–10 minutes was used.

Precursors for nanolaminate films were prepared by adding H_2SO_4 to $HfOCl_2$ or $ZrOCl_2$ as 46% sulfate relative to metal. Solutions were diluted to a metal concentration of 0.03–0.13 M. Alternating layers of HafSOx and ZircSOx were deposited in the same fashion as described for dielectric films.

The silicon substrates had a surface of SiO_2 or Ta metal. A 500-nanometer Ta surface was used for dielectric testing. A 200-nanometer SiO_2 surface was used for all other purposes. The surfaces were prepared for deposition by ultrasonic eleaning in (Decon Labs, Contrad 70) solution at 45 °C for 45 minutes, then rinsing the surfaces thoroughly with Millipore water before deposition.

XRD data were collected with a Rigaku RAPID diffractometer, employing Cu Kα radiation generated from a rotating anode at 50 kV and 270 mA. The incident beam angle was 7.6°, while the diffracted beam was collected with an image plate. XRR data were collected with Cu Kα radiation. Low angle reflections up to 10° (2θ) were collected at 0.005° steps. Transmission FTIR data were collected with a Nicolet 5PC spectrometer, with an uncoated substrate as reference. EMPA was collected.

MIM capacitor structures were completed by thermally evaporating circular contacts of Al (1.2 mm diameter) on deposited dielectrics. Parameters of dielectric

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constant and loss tangent were obtained. Bottom-gate transistor structures also were fabricated by sputtering inorganic channel materials without active heating. ZTO-channel devices were subsequently heated to 325 °C for 1 hour. Aluminum source and drain contacts were thermally evaporated. Transistor characterization was performed.

Example 4

This example describes a general method for producing smooth, dense, and pinhole-free ultra-thin nanolaminate films as thin as about 2 nm. Precursor solutions containing $HfOCl_2 \cdot 8H_2O$ or $ZrOCl_2 \cdot 8H_2O$, H_2O_2 (30%) and H_2SO_4(aq) were prepared as described in U.S. Patent Publication No. 2005/0242330 A1. The precursor solutions contained a metal ion concentration of about 0.05 M to 0.4 M with 70% H_2O_2 and 50% sulfate relative to metal. The difference in metal ion concentrations allowed for thickness per coat variation from 3 nm to 25 nm. Thin films were deposited on silica substrates with thermally grown SiO_2. Substrates were cleaned by using an ultrasonic bath with Contrad-70 solution at 45 °C for 60 minutes followed by a rinse with deionized water. Films were deposited by using a spin coater with a spin rate of 3000 rpm for 30 seconds followed by hotplate polymerization at 125 °C for 1-2 minutes. Spin-coating and polymerization steps were repeated until the desired thickness was reached. After the desired thickness had been reached, some films were heated to crystallization temperature. Other films were first treated in a 0.1 M-0.5 M NaOH bath for 1-2 minutes, then rinsed in a deionized water bath for 1-2 minutes before the thermal treatment.

Thin-film characterization using X-ray diffraction (XRD) analysis was performed on a Rigaku R-axis rapid with Cu Kα radiation. Atomic force microscopy (AFM) measurements were performed using a Digital Instruments Nanoscope III Mulitmode AFM operated in contact mode with a Veeco NP-20 SiN probe and a scan frequency of 1.15 Hz. X-ray reflectivity (XRR) measurements were performed using a Bruker Discover D8 and used to determine surface and interfacial roughness of the films. Compositional analyses were acquired on a Cameca SX-50 electron microprobe equipped with 4 tunable wavelength dispersive spectrometers. Accelerating voltages of 12, 16 and 22 kV were used and averaged

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over 5 points to monitor O, Cl, Na, S, and Si Kα intensities and Zr and Hf Lα intensities. Standards used for analysis were MgO, Hf, Zr, FeS_2 (pyrite), $Ca_5(PO_4)_3Cl$ (apatite), Si, and Si_3AlNaO_8 (albite). Corrections to the raw intensity were made by using Probe for Windows automation and analysis package. The StrataGEM compositional analysis software package was used for thin film geometry corrections by comparing experimental K-ratios to simulated values.

Amorphous, atomically flat, dense, pinhole-free thin films were deposited via spin coating for the as-deposited and exchanged films. FIG. 19 is an AFM image of an unexchanged HafSOx film with a roughness of about 0.1 nm. FIG. 20 is a TEM image of an HfO_2 film following ion exchange of HafSOx and thermal treatment at 850 °C. Unexchanged films remained smooth and amorphous up to 600 °C for Zr and 650 °C for Hf. However, after heating above these temperatures, films crystallized and became rough forming volcano-like features at the surface. FIG. 21 is an AFM image of a HfO_2 film deposited on silica. The HfO_2 film was formed by thermal decomposition of $HafSO_x$. The resulting film had a roughness of about 5 nm, resulting in volcano-like peaks. These features were most likely caused by the loss of SO_3. This was supported by thermal gravimetric analysis of Hf sulfate powder, where sulfate decomposition (SO_3 (g) → SO_2 (g) and ½ O_2 (g)) occurs above 700 °C.

To eliminate the volcano effects, films were treated in a 0.1-0.5M NaOH(aq) bath for 1-2 minutes to remove the SO_4^{2-} and Cl^- anions from the film before heating. NaOH previously has been shown to effectively exchange hydroxy anions for other anions in zirconium salts. The NaOH treatment caused a thickness reduction of 40-45% (giving layer thickness of 2-15 nm), but the treatment had little effect on the smoothness (~1Å) or amorphous nature of the films when heated below 500 °C or 550 °C for zirconia and hafnia, respectively.

FIG. 22 is an AFM image of a HafSOx film deposited on silica, subsequently treated with 0.1M NaOH and heated to 450 °C for 10 minutes. The resulting film had a roughness of approximately 0.1 nm. Films heated above these temperatures crystallized, yet remained smooth at temperatures up to 850 °C.

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FIG. 23 shows a HfO_2 film deposited on silica, subsequently treated with 0.1 M NaOH and heated to 850 °C for 10 minutes. The resulting crystallized film remained smooth with a roughness of about 0.2 nm.

A drop in crystallization temperature was seen in the X-ray diffraction plots (FIGS. 24-27). In FIGS. 24-27, the substrate peaks have been removed with software. The *'s represent the major tetragonal phase peaks. FIG. 24 is an XRD plot of the untreated HfO_2 film crystallized as a mixture of tetragonal and monoclinic phases at 700 °C. The HfO_2 plot is a reference plot for the monoclinic phase. In contrast, FIG. 25 is an XRD plot of the 0.1 M NaOH-treated hafnia film crystallized only in the monoclinic phase at 550 °C. The HfO_2 plot is a reference plot for the monoclinic phase. FIG. 26 is an XRD plot of untreated zirconia films crystallized in a mixed monoclinic and tetragonal phase at 650 °C. The ZrO_2 plot is a reference plot for the monoclinic phase. As seen in FIG. 27, the 0.13 M NaOH-treated zirconia films crystallized only in the tetragonal phase at 500 °C. Upon further heating, films developed both monoclinic and tetragonal phases. The tetragonal phases of HfO_2 and ZrO_2 have been observed in previous thin film studies. The lower crystallization temperature, crystallization and loss of thickness indicated that the NaOH treatment removed anions (SO_4^{2-} and Cl^-) from the thin films.

Electron probe microanalysis (EPMA) of a film deposited from the 0.4 M Hf solution and heated to 350 °C for 5 minutes gave a film with composition $HfO_{1.32}(SO_4)_{0.61}Cl_{0.15}$. The chlorine in the film was a result of kinetic trapping as a consequence of the rapid thermal dehydration. Films that were treated in the NaOH(aq) bath did not have measurable sulfur levels (less than 0.01 atomic percent), and less than 0.3 atomic percent Cl was observed. This confirmed that the sulfur and chlorine were both removed from the films in the NaOH(aq) bath. EPMA also verified that the residual sodium left in the film after the treatment was less than 0.3 atomic percent.

Example 5

In a specific embodiment of the approach described above, hydrated indium and gallium nitrate salts ($In(NO_3)_3 \cdot 0.5H_2O$ and $Ga(NO_3)_3 \cdot 9.5H_2O$) were dissolved in

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methanol (CH_3OH). Final concentrations were [In] = 0.288 M, [Ga] = 0.170 M. Zinc powder was then added to the solution, and the flask sealed. The final concentration of zinc was 0.2 M. Reacting over a period of 1-7 days, the powder was slowly oxidized and dissolved to bring the total metal ion concentration to 0.658 M. The methanolic solution was exposed to air, and the methanol was allowed to evaporate at room temperature. The solid residue remaining in the solution was then dissolved in H_2O to a total metal concentration of 0.395 M. This precursor solution was spin-coated on a SiO_2 substrate with a conductive back contact and annealed to 450 °C for 1-4 hours. Following annealing, a transparent, amorphous $InGa_{0.6}Zn_{0.7}O_{3.15}$ semiconductor film was obtained as shown in the SEM image of FIG. 28. Aluminum source and drain contacts were thermally evaporated onto the oxide semiconductor film through a shadow mask to produce a thin film transistor (TFT). Field effect mobility for these TFTs was shown to exceed 8 $cm^2 V^{-1} s^{-1}$.

Example 6

This example describes two general methods of bilayer inorganic lithographic processing. In one working embodiment, a HafSOx film with a thickness from about 30 nm to about 60 nm was solution deposited onto a SiO_2/Si substrate. The substrate was placed directly onto a hot-plate set at about 50 °C and heated to impart structural integrity to the film. The resulting film was acid insoluble. The substrate was then placed on a heated platen (about 50 °C to 200 °C) of an ink-jet printer, where copper formate lines were printed onto the substrate via a thermal ink-jet head. Copper formate decomposed and diffused into the HafSOx film on heating, rendering the film soluble. Following a rinse in water, additional heating to about 300 °C, and development in dilute acid, the drawn lines were clearly evident as shown in FIG. 29.

In another working embodiment, patterns also were produced via photolithography. Exposure of a $HfO_{2-x}(SO_4)_x$ bilayer film with deep UV light using an unfiltered deuterium lamp promoted copper formate decomposition for subsequent interdiffusion and development of the pattern shown in FIG. 30. Feature sizes were reduced to about 22 nm with electron beam writing. The interdiffusion process can be spatially controlled via electron-beam energies to draw patterns and

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objects on the nanoscale. Highly resolved patterns were produced at charge dose levels near 150 $\mu C/cm^2$, representing a sensitivity similar to that of many polymer resists. FIGS. 31 and 32 are two patterns produced by electron-beam writing at a dose of level of about 200 $\mu C/cm^2$. In FIG. 31, the line spacing is 500 nm as measured by an electron microscope.

Example 7

This example describes general methods for patterning a single-layer inorganic film. A single inorganic film containing peroxide or related coordinating species is spin-cast, liquid misted, or ink-jet printed onto an appropriate substrate. The film is heated at modest temperatures of less than 100°C to provide structural integrity to the film. The film is then exposed through a photomask to high-energy light, a maskless pattern via spatial light modulation, a defined laser beam, or electron beam to define a pattern or other preferred film features. Two examples of photogryaphically patterned films are shown in FIGS. 33 and 34. FIG. 33 is a patterned $ZrO_{2-x}(SO_4)_x$ film. FIG. 34 is a patterned TiO_2 film. The TiO_2 film was about 15-50 nm thick. It was patterned using an unfiltered deuterium lamp, followed by etching with 0.1-0.2 M HCl for less than 60 seconds. FIGS. 35-37 are $HfO_{2-x}(SO_4)_x$ films patterned by an electron beam. The films were about 30-60 nm thick. They were patterned using an electron beam at a dose level of 200 $\mu C/cm^2$, followed by etching with 5-12 M HCl for about 1-4 minutes.

In view of the many possible embodiments to which the principles of the disclosed invention may be applied, it should be recognized that the illustrated embodiments are only preferred examples of the invention and should not be taken as limiting the scope of the invention. Rather, the scope of the invention is defined by the following claims. We therefore claim as our invention all that comes within the scope and spirit of these claims.

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We claim:

1. A device comprising a thin film or laminate structure comprising at least one hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8.

2. The device according to claim 1 wherein the thin film or laminate has a permittivity value within the range of from about 9 to about 12, a breakdown field up to at least 6 MV cm^{-1}, and a leakage current near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}.

3. The device according to claim 1 where the compound further comprises lanthanum, and has a formula $M_{1-z}La_zO_{2-x-z/2}(SO_4)_x$ (MSOx:La), where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatombic ion charge), and any value for z in a range of from 0.0 to about 3.8.

4. The device according to claim 1 where the compound is HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, or ZircSOx:Ca, the device having leakage current less than 50 nA cm^{-2} and permittivity values of from about 9 to about 12.

5. The device according to claim 1 where the device is a field effect transistor comprising HafSOx:La and/or ZircSOx:La as a gate dielectric and zinc indium oxide and/or zinc tin oxide as channels, the transistor having an on-to-off ratio of greater than 10^6, and gate leakage currents are in the range of pA cm^{-2}.

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6. The device according to claim 1, further comprising an optical substrate where the thin film or laminate structure forms a coating on the optical substrate.

7. The device according to claim 6 where the coating is an antireflective coating and/or the coating is transparent to visible or ultraviolet light.

8. The device according to claim 6 where the optical substrate and coating define a dielectric mirror, an X-ray mirror, an interference filter, a diffractive grating, and/or a waveguide.

9. The optical device according to claim 7 where the coating is selectively doped to provide a doped light-emitting layer having luminescent ions selected from Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof.

10. The device according to claim 1 where the device is a master plate for imprint lithography and the thin film or laminate structure is deposited onto a flexible or glass substrate, the thin film or laminate structure comprises a first layer of HafSOx deposited onto the substrate and a second layer comprising ZircSOx:Cu, and where the laminate structure comprising the first and second layers is patterned by exposure to an energy source.

11. The master plate according to claim 10 where exposure to light or an electron beam through a mask causes the two layers to interdiffuse in exposed areas, thereby rendering previously undoped HafSOx layer soluble, the soluble HafSOx layer being removed to define at least partial printing features of the master plate.

12. A method for making a device, comprising:

providing a thin film or laminate structure, the structure comprising a substrate and one or more layers deposited onto the substrate;

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at least one of the one or more layers comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8; and

exposing the structure to an energy source.

13. The method according to claim 12 where the thin film or laminate structure comprises a substrate, a first layer for patterning, and a second layer comprising the hafnium and/or zirconium oxy hydroxy compound, where the second layer is a positive resist layer, exposure to an energy source converts the resist layer material into a developer-soluble material, and the method further comprises removing resist layer material exposed to the energy source by treating the resist layer with a developer solution to pattern the structure.

14. The method according to claim 12 where the thin film or laminate structure comprises a substrate, a first layer for patterning and a second layer comprising the hafnium and/or zirconium oxy hydroxy compound, where the second layer is a negative resist layer, exposure to an energy source causes the resist layer to polymerize, and the method further comprises patterning the structure by treating the structure with a developer to remove material not exposed to the energy source.

15. The method according to claim 13 where the positive resist comprises a bilayer, where a second layer of the bilayer comprises an acid-soluble Cu-doped zirconium oxide sulfate (ZircSOx:Cu) film deposited on an insoluble hafnium oxide sulfate (HafSOx) film, and where exposure to an energy source comprising light or an electron beam through a mask causes the ZircSOx:Cu film and the HafSOx film to interdiffuse in exposed areas, thereby rendering the HafSOx film soluble.

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16. The method according to claim 12 where the hafnium and/or zirconium oxy hydroxy compound comprises sulfate, and where the sulfate is subsequently removed by ion exchange with an aqueous basic solution, the basic solution comprising a Group I metal hydroxide, soluble Group II metal hydroxide, soluble Group III metal hydroxide, soluble lanthanide hydroxide, ammonium hydroxide, and/or aqueous tertiary amine, or a combination thereof.

17. The method according to claim 12 comprising:

providing a suitable substrate comprising a semiconductor material, a metal, glass, silica, a polymeric material, or combinations thereof;

solution depositing a first HafSOx film onto the substrate;

solution depositing a second ZircSOx:Cu film onto the first film to form a laminate structure;

exposing the laminate structure to an energy source to cause the HafSOx film and the ZircSOx:Cu film to interdiffuse in exposed areas, thereby rendering previously undoped HafSOx film soluble; and

developing the exposed structure to remove HafSOx film.

18. The method according to claim 12 where the thin film or laminate structure comprises a substrate, a first layer of insoluble hafnium oxide sulfate (HafSOx) deposited onto the substrate, and a second layer comprising copper formate deposited onto the first layer, and where the laminate structure comprising the first and second layers is heated to a temperature from about 50 °C to about 200 °C to cause the copper formate to decompose and interdiffuse with the HafSOx layer, thereby producing a soluble product, the soluble product being removed.

19. The method according to claim 12 where the thin film or laminate structure comprises a substrate and a first layer comprising a solid inorganic acid or base, the solid inorganic acid or base comprising a metal having an atomic number in the range of 21-78, the first layer further comprising a peroxide or other coordinating anion, where the first layer is soluble in acid or base, the first layer is

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heated to a temperature from about 50 °C to about 125 °C to produce a structurally rigid film, and exposure to a laser, an electron beam, and/or light through a mask causes exposed areas of the film to become less soluble than unexposed areas, the unexposed areas being removed to define a pattern in the film.

20. The method according to claim 19 where the film is exposed to an electron beam at a dose level of from greater than 0 $\mu C/cm^2$ to at least 400 $\mu C/cm^2$, more typically from about 2 $\mu C/cm^2$ to about 400 $\mu C/cm^2$, to define a pattern in the film.

21. The method according to claim 19 where the patterned film demonstrates structural integrity to less than about 3 nm.

22. The method according to claim 12, where the device includes a micro- or nano-channel array, and where the structure comprises a substrate, a first layer and a second layer, the second layer being a metal oxide layer, the method further comprising:

patterning the structure; and

exposing the structure to an energy source to form a durable material having a desired pattern produced by patterning the structure.

23. The method according to claim 22 further comprising stamping unit features of a desired size scale into a semi-solid hafnium or zirconium compound to form a stamped layer.

24. A device made according to the method of claim 22, the device selected from metal and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal- and ceramic-based systems, fibers for composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, and catalyst supports.

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25. A method for making a device having a corrosion barrier, comprising:

providing a device;

forming at least one corrosion barrier on the device comprising a metal oxide layer comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8; and

exposing the compound to an energy source to form the corrosion barrier.

26. A method for forming fibers, comprising:

providing a composition comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8;

forming a solution comprising the compound;

drawing the solution into fibers; and

converting the fibers into solid, stable fibers.

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27. A method for making a metal oxide film where the film comprises at least two metals, the method comprising:

making a solution comprising dissolving one or more soluble salts consisting essentially of a metal cation and one or more anions in a non-complexing, non-aqueous polar solvent, where at least one of the metal cations has a formal charge greater than 3^+ and the concentration of metal cations with a formal charge greater than 3^+ exceeds 50 mol% of the metal cations in the metal oxide film, and where the solvent has a boiling point less than about 150 °C;

raising the pH of the solution, where raising the pH comprises adding a basic aqueous solution, adding a small amount of a soluble basic oxide, adding a gaseous compound capable of forming a basic aqueous solution, adding an electropositive metal which may consume protons and is incorporated into the film, adding an aqueous or gaseous oxidizing agent which consumes protons or decomposes counter ions but is not incorporated into the film, or any combination thereof;

producing a solid by evaporating the non-aqueous solvent;

dissolving the solid in water;

depositing the dissolved solid onto a substrate to form a patterned or blanket liquid film; and

thermally curing the film.

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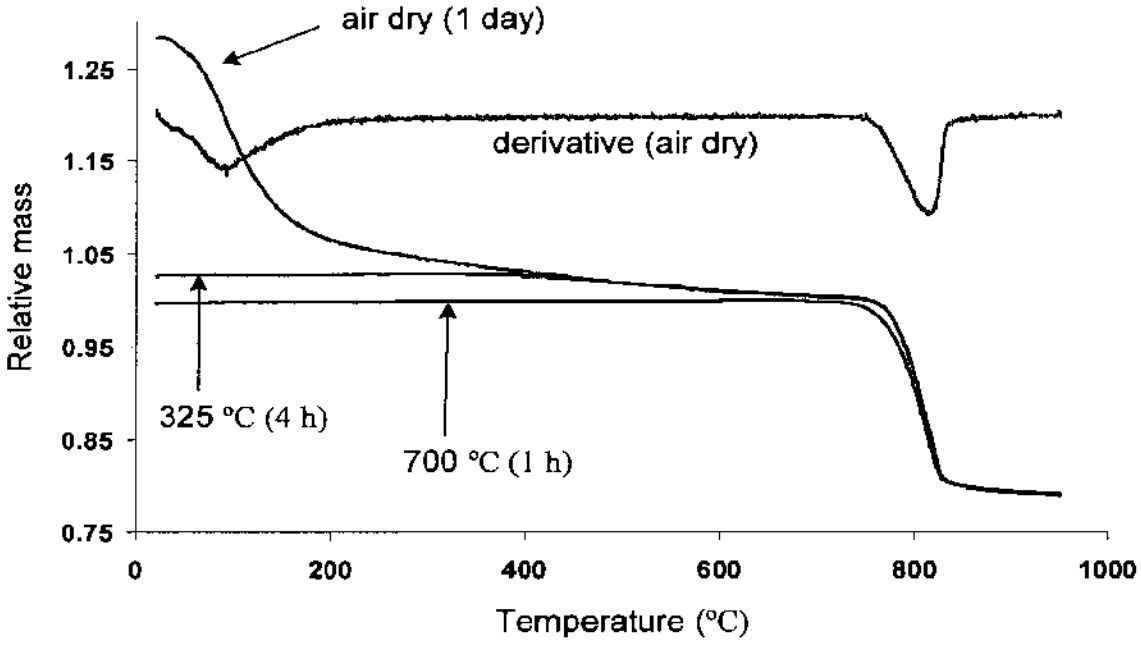


FIG. 1

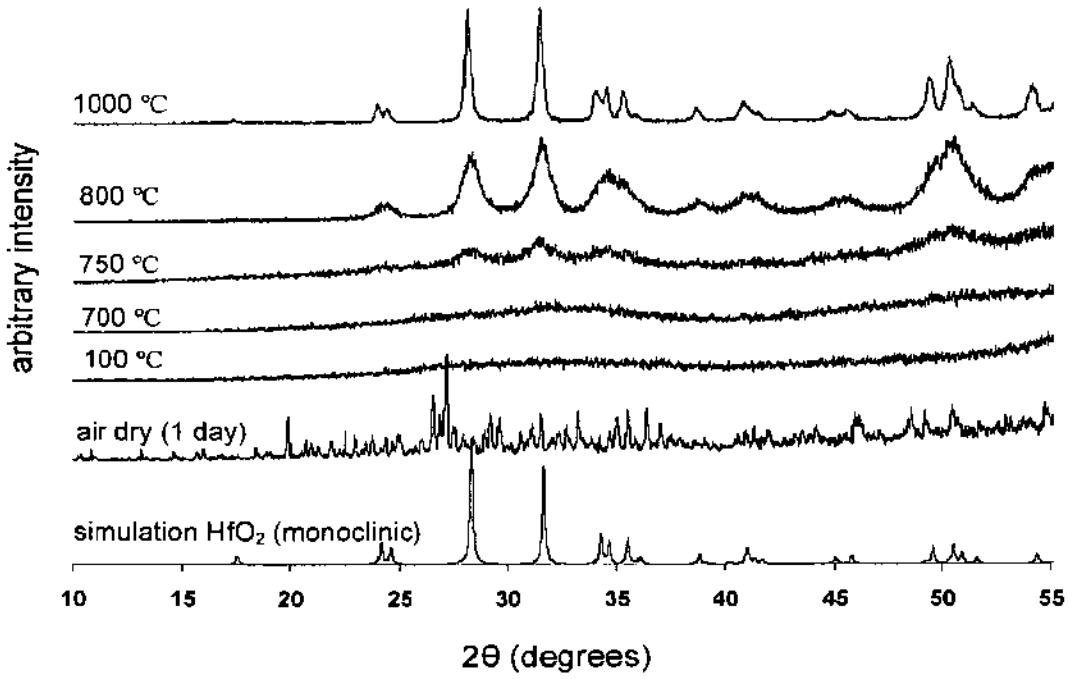


FIG. 2

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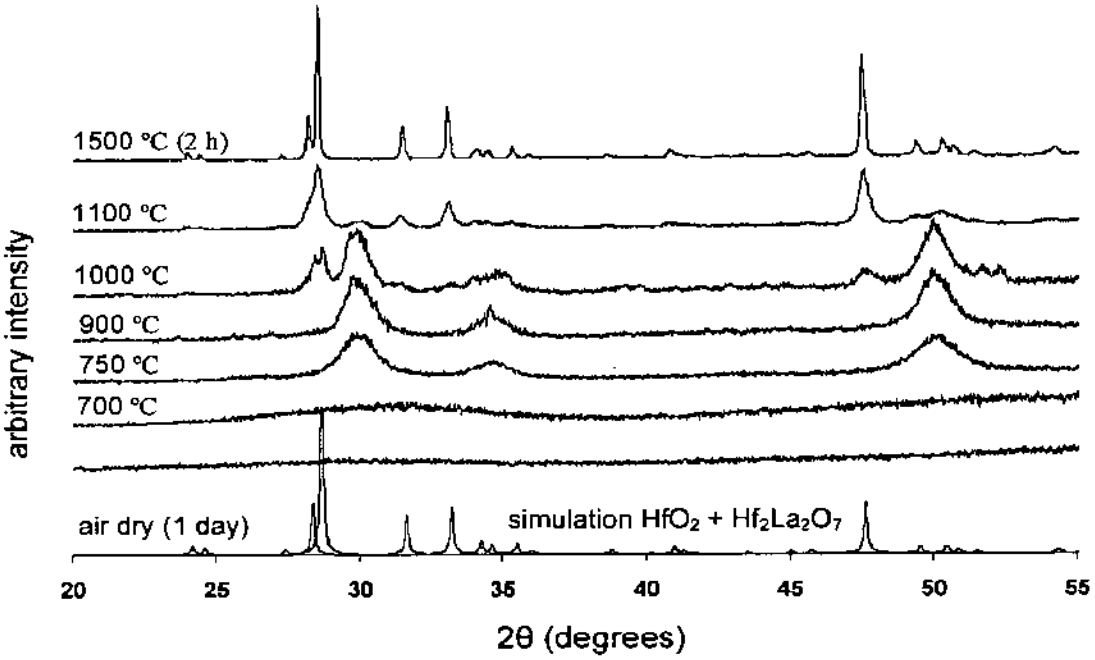


FIG. 3

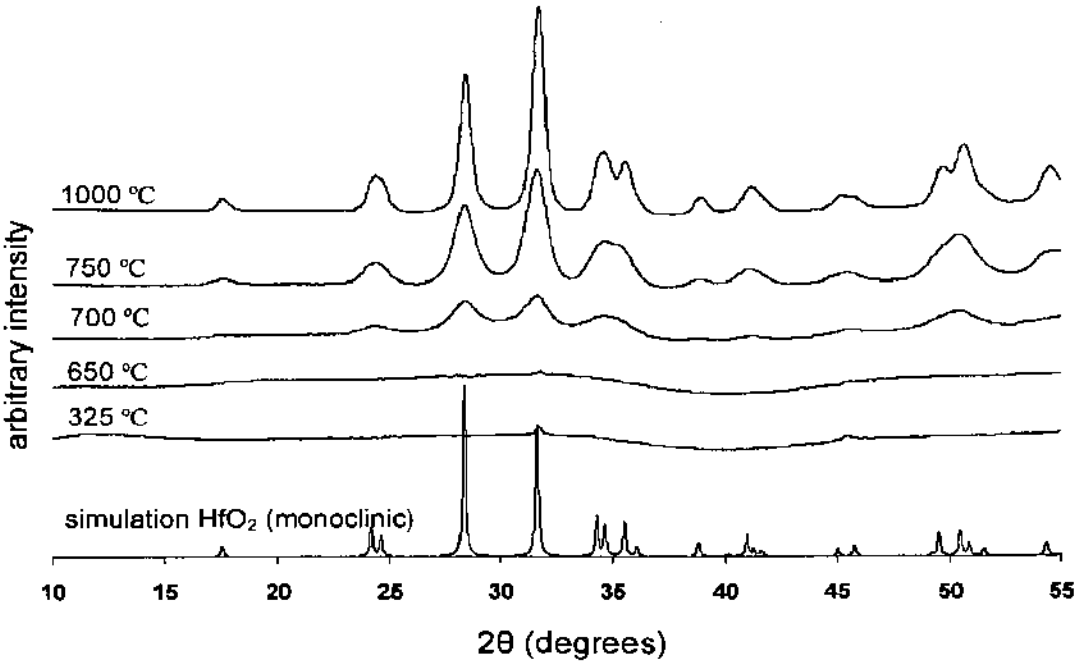


FIG. 4

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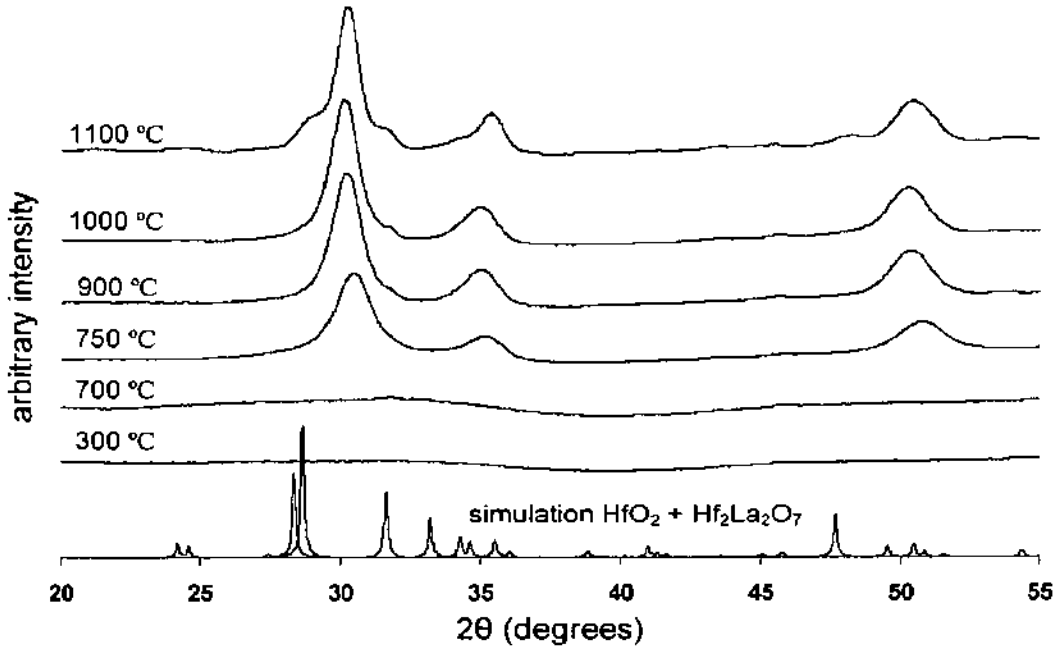


FIG. 5

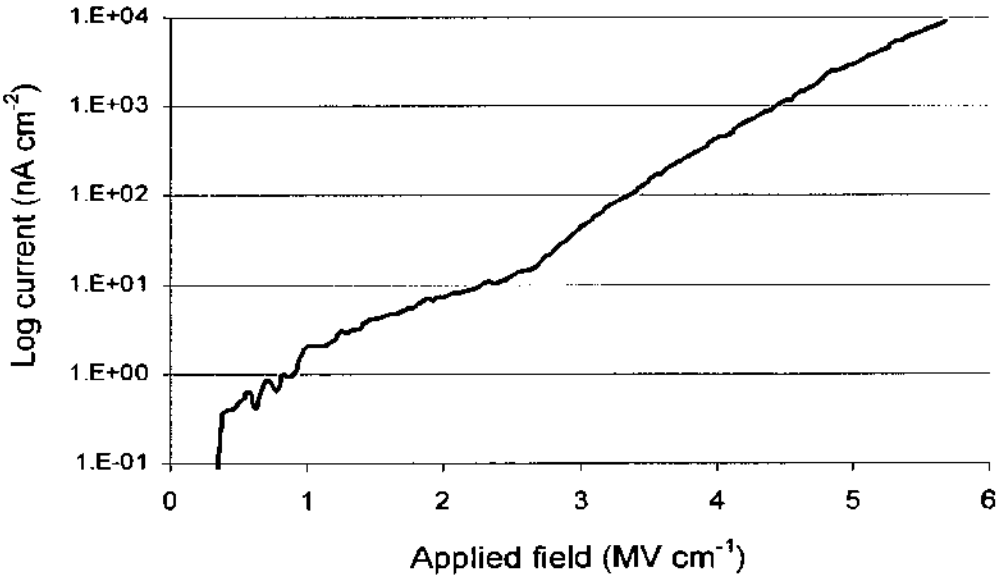


FIG. 6

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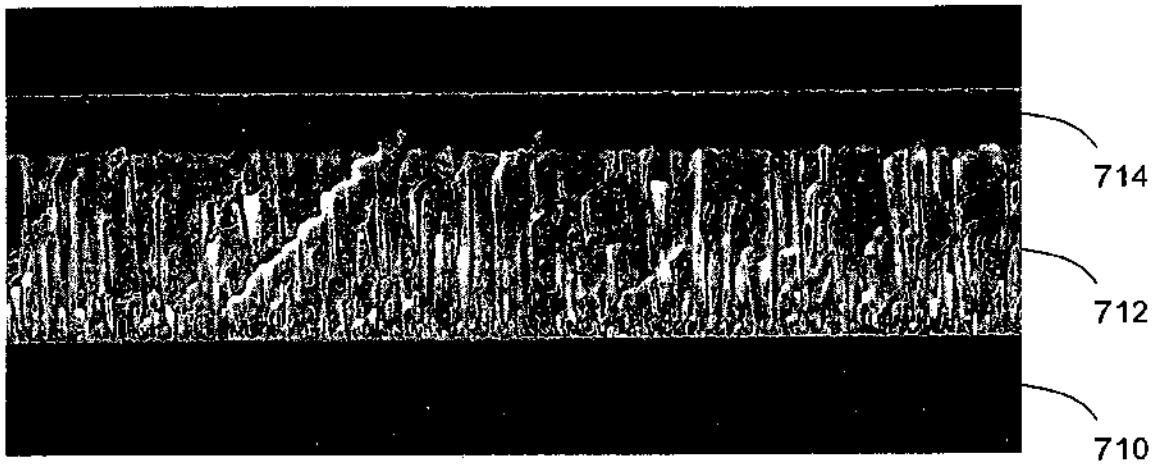


FIG. 7

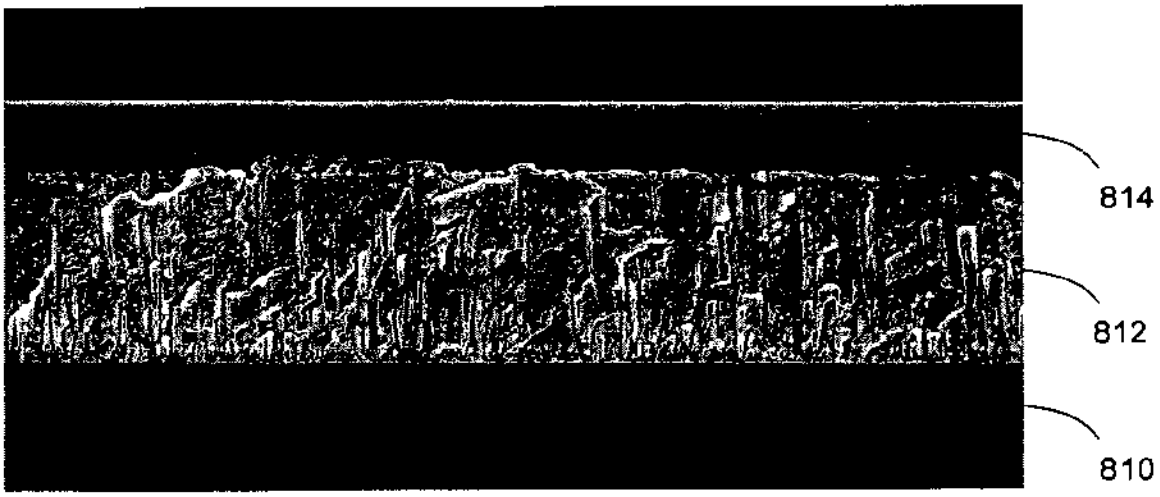


FIG. 8

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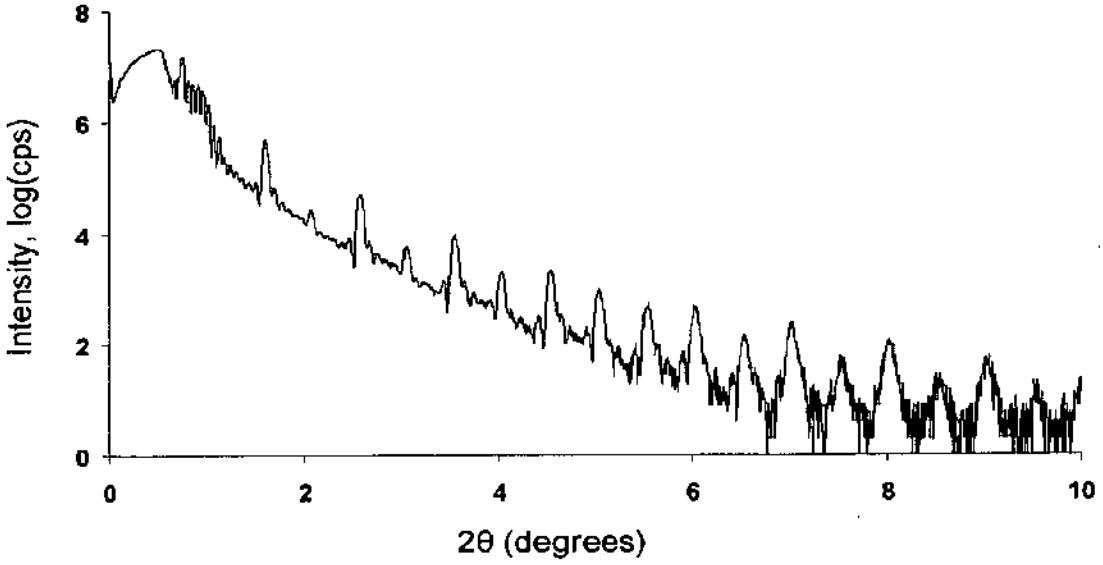


FIG. 9

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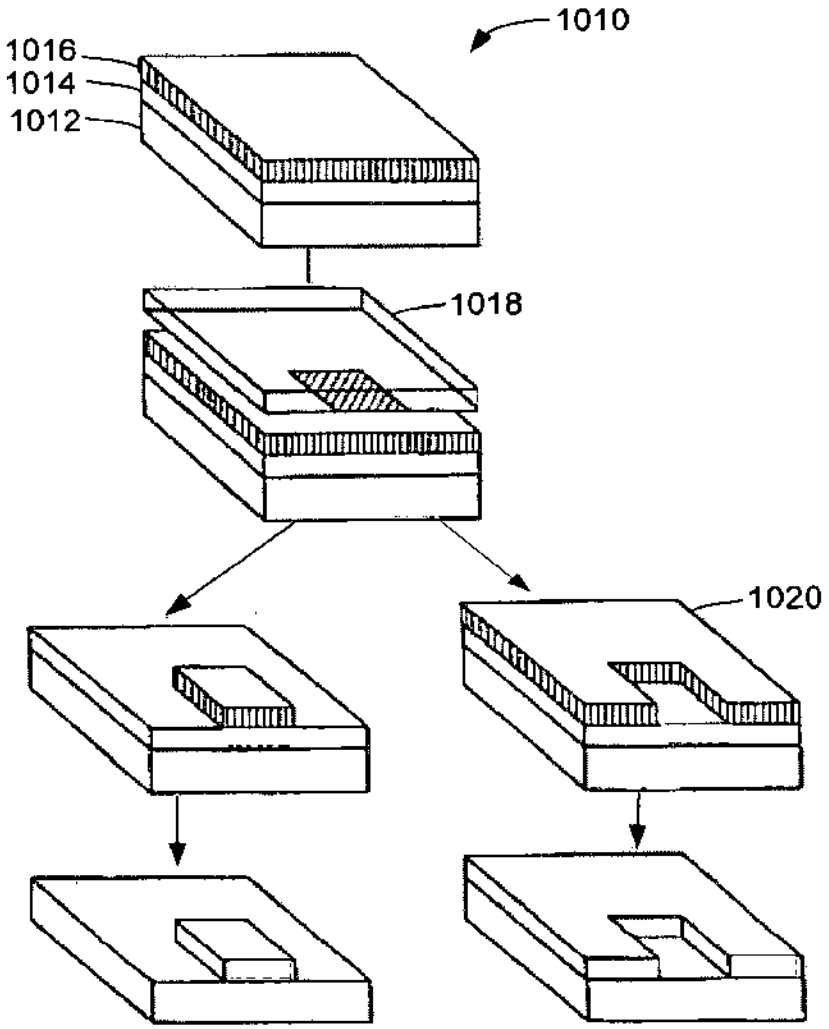


FIG. 10

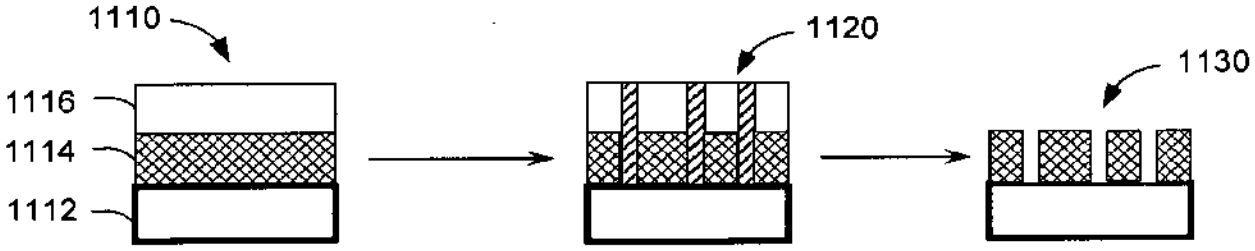


FIG. 11

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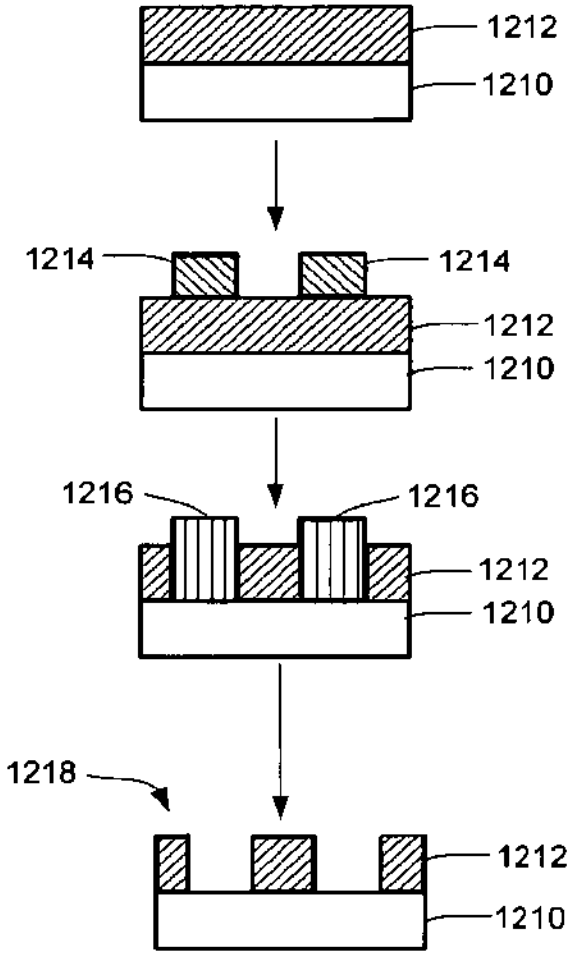


FIG. 12

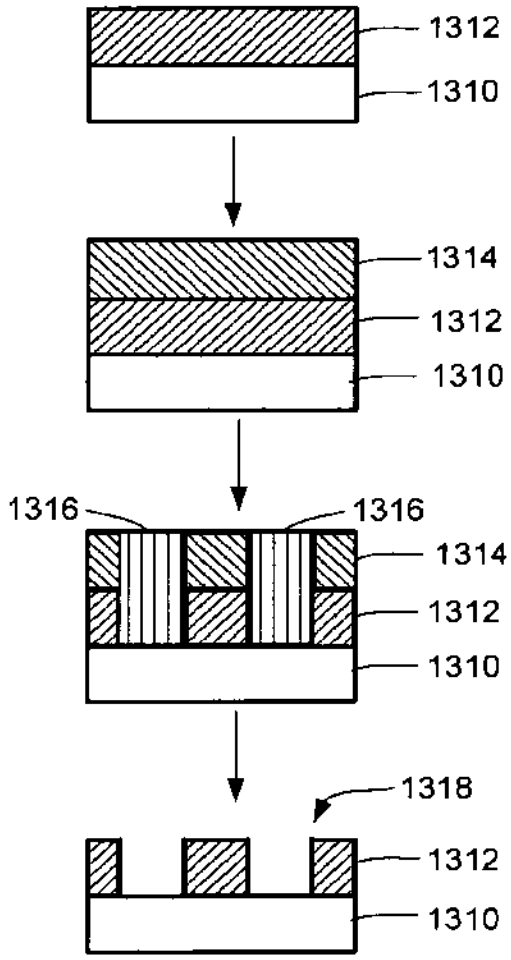


FIG. 13

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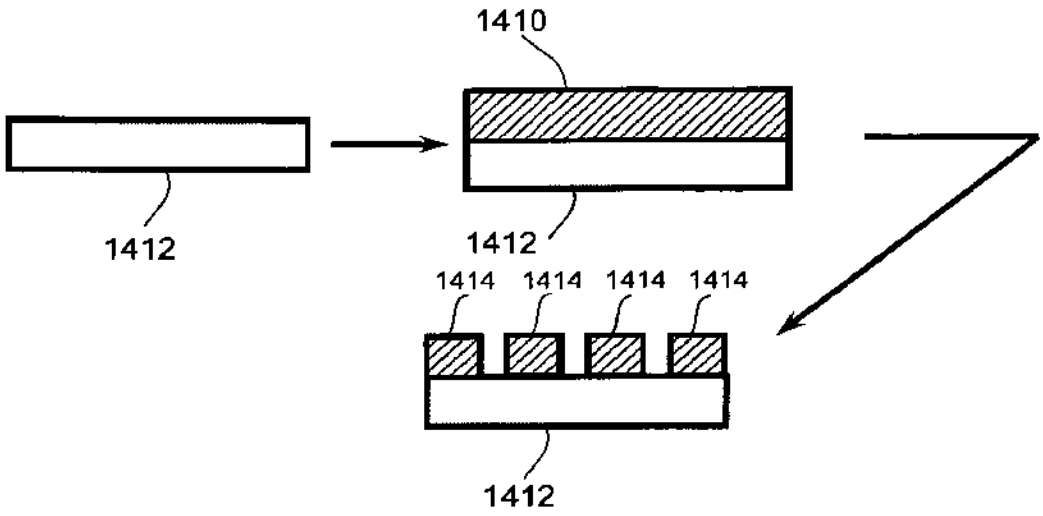


FIG. 14

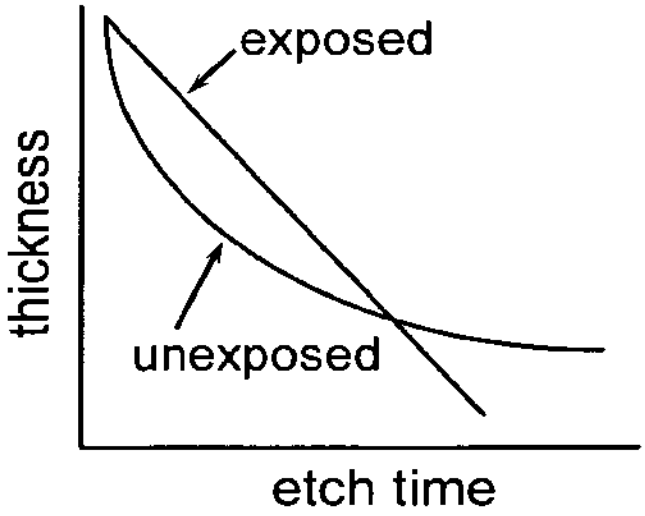


FIG. 15

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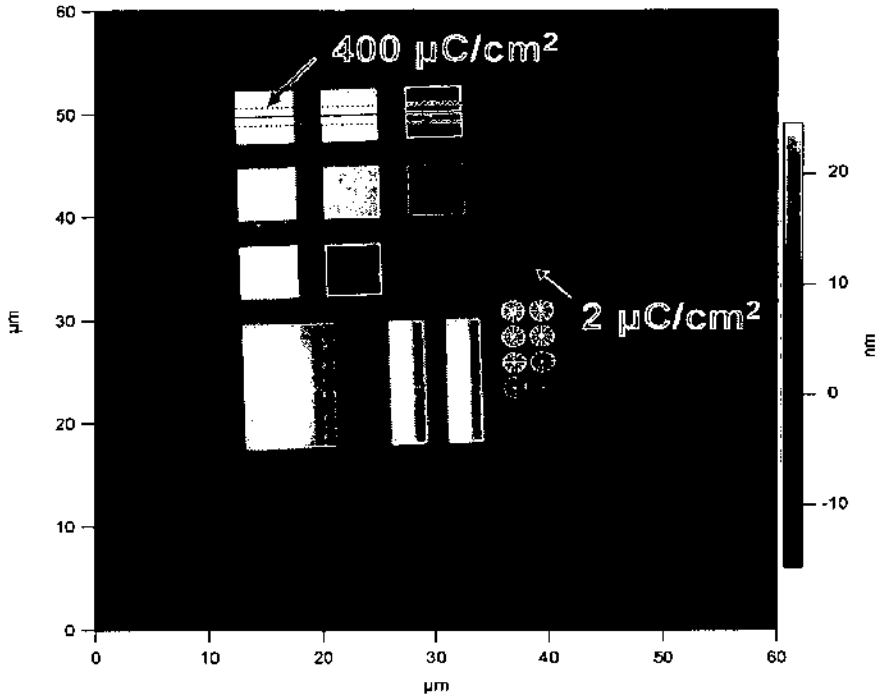


FIG. 16

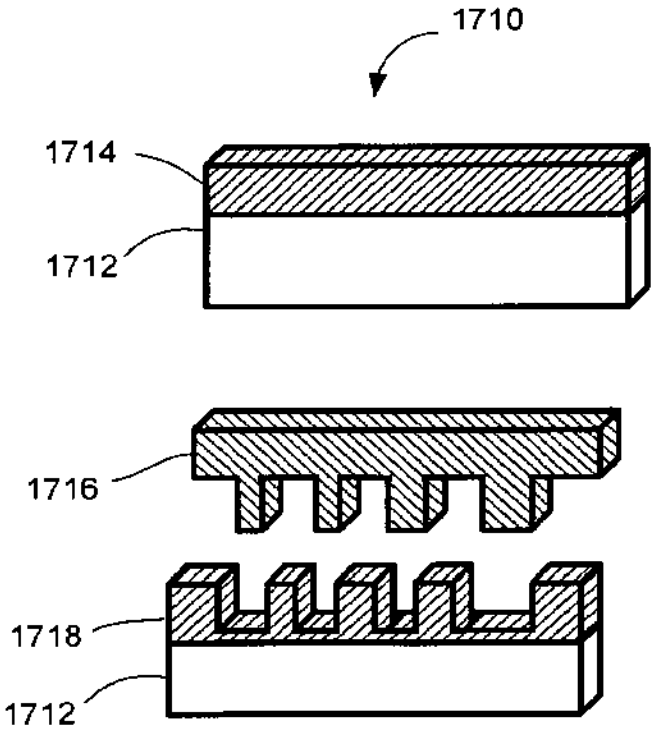


FIG. 17

SUBSTITUTE SHEET (RULE 26)

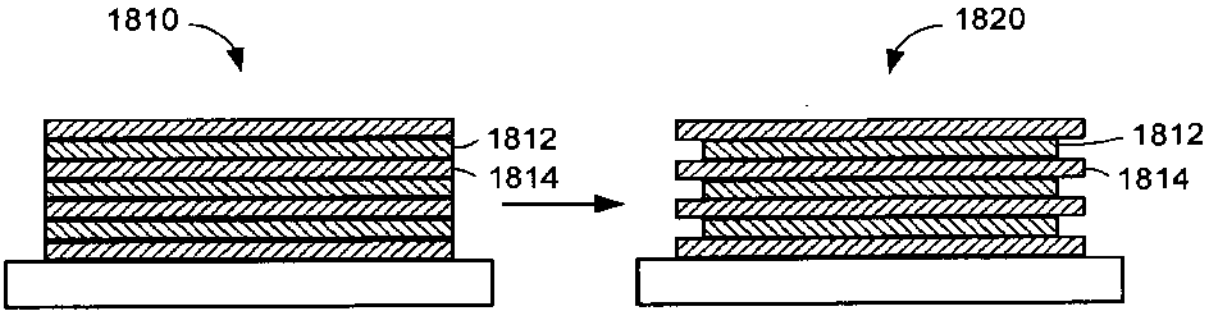


FIG. 18

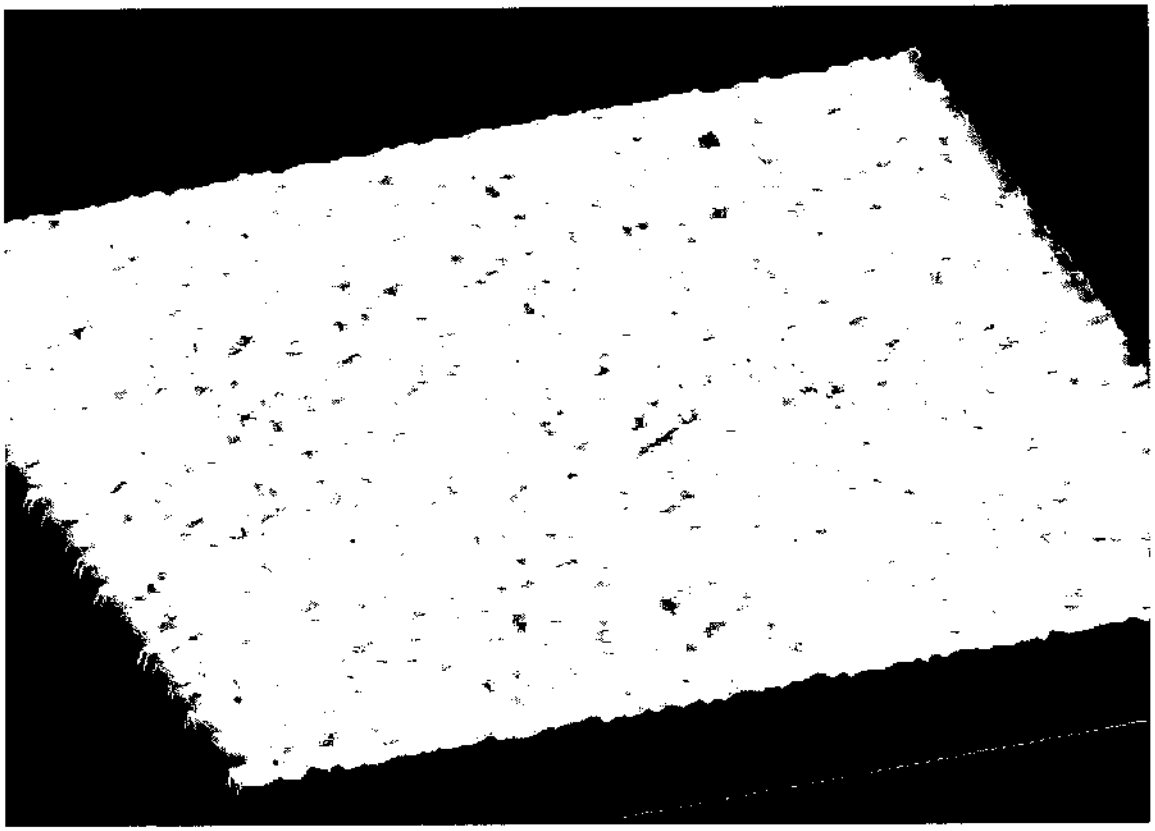


FIG. 19

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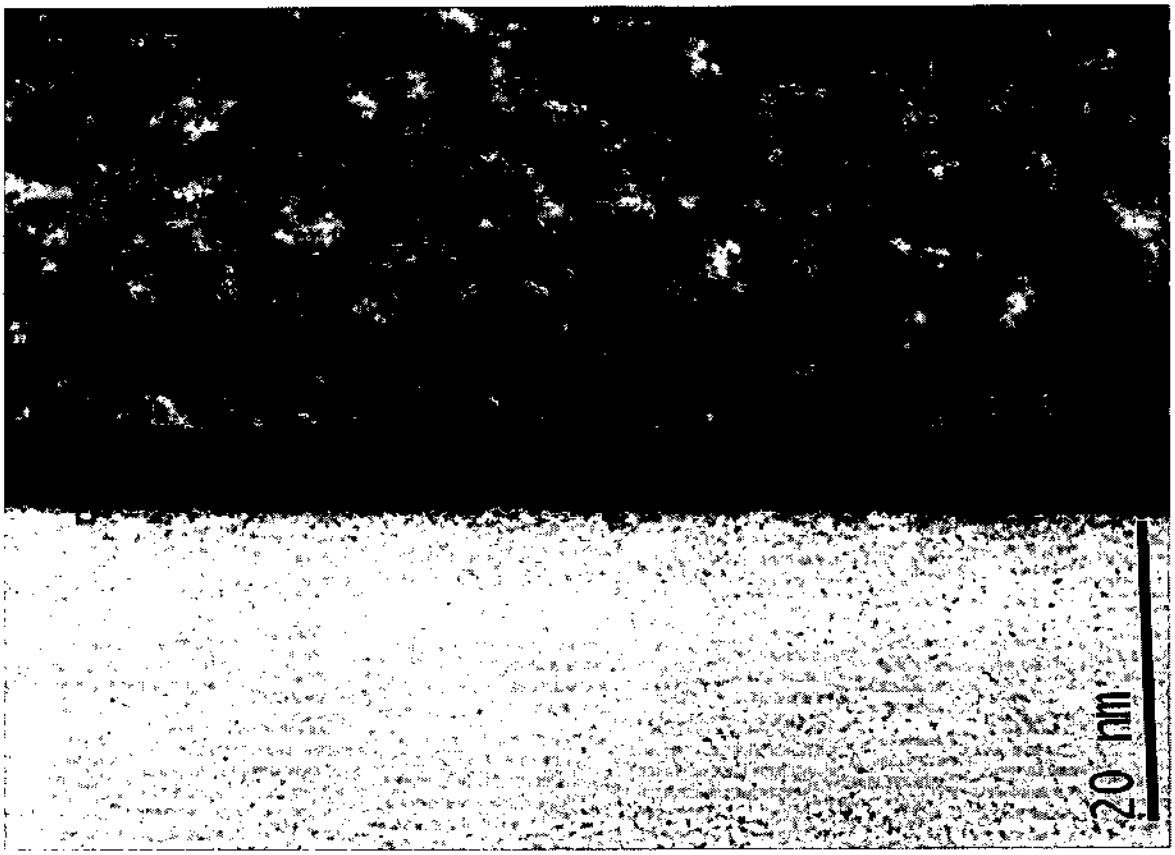


FIG. 20

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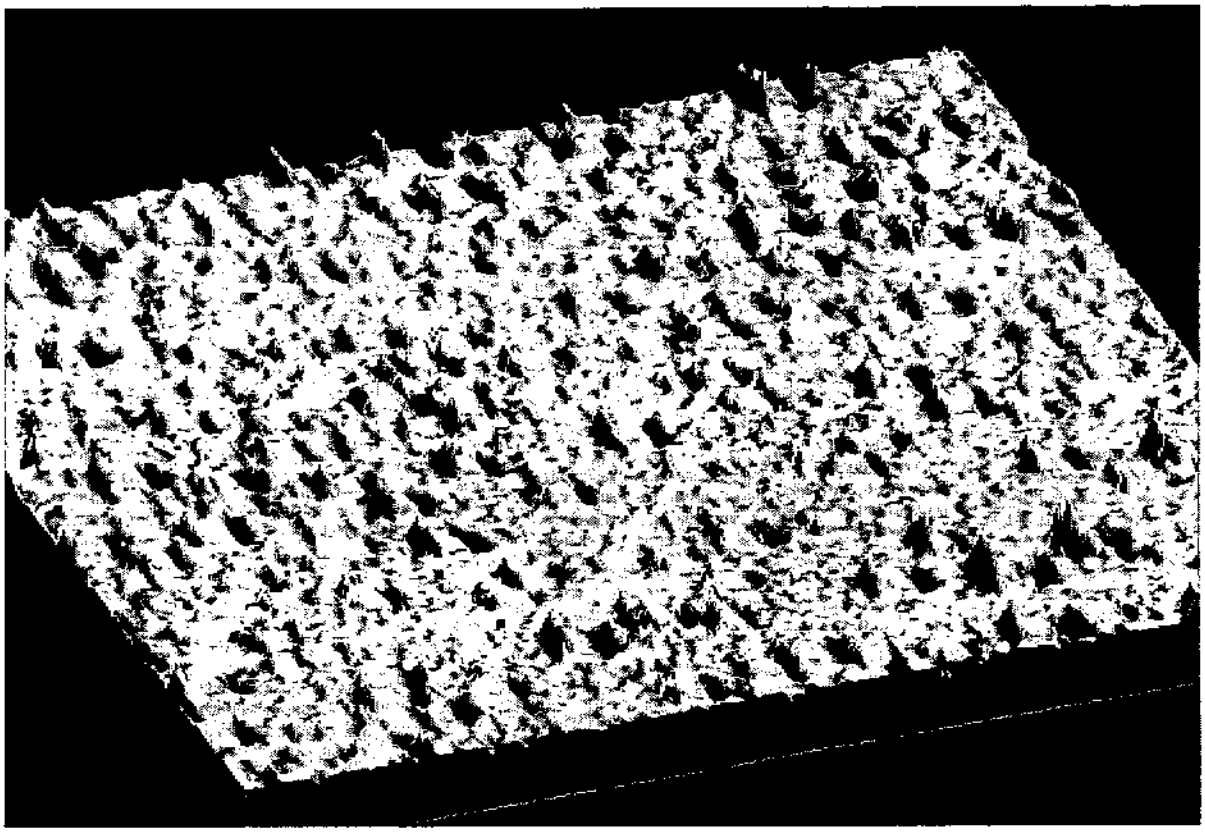


FIG. 21

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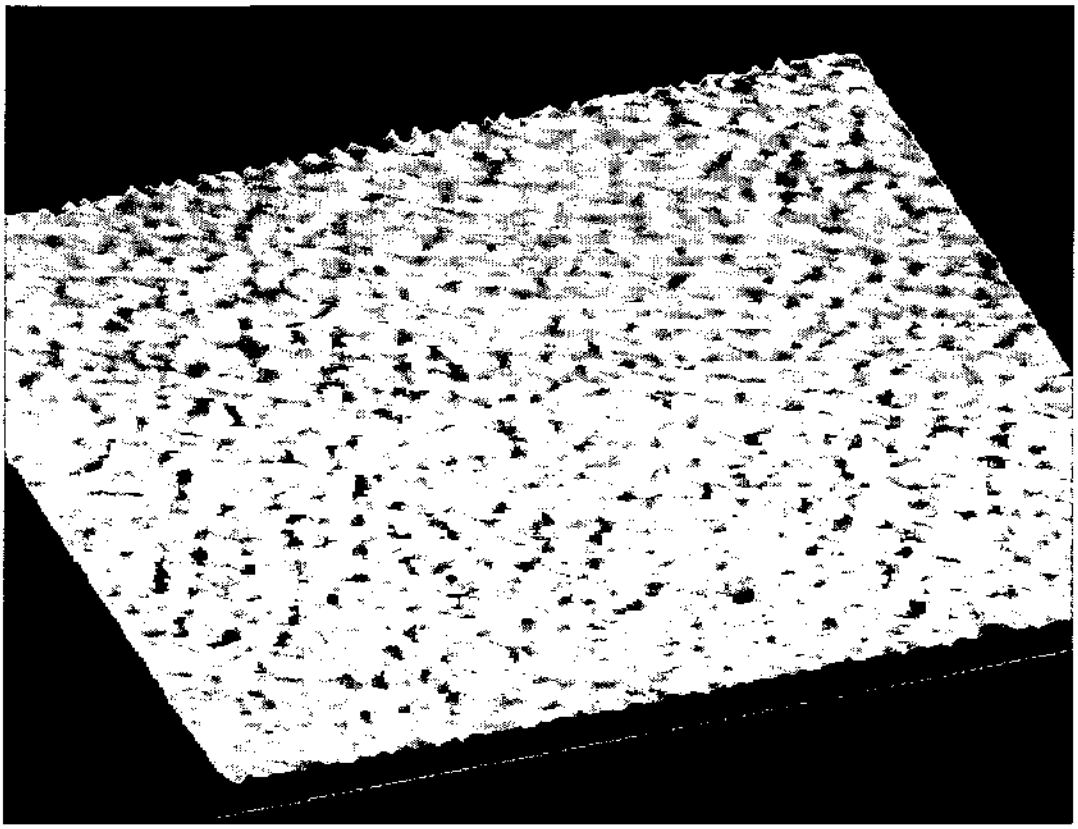


FIG. 22

Lam Research Ex. 1004 - Page 166 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

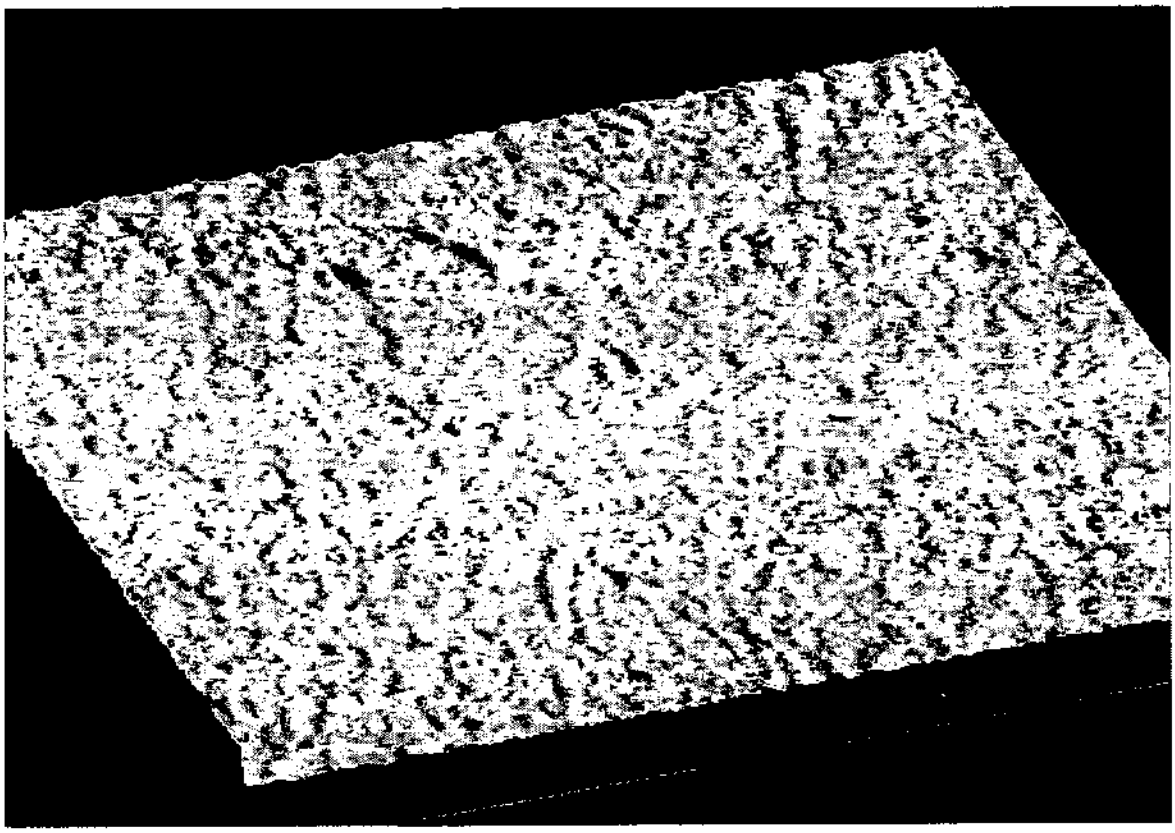


FIG. 23

Lam Research Ex. 1004 - Page 167 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

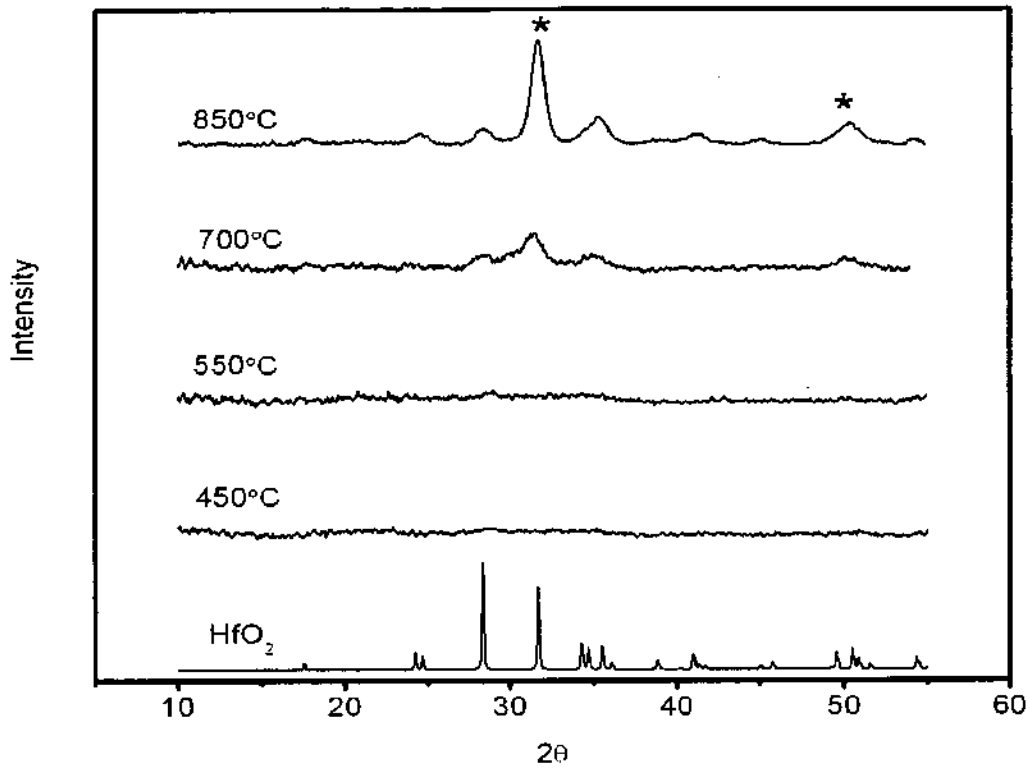


FIG. 24

SUBSTITUTE SHEET (RULE 26)
Lam Research Ex. 1004 - Page 168 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

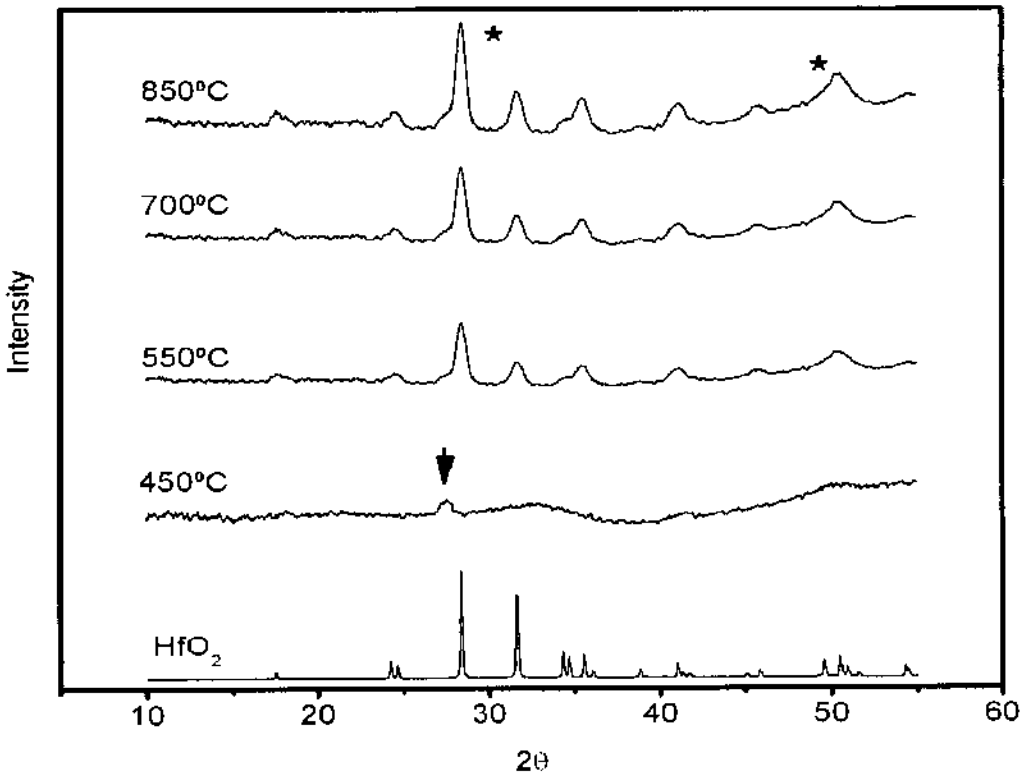


FIG. 25

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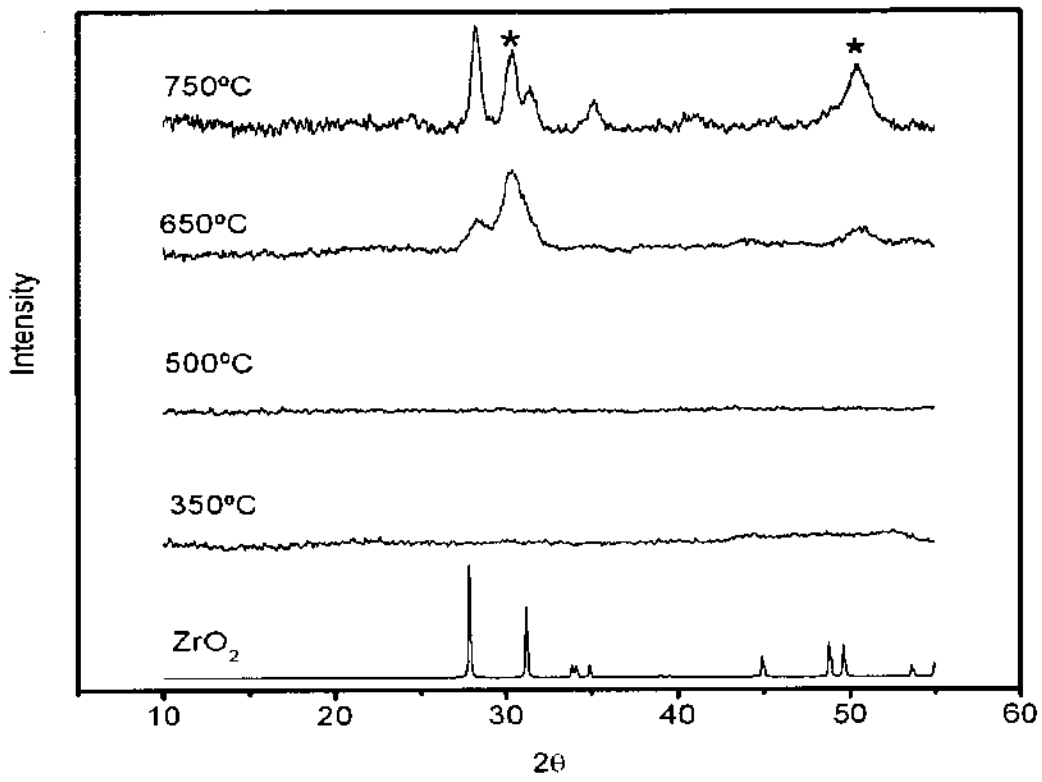


FIG. 26

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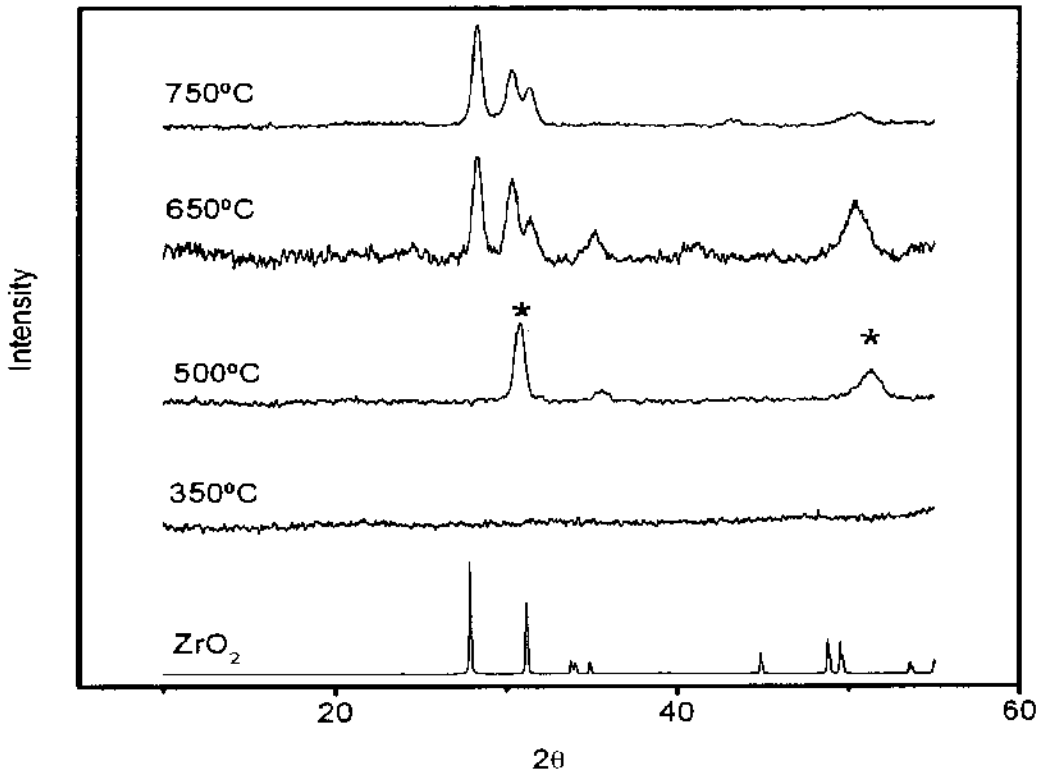


FIG. 27

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FIG. 28

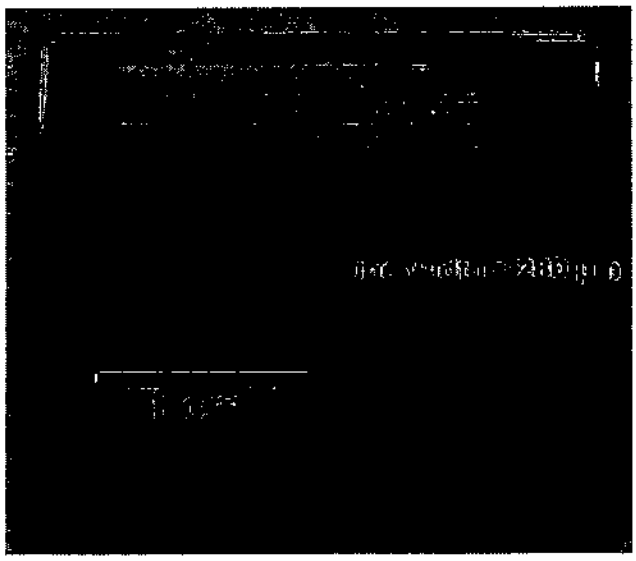


FIG. 29

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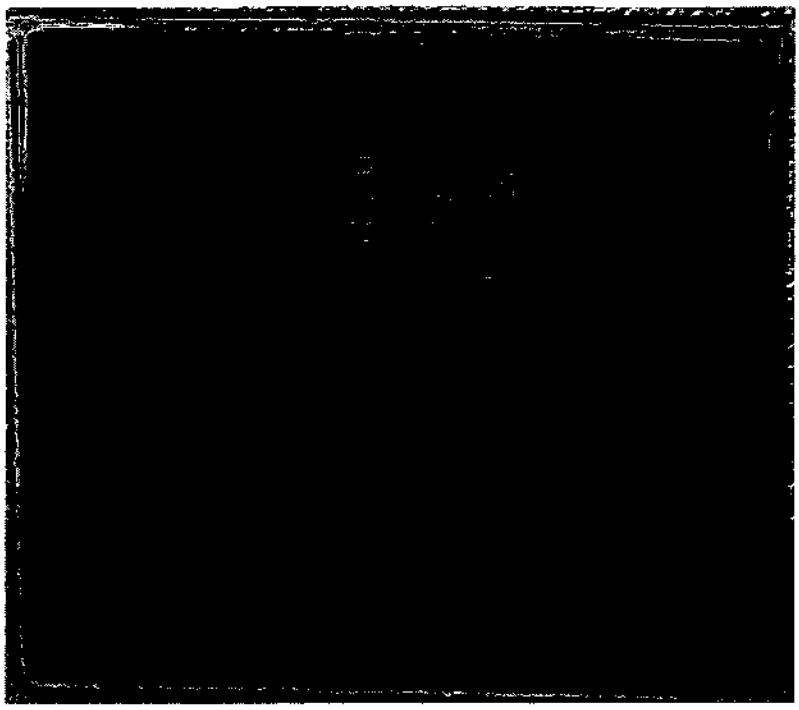


FIG. 30



FIG. 31



FIG. 32

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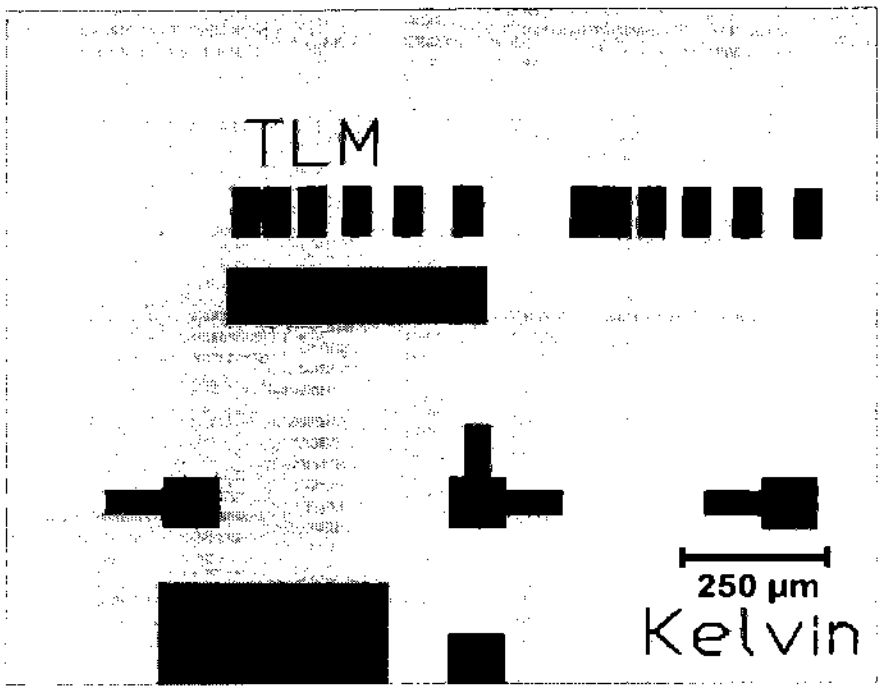


FIG. 33

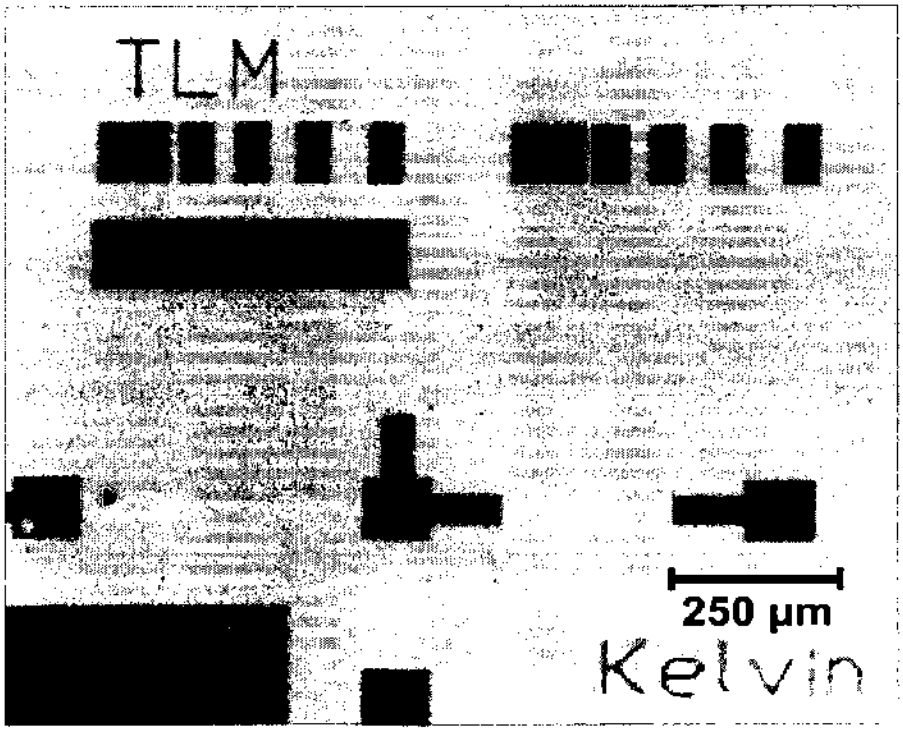


FIG. 34

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FIG. 35

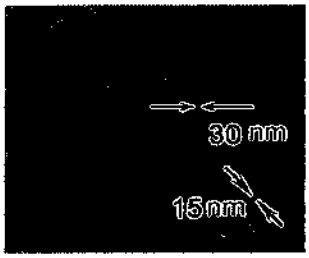


FIG. 36

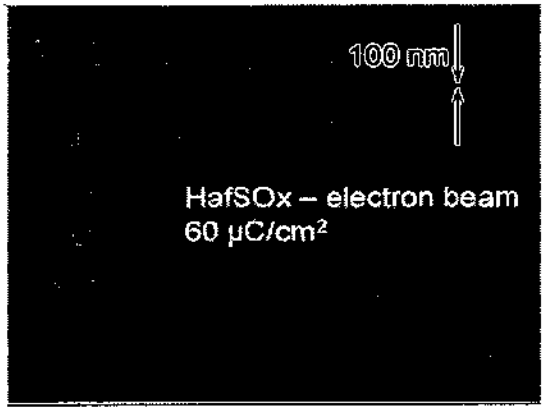


FIG. 37

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 07/23084

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08F 10/00, H01L 21/00 (2008.04)
USPC - 252/570; 438/151; 257/E21.01
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC - 252/570; 438/151; 257/E21.01

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Chemical Engineering and Biotech Research

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST: US Patents full-text; US PGPubs full-text; EPO Abstracts; and JPO Abstracts; Google
Terms: zirconium oxy hydroxy sulfate; hafnium oxy hydroxy sulfate; electronic device; photoresist; tungstate; lanthanum; photolithograph; optical and glass substrate; photo and resist.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2005/0242330 A1 (Herman et al.) 03 November 2005 (03.11.2005), para [0009] - [0012] and [0018]-[0029]; Figures	1-4, 12, 16, 25 --- 5-11, 13-15, 17-24, 26-27
Y	US 2006/0088962 A1 (Herman et al.) 27 April 2006 (27.04.2006), para [0006]-[0023]; Figures	5-11, 13-15, 17-24, 26
Y	US 3,385,915 A (Hamling) 28 May 1968 (28 May 1968), col 1, ln 40-45; col 2, ln 18-26	27

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 April 2008 (10.04.2008)	15 MAY 2008
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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(74) Agent: **SLATER, Stacey, C.**; Klarquist Sparkman, LLP, One World Trade Center, Suite 1600, Portland, OR 97204 (US).

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(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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— *with international search report (Art. 21(3))*

WO 2009/120169 A1

(54) **Title**: SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THE USE AND MANUFACTURE

(57) **Abstract**: Devices having a thin film or laminate structure comprising hafnium and/or zirconium oxy hydroxy compounds, and methods for making such devices, are disclosed. The hafnium and zirconium compounds can be doped, typically with other metals, such as lanthanum. Examples of electronic devices or components that can be made include, without limitation, insulators, transistors and capacitors. A method for patterning a device using the materials as positive or negative resists or as functional device components also is described. For example, a master plate for imprint lithography can be made. An embodiment of a method for making a device having a corrosion barrier also is described. Embodiments of an optical device comprising an optical substrate and coating also are described. Embodiments of a physical ruler also are disclosed, such as for accurately measuring dimensions using an electron microscope.

SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THEIR USE AND MANUFACTURE

FIELD

The present disclosure concerns embodiments of features and devices comprising inorganic metal oxide materials useful for creating spatially-defined structures for purposes including electronic and optical applications, and embodiments of methods for their manufacture and use.

ACKNOWLEDGMENT OF GOVERNMENT SUPPORT

Embodiments of the present disclosure have been developed using federal funding under DARPA grant number HR0011-06-1-0045. The United States government has certain rights in the invention.

BACKGROUND

Electronic devices currently are made using iterative process steps, such as sequential deposition and etching of materials. For devices comprising inorganic materials, metal-organic precursors have been used extensively for solution-based deposition of inorganic oxides. The presence of the organic moiety necessitates a high-temperature burnout step to remove the organic material. This step can cause significant volume change, crystallization and the phenomenon of "mud cracking." The associated defects inhibit the performance of these materials as coatings and within devices.

Methods for solution processing materials for electronic device applications have been patented. For example, Ostergard, U.S. Patent No. 6,946,677, entitled "Pre-Patterned Substrate for Organic Thin Film Transistor Structures and Circuits and Related Method for Making Same," describes forming a desired circuit configuration in the surface of a substrate, thereby pre-patterning the area to receive material useful for forming an organic thin film transistor (OTFT) structure and interconnecting conductive paths. According to the '677 patent, OTFT material is deposited in the pre-patterned area using printing techniques such as inkjet printing.

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Weng *et al.*, U.S. Patent No. 6,927,108, describes solution processing thin-film materials to form transistors. The '108 patent describes forming "conductive solution-processed thin film material contacts, semiconductor solution-processed thin film material active regions, and dielectric solution-processed thin film material isolations in a sequence and organization to form a solution-processed thin film structure capable of transistor operation."

U.S. Patent Publication No. 2005/0242330 A1, which is incorporated herein by reference, concerns hafnium and zirconium compounds useful for electronic applications. U.S. Patent Publication No. 2005/0242330 A1 names Dr. Douglas Keszler as an inventor, who also is an inventor of embodiments disclosed herein.

SUMMARY

U.S. Patent Publication No. 2005/0242330 A1 discloses compounds and solution deposition of inorganic compounds in a manner that addresses deficiencies of prior technologies. For example, solution deposition according to the present invention avoids using organic materials required for metal-organic deposition techniques, and hence also avoids organic burnout and the cracking problems associated with burnout.

One embodiment of the present invention concerns devices, such as electronic devices, having a thin film or laminate structure comprising at least one hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable. X may have any value in a range of from about 0.1 to about 3.5/(polyatomic ion charge). For example, x may be any value within the range of from about 0.1 to about 1.75 for a polyatomic ion with a charge of 2, such as the oxy hydroxy sulfate compounds. Z may have any value range within the range of from 0.0 to about 3.8.

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Particular embodiments concern thin films or laminates comprising a hafnium or zirconium oxy hydroxy sulfate compound having a formula $(MO_{2-x-z/2}(OH)_z(SO_4)_x)$, wherein M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 1.75, and any value for z in a range of from 0.0 to about 3.8. These compounds also are referred to as HafSOx and ZircSOx. The hafnium and zirconium compounds also can be doped, typically with other metals, such as calcium, cerium, lanthanum, or combinations thereof. Certain embodiments have used lanthanum as a dopant to produce compounds having a formula $M_{1-x}La_yO_{2-x-z/2-y/2}(OH)_z(SO_4)_x$ (MSOx:La), where the composition and stoichiometry are as stated above. A particular example of a lanthanum-doped compound is $Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$. Additional exemplary compounds include HafSOx:La, ZircSOx:La, HafSOx:Ce, or ZircSOx:Ca. In certain embodiments, sulfate is subsequently removed via ion exchange with an aqueous base, resulting in $M(OH)_x$ or MO_x films. Suitable aqueous bases include group I metal hydroxides, group II metal hydroxides, group III metal hydroxides, lanthanide hydroxides, ammonium hydroxide, and/or aqueous tertiary amines, among others. The absence of organic components in the $M(OH)_x$ allows the unique conversion and dehydration to metal oxide MO_x at low temperatures, using any suitable technique, such as via microwave and lamp drying or by laser processing.

Certain embodiments concern thin oxide films or laminates comprising complex compositions with two or more metals. At least one of the metal cations has a charge greater than or equal to 3^+, and the total concentration of cations with charge greater than or equal to 3^+ exceeds 50 mol% of the metal cations in the target oxide. A non-aqueous solution comprising dissolved salts and an amount of water is prepared. The amount of water is less than 20 mol% relative to the non-aqueous solvent. The pH of the solution is increased relative to the starting solution by adding a base or by reaction of free protons via oxidation-reduction mechanisms. The final solution pH depends upon the metal cations used, but will typically be in the range of about 2-9. The increased pH results in hydrolysis of water molecules bound to the cations and condensation of these resulting hydroxo-cations. The solvent is evaporated, and the resulting solid is dissolved or dispersed in water and

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subsequently applied to a substrate as a liquid film. The liquid film is then thermally cured at a temperature between about 100 °C and 600 °C for about 5-240 minutes.

Examples of electronic devices, or components of devices, that can be made according to this invention include, without limitation, insulators, such as a gate insulator in a field effect transistor, transistors, such as a field effect transistor, and capacitors, such as a MIM capacitor. Thin films and laminates made according to this embodiment had a permittivity value within the range of from about 9 to about 12, a breakdown field from at least 3 MV cm^{-1} up to about 6 MV cm^{-1}, and a leakage current near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}. Devices made using ZircSOx:Ca had a breakdown field of about 3.6 MV cm^{-1}, and a leakage current of less than about 50 nA cm^{-2}, more typically less than about 10 nA cm^{-2}.

Field effect transistors can be made using HafSOx:La and/or ZircSOx:La as gate dielectric materials. Certain disclosed embodiments used zinc indium oxide and/or zinc tin oxide as channels. Particular field effect transistors had an on-to-off ratio of greater than 10^6, and nA cm^{-2} gate leakage currents.

Another embodiment of the present invention concerns a method for patterning a device using an inorganic photoresist. A particular embodiment of the method comprises first providing a structure to be patterned. The structure typically comprises: a substrate, such as a semiconductor material, a metal, glass, a polymeric material, or combinations thereof; a material layer for patterning, such as silica; and a resist layer. The resist layer typically includes disclosed hafnium and/or zirconium oxy hydroxy compounds. The structure is exposed to an energy source, such as an electron beam or light, with particular examples using ultraviolet light. Thereafter, material is removed to pattern the device, or it is retained as an active, patterned component of the device.

The resist may be a positive resist or a negative resist. For example, the method can include exposing the resist layer to an energy source to convert the resist layer material into a developer-soluble material. The developer-soluble material is then removed using a developer. Suitable developers may include acids, bases, and/or ultrasonic agitation, among others. Again by way of example, the method can comprise removing resist layer material exposed to the energy source. Without limiting the invention to a particular theory of operation, at least for certain

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embodiments, exposure to the energy source may cause the resist layer to polymerize, making it relatively less soluble in a developer than prior to exposure to the energy source.

One embodiment of a positive resist comprises a bilayer. A first layer of the bilayer comprises a copper formate film deposited on a hafnium oxide sulfate (HafSOx) film. The copper formate film is soluble in acid and the undoped HafSOx film is insoluble in acid. Exposing the bilayer to light through a mask or to a focused electron beam causes the two films to interdiffuse in exposed areas, thereby rendering the previously undoped HafSOx film soluble.

Another embodiment of a bilayer process for making a resist comprises depositing a first layer of a solid acid or base, where the acid or base contains one or more metal atoms, onto a substrate. A liquid suspension containing an oxide precursor, such as copper formate, is applied in a desired pattern onto the first layer. Under heated conditions, the precursor decomposes to an oxide. The oxide subsequently reacts and interdiffuses with the first layer, forming a product that can be etched to reveal a pattern. An alternate embodiment comprises depositing oxide particles onto the first layer, with or without heating, resulting in a direct reaction to form a product that can be etched. A further embodiment comprises depositing a thin layer of the oxide precursor onto the first layer. A pattern of activated precursor is then formed by light exposure through a photomask or direct writing with a focused laser or electron beam.

Another embodiment of the present invention concerns a master plate for imprint lithography. The master plate comprises a substrate, such as a flexible or glass substrate, and at least one layer of a thin film or laminate structure comprising at least one disclosed hafnium and/or zirconium oxy hydroxy compound. A particular embodiment of a master plate includes a layer of HafSOx deposited onto the substrate, and a second layer, such as a ZircSOx:Cu layer. The master plate may be patterned by exposure to an energy source, such as exposure to light or an electron beam through a mask to cause the two films to interdiffuse in exposed areas. This renders previously undoped HafSOx film soluble, which is removed to at least partially define printing features of the master plate.

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In another embodiment, masks or templates can be fabricated using the films of the present invention in a single layer process. A thin film of an inorganic precursor, such as a solid acid or base, is deposited onto a substrate in combination with a peroxide or similar anion. The film is heated to produce a structurally rigid film. It is then exposed through a photomask or via a laser or electron beam to induce condensation/crosslinking in exposed areas. The solubility of the exposed areas decreases relative to the unexposed areas. The unexposed areas can then be selectively etched, producing a negative-tone image in the film. Positive-tone images also can be formed by preheating the film to higher temperatures before exposure. In some embodiments, an $M(OH)_x/H_2O_2$ film is formed by treating a film such as HafSOx with a mixture of sodium hydroxide and hydrogen peroxide. The resulting film is then patterned by exposure to light or an electron beam.

A method for forming a device also is described, comprising providing a structure to be patterned comprising a substrate, a material layer for patterning, and a metal oxide layer comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The structure is patterned and then exposed to an energy source to form a durable material having a desired pattern produced by patterning the structure. One embodiment of a device made according to the method can include a channel array, such as a micro- or nano-channel array. For such embodiments, the method for making the device can include stamping unit features of a desired size scale into a semi-solid hafnium or zirconium compound to form a stamped layer.

An embodiment of a method for making a device having a corrosion barrier also is described. Disclosed embodiments of the method comprise providing a device, and forming at least one corrosion barrier on the device. The corrosion barrier typically comprises a metal oxide layer comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The method also can include exposing the compound to an energy source to form the corrosion barrier. Examples of such devices include metal and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal and ceramic-based systems, fibers for

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composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, and catalyst supports.

An embodiment of a method for forming fibers also is disclosed. A solution is formed comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The solution is then drawn into fibers. The fibers may be converted into solid, stable forms by any suitable process, such as hydrolysis, annealing, air pyrolysis, and combinations thereof.

Embodiments of an optical device also are described. Particular disclosed embodiments of the device comprise an optical substrate, and a substrate coating comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The layer may be an antireflective coating. The optical substrate and coating may define, for example, a dielectric mirror, an X-ray mirror, an interference filter, a diffractive grating, and/or a waveguide. The optical device also may include a layer that is transparent, such as visibly transparent or transparent to ultraviolet light. The layer may be selectively doped to provide a doped layer having luminescent ions selected from Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof. Doping the layer can be used to produce a light-emitting layer.

Embodiments of a method for making a physical ruler also are disclosed. Certain embodiments comprise forming at least one acid-soluble layer by solution deposition of disclosed hafnium and/or zirconium oxy hydroxy compounds. At least one acid-insoluble layer is formed adjacent to the acid-soluble layer, the acid-insoluble layer being formed by solution deposition of disclosed hafnium and/or zirconium oxy hydroxy compounds. Repeating these steps produces alternating layers, and the method includes accurately determining widths of alternating acid-insoluble and acid-soluble layers. Width determination can be accomplished using any suitable method, such as X-ray reflectivity. Moreover, at least one layer is etched to define a digitated secondary reference pattern for measuring objects. Certain embodiments of such a device are useful for accurately measuring dimensions using an electron microscope.

The foregoing and other objects, features, and advantages of the invention will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 provides thermogravimetric analysis (relative mass versus temperature) (TGA) for HafSOx (x = 0.70) with various pretreatments and with samples heated under flowing $N_2(g)$ at a rate of 10 °C minute^{-1}.

FIG. 2 is an XRD pattern for HafSOx powders after heating at stated temperatures in air for 1 hour, except as noted.

FIG. 3 is an XRD pattern for HafSOx:32% La powders after heating at stated temperatures for 1 hour, except as noted.

FIG. 4 is an XRD pattern for HafSOx films after heating at given temperatures in air for 5 minutes, where the very small features at 31.8° and 45.6° are attributed to the substrate.

FIG. 5 is an XRD pattern for HafSOx:24% La thin films after heating at stated temperatures in air for 5 minutes.

FIG. 6 illustrates dielectric breakdown characteristics for HafSOx film.

FIG. 7 is an SEM showing one embodiment of HafSOx deposited on tantalum (Ta) metal on a silicon dioxide substrate.

FIG. 8 is an SEM for HafSOx:24% La deposited on Ta.

FIG. 9 is an XRR pattern for HafSOx/ZircSOx multilayer thin-film comprising 14 alternating layers (7 bilayers) having a bilayer thickness of 17.6 nm.

FIG. 10 is a schematic diagram illustrating positive or negative photoresist procedures.

FIG. 11 is a schematic diagram illustrating a positive resist using a bilayer system, the illustrated embodiment comprising a Cu-doped zirconium oxide sulfate (Cu:ZircSOx) film deposited on a hafnium oxide sulfate (HafSOx) film.

FIG. 12 is a schematic diagram illustrating a bilayer process for producing a patterned oxide on a substrate.

FIG. 13 is a schematic diagram illustrating a bilayer process for producing a patterned oxide on a substrate.

FIG. 14 is a schematic diagram illustrating a single layer process for producing a patterned film on a substrate.

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FIG. 15 is a graph of thickness versus etch time for a thermally pre-treated, single-layer film.

FIG. 16 is a film patterned by an electron beam.

FIG. 17 is a schematic diagram illustrating hot embossing lithography for use with semi-solid forms of compounds disclosed herein having much higher mechanical strength, chemical stability, and unique electrical and optical properties relative to organic polymers.

FIG. 18 is a schematic diagram illustrating one method for making a physical ruler for use in standardizing measurements in applications, such as electron microscopy.

FIG. 19 is an AFM image of an unexchanged HafSOx film deposited on silica.

FIG. 20 is a TEM image of HfO_2 following ion exchange of HafSOx and thermal treatment at 850 °C.

FIG. 21 is an AFM image of a HfO_2 film deposited on silica and formed from HafSOx thermal decomposition after heating above 700 °C.

FIG. 22 is an AFM image of a HafSOx film deposited on silica, treated with 0.1M NaOH, and heated to 450 °C for 10 minutes.

FIG. 23 is an AFM image of a HfO_2 film deposited on silica, treated with 0.1M NaOH and heated to 850 °C for 10 minutes.

FIG. 24 provides XRD plots of untreated hafnia films.

FIG. 25 provides XRD plots of treated hafnia films.

FIG. 26 provides XRD plots of untreated zirconia films.

FIG. 27 provides XRD plots of treated zirconia films.

FIG. 28 is an SEM image of an indium gallium zinc oxide semiconductor film deposited on silica.

FIG. 29 is a line pattern produced via ink-jet printing and inorganic diffusion-reaction.

FIG. 30 is a pattern produced by exposing a bilayer film to UV light.

FIG. 31 is a film patterned by electron-beam writing.

FIG. 32 is a film patterned by electron-beam writing.

FIG. 33 is a film patterned photographically.

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FIG. 34 is a film patterned photographically.

FIG. 35 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

FIG. 36 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

FIG. 37 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

DETAILED DESCRIPTION

Disclosed embodiments of the present invention concern devices, including electronic devices or components of electronic devices, which can be made by solution deposition of inorganic materials. Throughout this disclosure, the singular terms "a," "an," and "the" include plural referents unless the context clearly indicates otherwise. Similarly, the word "or" is intended to include "and" unless the context clearly indicates otherwise. The term "includes" means "comprises." All percentages recited herein are atomic percentages unless indicated otherwise. All patents and publications mentioned herein are incorporated by reference in their entirety, unless otherwise indicated. In case of conflict, the present specification, including explanations of terms, will control. The materials, methods, and examples recited herein are illustrative only and are not intended to be limiting.

I. Metal Oxide Sulfate Materials Generally and U.S. Patent Publication No. 2005/0242330 A1

The present disclosure concerns embodiments of a method for solution deposition of inorganic materials, typically solution deposition of metal oxide sulfate inorganic materials that are useful for electronic applications. Embodiments of these materials are described in U.S. Patent Publication No. 2005/0242330 A1. Certain portions of that published application, from paragraph 009 through paragraph 014, are paraphrased below. References to figures in this paraphrased text refer to the figures as published with the '330 publication.

> FIG. 1 illustrates one embodiment of a process for manufacturing a dielectric precursor material. Process 10 generally comprises providing a first reactant 12, such as a metal-containing cation, providing a second reactant 14, such as a polyatomic anion, and then reacting the polyatomic anion and the metal-containing cation. The metal-containing cation and the polyatomic anion may be in solution, such as an aqueous solution, when reacted together. In one embodiment, the metal-containing cation may be provided using an aqueous solution of a hafnium oxy halide, such as hafnium

oxy chloride ($HfOCl_2(aq)$). The polyatomic anion, such as sulfate (SO_4^{2-}), may be provided using an aqueous solution of sulfuric acid ($H_2SO_4(aq)$). These two reactants may be mixed together using processes and relative amounts suitable for making desired materials. The mixture may be heated.

The reaction may produce a precursor solution 16. Precursor solution 16 may be immediately used as desired, such as by being applied to a substrate. Optionally, precursor solution 16 may be at least partially dehydrated and then applied. In the example given above, the precursor solution may then form hafnium oxy-hydroxy sulfate ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$). With reference to the variables in this formula, x and z may be fixed or variable, and may have any value. For example, the value of x typically is from about 0.1 to about 1.9, and a value for z is from 0.0 to about 2.0. For one embodiment the values were x=0.5 and z=0. Hydroxyl groups may be a part of the metal-containing cation, and the compound may comprise hafnium oxy-hydroxy sulfate ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$).

In other embodiments, the polyatomic anion may include one or more of sulfate (SO_4^{2-}), borate (BO_3^{3-}), phosphate (PO_4^{3-}), tungstate (WO_4^{2-}) and silicate (SiO_4^{4-}). The metal-containing cation may comprise a metal suboxide, and may include one or more of hafnium (Hf^{4+}), titanium (Ti^{4+}), zirconium (Zr^{4+}), cerium (Ce^{4+}), tin (Sn^{4+}), tantalum (Ta^{5+}), niobium (Nb^{4+}), yttrium (Y^{3+}), molybdenum (Mo^{4+}), tungsten (W^{6+}), aluminum (Al^{3+}), gallium (Ga^{3+}), zinc (Zn^{2+}), chromium (Cr^{3+}), iron (Fe^{3+}), bismuth (Bi^{3+}), lanthanides, hafnium oxy-hydroxide ($HfO_y(OH)_z^{(4-2y-z)+}$), zirconium oxy-hydroxide ($ZrO_y(OH)_z^{(4-2y-z)+}$), titanium oxy-hydroxide ($TiO_y(OH)_z^{(4-2y-z)+}$), tantalum oxy-hydroxide ($TaO_y(OH)_z^{(5-2y-z)+}$), yttrium oxy-hydroxide ($YO_y(OH)_z^{(3-2y-z)+}$), niobium oxy-hydroxide ($NbO_y(OH)z^{(4-2y-z)+}$), molybdenum oxy-hydroxide ($MoO_y(OH)_z^{(4-2y-z)+}$), tungsten oxy-hydroxide ($WO_y(OH)_z^{(6-2y-z)+}$), aluminum oxy-hydroxide ($AlO_y(OH)_z^{(3-2y-z)+}$), gallium oxy-hydroxide ($GaO_y(OH)_z^{(3-2y-z)+}$), zinc oxy-hydroxide ($ZnO_y(OH)_z^{(2-2y-z)+}$), chromium oxy-hydroxide ($CrO_y(OH)_z^{(3-2y-z)+}$), iron oxy-hydroxide ($FeO_y(OH)_z^{(3-2y-z)+}$), bismuth oxy-hydroxide ($BiO_y(OH)_z^{(3-2y-z)+}$), and oxy-hydroxides of the lanthanide series. The value of y is related to the charge on the metal cation and the amount of hydroxide and other polyatomic anion that is bound to the metal cation.

Embodiments of the method using polyatomic anions and metal-containing cations disclosed herein may result in the formation of a dielectric precursor material that does not require using organics for forming complexes, i.e., the sources of the anion and the cation do not contain organics. However, organic materials can be used, if desired or necessary for certain embodiments. For example, a non-complexing organic, such as ethanol, may be used as a partial solvent in the precursor solution. If complexing organics are not included in the precursor material, the precursor solution typically does not have to be heated or annealed at temperatures as high as 400 °C or higher, to decompose/combust any organic materials once the precursor solution is applied to a substrate. Polymerization of the

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precursor solution upon heating and/or drying results in the formation of amorphous films and not polycrystalline materials, thereby allowing solutions-based-application of the dielectric material on a substrate.

In general, disclosed embodiments of the present process may be conducted at ambient conditions, such as atmospheric pressure in air. Accordingly, vacuum processing is not required, but may be utilized if desired. The process may be conducted at a temperature above ambient, such as in a range of from about 80 °C to about 850 °C, typically in a temperature range of from about 80 °C to at most 350 °C, and often at a temperature of at most 100 °C. These low pressure and low temperature processing steps may reduce the energy requirements for disclosed processes. Due to the low temperatures useful for processing the dielectric films, the films may be processed on or applied as a solution to low-temperature substrates, such as plastic substrates. The amorphous, non-crystalline dielectric precursor solution produced allows even, conformal coverage of the precursor solution on a substrate, such as on a wafer. The solution also may be applied in a predetermined, specific pattern, such as by using inkjet printing, so that no masking or etching steps are used. Accordingly, the process of the present disclosure may eliminate or reduce the usage of hazardous or toxic materials that may be used for the formation and removal of materials during photolithography processing on substrates. Thus the present process is time efficient and environmentally "green" relative to known processes. Moreover, the hafnium oxide and sulfate materials utilized in one example embodiment of the present disclosure may not be toxic materials.

Examples of materials used in the process of the present disclosure include compounds belonging to the family of compounds including hafnium oxy hydroxy sulfates ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$), hafnium oxy hydroxy tungstates ($HfO_{2-x-z/2}(OH)_z(WO_4)_x$), hafnium oxy hydroxy borates ($HfO_{2-x-z/2}(OH)_z(BO_3)_x$), hafnium oxy hydroxy phosphates ($HfO_{2-x-z/2}OH_z(PO_4)_x$), and hafnium oxy hydroxy silicates ($HfO_{2-x-z/2}OH_z(SiO_4)_x$). These materials may be polymerized at temperatures as low as 80 °C and may remain amorphous up to approximately 740 °C, and even as high as 1,200 °C. Material polymerization may be controlled by adjusting the heating rate, by using co-solvents, by other suitable methods, and by any and all combinations of such methods. Amorphous films of the present disclosure may reduce defect formation at grain boundaries and may reduce crack formation upon an amorphous-to-crystalline transition. Moreover, the dielectric films of the present disclosure may have a reasonably high dielectric constant, i.e., a dielectric constant higher than the dielectric constant of organic compounds. The ability to form high quality dielectrics by solution-based processing, such as inkjet printing applications, allows formation of low cost electronic components, such as field effect transistors or capacitors.

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FIG. 2 schematically illustrates one embodiment of a process for applying precursor solution 16 to form a dielectric material. Precursor solution 16, such as hafnium oxy sulfate, may be applied to a substrate 18, such as a wafer, by an applicator 20. In one embodiment, applicator 20 may comprise an inkjet printer having nozzles 22. The aqueous precursor solution 16 is ejected through nozzles 22 of the inkjet printer. In other embodiments, applicator 20 may comprise a spin-coater, a dip-coater, or a spray-coater such that the method of applying the precursor solution may comprise, respectively, spin-coating, dip-coating, or spray-coating. Due to the amorphous, solution-based properties of precursor solution 16, precursor solution 16 may allow good conformal coverage when applied. Once applied to the substrate surface, or to a film or films deposited on the substrate, the precursor solution may be dehydrated, such as by heating with a heater 24, or by other dehydration devices, to remove or reduce the amount of water in the precursor solution. This dehydration step may cause precipitation of an amorphous dielectric material 26, such as a hafnium oxy sulfate thin film, on wafer 18.

FIG. 3 is a graph showing possible solution concentrations for differing precursor concentrations for one embodiment of dielectric material precursor solutions 16 (see FIG. 1), in particular, for the reaction of sulfuric acid (H_2SO_4) with hafnium oxy chloride ($HfOCl_2$). More particularly, FIG. 3 shows a graph of total sulfate concentration (molarity (M)) versus total hafnium concentration (M). Region 28 represents a clear solution, i.e., a solution with no visually detectable precipitate therein, wherein region 28 is a region of excess sulfuric acid (H_2SO_4). Region 30 represents a clear solution, i.e., a solution with no visually detectable precipitate therein. Region 30 is a region of excess hafnium oxy chloride ($HfOCl_2$). Line 32 represents a stoichiometric line wherein sulfuric acid and hafnium oxy chloride are each present in a one-to-one ratio (1:1 stoichiometric ratio). Region 34 represents a precipitation area, i.e., a solution having a visually detectable precipitate therein. Region 34, or portions thereof, therefore, may represent solutions that are not best suited for forming smooth substantially defect free films by inkjet printing applications, but its use is not foreclosed. Accordingly, when precursor solution 16 (see FIG. 2) is applied through an inkjet printer application device 20 (see FIG. 2), it may be desirable that the concentration of the first and second reactants fall within either of regions 28 or 30, but not within solids region 34. Solids present in the solutions of region 34 may occlude nozzles 22, may form an unsmooth film, or may otherwise result in unfavorable precursor solution application. In other words, the solutions of regions 28 and 30 may represent possible precursor solution "inks" that may be applied through an inkjet printhead or by a dropper method.

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II. General Discussion

New thin-film dielectrics and nanolaminates have been developed using solution deposition, typically aqueous solution deposition, of smooth, dense films. Solution deposition techniques include spin coating and inkjet printing. Solution deposition may be followed by modest thermal treatment ($T < 325\ ^{\circ}C$).

A variety of analytical techniques have been used to define the chemistry of the materials made according to the present disclosure, both as powders and films. The quality and functionality of the films have been assessed by X-ray reflectivity, electronic microscopy, and performance in electronic devices. Dielectric characteristics have been determined for working embodiments, and include permittivity values covering the range of from about 9 to about 12; breakdown fields up to at least 6 MV cm^{-1}; and leakage currents near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}. The surface smoothness and pore-free nature of the films facilitate the production of unique nanolaminated structures having individual layers at least as thin as about 2 nanometers. Relatively high permittivity films can be realized using disclosed embodiments of the present invention, while also providing high-breakdown strengths and low-leakage currents in thin-film metal-insulator-metal (MIM) capacitors and thin-film transistors (TFTs). The exceptional characteristics of the insulating films also have allowed fabrication of unique nanolaminated structures.

Amorphous materials are desirable for use as thin-film dielectrics; they do not have grain boundaries, and hence are not susceptible to roughness and charge conduction associated with crystallites. Numerous oxides of hafnium and zirconium, e.g., the simple binaries, silicates, and aluminates, have been examined as candidates for high-permittivity dielectric applications. In multiple-component materials, crystallization can be inhibited to produce more robust breakdown characteristics relative to the pure binary oxides, though permittivity may be sacrificed. These dielectric films often are formed using a variety of metal-organic or metal-salt precursors and techniques such as atomic layer deposition (ALD), chemical vapor deposition (CVD), sol-gel processing, or combinations thereof. However, making useful dielectric films by solution deposition methods that are

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both dense and amorphous may require inhibiting crystallization and cracking, both during deposition and subsequent processing.

Certain disclosed embodiments of the present invention concern the development of metal oxide films. Metal oxides are exemplified herein generally by reference to hafnium and zirconium sulfate systems having representative formulas $HfO_{2-x}(SO_4)_x$ and $ZrO_{2-x}(SO_4)_x$, respectively, where $0.1 \leq x \leq 1.5$. These compounds are referred to herein by the acronyms HafSOx and ZircSOx, respectively. To define the chemistry and physical properties of these systems, HafSOx, and doped analogs thereof, such as the La-substituted derivative HafSOx:La, have been made, both as powders and thin films. Thin-film dielectric properties of HafSOx, ZircSOx, and selected derivatives have been assessed by fabricating capacitors and TFTs. These analyses revealed that very high-quality, dense films could be produced. Film thickness and fabrication of mixed HafSOx/ZircSOx nanolaminates can now be controlled by spin-coating processes.

A number of phases and crystal structures have been reported from examination of HfO_2-SO_3-H_2O and ZrO_2-SO_3-H_2O systems. Several structures are characterized as simple hydrates of formulations $Hf(SO_4)_2 \cdot nH_2O$ or $Zr(SO_4)_2 \cdot nH_2O$, exhibiting variations in the degree of hydration and in the structural dimensionality associated with the condensation of the metal atom, sulfate groups, and water. Materials rich in metal relative to sulfate are known, including $Zr_2(OH)_2(SO_4)_3 \cdot 4H_2O$; $Hf(OH)_2SO_4$, $Zr(OH)_2SO_4$, and their hydrates; $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13} \cdot 33H_2O$ and $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$; and $Zr_3O_5SO_4$ and its hydrate. All of these structures (with the possible exception of $Zr_3O_5SO_4$) are likely unstable when subjected to air at both room temperature and under moderate heating, resulting from changes in hydrogen bonding or dehydration. This allows the dehydration and condensation processes to be used to develop amorphous films.

Starting from aqueous solutions with selected fractions of sulfate relative to hafnium (variable x), HafSOx precipitates were induced by heating. FIG. 1 is a thermogravimetric analysis (TGA) of air-dried HafSOx precipitates. TGA is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature. Heating an air-dried HafSOx precipitate leads to mass loss in three domains. Similar characteristics have been observed for other

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HafSOx derivatives as well. The large mass loss below a temperature of about 200 °C is attributed to loss of incorporated water. Mass loss in the temperature range of from about 200 °C to about 700 °C is attributed mainly to elimination of more tightly bound hydroxyl species as water. The sharp mass loss that begins above about 700 °C, is attributed to sulfate decomposition according to $SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$. Assuming dehydrated HafSOx powder is converted completely to HfO_2 between 700 °C and 950 °C, the sulfate fraction can be calculated from the mass loss. Determining mass loss of samples revealed that increasing levels of sulfate in the mother solution yielded increasing levels of sulfate in precipitates. Specifically, the sulfate-to-hafnium ratio varied from about 46% to about 71% for dehydrated formulas of $HfO_{1.54}(SO_4)_{0.46}$ and $HfO_{1.29}(SO_4)_{0.71}$, respectively. The same maximum sulfate composition precipitated whether $H_2SO_4(aq)$ or $(NH_4)_2SO_4(aq)$ was used as the sulfate source; products with sulfate levels < 46% were not examined. The onset of sulfate loss occurred above 720 °C for all samples, though some variations in the thermogravimetric profiles were observed. Peak positions for the derivatives of these heating curves, as definable values, reveal decomposition between 793 °C and 817 °C for samples tested. The highest decomposition temperatures were observed for samples having maximum sulfate content with $H_2SO_4(aq)$ as the sulfate source.

Again with reference to FIG. 1, samples with maximum sulfate content also were heated prior to TGA measurements. Mass losses associated with water were reduced, and calculated sulfate contents were similar for both preheated and regular samples. This sulfate content of 70–71% mimics the compositions of the reported crystals $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$ and $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}\cdot 33H_2O$. From TGA studies, Ahmed, Fjellvåg, and Kjekshus (*Acta Chem. Scand.*, 53, 24 (1999) also found that sulfate decomposition for $Hf_{18}O_{23}(SO_4)_{13}$ and $Zr_{18}O_{23}(SO_4)_{13}$ occurs at temperatures higher than those for the Hf and Zr disulfates within their study, and higher than those for the basic sulfates $Hf(OH)_2SO_4\cdot H_2O$ and $Zr_3O_5SO_4$ reported by others. In addition to enhanced thermal stability, a sulfate-to-metal ratio of approximately 13:18 exhibits special stability within this system. As such, this composition may be suitable for purposes where solution processing and heating are required.

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The sulfate $La_2O_2SO_4$ has a decomposition temperature of greater than 1,300 °C. Lanthanum (La) was added to the mother HafSOx solution to produce additional compounds having modified physical properties, such as modified dehydration properties and thermal characteristics, one example being thermal stability. A mixed-metal system, $Hf_{1-z}La_zO_{2-x-z/2}(SO_4)_x$ (HafSOx:La), exemplifies such compounds. To produce such compounds a solution containing the precursor materials and 23% La (total metal) was heated to form precipitates. Chemical analysis indicated that only 3% La was found in the product. From TGA, a sulfate-to-metal ratio of 71% was established, and the decomposition (as derivative peak) at 820 °C was found to be consistent with maximal sulfate content. Co-precipitation was then induced by adding NH_3(aq) to a salt solution of the constituent species containing 32% La. The chemical composition of the product was analyzed, revealing the same fraction of La as that present in the mother solution. Thermal decomposition for this formula was markedly different from undoped HafSOx. Mass loss attributed to sulfate was apparent above 700 °C, though heating features were less abrupt and no constant mass was achieved with heating to 1,000 °C, even when heating at the slower rate of 2 °C minute^{-1}. For this heating rate, decomposition (as derivative peak) occurs at approximately 870 °C, though this value depends on heating conditions. Complete decomposition to the oxides was accomplished by heating to 1,500 °C, yielding the formula $Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$ for the dried precipitate.

XRD data were collected for precipitated HafSOx powders to establish temperature ranges for crystalline phases. After air drying, a complex diffraction pattern was recorded for samples having maximum sulfate content and H_2SO_4(aq) as the sulfate source; other samples exhibited no or diffuse diffraction. XRD data for HafSOx ($x = 0.70$) are shown in FIG. 2. After heating air dried samples for 1 hour at temperatures between from about 100 °C to about 700 °C, the material becomes amorphous. Crystalline peaks characteristic of monoclinic HfO_2 are observed after heating at 750 °C and above for 1 hour. As the onset of sulfate loss occurs at 720 °C by TGA, crystallization is found to coincide with sulfate loss. Inclusion of 3% La generates similar diffraction profiles for temperatures up to 1,000 °C.

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XRD data for HafSOx:32% La are shown in FIG. 3. Both the precipitated material and that heated to 700 °C are X-ray amorphous. Just as with unsubstituted HafSOx, a detectable crystalline phase forms between 700 °C and 750 °C (1 hour heating), which is the temperature interval over which sulfate begins to decompose. Yet with substitution of 32% La, monoclinic HfO_2 is not the detected phase. Rather, the diffraction profile is consistent with cubic (or tetragonal) HfO_2, the phases of HfO_2 often stabilized by lanthanide atom inclusion. High-temperature heating generates $Hf_2La_2O_7$ and monoclinic HfO_2 as predicted from consideration of the appropriate phase diagrams. Intermediate temperature oxide phases are consistent with work on the system ZrO_2-La_2O_3 by Zhang, Kershaw, Dwight and Wold (*J. Solid State Chem.*, 72, 131 (1988)), who found that 10–37% lanthanum stabilizes cubic zirconia at 900 °C, with phase separation occurring at 1,050 °C.

HafSOx and HafSOx:La thin films having thicknesses of from about 200 nanometers to about 300 nanometers were fabricated for materials characterization. Compositions for the films were determined with electron-probe microanalysis (EPMA), based on relative concentrations of Hf, La, Cl, and S. Oxygen levels are less precise by this method, so dehydrated formulas are expressed. Two representative HafSOx films heated at 325 °C (5 minutes) were determined to be $HfO_{0.985}(SO_4)_{0.67}Cl_{0.69}$ and $HfO_{0.915}(SO_4)_{0.85}Cl_{0.47}$, representing 67% and 85% sulfate relative to hafnium. The 85% sulfate film was further heated to 650 °C (5 minutes) and determined to be $HfO_{1.275}(SO_4)_{0.71}Cl_{0.03}$. Also, the HafSOx:La film heated at 330 °C (5 minutes) was determined to be $Hf_{0.76}La_{0.24}O_{0.73}(SO_4)_{0.96}Cl_{0.38}$. For HafSOx heated to 650 °C, the sulfate ratio was reduced to 71%, which matches the composition for heat precipitated HafSOx powders with maximal sulfate. For HafSOx:La, the measured fraction of La (24%) agrees well with the 23% La concentration in the precursor solution.

Transmission Fourier transform infrared (FTIR) analyses for HafSOx ($x \sim 0.67$ & 0.85), and HafSOx:La films were collected after heating for 5 minutes at selected temperatures. FTIR spectra were used to detect principally two functional groups. Absorption in the range 3000–3600 cm^{-1} is attributed to hydroxyl groups; and absorption in the range 1000–1200 cm^{-1} is attributed to sulfate groups. With heating, hydroxyl absorption diminishes over the range from about 325 °C to about

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600 °C, while sulfate stretches are nearly eliminated between about 650 °C and 700 °C for HafSOx films, and between about 700 °C and 750 °C for the HafSOx:La film. (The profiles for sulfate absorption are slightly distorted since SiO_2 from the substrates absorbs at a similar energy, but spectra are qualitatively correct.)

Thin-film XRD data were collected for HafSOx ($x \sim 0.67$ & 0.85) and HafSOx:24% La films after heating at indicated temperatures for 5 minutes each, as shown in FIGS. 4 and 5, respectively. For both HafSOx compositions, films are X-ray amorphous from about 325 °C to about 650 °C. Monoclinic HfO_2 is detected at about 700 °C and above. HafSOx:La films are amorphous from about 330 °C to about 700 °C, while a cubic phase is detected from about 750 °C to about 1000 °C. The cubic phase is apparently unstable at 1,100 °C, as separation into monoclinic HfO_2 and $Hf_2La_2O_7$ phases commences. For HafSOx and HafSOx:La films, loss of sulfate can be directly correlated with oxide crystallization, which is consistent with powder behavior.

Films of HafSOx, ZircSOx, and derivatives thereof, were deposited by spin-coating for use as dielectrics. MIM capacitors were tested to determine the parameters of permittivity and loss tangent at 1 kHz, as well as electric-field breakdown strength. "Breakdown" is defined as the field where current density surpasses 10 $\mu A\ cm^{-2}$. Similar tests were conducted for HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, and ZircSOx:Ca. FIG. 6 illustrates dielectric breakdown characteristics for HafSOx dielectric film where the aluminum dot contacts represent an area of 0.011 cm^2. HafSOx and ZircSOx films had breakdown fields of 4–6 MV cm^{-1}. A breakdown field of 3.6 MV cm^{-1} was found for ZircSOx:Ca. At an applied field of 1 MV cm^{-1}, all six variations exhibited leakage current less than 50 nA cm^{-2}, and leakage currents less than 10 nA cm^{-2} were observed for many compositions. Permittivity values of from about 9 to about 12, and loss tangent < 1% were measured for all variations.

Field-effect transistors (FETs) were fabricated with HafSOx:La or ZircSOx:La as the gate dielectrics and zinc indium oxide or zinc tin oxide as the channels. Current modulation was achieved; drain-to-source current saturated with increasing drain-to-source voltage, providing an on-to-off ratio greater than 10^6; and gate leakage currents are in the range of pA cm^{-2}. These results clearly indicate that

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HafSOx:La and ZircSOx:La films are sufficiently robust for device integration; the requirement for a quality dielectric/channel interface is also met.

As a new class of amorphous multi-component oxide dielectric films, HafSOx, ZircSOx, and their derivatives may be compared to other mixed systems, particularly aluminates and silicates, represented as $(MO_2)_{1-x}(Al_2O_3)_x$ and $(MO_2)_{1-x}(SiO_2)_x$ where M = Hf or Zr. Various film compositions for each of these systems have been deposited by conventional vapor phase techniques. In the cases of Hf or Zr aluminates and silicates with 20–50 mol% Al_2O_3 or SiO_2 (as common compositions for dielectric applications), crystallization typically occurs at about 800 °C to about 1,000 °C, in conjunction with phase segregation. For tested HafSOx powders and films, crystallization occurs at approximately 700 °C as sulfate decomposes. As dielectrics, these aluminates and silicates exhibit permittivity values of 10–15, compared to values of 9–12 for HafSOx and ZircSOx. This new class of oxide sulfate materials can be considered amorphous, moderate temperature, medium permittivity dielectrics.

Scanning electron microscopy (SEM) and X-ray reflectivity (XRR) were used to further examine film qualities. SEM images for HafSOx and HafSOx:La films are shown in FIGS. 7 and 8. These images reveal smooth surfaces and dense, uniform cross-sections for films having thicknesses in the range of from about 150 nanometers to about 300 nanometers, as typically used for dielectric testing. FIG. 7 shows a SiO_2 substrate 710 upon which a 506-nm layer of Ta metal 712 and a 160-nm HafSOx film 714 have been deposited. FIG. 8 shows a SiO_2 substrate 810 upon which a 512-nm layer of Ta metal 812 and a 192-nm HafSOx/La film 814 have been deposited.

As a stringent measure of reproducibility for thinner film fabrication, multilayer structures with a HafSOx/ZircSOx repeating motif were deposited and analyzed by XRR. The interference pattern from one XRR scan is shown in FIG. 9. Positions of peak maxima, representative of standing wave harmonics, were used to find the thickness of the repeating bilayer. By systematically varying the thicknesses of HafSOx and ZircSOx independently, the thicknesses of the individual layers were determined. Within a nanolaminate stack, single layers as thin as about

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3 nanometers were measured. As high order reflections in the diffraction pattern are observed, each bilayer was deposited with a variability < 0.5, including roughness.

Shrinking device dimensions have led to the need to replace thin, high leakage-current SiO_2 as a dielectric in Si CMOS technologies. The replacement dielectrics must exhibit a high permittivity, allowing thicker layers to exhibit the same device capacitance with smaller leakage currents. HfO_2 and ZrO_2 have attracted considerable attention as replacement gate dielectrics because of their desirable dielectric properties and thermal properties. One of the challenges for HfO_2 and ZrO_2 dielectrics is making smooth, dense, pinhole-free, ultra-thin films having a thickness less than or equal to 13 nm. Previously ultra-thin films have been formed using atomic layer deposition (ALD). Despite some promising results from ALD, the processing requires using a vacuum with long deposition times (1 Å/min), which leads to high costs and low throughput. This has driven some work on the solution based deposition of HfO_2 and ZrO_2. To date these films have not reached the same uniformity and density of the ALD films.

Using an exchange reaction, ultra-thin $M(OH)_x$ and MO_x films can be fabricated that rival ALD quality and are suitable for use in DRAM (dynamic random access memory) and Si CMOS (complementary metal-oxide semiconductor) technologies. For disclosed embodiments, the films are deposited in a sulfate form via inorganic condensation using spin-coating. For example, a semi-solid film can be formed with the composition $MO_x \cdot HCl \cdot H_2SO_4$. The sulfate is removed by ion exchange using an aqueous sodium hydroxide solution:

$$MO_x \cdot HCl \cdot H_2SO_4 + OH^-(aq) \rightarrow M(OH)_{2x} + Cl^-(aq) + SO_4^{2-}(aq)$$

The resulting hydroxo and/or oxide films are smooth, dense, and pinhole free. For example, HfO_2 films with a thickness of about 2 nanometers can fabricated from HafSOx films. Exchanged films are subjected to thermal treatments up to about 800 °C for about 10 seconds to 10 minutes, resulting in a film surface roughness of about 0.1 nanometer. Such film characteristics satisfy requirements for metal-dielectric gates in CMOS and related technologies, while replacing expensive atomic layer deposition processing with low-cost spin-on or misting techniques.

The deposited semi-solid hydrated hydroxo films allow for anion exchange without disruption of the films' morphology. For example, oxoanions such as SO_4^{2-},

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WO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-}, VO_4^{3-}, AlO_4^{5-}, GaO_4^{5-}, and their protonated forms, e.g., HPO_4^{2-}, $H_2PO_4^-$, and the halides F^-, Cl^-, Br^-, and I^-, can be selectively exchanged by placing the films in a metal salt bath, e.g., Na_2SO_4(aq). This provides opportunities to optimize film performance for electronic applications and other applications, such as ion exchange chromatography and filtration.

For some embodiments of oxide films, it is difficult to produce single-source precursor liquid suspensions that can be directly applied to a substrate to provide a complex composition, e.g., two or more metal atoms. The following methods allow the production of such liquid suspensions and their use as single-source precursors for deposition of films of suitable quality for device applications.

The following describes a general method for synthesizing an aqueous precursor solution and depositing metal oxide films using the precursor. The aqueous precursor is distinctive in that it comprises polymeric or oligomeric metal-hydroxo compounds condensed via hydrolysis in a non-aqueous polar solvent and subsequently transferred to an aqueous environment for deposition. Advantageous thin-film electrical and optical properties and processing temperatures are achieved by condensing metal hydroxides to dense solid oxides without deleterious organic contaminants. Disclosed embodiments of the synthetic method follow the general procedure: 1) dissolution of metal salt in polar solvent; 2) hydrolysis and condensation; 3) solvent evaporation; 4) dissolution in H_2O; and 5) solution deposition and curing.

One or more soluble salts comprising a metal cation (M^{a+}) and one or more anions (X^{b-}) are dissolved in a non-complexing, non-aqueous polar solvent such as aliphatic alcohols or nitriles, particularly lower (10 carbon atoms or fewer) alkyl alcohols and nitriles, such as methanol, ethanol, acetonitrile, or a mixture thereof. Many solvent systems are possible. Suitable solvents for a particular application can be selected by considering boiling point (typically less than 150 °C), low toxicity, and acid-base and redox properties compatible with intended solution-phase reactions. Metal sources may include simple ionic or molecular salts ($Zn(NO_3)_2$, $SnCl_4$, etc.); oxy or hydroxy salts ($ZrO(NO_3)_2$, ZnOHCl, etc.); or potentially organic salts ($Fe(CH_3CO_2)_2$, $Cu(CHOO)_2$, etc.). At least one of the metal cations must have a formal charge greater than or equal to 3^+ and the total concentration of such ions

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(M^{a+} where $a \geq 3$) should exceed 50 mol% of the metal cations in the target oxide. Concurrently, an amount of H_2O is introduced into the solution as hydrates of the metal salts described above, as a pure liquid, or a basic solution detailed below. The amount of water is determined by the cations chosen; typical amounts of water will not exceed 20 mol% of the non-aqueous polar solvent.

The pH of the solution is then raised relative to the starting pH by adding an appropriate base or by reaction of free protons via oxidation-reduction mechanisms. The increased pH drives hydrolysis of the H_2O ligands bound by the acidic ($a \geq 3$) cations and condensation of the resulting hydroxo-cations. The final solution pH depends upon the metal cations used, but will typically be in the range of about 2-9. This may be accomplished using one of the following techniques, or any and all combinations thereof:

a) Addition of a basic aqueous solution containing NH_4OH, $(NH_4)_3PO_4$, CsOH, or similar compounds. Specific compounds (NH_4OH) may be chosen to decompose or volatilize during subsequent processing. Other cations (e.g., Cs) or polyatomic anions
(e.g., PO_4^{-3}) may be used if they are intended to comprise part of the final oxide film to achieve unique morphological, optical, or electrical properties following dehydration.

b) Addition and dissolution of a small amount of a basic oxide such as CaO or SrO, with a similar goal of inclusion in the final oxide film.

c) Addition of NH_3 or other gaseous compounds, which form a basic solution in H_2O.

d) Addition of electropositive metal reducing agents, such as Zn, Al or Fe, which may consume protons through direct reduction to H_2, or as part of other proton-consuming oxidation-reduction processes such as the reduction of NO_3^-. Resultant cationic species are thereafter incorporated into the final oxide film.

e) Addition of aqueous or gaseous oxidizing or reducing agents such as N_2H_4, H_2CO, or H_2O_2 in liquid form, or as soluble salts, with a similar purpose of consuming protons or decomposing counter ions but without inclusion in the final oxide film.

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The solution may be stirred at room temperature, heated, or exposed to solvothermal conditions to promote thermohydrolysis and condensation, depending on the final composition desired. Following a suitable reaction period the solution will contain one or more soluble oligomeric or polymeric metal-hydroxo cationic species. These species may be homo or hetero-metallic in nature. The degree of condensation is limited by the restricted molar ratio of H_2O (aquo- and hydroxo-ligands) available, while the decreased polarity and size of the non-aqueous solvent relative to H_2O may prevent additional condensation and precipitation processes through steric effects or altered charge-screening properties.

Soluble metal species are isolated by evaporating the non-aqueous solvent. Isolated metal-hydroxo compounds may form crystalline or amorphous solids or gels depending on certain processing considerations, such as solvent, counterion, and hydrolysis ratio.

Precursor solutions for oxide films are prepared by dissolving or dispersing the isolated solid in H_2O. The resulting sol or solution is homogenous, and may or may not be thermodynamically stable.

Precursor solutions are applied to a substrate using any suitable technique, including printing, spin, spray, or dip-coating to form a patterned or blanket liquid film. Liquid films are thermally cured under atmospheric conditions for about 5-240 minutes at a temperature from about 100 °C to 600 °C. Vacuum or forming gas (e.g., H_2 and flowing N_2 or Ar) anneals may be used to alter oxygen stoichiometry or cation oxidation state as appropriate for the chemical or optoelectronic properties desired.

The smoothness and high atomic density of the films described herein allow fabrication of purely inorganic nanolaminates via solution processing. These films represent a new platform for developing a wide range of applications, as discussed further below.

III. Applications

A person of ordinary skill in the art will appreciate that the HafSOx and ZircSOx compounds, and films comprising such compounds, can be used to make a number of different devices, and can be used to practice a variety of processes

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utilizing such compounds. Metal-organic precursors have been extensively employed in the solution-based deposition of inorganic oxides. The presence of the organic moiety necessitates a high-temperature burnout step, which leads to significant volume change and generally to crystallization and the phenomenon of "mud cracking." These problems are eliminated by using disclosed embodiments of the present invention and suitable inorganic compositions to form amorphous HafSOx and ZircSOx films, where simple dehydration and polymerization lead to film quality preservation. To understand phase stability, representative HafSOx and HafSOx:La powders and films were characterized at various temperatures. Thin-films based on HafSOx and ZircSOx were deposited in multiple configurations in order to examine the quality and utility of the films. Several derivatives have been used to produce capacitor dielectrics. HafSOx:La and ZircSOx:La were used to form gate dielectrics in FET devices. Nanolaminate layers of HafSOx and ZircSOx exhibited remarkable smoothness with reproducibility within a couple atomic layers. Classes of films comprising HafSOx, ZircSOx, and their derivatives are useful, amongst other things, as electrical insulators, protective barriers, optical coatings, and/or as inorganic polymers for photolithography.

A. Patterned films for Resist, Imprint Lithography, and Printing

Photolithography is commonly used to transfer geometric shapes on a mask to the surface of a silicon wafer or other semiconductor. For the past four decades, photolithographic processing has been the driving force for the improvements in resolution and dimensional control of device features in the microelectronics industry. These advances have made possible the high-performance personal computers, cell phones, CD players, and other innumerable advanced electronic products that are now considered to be essential parts of our lives. The photolithographic advances that have made these products possible have largely centered on developing short-wavelength exposure tools and an extraordinary extension in the resolution and feature-size capabilities of polymer resists. As the quest for ever smaller features and device-yield improvements continue, however, the limitations and inefficiencies of polymer-based resist technology are becoming more evident.

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The smallest feature sizes realized via lithography have been produced by electron-beam writing of inorganic materials. The beam-dose energies required to produce these features, however, have been much too high to receive more than passing interest for use in a manufacturing environment.

During the deposition and processing of the films described herein, it is possible to control the film hydration level, which provides a method for controlling the interdiffusion of stacked films and their resulting physical and chemical properties. This controlled interdiffusion with resulting induced modifications in material solubility, coupled with the high quality of the films, was used to develop a new lithographic patterning method involving amorphous and crystalline films. This methodology involves depositing and reacting two distinct films, and it is designated as bilayer diffusion. In addition, small coordinating species such as peroxide (O_2^{2-}) can be incorporated into aqueous-based inorganic liquid suspensions and films to provide an additional, new lithographic patterning method. In this technique, energy (e.g., light, electron beam, heat) can be applied to films, inducing condensation reactions that alter the solubility of the film, thereby allowing lithographic patterning.

Patterns can be formed using a positive or negative photoresist. This process is illustrated schematically in FIG. 10 with reference to a laminate structure 1010 having a silicon substrate 1012, a silica layer 1014 and a resist layer 1016. For positive resists, the resist layer 1016 is exposed to an energy source, such as UV light, wherever the underlying material is to be removed. In these resists, exposure to the UV light changes the chemical structure of the resist layer 1016 so that it becomes more soluble in the developer. The exposed resist layer 1016 is then removed by the developer solution, leaving areas of the bare underlying material. In other words, "whatever shows, goes." The mask 1018, therefore, contains an exact copy of the pattern which is to remain on the wafer.

Negative resists behave in just the opposite manner. Exposure to the UV light causes the negative resist to polymerize, and it therefore is more difficult to dissolve. As a result, the negative resist 1020 remains on the surface wherever it is exposed, and the developer solution removes only the unexposed portions. Masks

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used for negative photoresists, therefore, contain the inverse (or photographic "negative") of the pattern to be transferred.

Resist materials in current use for electronics manufacture are organic polymers. These polymers exhibit coiling, morphologies, and diffusion chemistries that limit pattern resolution. Inorganic thin films of the present invention form the basis for a new resist technology. Here, negative resists can be realized by exposing the inorganic films in semi-solid form to light or electron beams, causing them to lose solvent, particularly water during dehydration, or small coordinating ligands such as O_2^{2-}. This hardens the films, rendering them insoluble in acid.

One embodiment of a positive resist can be made using a bilayer system. A first layer of the bilayer comprises a copper formate film deposited on a hafnium oxide sulfate (HafSOx) film. The copper formate film is soluble in acid and the undoped HafSOx film is insoluble in acid. Exposing the bilayer to light through a mask or to a focused electron beam causes the two films to interdiffuse in exposed areas, thereby rendering the previously undoped HafSOx film soluble.

One embodiment of this process is illustrated schematically in FIG. 11. With reference to FIG. 11, a laminate structure 1110 is first formed, such as by spin coating or inkjet coating suitable materials, in desired orders and thicknesses as required to define a working device. More specifically, a substrate material 1112 is first selected. A person of ordinary skill in the art will appreciate that any of a number of substrate materials potentially can be used to practice this embodiment of the present invention. Solely by way of example, and without limitation, suitable substrates include semiconductor materials, metals, glass, polymeric materials, and combinations thereof. As such the resist technology can be useful for a variety of applications in semiconductor manufacture. Once a suitable substrate 1112 is selected, a first layer 1114 of HafSOx is solution deposited onto the substrate 1112. Thereafter, a second layer, such as a layer 1116 of Cu:ZircSOx, is solution deposited onto layer 1114. The laminate structure 1110 is then subjected to an energy source, such as an electron beam or light, through a mask. Upon exposure to light or an electron beam through a mask, the two films interdiffuse in the exposed areas to render the previously undoped HafSOx film soluble to produce a laminate structure 1120. The exposed structure 1120 is then developed. The previously undoped

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HafSOx film is soluble, and hence is removed as indicated in laminate structure 1130.

On a flexible or glass substrate, the pattern illustrated in structure 1130 can be considered the master plate for imprint lithography or for generalized printing processes such as gravure printing. Forming a hardened patterned material of HafSOx in this way also provides a means for developing micro- and nano-channel arrays in the fabrication of devices for fluid control and delivery. Such devices could be applied in medical diagnostics, ink delivery, and chemical synthesis.

Another embodiment of a bilayer process is shown in FIG. 12. The process produces a patterned oxide on a selected substrate 1210. The substrate can, for example, be a glass, semiconductor wafer, metal, metal alloy, plastic, or a combination thereof. The first step of the process involves depositing a thin film 1212 (from about 1 nm to about 100 nm) of a solid acid or base, e.g., hydrated sulfate, phosphate, nitrate, silicate, aluminate, borate, or mixtures thereof, containing one or more of the metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu. In addition the solid acid/base can contain one or more of NH_3, OH, F, Cl, Br, I. The solid acid/base is preferably deposited via spin coating or printing; physical and vapor deposition are additional options. As one example, the solid acid can be deposited from an aqueous solution of $HfOCl_2$ and H_2SO_4(aq) via spin coating. The solid acid is heated sufficiently to produce a structurally rigid film 1212, such as by heating at about 50 °C for about 2 minutes. In the printing mode of operation, the substrate 1210 can be placed on a heated platen (about 25 – 300 °C), and an ink containing an oxide precursor 1214, e.g., copper formate, can be applied in a desired pattern by delivery through an ink-jet head or by bringing the substrate 1210 into contact with a template containing the precursor 1214. The template comprises a portion of a microcontact, letterpress, or gravure printer. Under heated conditions (greater than about 250 °C), the precursor 1214 decomposes to an oxide, subsequently reacting and interdiffusing with the solid acid, forming a product 1216 that can readily be washed or etched to reveal a pattern 1218. The oxide precursor also may be replaced by an ink suspension or paste containing fine oxide micro- or

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nanoparticles. Application of the fine particles with or without heating results in a direct reaction to form a product that can be etched to reveal a pattern.

An alternate embodiment is shown in FIG. 13 for producing a patterned oxide on a selected substrate 1310. The initial step involves depositing a solid acid 1312 or base onto the substrate. The oxide precursor 1314 is then applied as a blanket coat via spin coating, printing, chemical vapor, or physical vapor deposition. A pattern of activated precursor 1316 is then formed by exposure to an energy source, such as light, via a photomask. Suitable light sources include an unfiltered deuterium lamp or a light source producing light at 193 nm, among others. Alternatively, a pattern of activated precursor 1316 is formed by directly writing with a focused laser or electron beam. If necessary, the activated and patterned structure 1316 can then be heated to a temperature from about 125 °C to about 350 °C to promote interdiffusion of the two layers. The exposed areas can then be etched to produce the desired pattern 1318. A procedure to improve exposure sensitivity involves using a very thin layer (about 2 nm) of oxide precursor on the solid acid. The precursor layer is then covered with a layer of an oxide that is deposited via any suitable technique, such as chemical or physical vapor deposition or by solution casting of oxide nanoparticles. The layers interdiffuse following exposure of the thin layer of precursor.

The processes described above correlate to a positive resist technology. It is also possible to select solid acids/bases and precursors that will produce insoluble products. These products can be used to produce positive images in at least two ways. In one embodiment, the two layers completely interdiffuse to form a single insoluble layer. Following printing or exposure and development, the soluble portions of the film are then washed or etched to reveal a positive pattern. In an alternative approach, interdiffusion occurs only at the interface between the precursor and the solid acid/base to produce a thin, insoluble barrier layer. This barrier layer is then used to control the etching of the film stack to produce a positive image. The barrier layer is photosensitive. Prior to light exposure, it prevents reaction between the precursor and solid acid/base layers that would otherwise readily interdiffuse on contact. Once the barrier layer is photosensitized,

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it becomes a reactive oxide. The barrier is "broken," and the top layer can then interdiffuse with the lower layer.

Next-generation patterning, whether based on photo or imprinting, uses masks or templates, typically fabricated by electron-beam lithography. Many of these templates or masks are being fabricated with the hard mask HSQ (hydrogen silsesquioxane). HSQ masks are widely used for fabricating a variety of electronic, data storage, and microelectromechanical devices. HSQ is also under development as a hard master/template for imprint lithography.

Masks or templates can be fabricated using the films described herein in a single layer process as shown in FIG. 14. The first step of the process involves depositing a thin film (from about 1 nm to about 100 nm) of an inorganic precursor 1410 onto a substrate 1412. The inorganic precursor1410 may be a solid acid or base, e.g., hydrated sulfate, phosphate, nitrate, silicate, aluminate, borate, or mixtures thereof, containing one or more of the metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu in combination with peroxide or similar coordinating anion. In addition the solid acid/base and peroxide mixture can contain one or more of NH_3, OH, F, Cl, Br, I. The solid acid/base is preferably deposited via spin coating, liquid misting, or printing; physical and vapor deposition are additional options. As one example, the solid acid can be deposited from an aqueous solution of $HfOCl_2$ H_2SO_4(aq), and H_2O_2(aq) via spin coating. The solid acid is heated sufficiently, such as to a temperature of from about 50 °C to about 125 °C, and for a period of time from about 10 seconds to about 10 minutes to produce a structurally rigid film. The film is then exposed through a photomask or via a defined laser or electron beam to induce condensation in the exposed areas. The solubility of exposed areas 1414 decreases relative to unexposed regions, so the unexposed regions can be selectively etched in acid or base. Examples of acids or bases that can be used include hydrochloric acid, sulfuric acid, hydroxgen peroxide, sodium hydroxide, and tetramethyl ammonium hydroxide, among others. Typically, the concentration of the acids or bases used is within the range of about 0.1 M to about 1 M. The film is then developed in aqueous acid or base to etch the unexposed regions following an optional thermal cure at a temperature greater than about

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100 °C. This process produces a negative-tone image in the film. For many compositions, the resulting patterned films are amorphous, providing the means to realize high-resolution, small critical-dimension patterning without the limitations generally associated with crystalline films. By preheating the applied film to higher temperatures prior to field exposures, differential etching rates can be induced to realize positive-tone images. FIG. 15 demonstrates differential etching rates for thermally pre-treated, single-layer film. The graph demonstrates that thermal treatment affects etching rates such that exposed regions etch faster than unexposed regions following an initial time.

In another embodiment, a HafSOx film is treated with a mixture of sodium hydroxide and hydrogen peroxide, resulting in anion exchange and formation of a $M(OH)_x/H_2O_2$ film. Alternatively, a previously prepared $M(OH)_x$ film may be soaked in hydrogen peroxide to form a $M(OH)_x/H_2O_2$ film. The resulting $M(OH)_x/H_2O_2$ film is then patterned by exposure to light or an electron beam. These techniques provide a means for directly patterning simple of complex MO_x films without a polymer resist. For example, HfO_2 films may be directly patterned for use as high k dielectrics in Si CMOS circuits and printed electronics applications. In another example, a patterned TiO_2 film can be produced from a $Ti(OH)_x/H_2O_2$ film formed by solution deposition of $Ti(OH)_4$ in H_2O_2.

These methods substantially eliminate diffusion used in two-layer embodiments, lower exposure doses, and improve line-edge roughness and critical dimensions. FIG. 16 is an AFM (atomic force microscope) image of a HafSOx film patterned via a single-layer, negative tone process with an electron beam at dose levels ranging from greater than 0 $\mu C/cm^2$ to at least 400 $\mu C/cm^2$. The nanometer scale to the right of the image indicates the height of the features etched into the film. As shown in FIG. 16, features have been written via electron-beam exposure at dose levels as low as 2 $\mu C/cm^2$. This dose level is comparable to the best known chemically amplified polymer resists and 1000 times lower than that previously demonstrated for an inorganic resist. Features can be produced with a resolution of less than about 20 nm. In addition, the films demonstrate structural integrity (e.g., smooth, dense, pinhole-free) to less than 3 nm, nearly an order of magnitude smaller than that demonstrated for HSQ.

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The film application, heating, and etching steps associated with a polymer resist, as well as the vacuum and high-temperature processing steps of the inorganic material, have been eliminated in the patterning process. The resulting patterned film could be a functional component of an electronic device, a hard mask for subsequent patterning of the underlying substrate, or a template for imprinting. Except for the electron-beam exposure, all processing is conducted in a normal environment in air. Considering the elimination of several processing steps, the disclosed technique provides a new method to improve device production yields and lower fabrication costs. Relying on the exclusive use of aqueous chemistries, the process is also environmentally green, and washed products can be completely recovered and recycled. The technique has applications to many advancing technologies. Its use is not restricted only to the systems described herein.

B. Imprint Lithography

Hot embossing and photo-initiated imprint lithography are additional methods for producing patterns in HafSOx, ZircSOx and related materials. The hot-embossing process, illustrated schematically in FIG. 17, most commonly has been applied to creating patterns with organic polymers. The semi-solid form of HafSOx and related compositions provides an opportunity to pattern inorganic materials having much higher mechanical strength, chemical stability, and unique electrical and optical properties relative to organic polymers.

With reference to FIG. 17, HafSOx or related inorganic material, instead of an organic polymer, is solution deposited, such as by spin coating or inkjet printing, on a suitable substrate 1712 to form HafSOx layer 1714. Substrate 1712 and HafSOx layer 1714 define laminate structure 1710. A stamp 1716 with unit features of desired size scale, such as nanometer, micrometer or millimeter size scale, is pressed into the semi-solid HafSOx or related film layer 1714 to form stamped layer 1718. Stamped layer 1718 and substrate 1712 are then heated to harden the HafSOx. The stamp is then removed to define a patterned HafSOx material in patterned laminate structure 1720.

Alternatively, peroxide or related small, weakly coordinating ligand can be added to HafSOx, ZircSOx, and related materials. Subsequently, during the

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stamping step, the film can be exposed to short wavelength light, promoting chemical condensation and hardening of the patterned film. The stamp is then removed to define a pattern film. This technique represents a new innovation in step-and-flash imprint lithograpy (SFIL) that is commonly used to imprint polymer materials.

C. Measuring Device

The chemistry developed for the bilayer positive resist technology noted above also can be used to fabricate a physical ruler, as illustrated in FIG. 18, for use in standardizing measurements in suitable fields, such as electron microscopy. In this application, a nanolaminate 1810 of alternating acid-soluble layers 1812 and acid-insoluble layers 1814 is deposited. The acid soluble layers are formed by solution deposition of a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8. Typically this layer is doped with copper. The acid-insoluble layers are formed by solution deposition of a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8.

The widths of the layers 1812 and 1814 are accurately determined, such as by using X-ray reflectivity. The acid-soluble layers 1812 are then etched to reveal a

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finger-type pattern 1820 that can be used as a secondary reference in accurately measuring objects in an electron microscope.

D. Corrosion Barriers

The precursor liquid can be coated onto a suitable substrate, such as a metal or alloy or ceramic, to form a corrosion barrier. In addition, the liquid can be drawn into fibers, placed in a mold, or used alone. The liquid is converted into solid, stable form by any suitable process, including hydrolysis, annealing, or pyrolysis in air. Typically, this requires heating to temperatures, and for a period of time, effective to achieve the desired results, such as a temperature normally above 100 °C for at least a few seconds, more typically at least a few minutes.

Because of the atomically dense nature of the films, potential applications include, but are not limited to, thermal, corrosion and oxidation protection for metals and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal and ceramic-based systems, fibers for composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, catalyst supports, as well as many others. The ability to laminate the films provides an opportunity to randomize the location of defects in one layer relative to another, providing enhanced corrosion protection.

E. Optical Coatings

The precursor liquids can be coated as individual layers and in multilayer formats onto suitable optical substrates to produce antireflection coatings, dielectric mirrors, X-ray mirrors, interference filters, waveguides, planar coatings, and scratch-resistant surfaces. Multilayer periodicity is achieved by alternately depositing at least two material compositions. Single layer periodicity can be achieved by etching, as described for photolithography processes. The amorphous nature, sharp interfaces between layers, and abilities to control dielectric constants provides a process for realizing performance near theoretical limits.

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In multilayer or single layer configurations, which have been selectively deposited or etched, the periodic structure is appropriate for diffracting applications. Combinations of single or multiple materials and/or voids may define the structures. The use of void space allows for great contrast of physical properties within given structures. Functional characteristics may be enhanced or realized by the use of void space. Optical gratings may be similarly defined.

Because substantially smooth surface films can be deposited according to embodiments of the method disclosed herein, films may be used to planarize substrate layers such as metal, ceramics, and plastics that exhibit greater degrees of roughness.

F. Luminescent Films

A material may absorb energy and emit photons in a number of luminescent processes. The luminescent events may involve only the predominant phase (or host), or also may include added elements. A single material may serve as host for numerous luminescent additives. Many of the disclosed film compositions are visibly transparent with transparency potentially extending into the ultraviolet portion of the spectrum. These materials potentially function well as luminescent host materials. These materials can be selectively doped with common luminescent ions, including by way of example, and without limitation, Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof, to yield light-emitting films of interest for lighting and display applications.

G. Printed Electronics

Manufacturers are seeking new, efficient fabrication methods that eliminate the limitations of conventional vapor deposition and lithographic processing. Printing and related maskless techniques are widely regarded as paths forward for realizing advancement in manufacturing efficiencies for back-plane electronics.

The disclosed solution-processed thin films exhibit morphological and device-functional characteristics similar to those achieved by the most advanced vapor-phase processing methods. Solutions of the disclosed compositions can be imprinted, such as with microcontact, gravure, an inkjet printer or other suitable

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means. The resulting imprinted solutions can be used to fabricate stable inorganic transistor arrays exhibiting device mobilities of about 10 cm^2/Vs with dielectric leakage current densities less than about 20 nA/cm^2. Dielectric and semiconductor inks also can be printed onto glass substrates to produce transistor arrays having mobility of about 5 cm^2/Vs and dielectric leakage currents less than about 100 nA/cm^2. MIM capacitor arrays can be fabricated with relative dielectric constants greater than about 5 and leakage current densities less than about 50 nA/cm^2.

IV. EXAMPLES

The following examples are provided to exemplify particular features of working and/or hypothetical embodiments of the present invention. A person of ordinary skill in the art will appreciate that the scope of the present invention is not limited to the particular features stated in such examples.

Example 1

This example describes a general method that has been used to prepare solutions as sources for bulk precipitates or for use as thin film precursors. The following reagents were used: $HfOCl_2 \cdot 8H_2O$ (Alfa Aesar, 99+% excluding 1.5%Zr); $ZrOCl_2 \cdot 8H_2O$ (Wah Chang spectrographic grade); $La_2(SO_4)_3$ (Alfa Aesar, 99.9%); $La(NO_3)_3 \cdot 6H_2O$ (Johnson Matthey, 99.9%); $Ce_2(SO_4)_3 \cdot 8H_2O$ (Strem, 99%); CaO (Alfa Aesar, 99.95%); $(NH_4)_2SO_4$ (Mallinkrodt AR); H_2SO_4(aq) (EM Science, GR ACS, 95-98%); and NH_3(aq) (EM Science, GR ACS, 28-30%). All solutions were prepared by combining $HfOCl_2$ or $ZrOCl_2$ with $La_2(SO_4)_3$, $Ce_2(SO_4)_3$, or CaO as necessary for a total metal concentration of about 0.8 M, followed by addition of sulfate solution, for a total metal concentration of about 0.5 M. These solutions were directly used for heat-induced precipitation and spin-coating dielectric films. Additional modifications were made as necessary to serve as precursors for hydroxide precipitation reactions or nanolaminate depositions.

Example 2

This example describes a general method that has been used for bulk precipitation from solutions made according to Example 1. Precipitation was

induced by immersing tubes of solution in a boiling water bath for 40 minutes. For hydroxide-induced precipitation, $HfOCl_2$ and $La_2(SO_4)_3$ were mixed as 23% La (metal percent), followed by addition of solutions of $La(NO_3)_3$ and $(NH_4)_2SO_4$ to provide a hafnium concentration ([Hf]) of about 0.39 M, a lanthanum concentration ([La]) of about 0.18 M, and a sulfate ([SO_4]) concentration of about 0.42 M. 1.9 mole equivalents (relative to total metals) of saturated NH_3(aq) were then added quickly and the resulting mixture stirred for 1 minute. All precipitates were separated from the supernatant by paper filtration with suction, including several rinses with de-ionized water. The filtrates were dried at room temperature for 1 day. Samples were subsequently heated in alumina crucibles in ambient air at temperatures from about 100 °C to about 1,500 °C for about 1 to about 4 hours. XRD data was collected with a Siemens D5000 diffractometer, utilizing Cu Kα radiation. Thermogravimetric data were collected with a Shimadzu TGA-50 by heating samples (10–20 mg) in a Pt crucible under flowing N_2(g), typically at a rate of 10 °C $minute^{-1}$, and holding for 15 minutes at the highest temperature. Inductively coupled plasma atomic emission spectroscopy (ICPAES) was conducted with a Jobin Yvon JY2000 analysis setup. Samples were dissolved in digestion bombs at 200 °C for a few hours and diluted to measurable levels.

Example 3

This example describes a general method that has been used for deposition of thin films using solutions made according to Example 1. Thin-films of HafSOx, ZircSOx, and derivatives with added La, Ce, or Ca, were deposited on Si substrates by spin-coating at 3,000 rpm for 30 seconds, followed by immediate hotplate polymerization at 135° C for 1.5–2 minutes (additional heating on a 325 °C oven surface for 15 seconds to about 2 minutes may be required for certain derivatives). This process was repeated until desired deposited film thicknesses were obtained. A final oven anneal at 325 °C for 5–10 minutes was used.

Precursors for nanolaminate films were prepared by adding H_2SO_4 to $HfOCl_2$ or $ZrOCl_2$ as 46% sulfate relative to metal. Solutions were diluted to a metal concentration of 0.03–0.13 M. Alternating layers of HafSOx and ZircSOx were deposited in the same fashion as described for dielectric films.

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The silicon substrates had a surface of SiO_2 or Ta metal. A 500-nanometer Ta surface was used for dielectric testing. A 200-nanometer SiO_2 surface was used for all other purposes. The surfaces were prepared for deposition by ultrasonic cleaning in (Decon Labs, Contrad 70) solution at 45 °C for 45 minutes, then rinsing the surfaces thoroughly with Millipore water before deposition.

XRD data were collected with a Rigaku RAPID diffractometer, employing Cu Kα radiation generated from a rotating anode at 50 kV and 270 mA. The incident beam angle was 7.6°, while the diffracted beam was collected with an image plate. XRR data were collected with Cu Kα radiation. Low angle reflections up to 10° (2θ) were collected at 0.005° steps. Transmission FTIR data were collected with a Nicolet 5PC spectrometer, with an uncoated substrate as reference. EPMA was collected.

MIM capacitor structures were completed by thermally evaporating circular contacts of Al (1.2 mm diameter) on deposited dielectrics. Parameters of dielectric constant and loss tangent were obtained. Bottom-gate transistor structures also were fabricated by sputtering inorganic channel materials without active heating. ZTO-channel devices were subsequently heated to 325 °C for 1 hour. Aluminum source and drain contacts were thermally evaporated. Transistor characterization was performed.

Example 4

This example describes a general method for producing smooth, dense, and pinhole-free ultra-thin nanolaminate films as thin as about 2 nm. Precursor solutions containing $HfOCl_2 \cdot 8H_2O$ or $ZrOCl_2 \cdot 8H_2O$, H_2O_2 (30%) and H_2SO_4(aq) were prepared as described in U.S. Patent Publication No. 2005/0242330 A1. The precursor solutions contained a metal ion concentration of about 0.05 M to 0.4 M with 70% H_2O_2 and 50% sulfate relative to metal. The difference in metal ion concentrations allowed for thickness per coat variation from 3 nm to 25 nm. Thin films were deposited on silica substrates with thermally grown SiO_2. Substrates were cleaned by using an ultrasonic bath with Contrad-70 solution at 45 °C for 60 minutes followed by a rinse with deionized water. Films were deposited by using a spin coater with a spin rate of 3000 rpm for 30 seconds followed by hotplate

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polymerization at 125 °C for 1-2 minutes. Spin-coating and polymerization steps were repeated until the desired thickness was reached. After the desired thickness had been reached, some films were heated to crystallization temperature. Other films were first treated in a 0.1 M-0.5 M NaOH bath for 1-2 minutes, then rinsed in a deionized water bath for 1-2 minutes before the thermal treatment.

Thin-film characterization using X-ray diffraction (XRD) analysis was performed on a Rigaku R-AXIS RAPID with Cu Kα radiation. Atomic force microscopy (AFM) measurements were performed using a Digital Instruments Nanoscope III Mulitmode AFM operated in contact mode with a Veeco NP-20 SiN probe and a scan frequency of 1.15 Hz. X-ray reflectivity (XRR) measurements were performed using a Bruker Discover D8 and used to determine surface and interfacial roughness of the films. Compositional analyses were acquired on a Cameca SX-50 electron microprobe equipped with 4 tunable wavelength dispersive spectrometers. Accelerating voltages of 12, 16 and 22 kV were used and averaged over 5 points to monitor O, Cl, Na, S, and Si Kα intensities and Zr and Hf Lα intensities. Standards used for analysis were MgO, Hf, Zr, FeS_2 (pyrite), $Ca_5(PO_4)_3Cl$ (apatite), Si, and Si_3AlNaO_8 (albite). Corrections to the raw intensity were made by using Probe for Windows automation and analysis package. The StrataGEM compositional analysis software package was used for thin film geometry corrections by comparing experimental K-ratios to simulated values.

Amorphous, atomically flat, dense, pinhole-free thin films were deposited via spin coating for the as-deposited and exchanged films. FIG. 19 is an AFM image of an unexchanged HafSOx film with a roughness of about 0.1 nm. FIG. 20 is a TEM image of an HfO_2 film following ion exchange of HafSOx and thermal treatment at 850 °C. Unexchanged films remained smooth and amorphous up to 600 °C for Zr and 650 °C for Hf. However, after heating above these temperatures, films crystallized and became rough, forming volcano-like features at the surface. FIG. 21 is an AFM image of a HfO_2 film deposited on silica. The HfO_2 film was formed by thermal decomposition of $HafSO_x$. The resulting film had a roughness of about 5 nm, resulting in volcano-like peaks. These features were most likely caused by the loss of SO_3. This was supported by thermal gravimetric analysis of Hf sulfate

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powder, where sulfate decomposition
(SO_3 (g) → SO_2 (g) and ½ O_2 (g)) occurs above 700 °C.

To eliminate the volcano effects, films were treated in a 0.1-0.5 M NaOH(aq) bath for 1-2 minutes to remove the SO_4^{2-} and Cl^- anions from the film before heating. NaOH previously has been shown to effectively exchange hydroxy anions for other anions in zirconium salts. The NaOH treatment caused a thickness reduction of 40-45% (giving layer thickness of 2-15 nm), but the treatment had little effect on the smoothness (~1Å) or amorphous nature of the films when heated below 500 °C or 550 °C for zirconia and hafnia, respectively.

FIG. 22 is an AFM image of a HafSOx film deposited on silica, subsequently treated with 0.1 M NaOH and heated to 450 °C for 10 minutes. The resulting film had a roughness of approximately 0.1 nm. Films heated above these temperatures crystallized, yet remained smooth at temperatures up to 850 °C.

FIG. 23 shows a HfO_2 film deposited on silica, subsequently treated with 0.1 M NaOH and heated to 850 °C for 10 minutes. The resulting crystallized film remained smooth with a roughness of about 0.2 nm.

A drop in crystallization temperature was seen in the X-ray diffraction plots (FIGS. 24-27). In FIGS. 24-27, the substrate peaks have been removed with software. The *'s represent the major tetragonal phase peaks. FIG. 24 is an XRD plot of the untreated HfO_2 film crystallized as a mixture of tetragonal and monoclinic phases at 700 °C. The HfO_2 plot is a reference plot for the monoclinic phase. In contrast, FIG. 25 is an XRD plot of the 0.1 M NaOH-treated hafnia film crystallized only in the monoclinic phase at 550 °C. The HfO_2 plot is a reference plot for the monoclinic phase. FIG. 26 is an XRD plot of untreated zirconia films crystallized in a mixed monoclinic and tetragonal phase at 650 °C. The ZrO_2 plot is a reference plot for the monoclinic phase. As seen in FIG. 27, the 0.13 M NaOH-treated zirconia films crystallized only in the tetragonal phase at 500 °C. Upon further heating, films developed both monoclinic and tetragonal phases. The tetragonal phases of HfO_2 and ZrO_2 have been observed in previous thin film studies. The lower crystallization temperature, crystallization and loss of thickness indicated that the NaOH treatment removed anions (SO_4^{2-} and Cl^-) from the thin films.

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Electron probe microanalysis (EPMA) of a film deposited from the 0.4 M Hf solution and heated to 350 °C for 5 minutes gave a film with composition $HfO_{1.32}(SO_4)_{0.61}Cl_{0.15}$. The chlorine in the film was a result of kinetic trapping as a consequence of the rapid thermal dehydration. Films that were treated in the NaOH(aq) bath did not have measurable sulfur levels (less than 0.01 atomic percent), and less than 0.3 atomic percent Cl was observed. This confirmed that the sulfur and chlorine were both removed from the films in the NaOH(aq) bath. EPMA also verified that the residual sodium left in the film after the treatment was less than 0.3 atomic percent.

Example 5

In a specific embodiment of the approach described above, hydrated indium and gallium nitrate salts ($In(NO_3)_3 \cdot 0.5H_2O$ and $Ga(NO_3)_3 \cdot 9.5H_2O$) were dissolved in methanol (CH_3OH). Final concentrations were [In] = 0.288 M, [Ga] = 0.170 M. Zinc powder was then added to the solution, and the flask sealed. The final concentration of zinc was 0.2 M. Reacting over a period of 1-7 days, the powder was slowly oxidized and dissolved to bring the total metal ion concentration to 0.658 M. The methanolic solution was exposed to air, and the methanol was allowed to evaporate at room temperature. The solid residue remaining in the solution was then dissolved in H_2O to a total metal concentration of 0.395 M. This precursor solution was spin-coated on a SiO_2 substrate with a conductive back contact and annealed to 450 °C for 1-4 hours. Following annealing, a transparent, amorphous $InGa_{0.6}Zn_{0.7}O_{3.15}$ semiconductor film was obtained as shown in the SEM image of FIG. 28. Aluminum source and drain contacts were thermally evaporated onto the oxide semiconductor film through a shadow mask to produce a thin film transistor (TFT). Field effect mobility for these TFTs was shown to exceed 8 $cm^2 V^{-1} s^{-1}$.

Example 6

This example describes two general methods of bilayer inorganic lithographic processing. In one working embodiment, a HafSOx film with a thickness from about 30 nm to about 60 nm was solution deposited onto a SiO_2/Si substrate. The substrate was placed directly onto a hot-plate set at about 50 °C and

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heated to impart structural integrity to the film. The resulting film was acid insoluble. The substrate was then placed on a heated platen (about 50 °C to 200 °C) of an ink-jet printer, where copper formate lines were printed onto the substrate via a thermal ink-jet head. Copper formate decomposed and diffused into the HafSOx film on heating, rendering the film soluble. Following a rinse in water, additional heating to about 300 °C, and development in dilute acid, the drawn lines were clearly evident as shown in FIG. 29.

In another working embodiment, patterns also were produced via photolithography. Exposure of a $HfO_{2-x}(SO_4)_x$ bilayer film with deep UV light using an unfiltered deuterium lamp promoted copper formate decomposition for subsequent interdiffusion and development of the pattern shown in FIG. 30. Feature sizes were reduced to about 22 nm with electron beam writing. The interdiffusion process can be spatially controlled via electron-beam energies to draw patterns and objects on the nanoscale. Highly resolved patterns were produced at charge dose levels near 150 $\mu C/cm^2$, representing a sensitivity similar to that of many polymer resists. FIGS. 31 and 32 are two patterns produced by electron-beam writing at a dose of level of about 200 $\mu C/cm^2$. In FIG. 31, the line spacing is 500 nm as measured by an electron microscope.

Example 7

This example describes general methods for patterning a single-layer inorganic film. A single inorganic film containing peroxide or related coordinating species is spin-cast, liquid misted, or ink-jet printed onto an appropriate substrate. The film is heated at modest temperatures of less than 100°C to provide structural integrity to the film. The film is then exposed through a photomask to high-energy light, a maskless pattern via spatial light modulation, a defined laser beam, or electron beam to define a pattern or other preferred film features. Two examples of photographically patterned films are shown in FIGS. 33 and 34. FIG. 33 is a patterned $ZrO_{2-x}(SO_4)_x$ film. FIG. 34 is a patterned TiO_2 film. The TiO_2 film was about 15-50 nm thick. It was patterned using an unfiltered deuterium lamp, followed by etching with 0.1-0.2 M HCl for less than 60 seconds. FIGS. 35-37 are $HfO_{2-x}(SO_4)_x$ films patterned by an electron beam. The films were about 30-60 nm

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thick. They were patterned using an electron beam at a dose level of 200 $\mu C/cm^2$, followed by etching with 5-12 M HCl for about 1-4 minutes.

In view of the many possible embodiments to which the principles of the disclosed invention may be applied, it should be recognized that the illustrated embodiments are only preferred examples of the invention and should not be taken as limiting the scope of the invention. Rather, the scope of the invention is defined by the following claims. We therefore claim as our invention all that comes within the scope and spirit of these claims.

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We claim:

1. A device comprising a thin film or laminate structure comprising at least one hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to about 3.8.

2. The device according to claim 1 wherein the thin film or laminate has a permittivity value within the range of from about 9 to about 12, a breakdown field up to at least 6 MV cm^{-1}, and a leakage current near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}.

3. The device according to claim 1 where the compound further comprises lanthanum, and has a formula $M_{1-z}La_zO_{2-x-z/2}(SO_4)_x$ (MSOx:La), where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to about 3.8.

4. The device according to claim 1 where the compound is HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, or ZircSOx:Ca, the device having leakage current less than 50 nA cm^{-2} and permittivity values of from about 9 to about 12.

5. The device according to claim 1 where the device is a field effect transistor comprising HafSOx:La and/or ZircSOx:La as a gate dielectric and zinc indium oxide and/or zinc tin oxide as channels, the transistor having an on-to-off ratio of greater than 10^6, and gate leakage currents are in the range of pA cm^{-2}.

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6. The device according to claim 1, further comprising an optical substrate where the thin film or laminate structure forms a coating on the optical substrate.

7. The device according to claim 6 where the coating is an antireflective coating and/or the coating is transparent to visible or ultraviolet light.

8. The device according to claim 6 where the optical substrate and coating define a dielectric mirror, an X-ray mirror, an interference filter, a diffractive grating, and/or a waveguide.

9. The optical device according to claim 7 where the coating is selectively doped to provide a doped light-emitting layer having luminescent ions selected from Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof.

10. The device according to claim 1 where the device is a master plate for imprint lithography and the thin film or laminate structure is deposited onto a flexible or glass substrate, the thin film or laminate structure comprises a first layer of HafSOx deposited onto the substrate and a second layer comprising ZircSOx:Cu, and where the laminate structure comprising the first and second layers is patterned by exposure to an energy source.

11. The master plate according to claim 10 where exposure to light or an electron beam through a mask causes the two layers to interdiffuse in exposed areas, thereby rendering previously undoped HafSOx layer soluble, the soluble HafSOx layer being removed to define at least partial printing features of the master plate.

12. A method for making a device, comprising:

providing a thin film or laminate structure, the structure comprising a substrate and one or more layers deposited onto the substrate;

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at least one of the one or more layers comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to about 3.8; and

exposing the structure to an energy source.

13. The method according to claim 12 where the thin film or laminate structure comprises a suhstrate, a first layer for patterning, and a second layer comprising the hafnium and/or zirconium oxy hydroxy compound, where the second layer is a positive resist layer, exposure to an energy source converts the resist layer material into a developer-soluble material, and the method further comprises removing resist layer material exposed to the energy source by treating the resist layer with a developer solution to pattern the structure.

14. The method according to claim 12 where the thin film or laminate structure comprises a substrate, a first layer for patterning and a second layer comprising the hafnium and/or zirconium oxy hydroxy compound, where the second layer is a negative resist layer, exposure to an energy source causes the resist layer to polymerize, and the method further comprises patterning the structure by treating the structure with a developer to remove material not exposed to the energy source.

15. The method according to claim 13 where the positive resist comprises a bilayer, where a second layer of the bilayer comprises an acid-soluble Cu-doped zirconium oxide sulfate (ZircSOx:Cu) film deposited on an insoluble hafnium oxide sulfate (HafSOx) film, and where exposure to an energy source comprising light or an electron beam through a mask causes the ZircSOx:Cu film and the HafSOx film to interdiffuse in exposed areas, thereby rendering the HafSOx film soluble.

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16. The method according to claim 12 where the hafnium and/or zirconium oxy hydroxy compound comprises sulfate, and where the sulfate is subsequently removed by ion exchange with an aqueous basic solution, the basic solution comprising a Group I metal hydroxide, soluble Group II metal hydroxide, soluble Group III metal hydroxide, soluble lanthanide hydroxide, ammonium hydroxide, and/or aqueous tertiary amine, or a combination thereof.

17. The method according to claim 12 comprising:

providing a suitable substrate comprising a semiconductor material, a metal, glass, silica, a polymeric material, or combinations thereof;

solution depositing a first HafSOx film onto the substrate;

solution depositing a second ZircSOx:Cu film onto the first film to form a laminate structure;

exposing the laminate structure to an energy source to cause the HafSOx film and the ZircSOx:Cu film to interdiffuse in exposed areas, thereby rendering previously undoped HafSOx film soluble; and

developing the exposed structure to remove HafSOx film.

18. The method according to claim 12 where the thin film or laminate structure comprises a substrate, a first layer of insoluble hafnium oxide sulfate (HafSOx) deposited onto the substrate, and a second layer comprising copper formate deposited onto the first layer, and where the laminate structure comprising the first and second layers is heated to a temperature from about 50 °C to about 200 °C to cause the copper formate to decompose and interdiffuse with the HafSOx layer, thereby producing a soluble product, the soluble product being removed.

19. The method according to claim 12 where the thin film or laminate structure comprises a substrate and a first layer comprising a solid inorganic acid or base, the solid inorganic acid or base comprising a metal having an atomic number in the range of 21-78, the first layer further comprising a peroxide or other coordinating anion, where the first layer is soluble in acid or base, the first layer is

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heated to a temperature from about 50 °C to about 125 °C to produce a structurally rigid film, and exposure to a laser, an electron beam, and/or light through a mask causes exposed areas of the film to become less soluble than unexposed areas, the unexposed areas being removed to define a pattern in the amorphous or crystalline film.

20. The method according to claim 19 where the film is exposed to an electron beam at a dose level of from greater than 0 $\mu C/cm^2$ to at least 400 $\mu C/cm^2$, more typically from about 2 $\mu C/cm^2$ to about 400 $\mu C/cm^2$, to define a pattern in the film with linewidths extending below 5 nm.

21. The method according to claim 19 where the patterned film is amorphous or crystalline, demonstrating structural integrity to less than about 3 nm.

22. The method according to claim 12, where the device includes a micro- or nano-channel array, and where the structure comprises a substrate, a first layer and a second layer, the second layer being a metal oxide layer, the method further comprising:

patterning the structure; and

exposing the structure to an energy source to form a durable material having a desired pattern produced by patterning the structure.

23. The method according to claim 12 further comprising stamping unit features of a desired size scale into a semi-solid hafnium or zirconium compound and related organic-free semi-solids to form a stamped layer that is thermally or photo hardened.

24. A device made according to the method of claim 12, the device selected from metal and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal- and ceramic-based systems, fibers for

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composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, and catalyst supports.

25. A method for making a device having a corrosion barrier, comprising:

providing a device;

forming at least one corrosion barrier on the device comprising a metal oxide layer comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to about 3.8; and

exposing the compound to an energy source to form the corrosion barrier.

26. A method for forming fibers, comprising:

providing a composition comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy bydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to about 3.8;

forming a solution comprising the compound;

drawing the solution into fibers; and

converting the fibers into solid, stable fibers.

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27. A method for making a metal oxide film where the film comprises at least two metals, the method comprising:

making a solution comprising dissolving one or more soluble salts consisting essentially of a metal cation and one or more anions in a non-complexing, non-aqueous polar solvent, where at least one of the metal cations has a formal charge greater than or equal to 3^+ and the concentration of metal cations with a formal charge greater than or equal to 3^+ exceeds 50 mol% of the metal cations in the metal oxide film, and where the solvent has a boiling point less than about 150 °C;

raising the pH of the solution, where raising the pH comprises adding a basic aqueous solution, adding a small amount of a soluble basic oxide, adding a gaseous compound capable of forming a basic aqueous solution, adding an electropositive metal which may consume protons and is incorporated into the film, adding an aqueous or gaseous oxidizing agent which consumes protons or decomposes counter ions but is not incorporated into the film, or any combination thereof;

producing a solid by evaporating the non-aqueous solvent;

dissolving the solid in water;

depositing the dissolved solid onto a substrate to form a patterned or blanket liquid film; and

thermally curing the film.

28. A method for making a metal oxide film, comprising:

providing a thin film or laminate structure, the structure comprising a substrate and one or more layers deposited onto the substrate, at least one of the one or more layers comprising a metal-acid film, the metal-acid film comprising a metal cation and an acid anion;

removing the acid anion by ion exchange with an aqueous basic solution, the basic solution comprising a Group I metal hydroxide, soluble Group II metal hydroxide, soluble Group III metal hydroxide, soluble lanthanide hydroxide, ammonium hydroxide, and/or aqueous tertiary amine, or any combination thereof; and

exposing the structure to an energy source, the energy source comprising a thermal energy source, a microwave energy source, a light source, or a laser.

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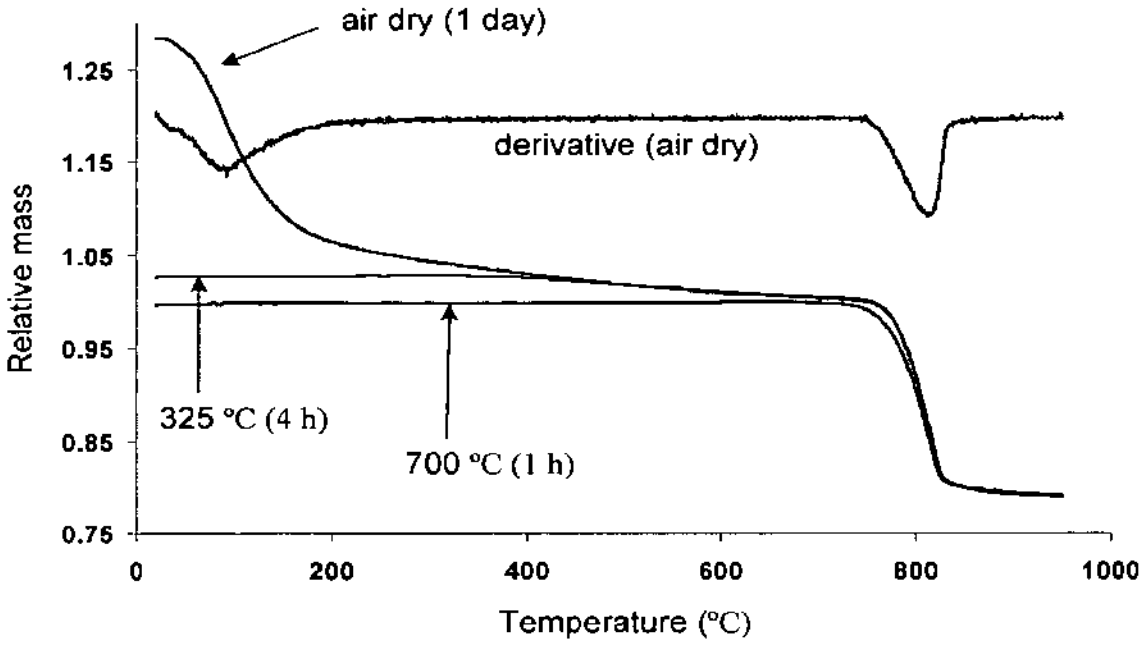

air dry (1 day)
derivative (air dry)
325 °C (4 h)
700 °C (1 h)
Relative mass
Temperature (°C)
1.25
1.15
1.05
0.95
0.85
0.75
0
200
400
600
800
1000

FIG. 1

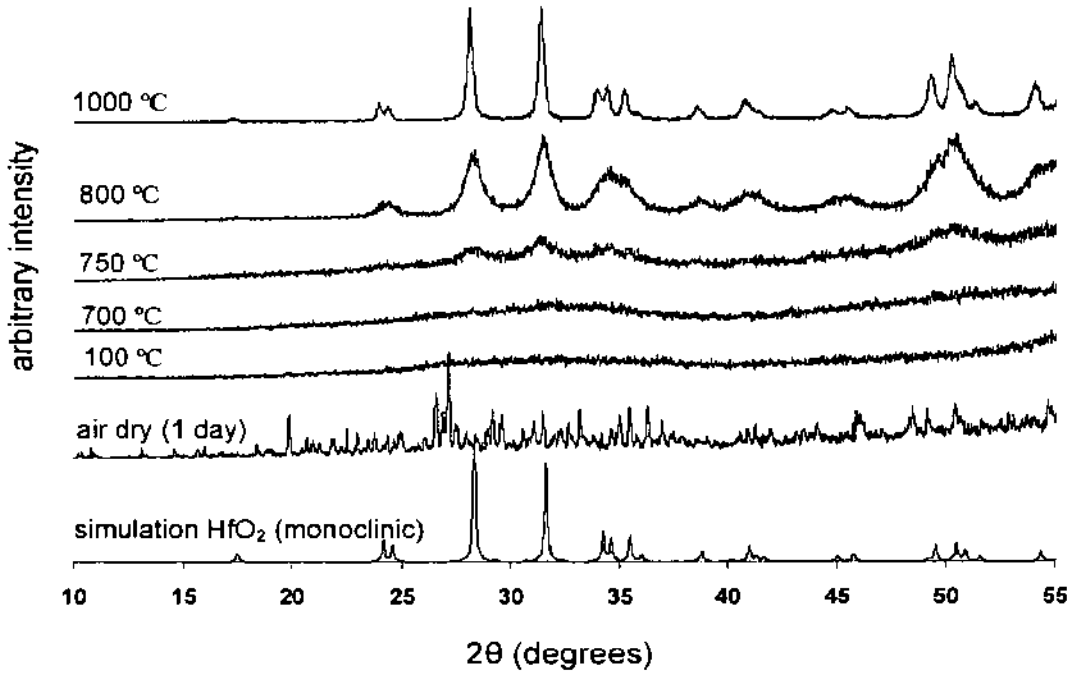

1000 °C
800 °C
750 °C
700 °C
100 °C
air dry (1 day)
simulation HfO2 (monoclinic)
arbitrary intensity
10
15
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 2

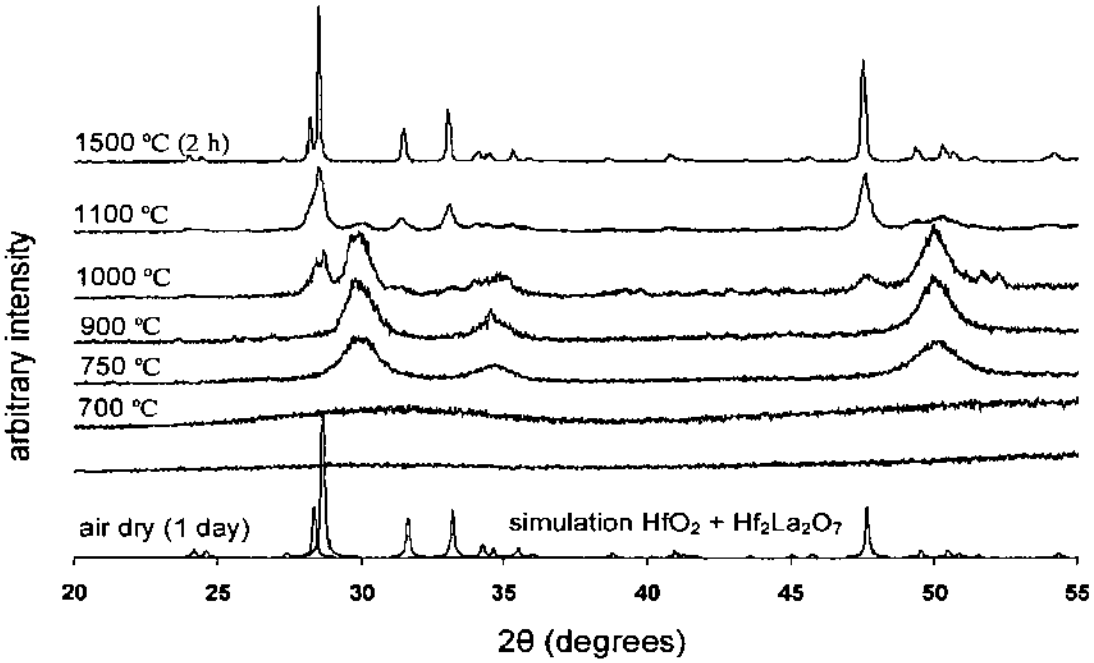

1500 °C (2 h)
1100 °C
1000 °C
900 °C
750 °C
700 °C
air dry (1 day)
simulation HfO_2 + $Hf_2La_2O_7$
arbitrary intensity
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 3

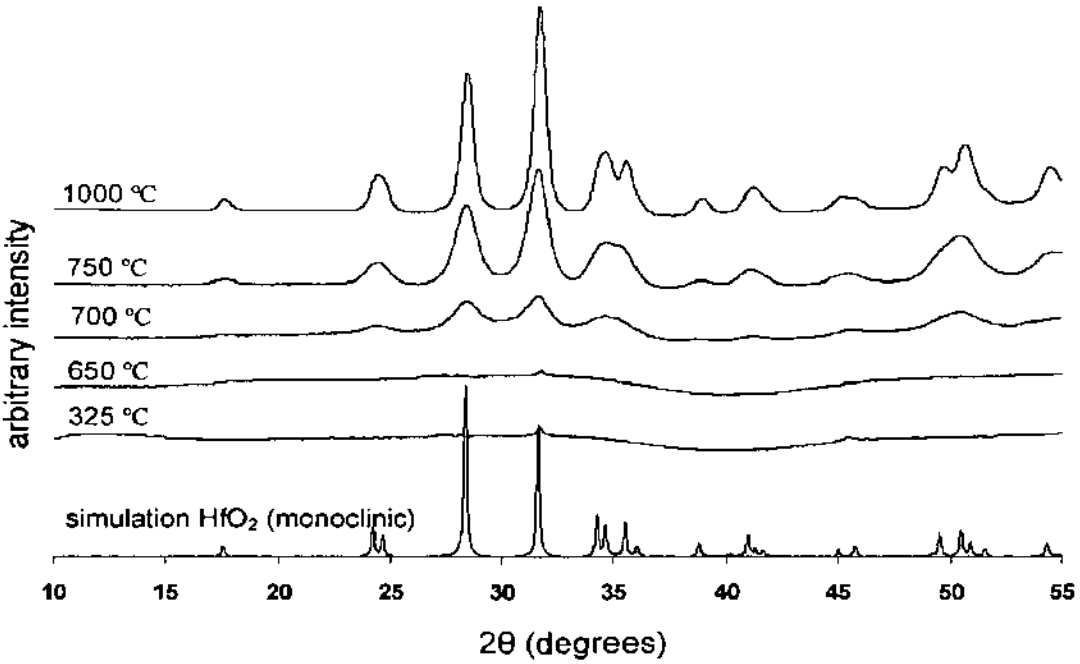

1000 °C
750 °C
700 °C
650 °C
325 °C
simulation HfO_2 (monoclinic)
arbitrary intensity
10
15
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 4

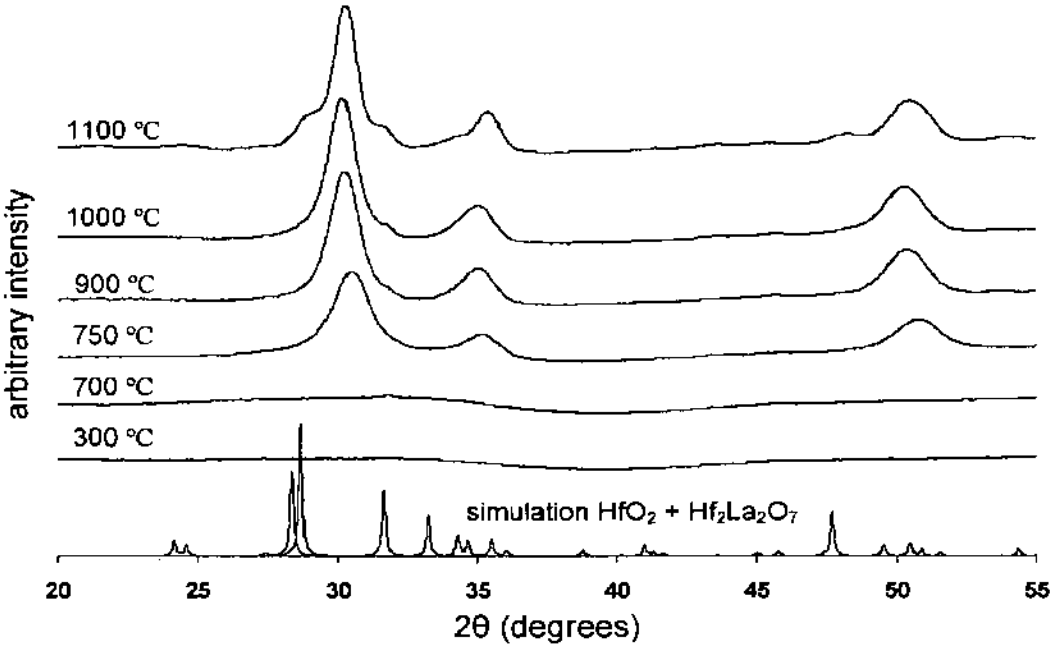

1100 °C
1000 °C
900 °C
750 °C
700 °C
300 °C
simulation HfO_2 + $Hf_2La_2O_7$
arbitrary intensity
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 5

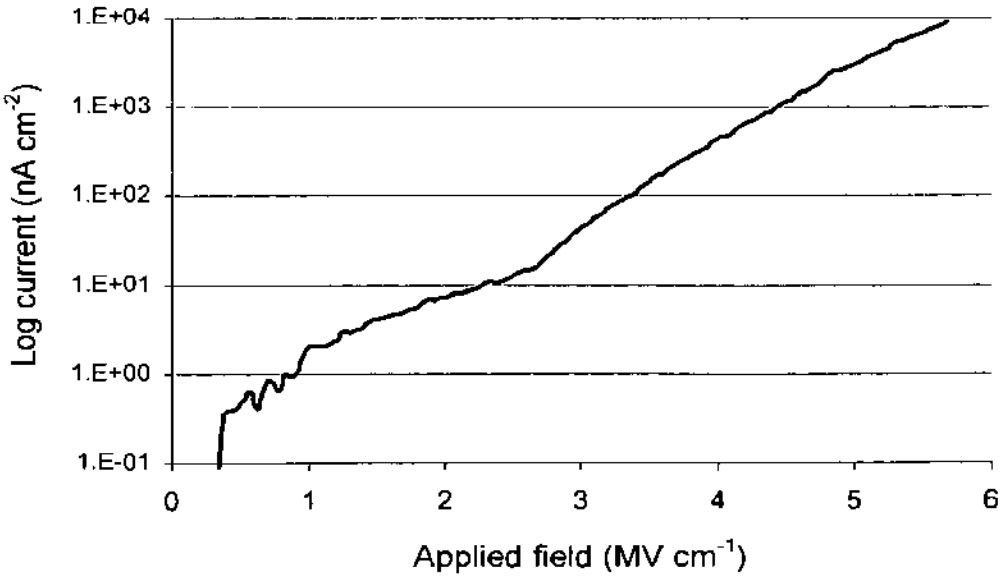

1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
Log current (nA cm^{-2})
0
1
2
3
4
5
6
Applied field (MV cm^{-1})

FIG. 6



FIG. 7

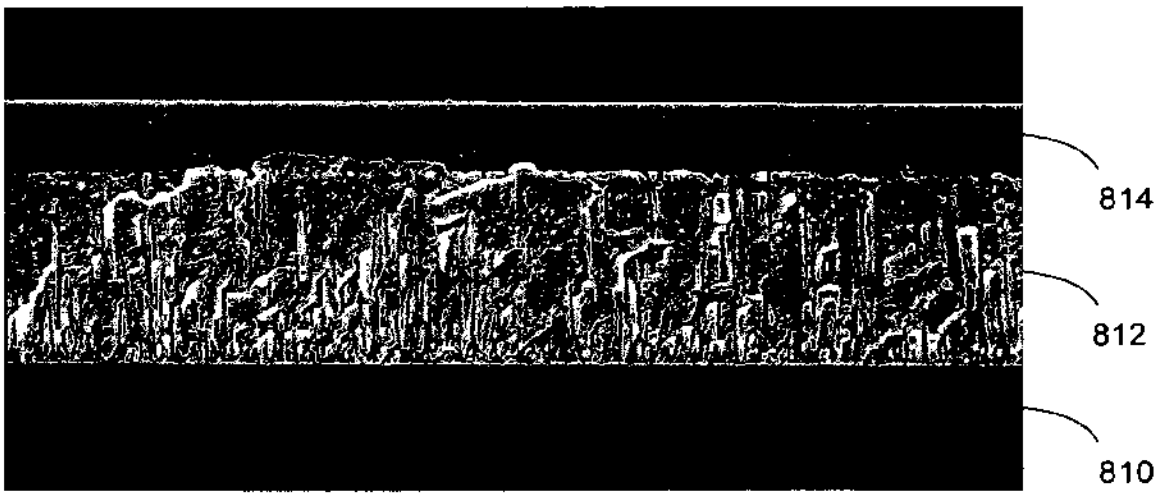


FIG. 8

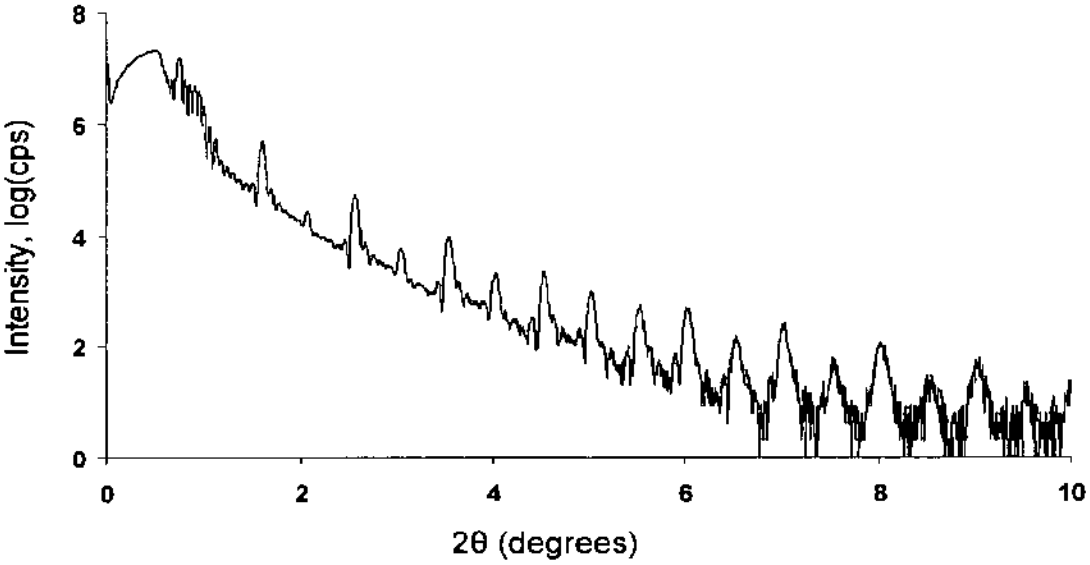


FIG. 9

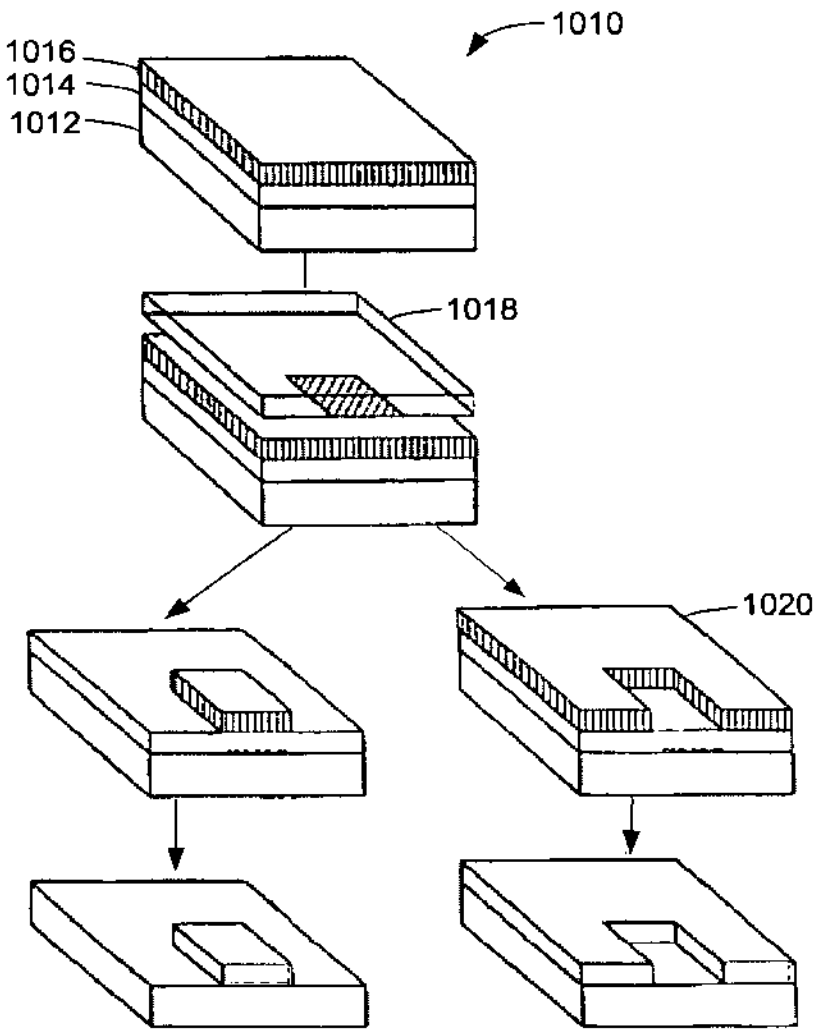


FIG. 10

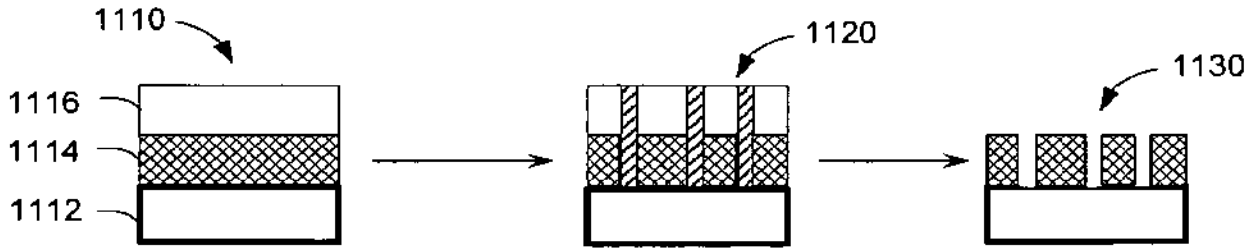


FIG. 11

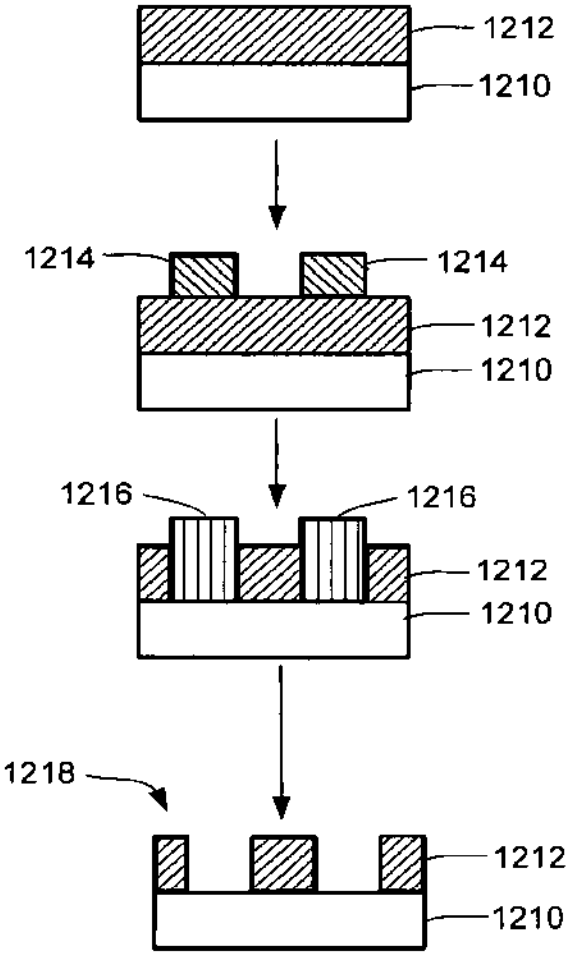

1212
1210
1214
1214
1212
1210
1216
1216
1212
1210
1218
1212
1210

FIG. 12

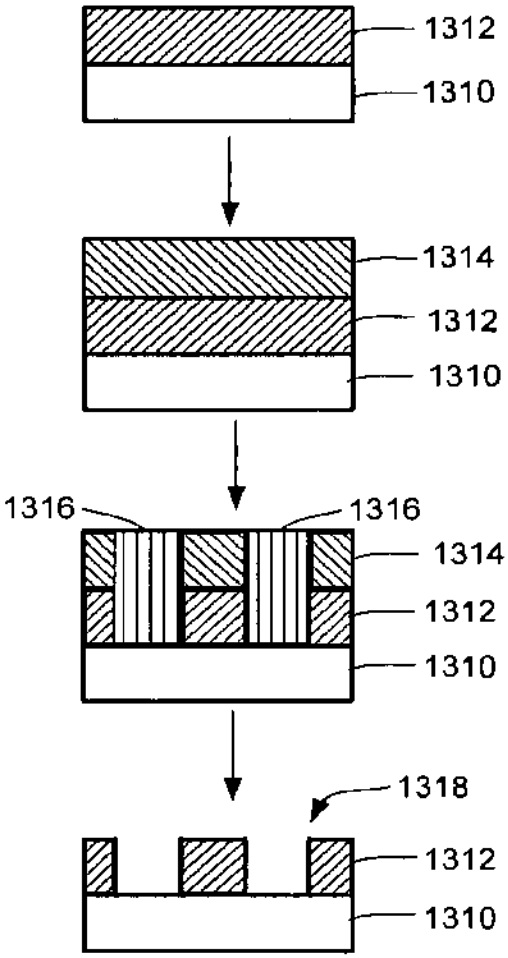

1312
1310
1314
1312
1310
1316
1316
1314
1312
1310
1318
1312
1310

FIG. 13

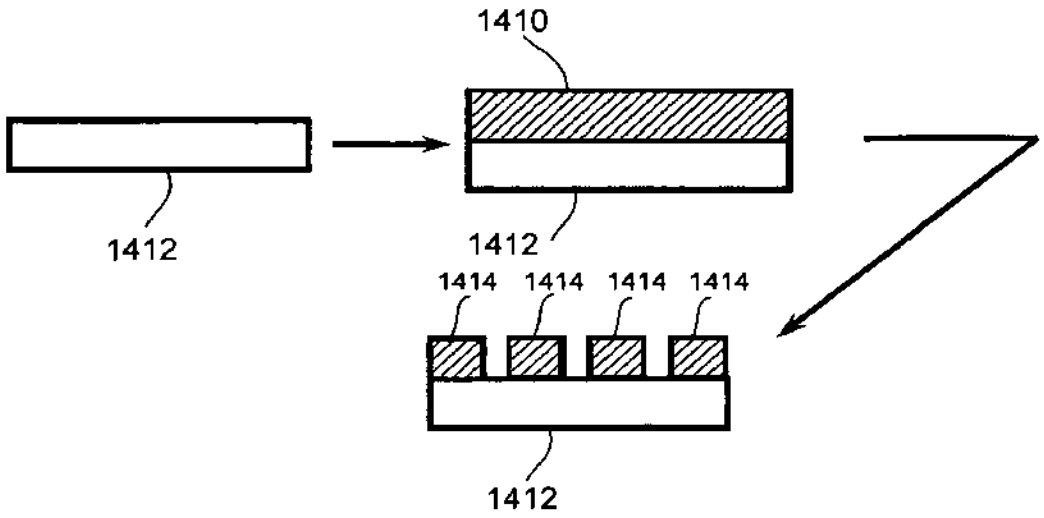

1410
1412
1412
1414
1414
1414
1414
1412

FIG. 14

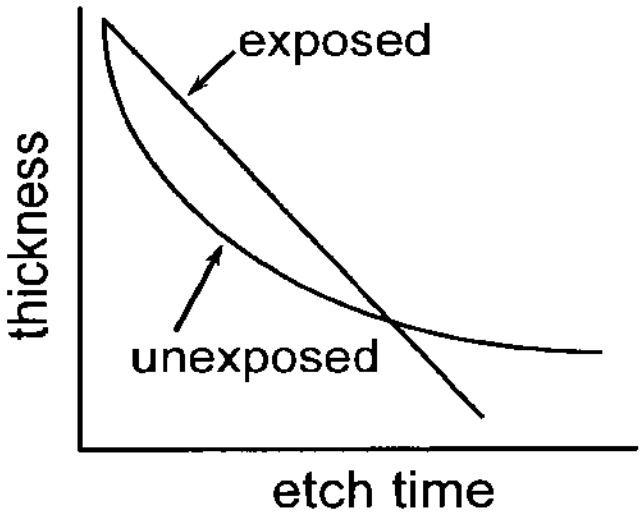

exposed
thickness
unexposed
etch time

FIG. 15

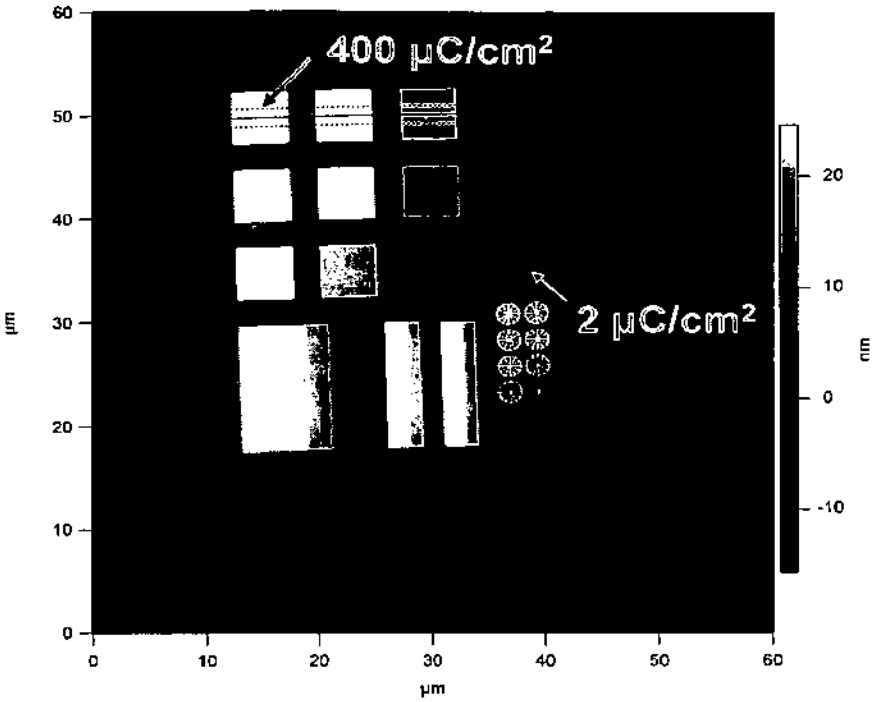

400 µC/cm²
2 µC/cm²
µm
nm
0
10
20
30
40
50
60
-10

FIG. 16

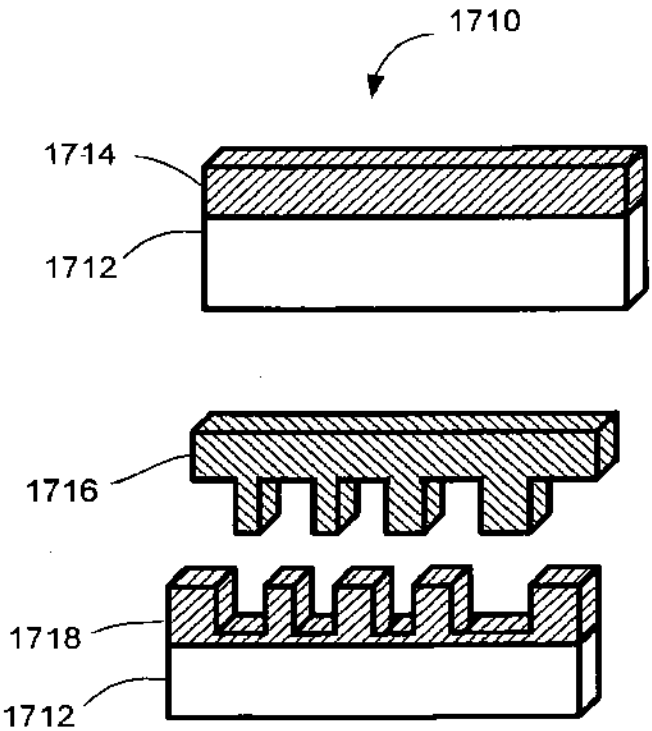

1710
1714
1712
1716
1718
1712

FIG. 17

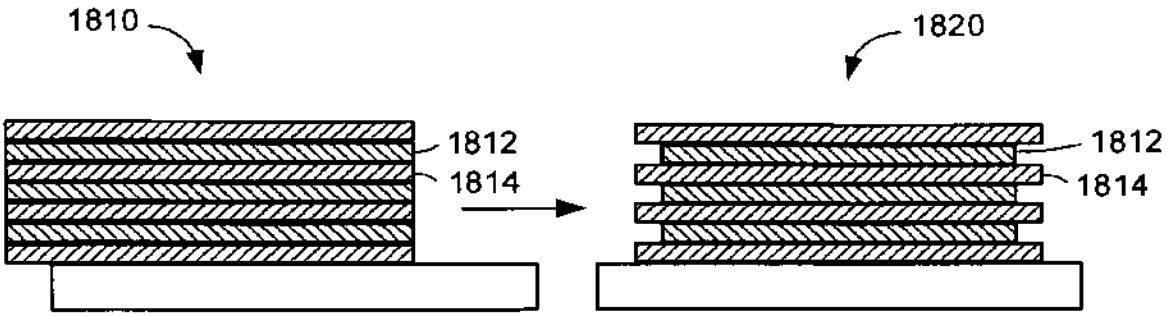


FIG. 18

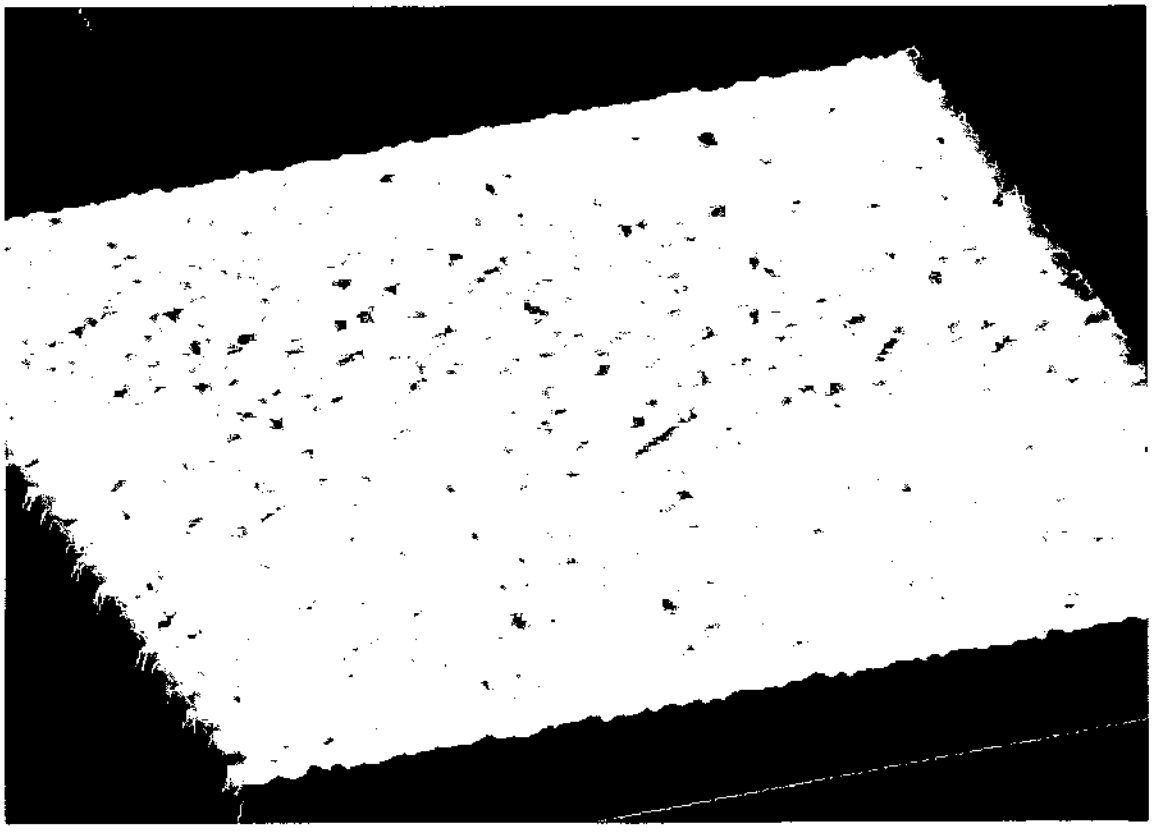


FIG. 19

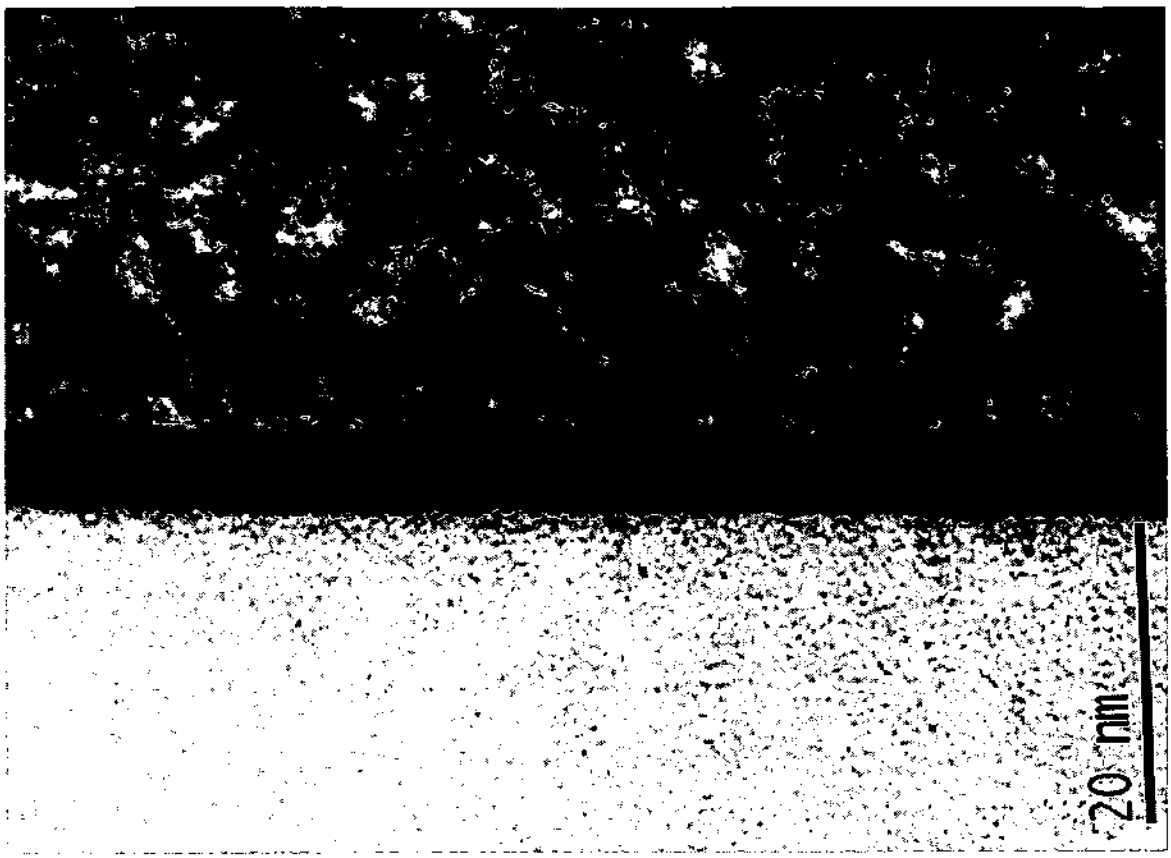


FIG. 20

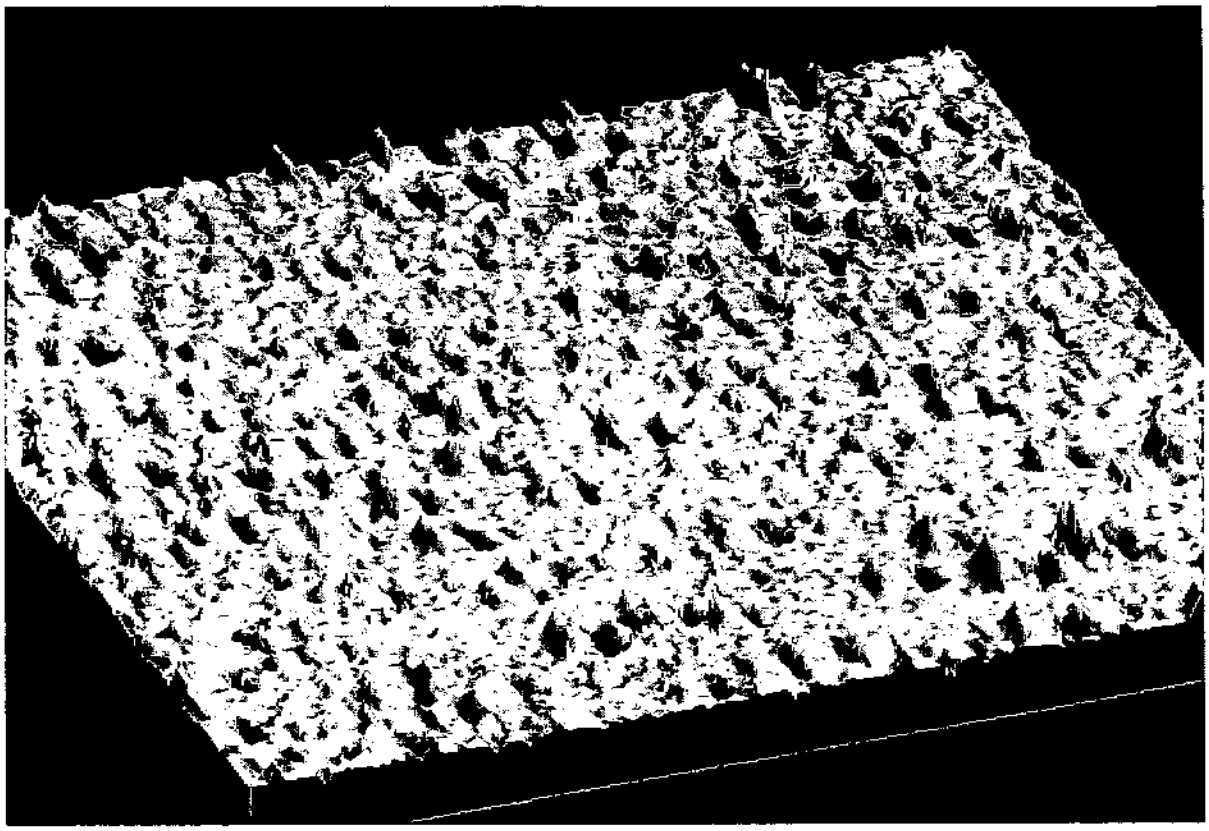


FIG. 21

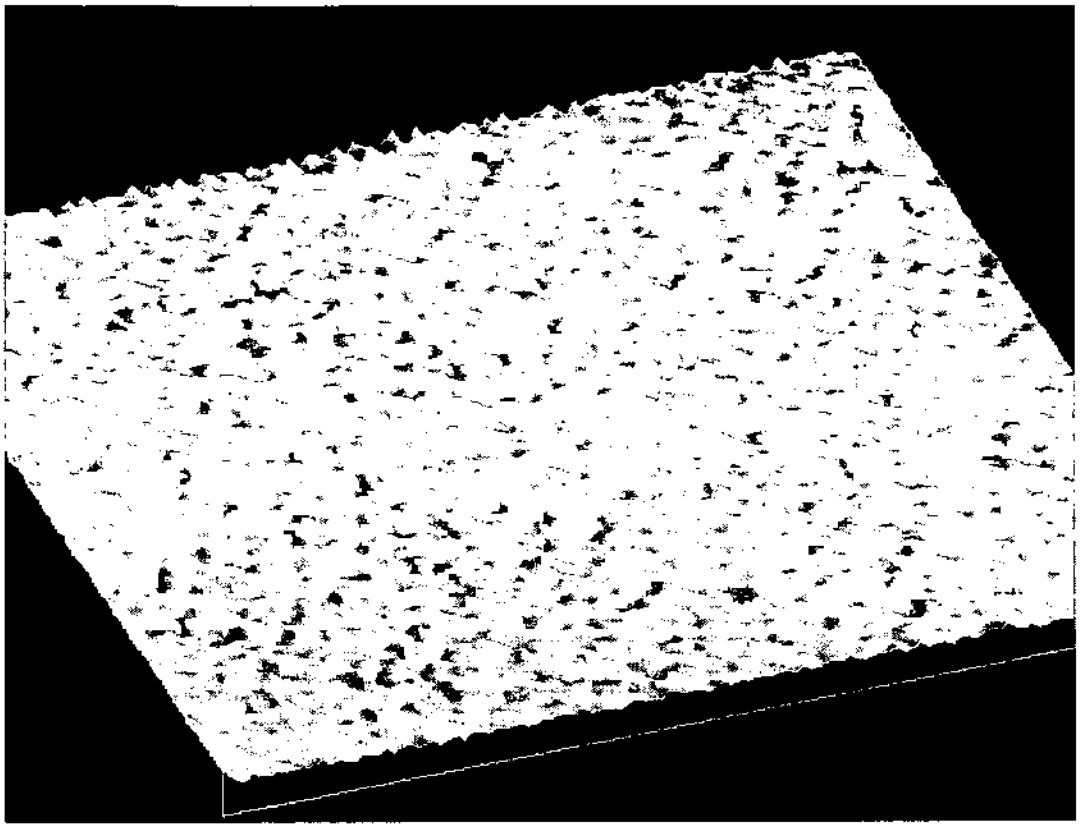


FIG. 22

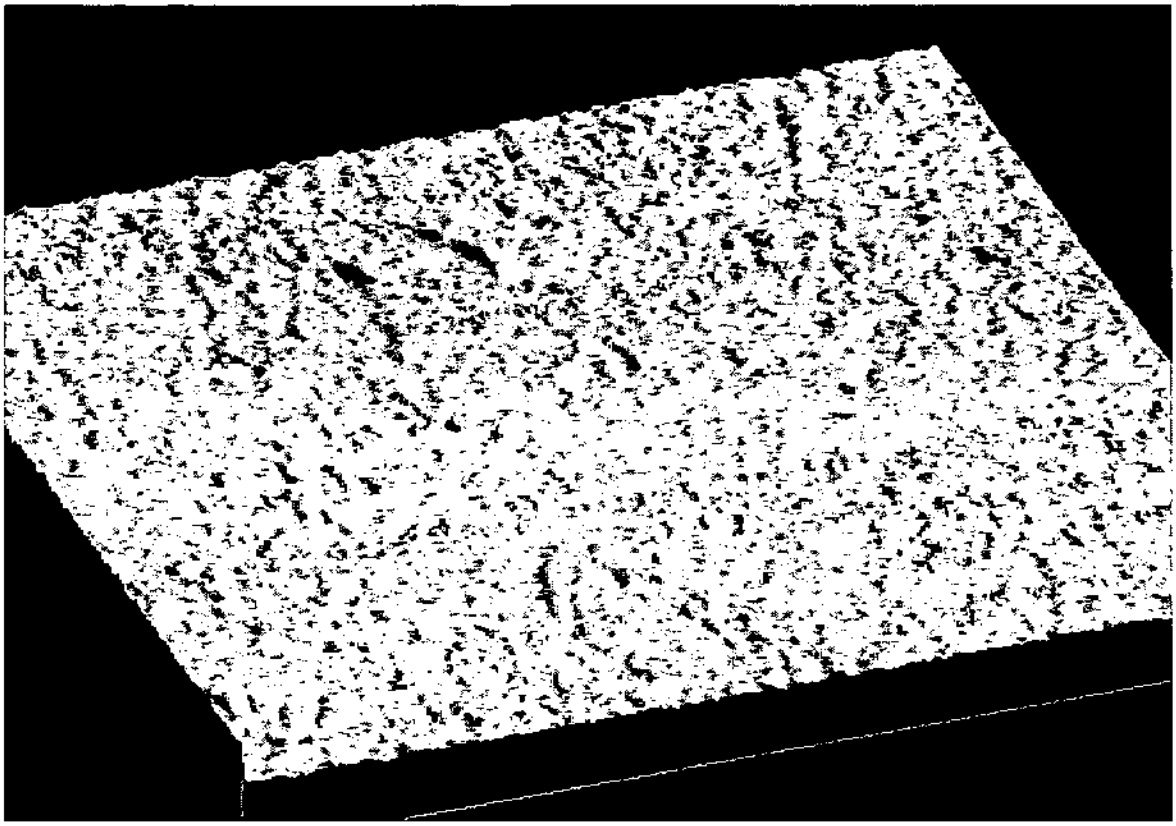


FIG. 23

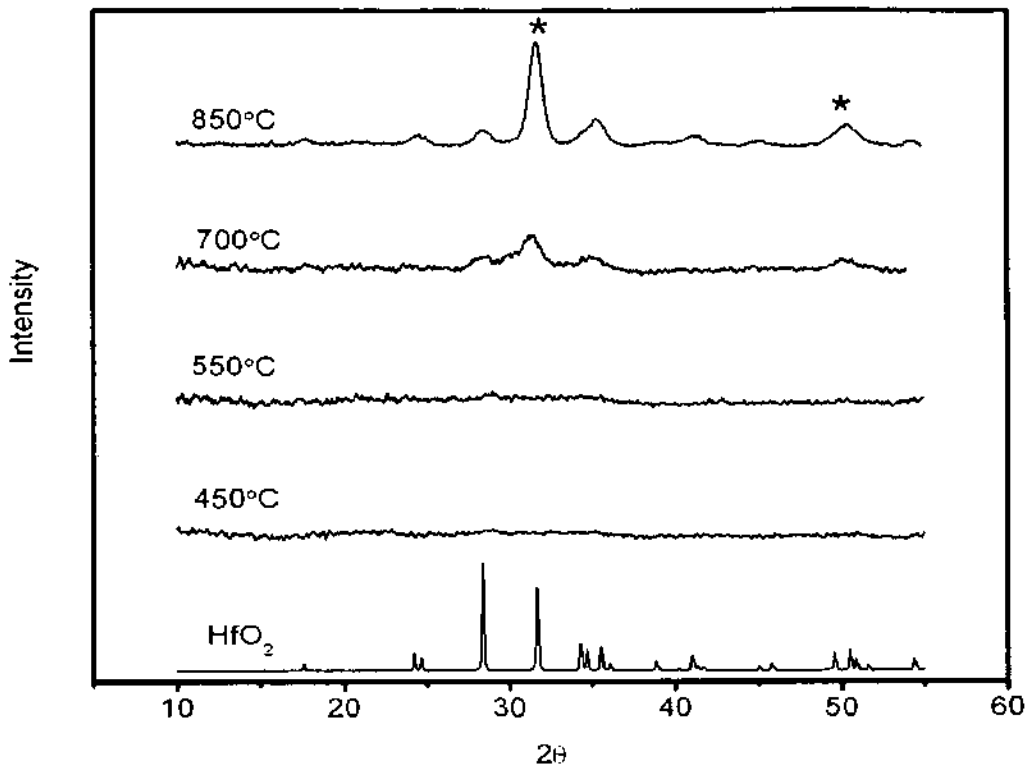


FIG. 24

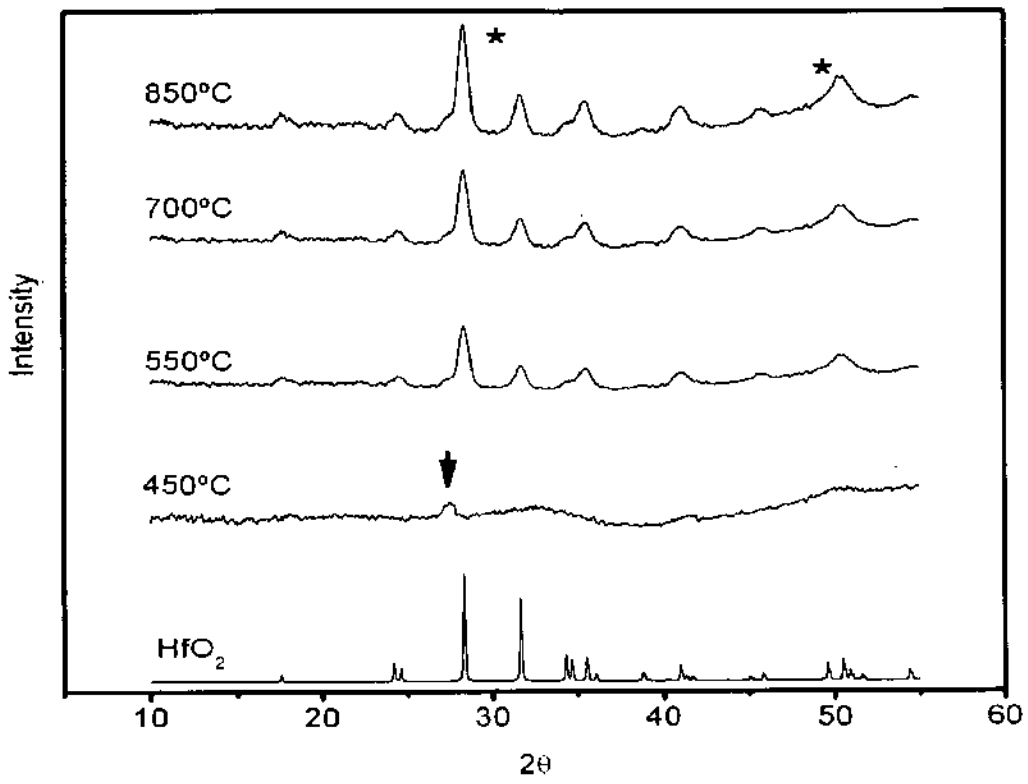


FIG. 25

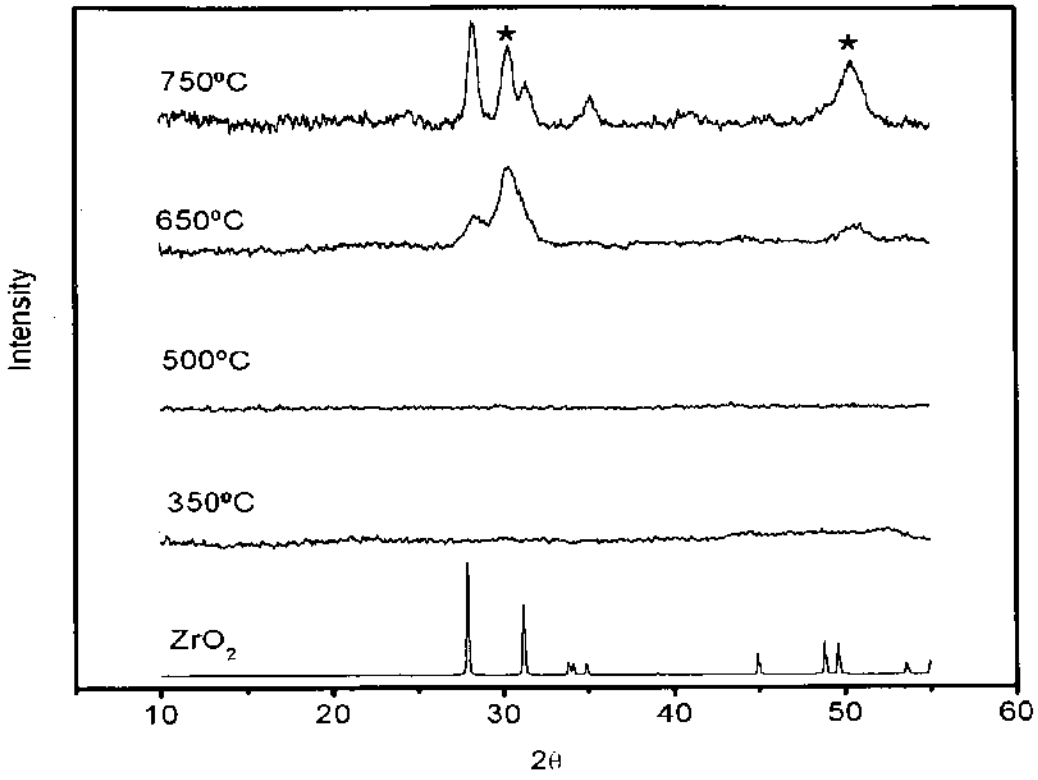


FIG. 26

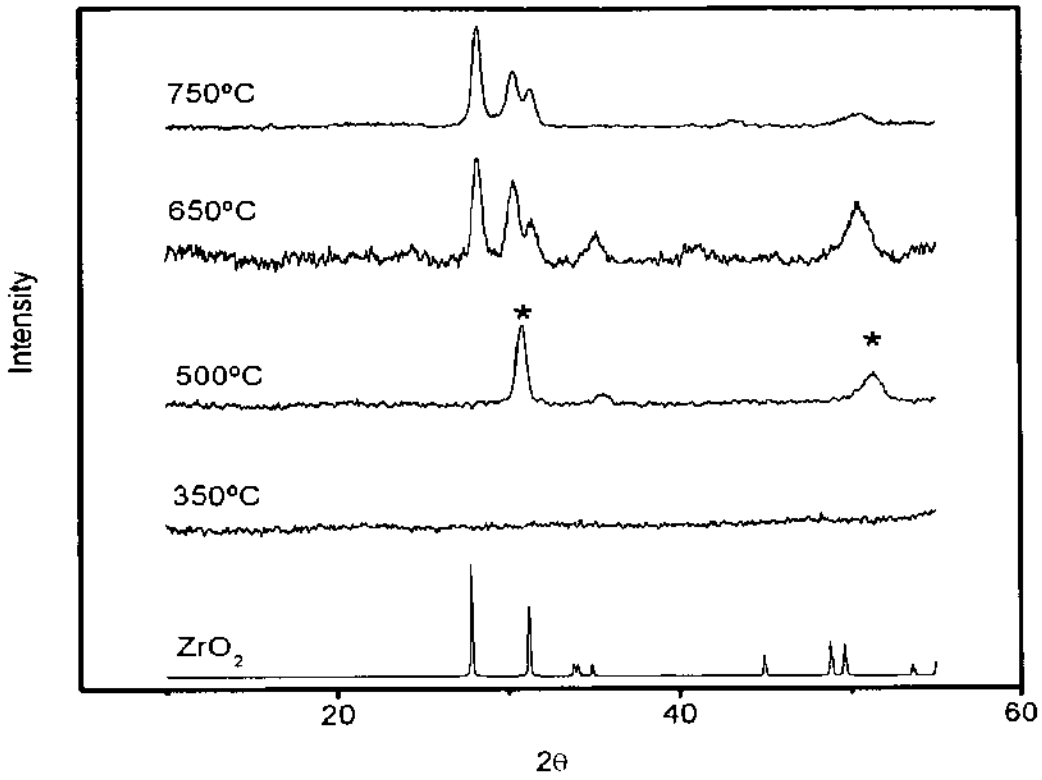


FIG. 27



FIG. 28

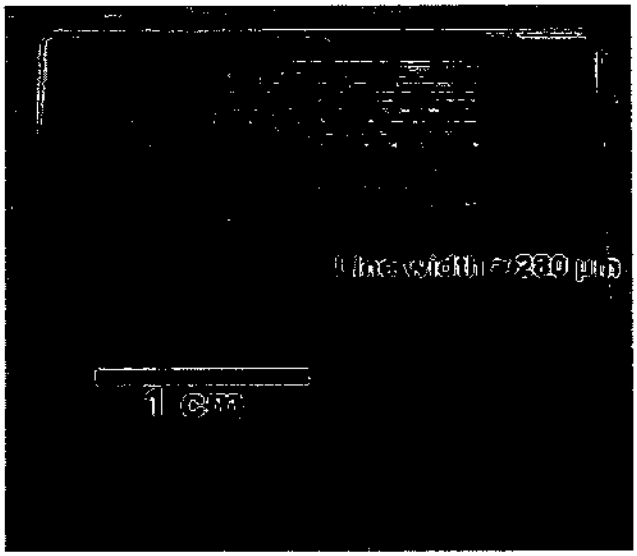


FIG. 29



FIG. 30



FIG. 31

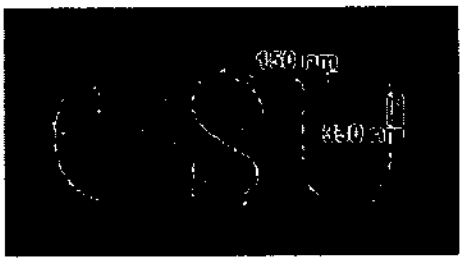


FIG. 32

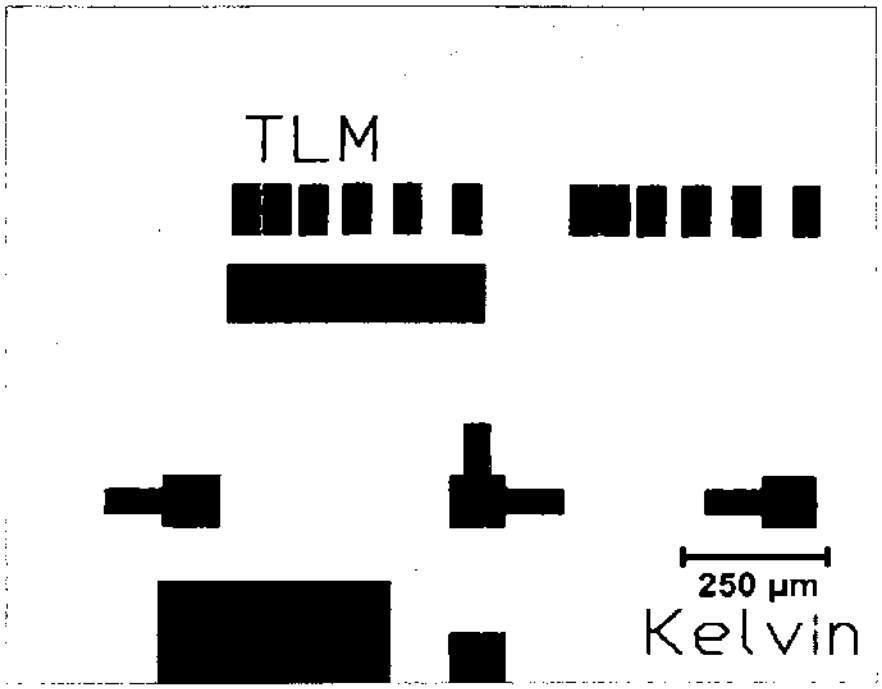


FIG. 33

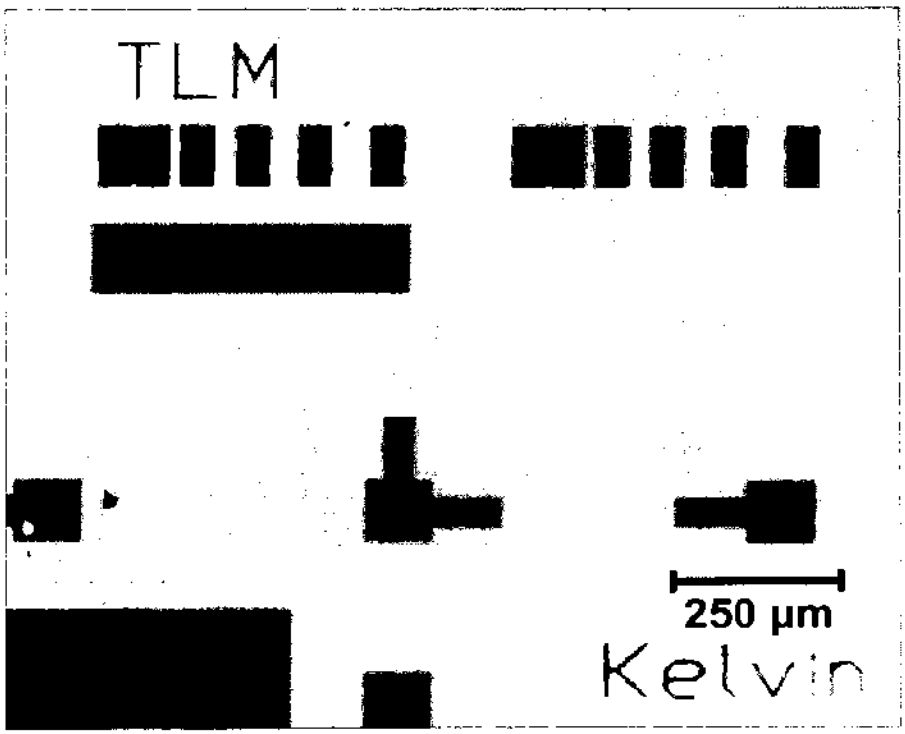


FIG. 34

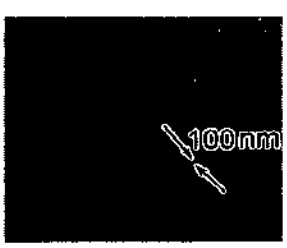


FIG. 35

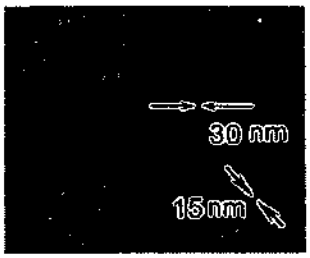


FIG. 36

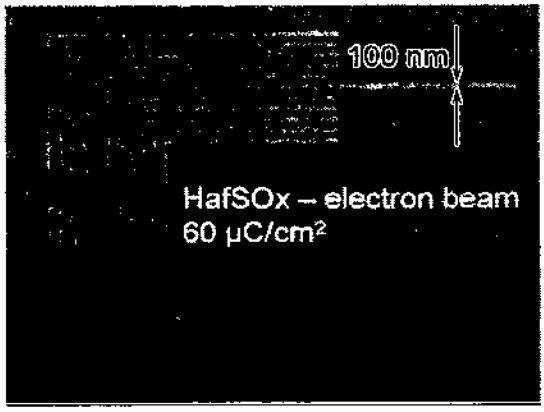


FIG. 37

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 08/04096

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - H01L 21/00 (2008.04)
USPC - 438/151; 257/E21.01
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC: 438/151; 257/E21.01
IPC(8): H01L 21/00 (2008.04)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 438/151; 257/E21.01; IPC(8): H01L 21/00 (2008.04) (text delimited)
Chemical Engineering and Biotech Research

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST: US Patents full-text; US PGPubs full-text; EPO Abstracts; and JPO Abstracts; Google
Terms: zirconium oxy hydroxy sulfate; hafnium oxy hydroxy sulfate; electronic device; photoresist; tungstate; lanthanum; photolithograph; optical and glass substrate; photo and resist, fibers, metal oxide, and dielectric.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2005/0242330 A1 (Herman et al.) 03 Nov. 2005 (03.11.2005), para [0009] - [0012], [0018]-[0029]; Figures	1, 2-4, 12, 16, 25, 28 --- 5-11, 13-15, 17-24, 26-27
Y	US 2006/0088962 A1 (Herman et al.) 27 Apr. 2006 (27.04.2006), para [0006]-[0023]; Figures	5-11, 13-15, 17-24, 27
Y	US 6,197,896 B1 (Aviram et al.) 06 March 2001 (06.03.2001), abstract; col 3, ln 50-56; col 5, ln 50-53)	10-11, 13-15, 17-24, 27
Y	US 3,385,915 A (Hamling) 28 May 1968 (28.05.1968), col 1, ln 40-45; col 2, ln 18-26	26

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 June 2008 (11.06.2008)	26 JUN 2008
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (April 2007)

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02

CONFIRMATION NO. 1662

PUBLICATION NOTICE

62274
DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

OC00000051240377

Title:PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

Publication No.US-2011-0293888-A1
Publication Date:12/01/2011

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Office of Public Records. The Office of Public Records can be reached by telephone at (703) 308-9726 or (800) 972-6382, by facsimile at (703) 305-8759, by mail addressed to the United States Patent and Trademark Office, Office of Public Records, Alexandria, VA 22313-1450 or via the Internet.

In addition, information on the status of the application, including the mailing date of Office actions and the dates of receipt of correspondence filed in the Office, may also be accessed via the Internet through the Patent Electronic Business Center at www.uspto.gov using the public side of the Patent Application Information and Retrieval (PAIR) system. The direct link to access this status information is currently http://pair.uspto.gov/. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

Lam Research Ex. 1004 - Page 251 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US02

Stowers et al. Confirmation No.: 1662

Application No.: 12/850,867 Examiner: Unknown

Filed: August 5, 2010 Group Art Unit: 1783

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING AND CORRESPONDING METHODS

PRELIMINARY AMENDMENT

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

Prior to examination, please amend the above-identified application as follows:

The present amendment comprises the following sections:

A. Amendments to the Claims; and

B. Remarks.

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

April 30, 2012
Date

/Mengmeng Fahrni/
Mengmeng Fahrni, Ph.D., Reg. # 57,717

AMENDMENTS TO THE CLAIMS

A detailed listing of all claims that are, or were, in the present application, irrespective of whether the claim(s) remains under examination in the application are presented below. The claims are presented in ascending order and each includes one status identifier. Those claims not cancelled or withdrawn but amended by the current amendment utilize the following notations for amendment: 1. deleted matter is shown by strikethrough; and 2. added matter is shown by underlining.

1. (Original) An aqueous inorganic patterning precursor solution comprising a mixture of water, metal suboxide cations, polyatomic inorganic anions and radiation sensitive ligands comprising peroxide groups, wherein the composition has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours without additional mixing.

2. (Original) The aqueous inorganic patterning composition of claim 1 having a metal suboxide cation concentration from about 0.01 M to about 1.4 M.

3. (Original) The aqueous inorganic patterning composition of claim 2 having a polyatomic anion concentration from about 0.75 to about 1.5 times the metal suboxide cation concentration.

4. (Original) The aqueous inorganic patterning composition of claim 1 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof.

5. (Original) The aqueous inorganic patterning composition of claim 1 wherein the polyatomic anions comprise sulfate.

6. (Original) The aqueous inorganic patterning composition of claim 1 wherein the polyatomic anions comprise borate, phosphate, tungstate, silicate or combinations thereof.

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7. (Original) The aqueous inorganic patterning composition of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

8. (Original) The aqueous inorganic patterning composition of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 7.

9. (Original) The aqueous inorganic patterning composition of claim 1 having a stability of at least 24 hours without additional mixing.

10. (Original) The aqueous inorganic patterning composition of claim 1 comprising Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or a combination thereof within an appropriate oxygenated ion.

11. (Original) A method for formation of a radiation sensitive inorganic coating precursor solution, the method comprising:

combining a first aqueous solution comprising metal suboxide cations, a complexing solution comprising a ligand having a peroxide group and a composition comprising a polyatomic inorganic anion to form the coating precursor solution, wherein the molar concentration ratio of ligands to metal suboxide cations is at least about 2.

12. (Original) The method of claim 11 wherein the first aqueous solution is mixed with the complexing solution to form a ligand-cation mixture solution prior to introduction of the inorganic anions.

13. (Original) The method of claim 12 wherein the ligand-cation mixture solution is aged at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion.

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14. (Original) A method for patterning an inorganic material on a substrate, the method comprising:

forming a layer of a radiation patternable coating material comprising a solvent, metal suboxide cations, ligands comprising a peroxide group and inorganic polyatomic anions to form a coated substrate;

heating the coated substrate to remove at least a portion of the solvent;

irradiating the coated substrate to a pattern of radiation to condense the coating at the irradiated locations; and

heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the coating with a developer.

15. (Original) The method of claim 14 wherein the radiation is ultraviolet light.

16. (Original) The method of claim 14 wherein the radiation is light having a wavelength of about 193 nm.

17. (Original) The method of claim 14 wherein the radiation is extreme ultraviolet light.

18. (Original) The method of claim 14 wherein the radiation comprises an electron beam.

19. (Original) The method of claim 14 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof and wherein the polyatomic anions comprise sulfate anions.

20. (Original) The method of claim 14 wherein the coating material comprises a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

21. (Original) The method of claim 14 wherein the formation of the coating is performed using spin coating, spray coating, dip coating or knife edge coating.

Lam Research Ex. 1004 - Page 255 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

22. (Original) The method of claim 14 wherein the layer of coating material has an average thickness from about 1 nm to about 40 nm.

23. (Original) The method of claim 14 wherein the radiation is directed through a mask to expose selected portions of the coated substrate.

24. (Original) The method of claim 14 wherein a laser beam or an electron beam is scanned over the coated substrate to expose selected portions of the coated substrate.

25. (Original) The method of claim 14 further comprising exposing the coated substrate with a developing composition to at least partially remove the coating composition at unexposed locations.

26. (Original) The method of claim 25 wherein the developing composition is contacted with the coated substrate for no more than about 75 seconds.

27. (Original) The method of claim 25 wherein the developing composition comprises tetramethyl ammonium hydroxide.

28. (Original) The method of claim 27 wherein the developing composition has a concentration of tetramethyl ammonium hydroxide of about 2.38 weight percent.

29. (Original) The method of claim 14 wherein the substrate is treated along a surface with a hydrophilic surface treatment prior to the forming of the radiation patternable coating material.

30. (Original) The method of claim 14 wherein the forming of the radiation patternable coating material comprises a plurality of coating steps to form a coating material of a selected thickness.

31.-38. (Cancelled)

Lam Research Ex. 1004 - Page 256 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

REMARKS

Claims 1-30 are pending. By this Amendment, claims 31-38 are cancelled without prejudice.

In view of the foregoing, it is submitted that this application is in condition for allowance. Favorable consideration and prompt allowance of the application are respectfully requested.

The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,

/Mengmeng Fahrni/

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Registration No. 57,717

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Moore Lake Plaza, Suite 205
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Fridley, MN 55432
Telephone: (404) 214-3664

Lam Research Ex. 1004 - Page 257 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Acknowledgement Receipt

EFS ID:	12658848
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	MengMeng Anne Fahrni
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	30-APR-2012
Filing Date:	05-AUG-2010
Time Stamp:	12:16:13
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Preliminary Amendment	preliminary_amendment.pdf	29961 a2d0df090c6c206aab2f8adaeb83f3f46260d5fa	no	1

Warnings:	
Information:	

2	Claims	Claims.pdf	166898 da18f855d018ce1b7f20cbe30ddab4dc3c0fce26	no	4
Warnings:					
Information:					
3	Applicant Arguments/Remarks Made in an Amendment	Remarks.pdf	21967 0df66c1dcd64a6732adf60a3449d39d3a81065d5	no	1
Warnings:					
Information:					
		Total Files Size (in bytes):	218826		

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If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

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If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number	Filing Date	☐ To be Mailed
12/850,867	08/05/2010	

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY ☒ RATE ($)	SMALL ENTITY ☒ FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	OTHER THAN SMALL ENTITY FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =		OR	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =			X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT 04/30/2012	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE ($)	SMALL ENTITY ADDITIONAL FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	* 30	Minus	** 38	= 0	X $30 =	0	OR	X $ =	
Independent (37 CFR 1.16(h))	* 3	Minus	***5	= 0	X $125 =	0	OR	X $ =	
☐ Application Size Fee (37 CFR 1.16(s))									
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
					TOTAL ADD'L FEE	0	OR	TOTAL ADD'L FEE	

AMENDMENT	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)	OR	RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =		OR	X $ =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =		OR	X $ =	
☐ Application Size Fee (37 CFR 1.16(s))									
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

Legal Instrument Examiner:
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This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Stower et al.
Art Unit	1783
Examiner Name	Gugliotta, Nicole T
Attorney Docket Number	5063.02US02

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4102683		1978-07-25	DiPiazza	
	2	4370405		1983-01-25	O'Toole et al.	
	3	4732841		1988-03-22	Radigan	
	4	4891303		1990-01-02	Garza et al.	
	5	4910122		1990-03-20	Arnold et al.	
	6	5672243		1997-09-30	Hsia et al.	
	7	6020269		2000-02-01	Wang et al.	
	8	6060380		2000-05-09	Subramanian et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	12850867
	Filing Date	2010-08-05
	First Named Inventor	Stower et al.
	Art Unit	1783
	Examiner Name	Gugliotta, Nicole T
	Attorney Docket Number	5063.02US02

	9	6194323		2001-02-27	Downey et al.	
	10	6268457		2001-07-21	Kennedy et al.	
	11	6287951		2001-09-11	Lucas et al.	
	12	6420088		2002-07-16	Angelopoulos et al.	
	13	6730454		2004-05-04	Pfeiffer et al.	
	14	7001821		2006-02-21	Aggarwal et al.	
	15	7256129		2007-08-14	Nam et al.	
	16	8053370		2011-08-11	Yang et al.	
	17	8092703		2012-01-10	Ishibashi et al.	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	12850867
	Filing Date	2010-08-05
	First Named Inventor	Stower et al.
	Art Unit	1783
	Examiner Name	Gugliotta, Nicole T
	Attorney Docket Number	5063.02US02

	1	20060234138		2006-10-19	Fehlhaber et al.	
	2	20080055597		2008-03-06	Sun et al.	
	3	20090174036		2009-07-09	Fuller et al.	
	4	20100184259		2010-07-22	Radigan et al.	
	5	20110293888		2011-12-01	Stowers et al.	

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							☐

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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	MEYERS ET AL., "Solution-Processed Aluminum Oxide Phosphate Thin-Flim Dielectrics" Chem Mater., 2007, 19, 4023-4029 Abstract Only	☐

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	12850867
	Filing Date	2010-08-05
	First Named Inventor	Stower et al.
	Art Unit	1783
	Examiner Name	Gugliotta, Nicole T
	Attorney Docket Number	5063.02US02

	2	NAKATTA ET AL., "Improvement of InGaZnO4 Thin Film Transistors Characteristics Utilizing Excimer Laser Annealing" The Japan Society of Applied Physics, 2009 Abstract Only	☐
	3	NEEF ET AL., "Effects of carbon/hardmask interactions on hardmask performance", Proceedings of SPIE, 7273, 2009, 72731-1 - 727311-7	☐
	4	OWEN ET AL., "1/8 μm optical lithography" J. Vac. Sci. Technol. B 10, 3032 1992 Abstract Only	☐
	5	STOWERS ET AL., "Directly patterned inorganic hardmask for EUV lothography," Proc. SPIE 7969, 796915 (2011); Http://dx.doi.org/10.1117/12.879542	☐
	6	WANG ET AL.,"TiO2 micro-devices fabricated by laser direct writing" Optics Express, August 29, 2011, 19, 17390-17935	☐

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Examiner Signature		Date Considered	

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

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Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Stower et al.
Art Unit	1783
Examiner Name	Gugliotta, Nicole T
Attorney Docket Number	5063.02US02

CERTIFICATION STATEMENT

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OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☐ Fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ None

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Mengmeng Fahrni/	Date (YYYY-MM-DD)	2012-08-28
Name/Print	Mengmeng Fahrni, Ph.D.	Registration Number	57,717

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2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt

EFS ID:	13605133
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	MengMeng Anne Fahrni
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	28-AUG-2012
Filing Date:	05-AUG-2010
Time Stamp:	14:20:54
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	US_IDS_Form__SB_08a.pdf	613926 fc8300cf177151e0f732762bc202ff7f7ffef6c4	no	6

Warnings:	
Information:	

2	Non Patent Literature	MEYERS_ET_AL_2007.pdf	302644 df56ca6eab95ce5fd87a493e254024ea78aa3587	no	1
Warnings:					
Information:					
3	Non Patent Literature	NAKATTA_ET_AL_2009.pdf	215028 f1e868e64d08ba7cd2cb1246c97eb46e80a81cfa	no	1
Warnings:					
Information:					
4	Non Patent Literature	NEEF_ET_AL_2009.pdf	7675946 0bbc6d7c3399751b5bb9073701c8b4c6e7966828	no	7
Warnings:					
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5	Non Patent Literature	OWEN_ET_AL_1992.pdf	375223 301894d60e5deee7835f30fe2388727639521ffd	no	1
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6	Non Patent Literature	STOWERS_ET_AL_2011.pdf	250889 b84df214fc336d69049657d41ed4f36ddf71a9cb	no	1
Warnings:					
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7	Non Patent Literature	WANG_ET_AL.pdf	716829 cb530443a2dba43f49c6e25c2c6425079addae5b	no	6
Warnings:					
Information:					
			Total Files Size (in bytes):	10150485	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Stowers
Art Unit	1781
Examiner Name	Gugliotta, Nicole T
Attorney Docket Number	5063.02US02

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							☐

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	12850867
	Filing Date	2010-08-05
	First Named Inventor	Stowers
	Art Unit	1781
	Examiner Name	Gugliotta, Nicole T
	Attorney Docket Number	5063.02US02

	1	Supplementary European Search Report From Corresponding European Patent Application No. 11168027.8 Dated January 6, 2012, 8 Pages.	☐

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EXAMINER SIGNATURE

Examiner Signature		Date Considered	

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First Named Inventor	Stowers
Art Unit	1781
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Attorney Docket Number	5063.02US02

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☐ See attached certification statement.

☐ Fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ None

SIGNATURE

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Signature	/Mengmeng Fahrni/	Date (YYYY-MM-DD)	2012-10-23
Name/Print	Mengmeng Fahrni, Ph.D.	Registration Number	57717

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EFS ID:	14055423
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	MengMeng Anne Fahrni
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	23-OCT-2012
Filing Date:	05-AUG-2010
Time Stamp:	16:04:05
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	US_IDS_Form__SB_08a.pdf	612441 b39f224f0b17dbbe35e2a0911dc18398d12ff8ad	no	4

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2	Non Patent Literature	EP_Search_Report.pdf	470232 10432eb681874b57d0aa9908dceb95f882ef5d94	no	8

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PTO/SB/08a (01-10)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

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Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1781
Examiner Name	Nicole T. Gugliotta
Attorney Docket Number	5063.02US02

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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	1	2007-514182	JP	A	2008-05-31	Punsalan et al.	corresponds to WO 2005/043246	☐
	2	10-2008-7010346	KR		2008-10-08	Keszler et al.	corresponds to US 2011/0045406	☐
	3	2005/043246	WO		2005-05-12	Punsalan et al.		☐

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
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	Filing Date	2010-08-05
	First Named Inventor	Jason K. Stowers
	Art Unit	1781
	Examiner Name	Nicole T. Gugliotta
	Attorney Docket Number	5063.02US02

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	1	Office Action from copending Korean Application No. 10-2011-0052919 dated March 14, 2013	☐
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Examiner Signature		Date Considered	

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☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☐ Fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ None

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Peter S. Dardi/	Date (YYYY-MM-DD)	2013-07-10
Name/Print	Peter S. Dardi, Ph.D.	Registration Number	39,650

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(54)【発明の名称】パターニングされたセラミック薄膜及びそれを製造するための方法

[0002] 燃料電池は、燃料（限定はしないが、水素、プロパン、メタン、一酸化炭素などを含む）と酸化剤との、電気及び熱への電気化学エネルギー変換を利用する。燃料電池は、携帯用電源として、一次電池及び二次電池に取って代わり得るものとして期待されている。燃料電池では、燃料（通常、水素の発生源を含む）は、通常は酸素の発生源で酸化され、（主に）水及び二酸化炭素が生成される。燃料極における酸化反応では電子が遊離し、その反応を、電子を消費する空気極での還元反応と組み合わせることにより、負荷を通る有用な電圧及び電流がもたらされる。

[0003] 燃料電池は、モータ、ライト、電気機器などに電源を供給するために用い得る直流（ＤＣ）電圧を与える。固体酸化物燃料電池（ＳＯＦＣ）は、燃料電池の１つのタイプであり、携帯用途において有用である。高性能の燃料電池デバイスを得るために一般的に望ましい材料特性によって、それら燃料電池デバイスの製造はかなり困難なものとなっている。

[0004] 図面においては、同様の符号は、必ずしも同じではないが、同様の構成要素に対応する。簡潔にするために、予め説明した機能を有する符号は、それらの番号が現われる後続の図面では必ずしも説明しない場合がある。

[0005] パターニング及び加熱技法と共に液体前駆体溶液を用いることにより、比較的簡単に、迅速に、且つ効率的に、新規のパターニングされたセラミック薄膜を形成し得ることを見出した。これらのパターニングされたセラミック薄膜は、イオン伝導性セラミック、燃料電池内のパターニングされた電極、ハードセラミックコーティング、透明導電性酸化物、及び透明半導電性酸化物をはじめとする、種々の応用形態において用いることができる。

[0006] ここで図１Ａを参照すると、パターニングされたセラミック薄膜を形成するための一実施形態は、基材１４上に

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液体前駆体溶液を付着させて、液体薄膜１２を形成するステップを包含する。

[0007] 基材１４のために任意の適切な材料を選択できることを理解されたい。一実施形態では、基材１４は、単結晶シリコン、多結晶シリコン、酸化シリコン含有誘電体基材、アルミナ、サファイア、セラミック及び／又はその混合物である。本発明の他の実施形態では、シリコンウェーハが最適な基材１４である。

[0008] 一実施形態では、液体前駆体溶液は、フォトレジスト中に、１つ又は複数の金属塩を溶解させることによって生成される。望ましい電気的、化学的及び／又は機械的性能、及び／又は信頼性を有するような、パターニングされたセラミック薄膜を過度に汚さない、任意の適切な金属塩（限定はしないが、金属塩の塩成分の例には、硝酸塩、硫酸塩及び／又は塩化物が含まれる）を選択し得ることを理解されたい。一実施形態では、金属塩は、硝酸セリウム及び／又は硝酸サマリウムである。

[0009] 多くの金属塩が水溶性である。それ故、金属塩の溶解は、水溶性のフォトレジストが用いられるなら、容易に遂成されるであろう。しかしながら、ほとんどのフォトレジストは水溶性ではない。フォトレジストは金属塩のキャリアとしての役割を果たすことができることを理解されたい。

[0010] 場合によっては、フォトリソグラフィにおいて用いられるいくつかの標準的なフォトレジストは、本発明の実施形態に適していない場合もあることを理解されたい。場合によっては、本発明の実施形態において有用なフォトレジストを、従来のフォトレジストの代わりに用いる結果として、加熱後に適切なセラミック薄膜が形成されない場合もあることを理解されたい。どの理論にも囚われるわけではないが、望ましいフォトレジストは、金属カチオンを安定化させて、実質的に均質な液体前駆体溶液の生成を促進することができる官能基を有するものと考えられる。限定はしないが、適切なフォトレジストの一例は、金属カチオンを配位結合するための役割を果たし得る、反復単位の末端にケトン基を有するフォトレジストである。限定はしないが、本発明の実施形態において適するフォトレジストの例は、ジアクリレートである。一実施形態では、フォトレジストは、テトラエチレングリコールジアクリレート、ポリビニルフェノール（ＰＶＰ）、ポリ（４－ビニルフェノール）、ポリ（４－ヒドロキシスチレン）、及び／又は任意のＤＮＱ（ジアゾナフトキノン）－ノボラック系レジストである。

[0011] 用いられる金属塩の量は、選択した金属塩及びその溶解度に依存することを理解されたい。一実施形態では、フォトレジストに対する金属塩の濃度は、フォトレジスト１リットル当たり最大約５モルの金属とすることができる。

[0012] 液体前駆体溶液は、フォトレジスト中に金属塩が実質的に完全に溶解している真の意味での溶液であることを理解されたい。完全に混和性の液体前駆体溶液を得るために、実質的に全ての固形物がフォトレジストに溶解するまで、その溶液を混合することができる。実質的に混和性の溶液は、一般的に、その中に粉末微粒子を全く含まない。そのような完全に混和性の溶液は多くの理由から好都合であり、例えば、パターニングされるべき線幅が、粉末微粒子の大きさ以下である場合に好都合であろう。

[0013] 一般的に、金属塩をフォトレジストに概ね完全に溶解するのにかかる時間は、用いられる材料に依存する。本発明の一実施形態では、全溶解時間は約２時間である。金属塩が実質的に完全に溶解しない場合には、結果として生じる液体薄膜１２は、望ましくない不均質な特性を有する可能性がある。

[0014] 本発明の一実施形態では、液体前駆体溶液を基材１４上に付着する前に、任意選択的に、液体前駆体溶液に１つ又は複数の添加剤を混ぜることができる。添加剤を混ぜることによって、液体前駆体溶液が基材１４に被着された（applied）後の熱硬化及び紫外線硬化を支援することができる。任意の適切な添加剤を選択できることを理解されたい。一実施形態では、適切な光開始剤添加剤は、限定はしないが、２，５ジメチル２，５－ジ－ｔ－ブチルペルオキシヘキサン（アトフィナ・ケミカルズ社（ATOFINA Chemicals Inc.）（ペンシルバニア州、フィラデルフィア）から商品名ＬＵＰＥＲＯＸ　１０１で市販）、α，α－ジメトキシ－α－フェニルアセトフェノン（チバ・スペシャルティ・ケミカルズ社（Ciba Specialty Chemicals）（ニューヨーク州、テリータウン）から商品名ＩＲＧＡＣＵＲＥ　６５１で市販）、及び／又はその混合物を含む。

[0015] 本発明の一実施形態では、液体前駆体溶液は、限定はしないが、スピンコーティング、スクリーン印刷、ディップコーティング、メニスカスコーティング及びスプレーコーティングをはじめとする付着技術を用いて、基材１４上に付着される。スピンコーティングは一般的に、非常に薄い膜厚及び細かく複雑な幾何学的形状を形成する。一実施形態では、薄膜厚は、約１μｍ以下である。スクリーン印刷は、一般的に、より厚い膜厚及びより大きな幾何学的形状を形成する。他の実施形態では、その厚い膜厚は、約１０μｍ以上である。

[0016] 一実施形態では、液体薄膜１２は、約０．０５μｍ～約０．５μｍの範囲の厚みを有する。他の実施形態では、液体薄膜１２は、約０．２５μｍの厚みを有する。

[0017] 本発明の一実施形態に従って、より厚い薄膜１２は、基材１４上に液体前駆体溶液の多数の層１２を付着するこ

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とによって形成できることに留意されたい。

[0018] ここで図１Ｂを参照すると、本発明のその実施形態の方法は、さらに、液体薄膜１２をパターニングするステップを含む。液体薄膜１２は、任意の適切な形状、大きさ及び／又は構造にパターニングできることを理解されたい。

[0019] 液体薄膜１２をパターニングするために、任意の適用可能なネガ型又はポジ型フォトリソグラフィ技法を選択することができる。

[0020] 一実施形態では、パターニングは、液体薄膜１２の一部をマスクするステップを含む。マスク１６は液体薄膜１２上に配置され、液体薄膜１２の一部２２がマスクされ、液体薄膜１２の他の部分２４はマスクされないようにする。

[0021] パターニングするステップはさらに、その上にマスク１６がある状態で、液体薄膜１２を光源１８に露光するステップを含む。任意の適切な光源１８を用いることができることを理解されたい。本発明の一実施形態では、ＵＶランプ（３６５ｎｍ、２００Ｗ／ｉｎ．ｉｎ）にて、液体薄膜１２は露光される。光源１８は、液体薄膜１２のマスクされた部分２２、マスクされていない部分２４のいずれかを硬化させる（ポジ型フォトリソグラフィが用いられるか、ネガ型フォトリソグラフィが用いられるかに依存する）。

[0022] 限定はしないが、図１Ｂは、ポジ型フォトリソグラフィ技法が用いられる、本発明の一実施形態の例である。この技法を用いる場合、液体薄膜１２のマスクされた部分２２は硬化し、液体薄膜１２のマスクされていない部分２４は硬化しない。

[0023] 本発明の一実施形態では、液体薄膜１２が光源１８に露光された後に、本方法はさらに、任意選択的に、液体薄膜１２を加熱乾燥するステップを含むことができる。露光後の加熱乾燥には、低温での加熱乾燥を用いることができることを理解されたい。一実施形態では、加熱乾燥温度は約５０℃～約２５０℃の範囲を有する。他の実施形態では、加熱乾燥温度は約１００℃である。

[0024] ここで図１Ｃを参照すると、本発明の方法の一実施形態では、パターニングするステップはさらに、液体薄膜１２の硬化していない部分を除去して、パターニングされた液体薄膜２０を残すステップを含む。液体薄膜１２の硬化していない部分の除去は、限定はしないが、溶媒剥離をはじめとする、任意の適切な手段によって達成できることを理解されたい。一実施形態では、除去は、液体薄膜１２の硬化していない部分をイソプロピルアルコールに溶解することによって実施される。

[0025] 一実施形態では、本方法は、パターニングされた液体薄膜２０を加熱して、液体前駆体溶液から、残った有機化合物を除去するステップを含む。任意の適切な加熱処理を用い得ることを理解されたい。一実施形態では、パターニングされた液体薄膜２０を約５５０℃～約６００℃の範囲の温度において燃焼させる。さらに別の実施形態では、燃焼温度は約５４０℃～約１０５０℃の範囲を有する。場合によっては、さらに高い温度によって、異物を除去するのを助けることができ、且つ／又はパターニングされたセラミック薄膜１０の所望の形態又は相を達成するのを助けることができる。

[0026] パターニングされた液体薄膜２０の線幅Ｗは任意の適切な幅とし得ることを理解されたい。しかしながら、一実施形態では、その幅は約０．５μｍ～約２ｍｍの範囲を有する。

[0027] パターニングされたセラミック薄膜１０の実施形態は、約０．２μｍ～約０．３μｍの範囲の厚みを有することができる。この範囲内の厚みを有するパターニングされたセラミック薄膜１０では、概ね亀裂が生じないことを理解されたい。

[0028] ここで図２Ａ～図２Ｃを参照すると、パターニングされたセラミック薄膜１０を形成するための一実施形態は、図１Ａ～図１Ｃに関連して先に説明されたようなステップを含む。しかしながら、それとは対照的に、特に図２Ｂを参照すると、パターニングするステップはネガ型フォトリソグラフィ技法を用いる。液体薄膜１２の一部２２がマスクされ、液体薄膜１２の一部２４がマスクされないように、マスク１６が液体薄膜１２の一部の上に配置される。

[0029] ネガ型フォトリソグラフィを用いるこの実施形態では、マスクされた部分２２は硬化せず、液体薄膜１２のマスクされない部分２４が硬化する。

[0030] ここで図２Ｃを参照すると、本発明の実施形態の方法はさらに、液体薄膜１２の硬化していない部分２４を除去するステップを含む。図２Ｃは、パターニングされた液体薄膜２０’が用いられるマスク１６（図２Ｂに示される）の逆の構造である、本発明の別の実施形態を示す。

[0031] さらに例示するために、以下の実施例が与えられる。この実施例は例示目的で与えられており、特許請求される

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発明内容の範囲を制限するものと解釈されるべきでないことを理解されたい。

[0032] 硝酸セリウム6．９４ｇ及び硝酸サマリウム１．７８ｇを、４０ｃｃのテトラエチレングリコールジアクリレートに加え、液体前駆体溶液を形成した。加熱及び紫外線硬化を助けるために、６ｃｃのＬＵＰＥＲＯＸ（商標）光開始剤及び重量比で５％のＩＲＧＡＣＵＲＥ６５１を液体前駆体溶液に追加した。その溶液を２時間にわたって混合し、その混合物が完全に溶解し、透明な溶液が得られるようにした。

[0033] その後、液体前駆体溶液をシリコンウェーハ上にスピンコーティングした。シャドーマスク及び紫外線露光を用いて、液体薄膜をパターニングした。露光後に、パターニングされた液体薄膜の硬化していない部分をイソプロピルアルコールで除去した。その後、パターニングされた液体薄膜を、約５４０℃で燃焼させて、液体前駆体溶液の有機化合物部分を除去し、且つ所望のサマリウムドープセリア（ＳＤＣ）のパターニングされたセラミック薄膜を残した。ＳＤＣのパターニングされた薄膜は、燃料電池内（例えば、固体酸化物燃料電池（ＳＯＦＣ）内の）燃料極として用いるのに適しているであろう。

[0034] ここで図３を参照すると、結果として形成されたＳＤＣのパターニングされたセラミック薄膜の平面図の倍率３５×のＳＥＭが示されている。

[0035] パターニングされたセラミック薄膜の実施形態は、限定はしないが、イオン伝導性セラミック（例えば電解質）、ハードセラミックコーティング、透明導電性酸化物（限定はしないが、その１つの実施形態は酸化インジウムスズである）及び透明半導電性酸化物（限定はしないが、その一例は酸化亜鉛である）、強誘電性酸化物（限定はしないが、その一例はジルコン酸チタン酸鉛である）、誘電性酸化物（限定はしないが、その例には、酸化アルミニウム及び酸化ジルコニウムが含まれる）、並びに燃料極及び空気極をはじめとする、種々の応用形態において用い得ることを理解されたい。電解質、燃料極及び空気極は、燃料電池において用いるのに適しているであろう。

[0036] ここで図４を参照すると、本発明の一実施形態では、燃料電池１００は、電解質２８と電気化学的に接触している少なくとも１つの電極２６、３０を含む。電極２６、３０は、燃料極２６又は空気極３０として用い得ることを理解されたい。さらに、電解質２８、燃料極２６及び／又は空気極３０は、本発明の実施形態によるパターニングされたセラミック薄膜１０とし得ることを理解されたい。

[0037] 図４は、デュアルチャンバ型燃料電池１００の簡略化された概略図である。燃料電池１００はシングルチャンバ型燃料電池であってもよいことを理解されたい。

[0038] さらに、燃料電池１００として、固体酸化物燃料電池、プロトン伝導性セラミック燃料電池、ポリマー電解質膜（ＰＥＭ）燃料電池、溶融炭酸塩燃料電池、固体酸燃料電池及び直接メタノールＰＥＭ燃料電池のうちの１つを用い得ることを理解されたい。

[0039] 本発明の燃料電池１００の実施形態では、酸化剤３４が空気極３０に運ばれ、反応剤３２が燃料極２６に運ばれる。一実施形態では、反応剤３２は燃料であり、酸化剤３４は酸素、空気、その混合物のうちの１つである。燃料電池１００に、任意の適切な燃料／反応剤３２を用い得ることを理解されたい。一実施形態では、燃料／酸化剤３２は、水素、メタン、エタン、プロパン、ブタン、ペンタン、メタノール、エタノール、より高次の直鎖又は混合炭化水素、例えば天然ガス又はガソリン（低硫黄の炭化水素、例えば、低硫黄ガソリン、低硫黄灯油、低硫黄ディーゼルが望ましい）、その混合物から選択される。別の実施形態では、燃料／反応剤３２は、ブタン、プロパン、メタン、ペンタン及びその混合物から成る群から選択される。内部で直に接触改質（reformation）するのに適している、対象とする作動温度範囲内で蒸気圧が適切である、及び類似のパラメータにおいて適している燃料を選択することができる。

[0040] 燃料電池１００がシングルチャンバ燃料電池である場合には、反応剤３２及び酸化剤３４の気体混合物を燃料極２６及び／又は空気極３０に向かって誘導できることに留意されたい。

[0041] 燃料電池１００を使用する方法の一実施形態は、燃料電池１００を電気的負荷しに、及び／又は蓄積デバイスＳに動作可能に接続するステップを含む。電気的負荷しは、限定はしないが、コンピュータ、ポータブル電子機器（例えば、携帯情報端末（ＰＤＡ）、ポータブル電動工具など）、及び通信装置、ポータブル又はそれ以外の民生品及び軍需品のありとあらゆるものをはじめとする、多数の装置を含むことができる。電気蓄積デバイスＳは、限定はしないが、例として、コンデンサ、バッテリ及びパワーコンディショニングデバイスのありとあらゆるものを含むことができる。いくつかの例示的なパワーコンディショニングデバイスは、無停電電源、ＤＣ／ＡＣコンバータ、ＤＣ電圧コンバータ、電圧レギュレータ、電流リミッタなどを含む。

[0042] 場合によっては、燃料電池１００は、輸送業、例えば電気自動車、及び公益事業、例えば発電所において用いるのに適しているものと考えられる。

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[0043] パターニングされたセラミック薄膜１０を使用する方法の一実施形態は、パターニングされたセラミック薄膜１０を、あるデバイス内に動作可能に配置するステップを含む。パターニングされたセラミック薄膜１０が、イオン伝導性セラミック、電極、ハードセラミックコーティング、透明導電性酸化物、透明半導電性酸化物、強誘電性酸化物、及び／又は誘電性酸化物として使用されるのに相応しいように、任意の適切なデバイスを選択できることを理解されたい。

[0044] 本発明の実施形態は、数多くの利点を提供することができ、そのいくつかの例は、限定はしないが、以下のものを含む。本発明の実施形態は、硬質及び脆性のセラミック薄膜をパターニングする必要性を実質的に避けながら、パターニングされたセラミック薄膜を形成する方法を提供できる点で好都合である。さらに、パターニングされたセラミック薄膜１０の実施形態は、イオン伝導性セラミック、電極、ハードセラミックコーティング、透明導電性酸化物、透明半導電性酸化物、強誘電性酸化物、及び／又は誘電性酸化物として用いることができる点で好都合である。

[0045] 本発明のいくつかの実施形態を詳細に説明してきたが、開示される実施形態を変更できることは当業者には明らかであろう。それゆえ、これまでの説明は、限定するものではなく、例示するものと見なされるべきであり、その真の範囲は添付の特許請求の範囲において定められる範囲である。

【請求項 1】
パターニングされたセラミック薄膜（１０）を形成する方法であって、

基材（１４）上に液体前駆体溶液を付着させ、それによって液体薄膜（１２）を形成することであって、前記液体前駆体溶液が、フォトレジスト中に溶解している少なくとも１つの可溶性金属塩を有する、形成すること；

前記液体薄膜（１２）をパターニングすること；及び

前記パターニングされた液体薄膜（２０、２０’）を加熱し、それによって前記パターニングされたセラミック薄膜（１０）を形成すること、

を包含し、

前記パターニングされたセラミック薄膜（１０）が、イオン伝導セラミック、電極、ハードセラミックコーティング、透明導電性酸化物、透明半導電性酸化物、強誘電性酸化物、及び誘電性酸化物のうちの少なくとも１つとして用いるように構成される、方法。

【請求項 2】
前記少なくとも１つの可溶性金属塩が、金属カチオン及び塩アニオンを含み、前記塩アニオンが、硝酸塩、硫酸塩、塩化物及び／又はその混合物を含む、請求項１に記載の方法。

【請求項 3】
前記少なくとも１つの可溶性金属塩が、前記フォトレジスト内に実質的に完全に溶解しており、前記液体前駆体溶液が実質的に完全に混和性である、請求項１又は２に記載の方法。

【請求項 4】
前記液体前駆体溶液内に少なくとも１つの添加剤が混合されている、請求項１～３の何れか一項に記載の方法。

【請求項 5】
前記フォトレジストが、ジアクリレート、ポリビニルフェノール（ＰＶＰ）、ポリ（４－ビニルフェノール）、ポリ（４－ヒドロキシスチレン）、ＤＮＱ（ジアゾナフトキノン）－ノボラック及びその混合物のうちの少なくとも１つである、請求項１～４の何れか一項に記載の方法。

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【請求項 6】
パターニングすることが、

前記液体薄膜（１２）の所定の部分をマスクすることであって、前記液体薄膜（１２）がマスクされた部分（２２）とマスクされていない部分（２４）とを有する、マスクすること；

前記液体薄膜（１２）を光源（１８）に露光することであって、それによって前記マスクされた部分（２２）及び前記マスクされない部分（２４）のうちの一方が硬化する、露光すること；及び

硬化していない部分を除去すること、

を含む、請求項１～５の何れか一項に記載の方法。

【請求項 7】
前記硬化していない部分を除去する前に、前記露光された液体薄膜（１２）を約５０℃～約２５０℃の範囲の温度において加熱乾燥することをさらに含む、請求項１～６の何れか一項に記載の方法。

【請求項 8】
前記除去することが、溶媒剥離によって達成される、請求項１～７の何れか一項に記載の方法。

【請求項 9】
前記加熱することが、約５４０℃～約１０５０℃の範囲の温度において、前記パターニングされた液体薄膜（２０、２０’）を燃焼させることによって達成される、請求項１～８の何れか一項に記載の方法。

【請求項 10】
前記基材（１４）が、シリコン、単結晶シリコン、多結晶シリコン、酸化シリコン含有誘電体基材、アルミナ、サファイア、セラミック及び／又はその混合物である、請求項１～９の何れか一項に記載の方法。

【請求項 11】
前記パターニングされたセラミック薄膜（１０）が、或る線幅（W）を有し、前記線幅（W）が、約０．５μm～約２mmの範囲にある、請求項１～１０の何れか一項に記載の方法。

【請求項 12】
燃料電池（１００）であって、

前記燃料電池（１００）内に動作可能に配置される少なくとも１つの電極（２６、３０）と；

前記少なくとも１つの電極（２６、３０）と電気化学的に接触している電解質（２８）と、

を含んで成り、

前記電極（２６、３０）及び前記電解質（２８）の少なくとも一方が、パターニングされたセラミック薄膜（１０）を含み、前記パターニングされたセラミック薄膜（１０）が、

基材（１４）上に液体前駆体溶液を付着させ、それによって液体薄膜（１２）を形成することであって、前記液体前駆体溶液が、フォトレジスト中に溶解している少なくとも１つの可溶性金属塩を有する、形成すること；

前記液体薄膜（１２）をパターニングすること；及び

前記パターニングされた液体薄膜（２０、２０’）を加熱し、それによって前記パターニングされたセラミック薄膜（１０）を形成すること、

を包含するプロセスによって生成される、燃料電池。

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【請求項 13】
前記電極（２６、３０）が、燃料極（２６）又は空気極（３０）である、請求項１２に記載の燃料電池。

【請求項 14】
電子デバイス（Ｌ、Ｓ）であって：

負荷（Ｌ）と；

前記負荷（Ｌ）に接続される請求項１２又は１３に記載の燃料電池（１００）と、

を含んで成る、電子デバイス。

【請求項 15】
パターニングされたセラミック薄膜（１０）を使用する方法であって、前記パターニングされたセラミック薄膜（１０）が：

基材（１４）上に液体前駆体溶液を付着させ、それによって液体薄膜（１２）を形成することであって、前記液体前駆体溶液が、フォトレジスト中に溶解している少なくとも１つの可溶性金属塩を有する、形成すること；

前記液体薄膜（１２）をパターニングすること；及び

前記パターニングされた液体薄膜（２０、２０’）を加熱し、それによって前記パターニングされたセラミック薄膜（１０）を形成すること；

を包含するプロセスによって形成されており、

前記パターニングされたセラミック薄膜（１０）を使用する方法が、デバイス（Ｌ、Ｓ）内に前記パターニングされたセラミック薄膜（１０）を動作可能に配置することを含み、前記パターニングされたセラミック薄膜（１０）が、イオン伝導性セラミック、電極、ハードセラミックコーティング、透明導電性酸化物、透明半導電性酸化物、強誘電性酸化物、及び誘電性酸化物のうちの少なくとも１つを構成する、方法。

【請求項 16】
燃料電池（１００）を使用する方法であって：

前記燃料電池（１００）を負荷（Ｌ）に動作可能に接続することを含み、前記燃料電池（１００）が、パターニングされたセラミック薄膜（１０）を含む電極（２６、３０）及び電解質（２８）のうちの少なくとも１つを含み、前記パターニングされたセラミック薄膜（１０）が、

基材（１４）上に液体前駆体溶液を付着させ、それによって液体薄膜（１２）を形成することであって、前記液体前駆体溶液が、フォトレジスト中に溶解している少なくとも１つの可溶性金属塩を有する、形成すること；

前記液体薄膜（１２）をパターニングすること；及び

前記パターニングされた液体薄膜（２０、２０’）を加熱し、それによって前記パターニングされたセラミック薄膜（１０）を形成すること、

を包含するプロセスによって形成される、方法。

【請求項 17】
セラミック薄膜（１０）であって：

或るパターンを有する金属有機液体前駆体溶液と；

その中に前記パターンを有する前記セラミック薄膜（１０）へと前記前駆体溶液を変換するための手段と、

を含んで成り、

前記セラミック薄膜が、イオン伝導性セラミック、電極、ハードセラミックコーティング、透明導電性酸化物、

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透明半導電性酸化物、強誘電性酸化物、及び誘電性酸化物のうちの少なくとも１つとして用いるように構成されている、セラミック薄膜。

【請求項 18】

パターニングされたセラミック薄膜（１０）を形成する方法であって：

基材（１４）上に液体前駆体溶液を付着させ、それによって液体薄膜（１２）を形成することであって、前記液体前駆体溶液が、フォトレジスト中に溶解している少なくとも１つの可溶性金属塩を有し、前記少なくとも１つの可溶性金属塩が、前記フォトレジスト中に実質的に完全に溶解しており、前記液体前駆体溶液が、実質的に完全に混和性である、形成すること；

前記液体薄膜（１２）をパターニングすることであって、

前記液体薄膜（１２）の所定の部分をマスクすることであって、前記液体薄膜（１２）がマスクされた部分（２２）とマスクされていない部分（２４）とを有する、マスクすること；

前記液体薄膜（１２）を光源（１８）に露光することであって、それによって前記マスクされた部分（２２）及び前記マスクされていない部分（２４）のうちの一方が硬化する、露光すること；及び

前記硬化していない部分を除去すること、

を含む、パターニングすること；並びに

前記パターニングされた液体薄膜（２０、２０’）を、有機物質を実質的に除去するのに十分な温度で燃焼し、それによって前記パターニングされたセラミック薄膜（１０）へとすること、

を包含し、

前記パターニングされたセラミック薄膜（１０）が、イオン伝導性セラミック、電極、ハードセラミックコーティング、透明導電性酸化物、透明半導電性酸化物、強誘電性酸化物、及び誘電性酸化物のうちの少なくとも１つとして用いるように構成される、方法。

【請求項 19】

前記液体薄膜（１２）が、約０．０５μｍ～約０．５μｍの範囲の厚みを有する、請求項１８に記載の方法。

【請求項 20】

前記パターニングされたセラミック薄膜（１０）が、約０．２μｍ～約０．３μｍの範囲の厚みを有する、請求項１８又は１９の何れかに記載の方法。

(57)【要約】

パターニングされたセラミック薄膜（１０）は、イオン伝導性セラミック、電極、ハードセラミックコーティング、透明導電性酸化物、透明半導電性酸化物、強誘電性酸化物、及び誘電性酸化物として有用である。そのセラミック薄膜（１０）は液体前駆体溶液から形成することができる。

【選択図】なし

【図 1A】

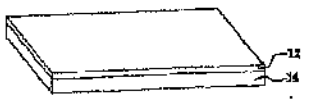


FIG. 1A

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Lam Research Ex. 1004 - Page 287 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

【図 1B】

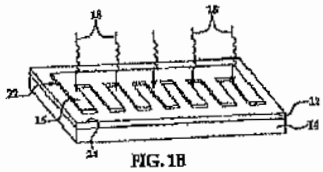


FIG. 1B

【図 1C】

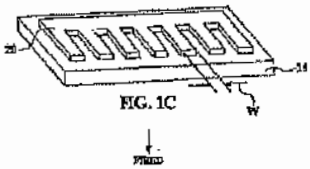


FIG. 1C

【図 2A】

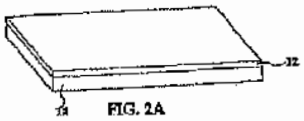


FIG. 2A

【図 2B】

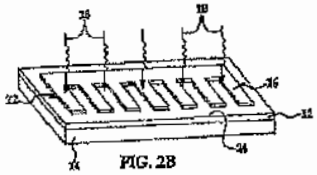


FIG. 2B

【図 2C】

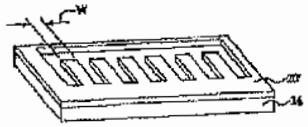
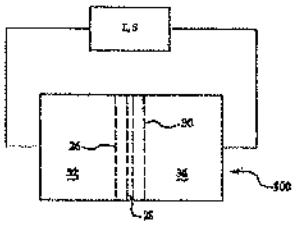


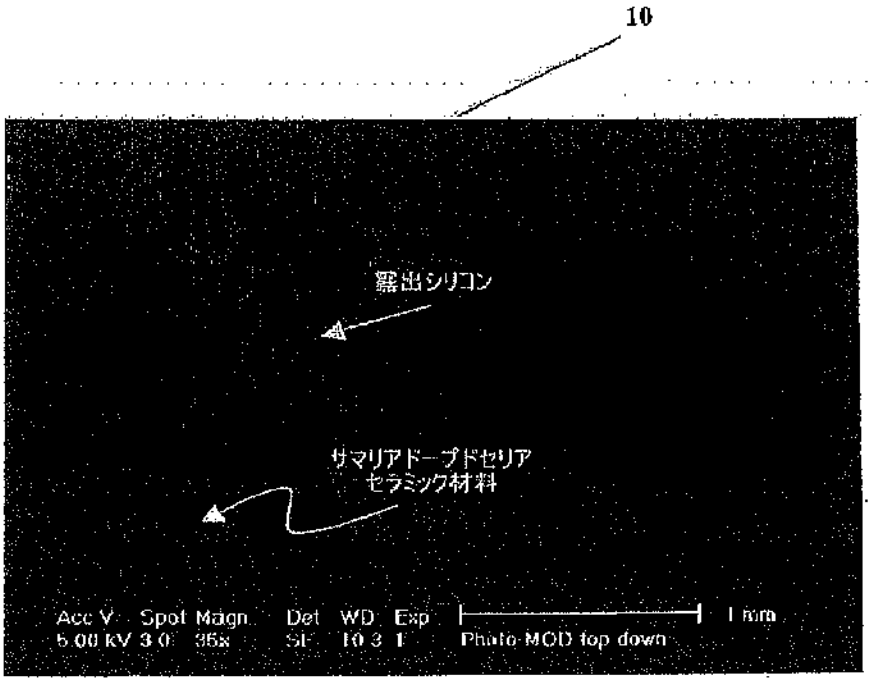
FIG. 2C

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【図 4】



【図 3】



【請求項 1】

パターニングされたセラミック薄膜（１０）を形成する方法であって

基材（１４）上に液体前駆体溶液を付着させ、それによって液体薄膜（１２）を形成することであって、前記液体前駆体溶液が、フォトレジスト中に溶解している少なくとも１つの可溶性金属塩を有する、形成すること；

前記液体薄膜（１２）をパターニングすること；及び

前記パターニングされた液体薄膜（２０、２０’）を加熱し、それによって前記パターニングされたセラミック

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薄膜（１０）を形成すること、

を包含し、

前記パターニングされたセラミック薄膜（１０）が、イオン伝導セラミック、電極、ハードセラミックコーティング、透明導電性酸化物、透明半導電性酸化物、強誘電性酸化物、及び誘電性酸化物のうちの少なくとも１つとして用いるように構成される、方法。

【請求項 2】

前記少なくとも１つの可溶性金属塩が、金属カチオン及び塩アニオンを含み、前記塩アニオンが、硝酸塩、硫酸塩、塩化物及び／又はその混合物を含み、前記少なくとも１つの可溶性金属塩が、前記フォトレジスト中に実質的に完全に溶解しており、前記液体前駆体溶液が、実質的に完全に混和性である、請求項１に記載の方法。

【請求項 3】

前記パターニングすることが、

－ 前記液体薄膜（１２）の所定の部分をマスクすることであって、前記液体薄膜（１２）がマスクされた部分（２２）とマスクされない部分（２４）とを有する、マスクすること；

－ 前記液体薄膜（１２）を光源（１８）に露光することであって、それによって前記マスクされた部分（２２）及び前記マスクされない部分（２４）のうちの一方が硬化する、露光すること；及び

－ 前記硬化していない部分を除去すること、

を包含する、請求項１又は２に記載の方法。

【請求項 4】

前記硬化していない部分を除去する前に、前記露光された液体薄膜（１２）を約５０℃～約２５０℃の範囲の温度において加熱乾燥することをさらに含み、前記加熱することが、約５４０℃～約１０５０℃の範囲の温度において前記パターニングされた液体薄膜（２０、２０’）を燃焼させることによって達成される、請求項１～３の何れか一項に記載の方法。

【請求項 5】

セラミック薄膜（１０）であって、

－ 或るパターンを有する金属有機液体前駆体溶液と；

－ その中に前記パターンを有する前記セラミック薄膜（１０）へと前記前駆体溶液を変換するための手段と、

を含み、

－ 前記セラミック薄膜が、イオン伝導性セラミック、電極、ハードセラミックコーティング、透明導電性酸化物、透明半導電性酸化物、強誘電性酸化物、及び誘電性酸化物のうちの少なくとも１つとして用いるように構成される、セラミック薄膜。

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60601360023 **INTERNATIONAL SEARCH REPORT**

International Application No
PCT/US2004/036770

A. CLASSIFICATION OF SUBJECT MATTER
INV. G03F7/004 H01M8/12 H01M4/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G03F H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2002/083863 A1 (S. MITAMURA) 4 July 2002 (2002-07-04) page 2, paragraph 22 - paragraph 25 page 4, paragraph 46 - paragraph 49 claims 15,16	1,3-11, 15,17-20 2
X	US 5 942 376 A (H. UCHIDA ET AL.) 24 August 1999 (1999-08-24) figures 1,4,5 column 7, line 63 - line 67 claims 1,10	1,3,4, 6-11, 18-20
Y	US 2003/157250 A1 (S. P. MUKHERJEE ET AL.) 21 August 2003 (2003-08-21) page 1, paragraph 2 page 3, paragraph 34 claim 13	2

-/—

[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

* Special categories of cited documents:

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"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 April 2006	22/05/2006

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Dupart, J.-M. 10.11.2006

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/035770

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 399 233 B1 (C. E. MILLIKEN ET AL.) 4 June 2002 (2002-06-04) figures 1,3,4 column 3, line 37 - line 43 column 7, line 39 - line 47 column 10, line 55 - line 67 column 11, line 1 - line 4	12-14, 16,17
X	US 6 361 892 B1 (R.C. RUHL ET AL.) 26 March 2002 (2002-03-26) figures 1,3 column 1, line 13 - line 15 column 8, line 27 - line 28 column 8, line 43 - line 60	12-14
A	EP 0 296 719 A (HEWLETT-PACKARD COMPANY) 28 December 1988 (1988-12-28) column 3, line 36 - line 52 column 4, line 20 - line 21 column 5, line 22 - line 24 column 6, line 22 - line 31	1-11, 18-20
A	US 4 952 555 A (J.V. MANTESE ET AL.) 28 August 1990 (1990-08-28) column 8 - column 10	1-11, 18-20

4

Form PCT/ISA/210 (continuation of second sheet) (January 2004)

page 2 of 2

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2004/035779

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (January 2004)

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International Application No. PCT/US2004/035770

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-11, 18-20

a method of making a patterned ceramic film

2. claims: 12,13

a fuel cell

3. claim: 14

an electronic device

4. claim: 15

a method of using a patterned ceramic film

5. claim: 16

a method of using a fuel cell

6. claim: 17

a ceramic film

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US2004/035770

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002083863 A1	04-07-2002	NONE	
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		US 5041420 A	20-08-1991
US 4952556 A	28-08-1990	NONE	

Form PCT/ISA/210 (patent family annex) (January 2004)

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(51)Int.Cl.　　F I　　テーマコード（参考）

H01M 8/02 (2006.01)　　H01M 8/02　　E

(81)指定国　AP(BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), EA(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), EP(AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OA(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG), AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW

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Fターム(参考)　2H025 AA10 AB20 AC01 AD01 AD03 BC13 BC42 BE01 CA00 CB17
CB28 FA20 FA39
2H096 AA30 BA05 BA06 BA10 EA02 HA30 JA04 LA30
5H018 AA06 AS02 AS03 BB01 BB08 EE13 HH03
5H026 AA06 BB00 BB01 BB04 EE13 HH03

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Detail Information

Last Issued Pub. Doc.

All Search List

Prev Next List

Application No.

10-2008-7010346

10-2008-0090383

KPA Examined Pub D KPA Unexam. Pub. D KPA XML

Solution processed thin films and laminates, devices comprising such thin films and laminates, and method for their use and manufacture

View Details Full-doc. of Unex. Pub. Full-doc. of Exam. Pub. Registration Judgment

View Details Biographical Information Legal Status Claim Designated States Priority

Int'l Cl.	H01B 1/12(2006.01)
Application No.(Date)	1020087010346 (2008.04.29)
Applicant	THE STATE OF OREGON ACTING BY AND THROUGH THE STATE BOARD OF HIGHER EDUCATION ON BEHALF OF OREGON STATE UNIVERSITY
Translation submission Date	(2008.04.29)
Registration No.(Date)	1012073810000 (2012.11.27)
Unex. Pub. No.(Date)	1020080090383 (2008.10.08)
Publication No.(Date)	(2012.12.05)
Int'l Application No.(Date)	PCT/US2007/023084(2007.10.31)
Int'l Unex. Pub. No.(Date)	WO 2008/082448(2008.07.10)
Final administrative status	Decision to grant (Reexamination)
Registration Status	Registered
Priority Info. (Country / No. / Date)	US (US) | 60/556,070 | 2006.11.01
Trial Info	Trial Info
Chief / Ministerial Amendment	/

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1. (WO2008082448) SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THEIR USE AND MANUFACTURE

PCT Biblio. Data | Description | Claims | National Phase | Notices | Drawings | Documents

Latest bibliographic data on file with the International Bureau

PermaLink

Pub. No.: WO/2008/082448 **International Application No.:** PCT/US2007/023084
Publication Date: 10.07.2008 **International Filing Date:** 31.10.2007

IPC: ***C08F 10/00*** (2006.01), ***H01L 21/00*** (2006.01)

Applicants: **STATE OF OREGON ACTING BY AND THROUGH THE STATE BOARD OF HIGHER EDUCATION ON BEHALF OF OREGON STATE UNIVERSITY** [US/US]; Office Of Technology Transfer, 312 Kerr Administrative Building, Corvallis, OR 97331-2140 (US) *(For All Designated States Except US).*
KESZLER, Douglas, A. [US/US]; (US) *(For US Only).*
ANDERSON, Jeremy [US/US]; (US) *(For US Only).*
HERSH, Peter, A. [US/US]; (US) *(For US Only).*
STOWERS, Jason, K. [US/US]; (US) *(For US Only).*
MEYERS, Stephen, T. [US/US]; (US) *(For US Only)*

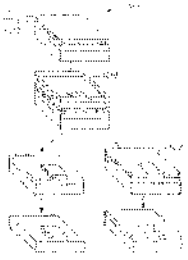
Inventors: **KESZLER, Douglas, A.**; (US).
ANDERSON, Jeremy; (US).
HERSH, Peter, A.; (US).
STOWERS, Jason, K.; (US).
MEYERS, Stephen, T.; (US)

Agent: **SLATER, Stacey, C.**; Klarquist Sparkman, Llp, One World Trade Center, Suite 1600, 121 Sw Salmon Street, Portland, OR 97204 (US)

Priority Data: 60/856,070 01.11.2006 US

Title **(EN)** SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THEIR USE AND MANUFACTURE
(FR) FILMS ET STRATIFIÉS MINCES TRAITÉS EN SOLUTION, DISPOSITIFS COMPRENANT DE TELS FILMS ET STRATIFIÉS MINCES, ET PROCÉDÉ POUR LEUR UTILISATION ET LEUR FABRICATION

Abstract: **(EN)**Devices having a thin film or laminate structure comprising hafnium and/or zirconium oxy hydroxy compounds, and methods for making such devices, are disclosed. The hafnium and zirconium compounds can be doped, typically with other metals, such as lanthanum. Examples of electronic devices or components that can be made include, without limitation, insulators, transistors and capacitors. A method for patterning a device using a positive or negative resist also is described. For example, a master plate for imprint lithography can be made. An embodiment of a method for making a device having a corrosion barrier also is described. Embodiments of an optical device comprising an optical substrate and coating also are described. Embodiments of a physical ruler also are disclosed, such as for accurately measuring dimensions using an electron microscope.



(FR)L'invention concerne des dispositifs ayant une structure de film mince ou de stratifié mince comprenant des composés hydroxy oxy d'hafnium et/ou de zirconium, et des procédés pour fabriquer de tels dispositifs. Les composés d'hafnium et de zirconium peuvent être dopés, typiquement avec d'autres métaux tels que le lanthanum. Des exemples de dispositifs ou composants électroniques pouvant être fabriqués comprennent, sans limitation, des isolateurs, des transistors et des condensateurs. L'invention concerne également un procédé pour réaliser un motif sur un dispositif, le procédé utilisant un résist positif ou négatif. Par exemple, une plaque maître pour une impression lithographique peut être réalisée. Un mode de réalisation d'un procédé pour réaliser un dispositif ayant une barrière à la corrosion est également décrit. Des modes de réalisation d'un dispositif optique comprenant un substrat optique et un revêtement sont également décrits. Des modes de réalisation d'une règle physique sont également divulgués, tel que pour mesurer de façon précise des dimensions à l'aide d'un microscope à électrons.

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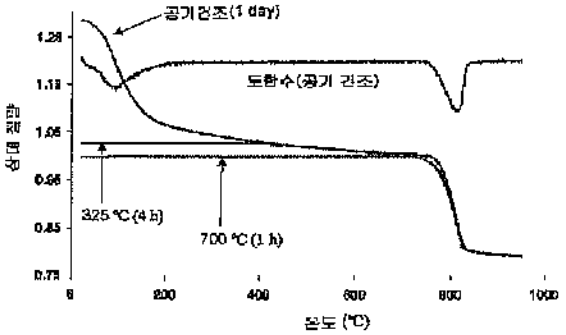
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발명의 국문명칭유황 처리된 박막들 및 적층체들, 상기 박막들 및적층체들을 포함하는 장치들, 및 그들의 사용 방법 및 제조방법

(57) 요 약

하프늄 및/또는 지르코늄 옥시 히드록시 화합물들을 포함하는 박막 또는 적층체 구조물을 갖는 소자들 및 그러한 소자들의 제조 방법이 개시된다. 상기 하프늄 및 지르코늄 화합물들은 란탄과 같은, 통상 다른 금속으로 도핑될 수 있다. 제조될 수 있는 전자 소자 또는 부품의 예는, 결연체, 트랜지스터 및 캐패시터를 포함하지만 이기에 한정되지 않는다. 포지티브 또는 네거티브 레지스트를 사용하여 소자를 패터닝하기 위한 방법이 설명된다. 예를 들면, 임프린트 리소그래피에 대하여 마스터 플레이트가 사용될 수 있다. 부식 장벽을 갖는 소자를 제조하기 위한 방법의 구현예도 설명된다. 광학 기판과 코팅을 포함하는 광학 소자의 구현예들도 설명된다. 전자 현미경을 이용하여 치수를 정확하게 측정하기 위한 것과 같은 물리적 자의 구현예도 설명된다.

대 표 도 - 도1



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특허청구의 범위

청구항 1

하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 $(MO_{2-x-z/2}(OH)_x(SO_4)_z)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 $(MO_{2-x-z/2}(OH)_x(WO_4)_z)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 $(MO_{2-3x/2-z/2}(OH)_x(BO_3)_z)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 $(MO_{2-3x/2-z/2}(OH)_x(PO_4)_z)$ 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 $(MO_{2-2x-z/2}(OH)_x(SiO_4)_z)$ 화합물 중에서 적어도 하나를 포함하는 박막 또는 적층체 구조물을 포함하는 소자.

(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음)

청구항 2

제 1 항에 있어서,

상기 박막 또는 적층체가 약 8 내지 약 12의 범위에서 값을 갖는 유전율, 적어도 6 MV cm^{-1}까지의 항복 전계, 및 1 MV cm^{-1}의 전계 강도에서 거의 1 nA cm^{-2}의 누설 전류를 갖는 것을 특징으로 하는 소자.

청구항 3

제 1 항에 있어서,

상기 화합물이 란탄을 더 포함하고, 화학식 $M_{1-z}La_zO_{2-x-z/2}(SO_4)_x$ (MSOx:La)를 갖는 것을 특징으로 하는 소자.(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 약 3.8의 범위에서 어떤 값이든 가질 수 있음)

청구항 4

제 1 항에 있어서,

상기 화합물이 HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, 또는 ZircSOx:Ca이고, 상기 소자가 50 nA cm^{-2} 미만의 누설 전류와 약 8 내지 약 12의 값을 갖는 유전율을 갖는 것을 특징으로 하는 소자.

청구항 5

제 1 항에 있어서,

상기 소자가 HafSOx:La 및/또는 ZircSOx:La을 게이트 유전체로서, 아연 인듐 산화물 및/또는 아연 주석 산화물을 채널로서 포함하는 전계효과 트랜지스터이고, 상기 트랜지스터가 10^6보다 큰 온-투-오프 비율(on-to-off ratio) 및 pA cm^{-2} 범위의 값을 갖는 게이트 누설 전류를 갖는 것을 특징으로 하는 소자.

청구항 6

제 1 항에 있어서,

광학 기판을 더 포함하고, 상기 박막 또는 적층체 구조물이 상기 광학 기판 위에 코팅을 형성하는 것을 특징으로 하는 소자.

청구항 7

제 6 항에 있어서,

상기 코팅이 반사방지 코팅이고, 및/또는 상기 코팅이 가시광선 또는 자외선에 대하여 투명한 것을 특징으로 하는 소자.

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청구항 8

제 6 항에 있어서,

상기 광학 기판과 코팅이 유전체 거울(dielectric mirror), X-선 거울, 간섭 필터, 회절 격자, 및/또는 도파로(waveguide)를 정의하는 것을 특징으로 하는 소자.

청구항 9

제 7 항에 있어서,

상기 코팅이 Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+} 및 이들의 조합으로부터 선택되는 발광성 이온을 포함하는 도핑된 발광층을 제공하기 위하여, 선택적으로 도핑된 것을 특징으로 하는 소자.

청구항 10

제 1 항에 있어서,

상기 소자가 임프린트 리소그래피를 위한 마스터 플레이트이고, 상기 박막 또는 적층체 구조물이 가요성 또는 유리 기판 위에 증착되고, 상기 박막 또는 적층체 구조물이 상기 기판 위에 증착된 HafSOx의 제1층과 ZirnSOx:Cu를 포함하는 제2층을 포함하고, 상기 제1층 및 제2층을 포함하는 적층체 구조물이 에너지 공급원에 노출됨으로써 패터닝되는 것을 특징으로 하는 소자.

청구항 11

제 10 항에 있어서,

마스크를 통해 빛 또는 전자빔에 노출시키는 것이 상기 두 층들의 상호확산(interdiffuse)을 노출된 영역에서 일으키고, 그에 의하여 노출 이전에는 도핑되지 않았던 HafSOx 층을 가용하게(soluble) 만들고, 가용하게 된 상기 HafSOx 층이 제거되어 상기 마스터 플레이트의 적어도 부분적인 프린팅 구조물을 정의하는 것을 특징으로 하는 소자.

청구항 12

박막 또는 적층체 구조물을 제공하는 단계; 및

상기 구조물을 에너지 공급원에 노출시키는 단계;

를 포함하고,

상기 구조물은 기판과 상기 기판 위에 증착된 하나 또는 그 이상의 층들을 포함하고,

상기 하나 또는 그 이상의 층들의 적어도 하나는 하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 $(MO_{2-x-z/2}(OH)_z(SO_4)_x)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 $(MO_{2-z-z/2}(OH)_z(WO_4)_x)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 $(MO_{2-3x/2-z/2}(OH)_z(BO_3)_x)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 $(MO_{2-3x/2-z/2}(OH)_z(PO_4)_x)$ 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 $(MO_{2-2x-z/2}(OH)_z(SiO_4)_x)$ 화합물을 포함하는 소자의 제조 방법.

(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음)

청구항 13

제 12 항에 있어서,

상기 박막 또는 적층체 구조물은 기판, 패터닝을 위한 제1층, 및 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 제2층을 포함하고, 상기 제2층은 포지티브 레지스트층으로서 에너지 공급원에 노출되면 상기 레지스트층 물질이 현상액에 녹을 수 있는 물질로 전환되고,

상기 구조물을 패터닝하기 위하여 상기 레지스트층을 현상액으로 처리함으로써 상기 에너지 공급원에 노출된 레

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지스트층 물질을 제거하는 단계를 더 포함하는 것을 특징으로 하는 방법.

청구항 14

제 12 항에 있어서,

상기 박막 또는 적층체 구조물은 기판, 패터닝을 위한 제1층, 및 하프늄 및/또는 지르코늄 옥시 하드록시 화합물을 포함하는 제2층을 포함하고, 상기 제2층은 네거티브 레지스트층으로서 에너지 공급원에 노출되면 상기 레지스트층이 중합되고,

상기 에너지 공급원에 노출되지 않은 물질을 제거하기 위하여 현상물질(developer)로 상기 구조물을 처리함으로써 상기 구조물을 패터닝하는 단계를 더 포함하는 것을 특징으로 하는 방법.

청구항 15

제 13 항에 있어서,

상기 포지티브 레지스트가 이중층(bilayer)을 포함하고, 상기 이중층의 제2층이 불용성 하프늄 옥사이드 설페이트(HafSOx) 막 위에 증착되고 산에 녹을 수 있으며 Cu-도핑된 지르코늄 옥사이드 설페이트(ZircSOx:Cu) 막을 포함하고,

마스크를 통해 빛 또는 전자빔을 포함하는 에너지 공급원에 노출시키는 것이 상기 ZircSOx:Cu 막과 상기 HafSOx 막의 상호확산을 노출된 영역에서 일으키고, 그에 의하여 HafSOx 막을 가용하게 만드는 것을 특징으로 하는 방법.

청구항 16

제 12 항에 있어서,

상기 하프늄 및/또는 지르코늄 옥시 히드록시 화합물이 설페이트를 포함하고, 상기 설페이트가 염기성 수용액과의 이온 교환에 의하여 후속 제거되고, 상기 염기성 용액이 1족 금속 히드록사이드, 가용성 2족 금속 히드록사이드, 가용성 3족 금속 히드록사이드, 가용성 란탄계 히드록사이드, 암모늄 히드록사이드 및/또는 수성(aqueous) 3차 아민, 또는 이들의 조합을 포함하는 것을 특징으로 하는 방법.

청구항 17

제 12 항에 있어서,

반도체 물질, 금속, 유리, 실리카, 고분자 물질, 또는 이들의 조합을 포함하는 적절한 기판을 제공하는 단계;

상기 기판 위에 HafSOx의 제 1 막을 용액 증착하는 단계;

적층체 구조물을 형성하기 위하여, 상기 제 1 막 위에 ZircSOx:Cu의 제 2 막을 용액 증착하는 단계;

상기 HafSOx 막과 상기 ZircSOx:Cu 막이 노출된 영역에서 상호확산하고 그에 의하여 노출 이전에는 도핑되지 않았던 HafSOx 막을 가용하게 만들기 위해, 상기 적층체 구조물을 에너지 공급원에 노출시키는 단계; 및

HafSOx 막을 제거하기 위하여 상기 노출된 구조물을 현상하는 단계;

를 포함하는 것을 특징으로 하는 방법.

청구항 18

제 12 항에 있어서,

상기 박막 또는 적층체 구조물이 기판, 상기 기판 위에 증착된 불용성 하프늄 옥사이드 설페이트(HafSOx)의 제 1 층, 및 상기 제 1 층 위에 증착되고 포름산 구리염(copper formate)을 포함하는 제 2 층을 포함하고,

상기 포름산 구리염의 분해와 상기 HafSOx 층과의 상호확산을 유발하고 그에 의하여 가용성 생성물을 생성하고 상기 가용성 생성물을 제거하기 위해, 상기 제 1 층 및 제 2 층을 포함하는 상기 적층체 구조물이 약 50 ℃ 내지 약 200 ℃의 온도로 가열되는 것을 특징으로 하는 방법.

청구항 19

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제 12 항에 있어서,

상기 박막 또는 적층체 구조물이 기판 및 고체 무기 산 또는 염기를 포함하는 제 1 층을 포함하고, 상기 고체 무기 산 또는 염기가 21번 내지 78번 범위의 원자 번호를 갖는 금속을 포함하고, 상기 제 1 층이 과산화물 또는 다른 배위 음이온을 더 포함하고, 상기 제 1 층이 산 또는 염기에 가용하며,

구조적으로 단단한 막을 제조하기 위하여 약 50 ℃ 내지 약 125 ℃의 온도로 상기 제 1 층이 가열되고, 마스크를 통하여 레이저, 전자빔 및/또는 빛에 노출시키는 것이 상기 막의 노출된 영역이 노출되지 않은 영역에 비하여 더 낮은 용해도를 갖도록 함으로써 노출되지 않은 영역이 제거되고 상기 막에 패턴이 생성되는 것을 특징으로 하는 방법.

청구항 20

제 19 항에 있어서,

상기 막에 패턴을 생성하기 위하여 상기 막이 0 $\mu C/cm^2$ 보다 크고 적어도 400 $\mu C/cm^2$까지의 도스 레벨, 더욱 일반적으로는 약 2 $\mu C/cm^2$ 내지 약 400 $\mu C/cm^2$의 도스 레벨로 전자빔에 노출되는 것을 특징으로 하는 방법.

청구항 21

제 19 항에 있어서,

패터닝된 상기 막이 약 3 nm 미만의 구조적 집적도(integrity)를 보이는(demonstrate) 것을 특징으로 하는 방법.

청구항 22

제 12 항에 있어서,

상기 소자가 마이크로- 또는 나노-채널 어레이를 포함하고, 상기 구조물이 기판, 제 1 층, 및 제 2 층을 포함하고, 상기 제 2 층은 금속 산화물 층이고, 상기 방법이

상기 구조물을 패터닝하는 단계; 및

상기 구조물을 패터닝함으로써 생성된 원하는 패턴을 갖는 네구성이 있는 물질을 형성하기 위하여 상기 구조물을 에너지 공급원에 노출시키는 단계;

를 더 포함하는 것을 특징으로 하는 방법.

청구항 23

제 22 항에 있어서,

스탬핑(stamping)된 층을 형성하기 위하여 반-고체(semi-solid) 하프늄 또는 지르코늄 화합물에 원하는 크기 스케일의 단위 지형물(feature)들을 스탬핑하는 단계를 더 포함하는 것을 특징으로 하는 방법.

청구항 24

상기 소자가 금속 및 금속/세라믹-계 열 보호(thermal protection) 시스템, 유기계 디스플레이 및 전자 제품, 태양 전지, 고 방사율(emissivity) 코팅, 산화물계 세라믹 매트릭스 시스템에 대한 계면 코팅, 인광체(phosphor) 위의 보호 코팅, 금속- 및 세라믹계 시스템에 대한 주변적 장벽 코팅, 복합체 및 섬유 레이저용 섬유, 용해 금속 처리에서의 부식 방지, 단열용 모노리딕 물질 및 촉매 담체로부터 선택되고, 청구항 22의 방법에 의하여 제조되는 소자.

청구항 25

소자를 제공하는 단계;

하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 $(MO_{2-x-z/2}(OH)_x(SO_4)_z)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 $(MO_{2-x-z/2}(OH)_x(WO_4)_z)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 $(MO_{2-3x/2-}$

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$_{z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) 화합물을 포함하는 금속 산화물 층을 포함하는 소자 위에 적어도 하나의 부식 장벽을 형성하는 단계(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음); 및

상기 부식 장벽을 형성하기 위해 상기 화합물을 에너지 공급원에 노출시키는 단계;

를 포함하는 부식 장벽을 갖는 소자의 제조 방법.

청구항 26

하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) 화합물을 포함하는 조성물을 제공하는 단계(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음);

상기 화합물을 포함하는 용액을 형성하는 단계;

상기 용액을 섬유들(fibers) 내부로 인입시키는 단계; 및

상기 섬유들을 고체로 전환시켜 안정한 섬유로 만드는 단계;

를 포함하는 섬유의 제조 방법.

청구항 27

적어도 두 금속을 포함하는 금속 산화물 막의 제조 방법으로서,

용액을 제조하는 단계로서, 금속 양이온 및 하나 또는 그 이상의 음이온으로 필수적으로 구성되는 하나 또는 그 이상의 가용성 염을 착화합물을 형성하지 않는(non-complexing) 비수계 극성 용매에 용해시키는 단계를 포함하고, 금속 양이온들의 적어도 하나가 3+보다 큰 형식 전하를 갖고, 3+보다 큰 형식 전하를 갖는 금속 양이온들의 농도가 상기 금속 산화물 막 내의 금속 양이온들의 50 몰%를 초과하고, 상기 용매가 150 ℃ 미만의 끓는점을 갖는, 용액을 제조하는 단계;

상기 용액의 pH를 증가시키되, 상기 pH를 증가시키는 단계는 염기성 수용액을 첨가하는 단계, 가용성 염기 산화물을 소량 첨가하는 단계, 염기성 수용액을 형성할 수 있는 기체 화합물을 첨가하는 단계, 양성자를 소비할 수 있고 상기 막 내에 통합되는 양전성(electropositive) 금속을 첨가하는 단계, 양성자를 소비하기나 상대 이온(counter ion)을 분해하지만 상기 막 내에 통합되지 않는 수계 또는 기체 산화제를 첨가하는 단계, 또는 이들 단계들의 조합을 포함하는, 상기 용액의 pH를 증가시키는 단계;

상기 비수계 용매를 증발시킴으로써 고체를 제조하는 단계;

상기 고체를 물에 용해시키는 단계;

패터닝된 또는 블랭킷 액막을 형성하기 위해 상기 용해된 고체를 기판 위에 증착하는 단계; 및

상기 막을 열적으로 경화하는 단계;

를 포함하는 금속 산화물 막의 제조 방법.

명 세 서

기 술 분 야

[0001] 본 개시는 전자 및 광학적 용용을 포함하는 목적들에 대하여 공간적으로 정의되는 구조물을 만드는 데 유용한

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무기 금속 산화물 물질을 포함하는 소자들 및 특징들의 구현예들 및 그들의 제조 방법 및 사용 방법의 구현예들에 관한 것이다.

[0002] <관련 출원의 상호 참조>

[0003] 본 출원은 2006년 11월 1일에 출원되었고, 그 전부가 여기에 인용되어 통합되는 미합중국 비정규출원 제60/856,070호의 선행 출원일의 이익을 주장한다.

[0004] <정부 지원의 감사>

[0005] 본 개시의 구현예들은 DARPA 보조금 번호 HR0011-06-1-0045의 연방 기금을 이용하여 개발되었다. 미합중국 정부는 본 발명의 특정 권리를 갖는다.

배 경 기 술

[0006] 전자 소자들은 일반적으로 물질의 순차적인 증착 및 식각과 같은 반복적인 공정 단계들을 이용하여 제조된다. 무기 물질들을 포함하는 소자들에 있어서, 금속-유기 전구체들이 무기 산화물들의 용액-기반(solution-based) 증착에 대하여 널리 사용되어 왔다. 유기 모이어티(moiety)의 존재는 유기 물질의 제거를 위해 고온 소각(burnout) 단계가 필요하게 한다. 이 단계는 상당한 부피 변화, 결정화 및 "머드 크래킹(mud cracking)"이라고 하는 현상을 일으킬 수 있다. 이와 관련된 결함들이 이 물질들의 피복으로서의 그리고 소자들 내에서의 성능을 저해한다.

[0007] 전자 소자 응용에 있어서 용액 처리 물질을 위한 방법들이 특허받아 왔다. 예를 들면, Ostergard의 미합중국 특허 제6,946,677호 "Pre-Patterned Substrate for Organic Thin Film Transistor Structures and Circuits and Related Method for Making Same"은 원하는 회로구성을 기판의 표면에 형성하는 단계, 및 그에 의하여 유기박막 트랜지스터(OTFT: organic thin film transistor) 구조 및 상호 연결하는 도전성 경로들을 형성하기에 유용한 물질을 수용하기 위해 상기 영역을 예비-패터닝(pre-patterning)하는 단계를 설명한다. 상기 미합중국 특허 제6,946,677호에 따르면, OTFT 물질은 잉크젯 프린팅과 같은 프린팅 기술을 이용하여 예비-패터닝된 영역에 증착된다.

[0008] Weng 등의 미합중국 특허 제6,927,108호는 트랜지스터를 형성하기 위한 박막 물질들의 용액 처리를 설명한다. 상기 미합중국 특허 제6,927,108호는 "트랜지스터 동작이 가능한 용액-처리된 박막 구조를 형성하기 위해 순차적으로 조직화된 도전성 용액-처리된 박막 물질 콘택들, 반도체 용액-처리된 박막 물질 활성 영역들, 및 유전 용액-처리된 박막 물질 절연들"을 형성하는 단계를 설명한다.

[0009] 미합중국 특허공개 제2005/0242330A1호는 전자 응용에 유용한 하프늄 및 지르코늄 화합물들에 관한 것으로서, 여기에 인용되어 통합된다. 미합중국 특허공개 제2005/0242330A1호는 발명자로서 Douglas Keszler 박사를 지명하고 있으며 그는 여기에 개시된 구현예들의 발명자이기도 하다.

발명의 상세한 설명

[0010] 미합중국 특허공개 제2005/0242330A1호는 선행 기술의 결함을 해결하는 방식으로 무기 화합물의 용액 증착과 화합물을 개시한다. 예를 들면, 본 발명에 따른 용액 증착은 금속-유기 증착 기술에 대하여 요구되는 유기 물질의 사용을 피할 수 있고, 따라서 유기물질의 소각(burnout)을 피할 수 있고, 소각에 따라 관련되는 크래킹 문제를 피할 수 있다.

[0011] 본 발명의 일 구현예는 하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 $(MO_{2-x-z/2}(OH)_x(SO_4)_z)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 $(MO_{2-x-z/2}(OH)_x(WO_4)_z)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 $(MO_{2-3x/2-z/2}(OH)_x(BO_3)_z)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 $(MO_{2-3x/2-z/2}(OH)_x(PO_4)_z)$ 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 $(MO_{2-x-z/2}(OH)_x(SiO_4)_z)$ 화합물 중에서 적어도 하나를 포함하는 박막 또는 적층체 구조물을 포함하는, 전자 소자와 같은, 소자에 관한 것이다. 여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있다. x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있다. 예를 들면, 옥시 히드록시 설페이트 화합물들과 같이 전하가 2인 다원자 이온에 대해서는 x는 약 0.1 내지 약 1.75의 범위 내에서 어떠한 값이든 가질 수 있다. z는 0.0 내지 약 3.8의 범위에서 어떤 값이든 가질 수 있다.

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[0012] 특정 구현예들은 화학식 $(MO_{2-x-x/2}(OH)_z(SO_4)_x)$를 갖는 하프늄 또는 지르코늄 옥시 하드록시 설페이트 화합물을 포함하는 박막 또는 적층체에 관한 것이다. (여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 1.75의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 약 3.8의 범위에서 어떤 값이든 가질 수 있음) 이들 화합물들은 HafSOx 및 ZircSOx로 불리기도 한다. 상기 하프늄 및 지르코늄 화합물들은 통상 칼슘, 세륨, 란탄, 또는 이들의 조합과 같은 다른 금속들로 도핑될 수도 있다. 특정 구현예들은 화학식 $M_{1-y}La_yO_{2-(x-z/2-y/2)}(OH)_z(SO_4)_x$ (MSOx:La)를 갖는 화합물을 제조하기 위해 도펀트로서 란탄을 사용하였다. 여기서, 조성과 양론은 위에서 언급한 바와 같다. 란탄-도핑된 화합물의 특정 예는 $Hf_{0.69}La_{0.32}O_{1.48}(SO_4)_{0.36}$이다. 추가적인 예시적인 화합물들은 HafSOx:La, ZircSOx:La, HafSOx:Ce, 또는 ZircSOx:Ca를 포함한다. 특정 구현예에서, 설페이트는 수성 염기와의 이온 교환을 통해 후속적으로 제거되고, M(OH)x 또는 MOx 막을 가져오게 된다. 적합한 수성 염기들은, 무엇보다도, 1족 금속 하드록사이드들, 2족 금속 하드록사이드들, 3족 금속 하드록사이드들, 란탄화 하드록사이드들, 암모늄 하드록사이드, 및/또는 수성 3차 아민류를 포함한다.

[0013] 특정 구현예들은 둘 또는 그 이상의 금속을 갖는 착제(complex) 조성물을 포함하는 얇은 산화물 막 또는 적층체들에 관한 것이다. 상기 금속 양이온들의 적어도 하나는 3+보다 큰 전하를 갖고, 3+보다 큰 전하를 갖는 양이온들의 총 농도는 목표 산화물 내의 금속 양이온들의 50 몰%를 넘는다. 용해된 염들과 소정량의 물을 포함하는 비-수계 용액이 제조된다. 물의 양은 비-수계 용매의 20 몰% 미만이다. 상기 용액의 pH는 염기를 첨가함에 의하여 또는 산화-환원 메커니즘을 통한 자유 양성자의 반응에 의하여 최초 용액에 비하여 증가된다. 최종 용액의 pH는 사용되는 금속 양이온에 의존하지만, 약 2 내지 8의 범위에 있을 것이다. 증가된 pH는 양이온에 결합된 물 분자들의 가수분해와 그 결과로서 얻어지는 이들 하드록소-양이온들의 응축을 가져온다. 상기 용매는 증발되고, 그 결과 고체는 물에 용해 또는 분산되게 되고 이어서 기판에 액체 막으로서 적용된다. 그런 후, 상기 액체 막은 100 ℃ 내지 600 ℃ 사이의 온도에서 약 5 분 내지 240 분 동안 열적으로 경화된다.

[0014] 본 발명에 따라 제조될 수 있는 전자 소자들 또는 소자 부품들의 예는 전계 효과 트랜지스터에서 게이트 절연막과 같은 절연체류, 전계 효과 트랜지스터와 같은 트랜지스터류, 및 MIM 캐패시터와 같은 캐패시터류를 포함하지만 여기에 한정되지 않는다. 본 구현예에 따라 제조된 박막들 및 적층체들은 약 8 내지 약 12의 범위에서 유전율 값을 갖고, 적어도 3 MV cm^{-1}에서 약 6 MV cm^{-1}까지의 항복 전계를 갖고, 1 MV cm^{-1}의 전계 강도에서 거의 1 nA cm^{-2}의 누설 전류를 가졌다. ZircSOx:Ca를 이용하여 제조한 소자들은 약 3.6 MV cm^{-1}의 항복 전계, 약 50 nA cm^{-2} 미만, 더욱 전형적으로는 약 10 nA cm^{-2} 미만의 누설 전류를 가졌다.

[0015] HafSOx:La 및/또는 ZircSOx:La를 게이트 유전체 물질로서 이용하여 전계 효과 트랜지스터들을 제조할 수 있다. 개시된 특정 구현예들은 채널로서 아연 인듐 산화물 및/또는 아연 주석 산화물을 사용하였다. 특정 전계 효과 트랜지스터들은 10^6보다 큰 온-투-오프 비율(on-to-off ratio), 및 nA cm^{-2}의 게이트 누설 전류를 가졌다.

[0016] 본 발명의 또 다른 구현예는 포토레지스트를 이용하여 소자를 패터닝하는 방법에 관한 것이다. 본 방법의 특정 구현예는 먼저 패터닝될 구조물을 제공하는 단계를 포함한다. 상기 구조물은 통상 반도체 물질, 금속, 유리, 고분자 물질, 또는 이들의 조합과 같은 기판; 실리카와 같이, 패터닝을 위한 물질층; 및 레지스트 층을 포함한다. 상기 레지스트 층은 통상 개시된 하프늄 및/또는 지르코늄 옥시 하드록시 화합물을 포함한다. 상기 구조물은 전자빔 또는 빛, 특히 예를 들면 자외선 광과 같은 에너지 공급원에 노출된다. 그런 후, 상기 소자를 패터닝하기 위해 물질이 제거되거나 소자의 활성, 패터닝된 부품으로서 유지된다.

[0017] 상기 레지스트는 포지티브 레지스트 또는 네거티브 레지스트일 수 있다. 예를 들면, 상기 방법은 상기 레지스트층을 에너지 공급원에 노출시켜 상기 레지스트 층 물질을 현상액(developer)에 용해될 수 있는 물질로 전환시키는 단계를 포함할 수 있다. 상기 현상액에 용해될 수 있는 물질은 그 후 현상액을 이용하여 제거된다. 적합한 현상액들은, 무엇보다도, 산, 염기, 및/또는 초음파 교반(ultrasonic agitation)을 포함할 수 있다. 다시 예로서, 상기 방법은 에너지 공급원에 노출된 레지스트층 물질을 제거하는 단계를 포함할 수 있다. 본 발명을 특정 작동 이론에 한정됨이 없이, 적어도 특정 구현예에 대하여, 에너지 공급원에 대한 노출은 레지스트 층의 중합을 일으킬 수 있고, 에너지 공급원에 노출되기 전에 비하여 현상액에 상대적으로 덜 용해되게 만들 수 있다.

[0018] 포지티브 레지스트의 한 구현예는 이중층을 포함한다. 상기 이중층의 제1층은 하프늄 옥사이드 설페이트(HafSOx) 막 위에 증착된 포름산 구리의 막을 포함한다. 상기 포름산 구리의 막은 산에 가용성이고, 도핑되지 않은 HafSOx 막은 산에 불용성이다. 상기 이중층을 마스크를 통해 빛에 노출시키거나 포커스를 맞춘 전자빔에

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노출시키는 것은 노출된 영역에서 두 막들이 상호확산하도록 하며, 그에 의하여 그 이전에 도핑되지 않았던 HafSOx 막을 가용성이 되게 한다.

[0019] 레지스트를 제조하기 위한 이중층 공정의 다른 구현예는 고체 산 또는 염기의 제 1 층을 기판 위에 증착하는 단계를 포함하고, 상기 산 또는 염기는 하나 또는 그 이상의 금속 원자를 포함한다. 포름산 구리와 같은 산화물 전구체를 포함하는 현탁액을 상기 제 1 층 위에 원하는 패턴으로 적용한다. 가열 조건 하에서, 상기 전구체는 분해되어 옥사이드가 된다. 이어서 상기 산화물은 상기 제 1 층과 반응 및 상호확산하여 식각을 통해 패턴을 드러낼 수 있는 생성물을 형성한다. 선택적인 구현예는 산화를 입자를 가열과 함께, 또는 가열함이 없이 상기 제 1 층 위에 증착하고, 식각될 수 있는 생성물을 형성하는 직접 반응을 가져오는 단계를 포함한다. 추가적인 구현예는 산화물 전구체의 박층을 상기 제 1 층 위에 증착하는 단계를 포함한다. 그런 후, 포토마스크를 통해 빛에 노출시키거나 또는 포커스를 맞춘 레이저 또는 전자빔으로 직접 기록함으로써 활성화된 전구체의 패턴이 형성된다.

[0020] 본 발명의 또 다른 구현예는 임프린트 리소그래피를 위한 마스터 플레이트에 관한 것이다. 상기 마스터 플레이트는 가요성 또는 유리 기판과 같은 기판을 포함하고, 박막 또는 적층체 구조물의 적어도 한 층이 적어도 하나의 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함한다. 마스터 플레이트의 특정 구현예는 상기 기판 위에 증착된 HafSOx의 층과 ZircSOx:Cu 층과 같은 제 2 층을 포함한다. 상기 마스터 플레이트는 노출된 영역에서 두 막들이 상호확산하도록 하기 위하여 마스크를 통해 빛 또는 전자빔에 노출시키는 것과 같이 에너지 공급원에 노출시킴으로써 패턴될 수 있다. 이것은 이전에 도핑되지 않았던 HafSOx 막이 가용성이 되어, 제거됨으로써 마스터 플레이트의 프린팅 피처들을 적어도 부분적으로 정의한다.

[0021] 또 다른 구현예에서, 단일층 공정에서 본 발명의 막들을 이용하여 마스크 또는 템플릿을 제조할 수 있다. 고체 산 또는 염기와 같은, 무기 전구체의 박막이 퍼옥사이드 또는 유사한 용이온과 함께 기판 위에 증착된다. 상기 막은 구조적으로 강직한 막을 생성하기 위해 가열된다. 그런 후, 노출된 영역에서 응축/가교를 유발하기 위해 포토마스크를 통해 또는 레이저 또는 전자빔을 통해 노출된다. 노출된 영역의 용해도는 노출되지 않은 영역에 비하여 감소된다. 그런 후, 노출되지 않은 영역은 선택적으로 식각되어 막 내에 네거티브-톤의 이미지를 생성할 수 있다. 노출시키기 전에 상기 막을 더 높은 온도로 예열함으로써 포지티브-톤의 이미지들도 형성될 수 있다. 일부 구현예들에서, HafSOx와 같은 막을 수산화나트륨과 과산화수소의 혼합물로 처리함으로써 $M(OH)_x/H_2O_2$ 막이 형성된다. 그런 후, 그 결과로서 얻어지는 막은 빛에 또는 전자빔에 노출시킴으로써 패터닝된다.

[0022] 기판, 패터닝을 위한 물질층, 및 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 금속 산화물층을 포함하는 패터닝될 구조물을 제공하는 단계를 포함하는 소자의 형성 방법이 또한 설명된다. 상기 구조물은 패터닝되고 그런 후 에너지 공급원에 노출되어, 상기 구조물을 패터닝함으로써 생성된 원하는 패턴을 갖는 내구성이 있는 물질을 형성한다. 상기 방법에 따라 제조된 소자의 일구현예는 마이크로- 또는 나노-채널 어레이와 같은 채널 어레이를 포함할 수 있다. 그러한 구현예들에 대하여, 상기 소자를 만들기 위한 방법은 반-고체 하프늄 또는 지르코늄 화합물에 원하는 크기 스케일의 단위 피처들을 스탬핑하여 스탬핑된 층을 형성하는 단계를 포함할 수 있다.

[0023] 부식 장벽을 갖는 소자를 제조하기 위한 방법의 구현예도 설명된다. 상기 방법의 개시된 구현예들은 소자를 제공하는 단계 및 상기 소자 위에 적어도 하나의 부식 장벽을 형성하는 단계를 포함한다. 부식 장벽은 통상 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 금속 산화물층을 포함한다. 상기 방법은 부식 장벽을 형성하기 위해 상기 화합물을 에너지 공급원에 노출시키는 단계를 포함할 수도 있다. 그러한 소자들의 예는 금속 및 금속/세라믹-계 열 보호(thermal protection) 시스템, 유기계 디스플레이 및 전자 제품, 태양 전지, 고 방사율(emissivity) 코팅, 산화물계 세라믹 메트릭스 시스템에 대한 계면 코팅, 인광체(phosphor) 위의 보호 코팅, 금속- 및 세라믹계 시스템에 대한 주변적 장벽 코팅, 복합체 및 섬유 레이저용 섬유, 용해 금속 처리에서의 부식 방지, 단열용 모노리딕 물질 및 축매 담체를 포함한다.

[0024] 섬유를 형성하기 위한 방법의 구현예도 설명된다. 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 용액이 형성된다. 그런 후, 상기 용액은 섬유 내부로 인입된다. 상기 섬유는 가수분해, 어닐링, 공기 열분해 및 이들의 조합과 같이 적절한 어떠한 방법에 의해서든 교체, 안정한 형태로 전환될 수 있다.

[0025] 광학 소자의 구현예들도 또한 설명된다. 상기 소자의 특히 개시된 구현예들은 광학 기판과, 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 기판 코팅을 포함한다. 상기 층은 반사방지 코팅일 수 있다. 상기 광학 기판 및 코팅은, 예를 들면, 유전체 거울(dielectric mirror), X-선 거울, 간섭 필터, 회절 격자, 및/또는 도파로(waveguide)를 정의할 수 있다. 상기 광학 소자는 시각적으로 후밍하거나 또는 자외선 빛에 투명

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한 것과 같이 투명한 층을 포함할 수도 있다. 상기 층은 Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+} 및 이들의 조합으로부터 선택되는 발광 이온들을 갖는 도핑된 층을 제공하기 위해 선택적으로 도핑될 수 있다. 상기 층을 도핑하는 단계는 발광층을 생성하기 위해 사용될 수 있다.

[0026] 물리적 자를 제조하기 위한 방법의 구현예들도 개시된다. 특정 구현예들은 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물의 용액 증착에 의하여 적어도 하나의 산-가용성 층을 형성하는 단계를 포함한다. 적어도 하나의 산-불용성 층이 상기 산-가용성 층에 인접하여 형성되고, 상기 산-불용성 층은 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물의 용액 증착에 의하여 형성된다. 이들 단계들의 반복은 교호하는 층들을 생성하고, 상기 방법은 교호하는 산-불용성 및 산-가용성 층들의 폭들을 정확하게 결정하는 단계를 포함한다. 폭의 결정은 X-선 반사와 같이 적절한 어떠한 방법을 이용해서든 달성될 수 있다. 게다가, 적어도 하나의 층이 식각되어 측정하는 목적물에 대하여 손가락 모양의 2차 참조 패턴을 정의한다. 그러한 소자의 특정 구현예들은 전자 현미경을 이용하여 치수를 정확하게 측정하는 데 유용하다.

[0027] 본 발명의 위에서의 그리고 다른 목적들, 피처들 및 장점들은 첨부된 도면을 참조하여 진행되는 다음의 상세한 설명으로부터 더욱 명백해질 것이다.

[0028] 본 발명의 개시된 구현예들은 무기 물질들의 용액 증착(solution deposition)에 의하여 제조될 수 있는, 전자 소자들 또는 전자 소자들의 부품들을 포함하는 소자들에 관한 것이다. 본 개시에 걸쳐서, 단수를 나타내는 "하나의(a, an)" 및 "상기"는 문맥상 명백히 달리 표시되지 않는 한 복수의 피지칭물(referent)도 포함한다. 유사하게, "또는"이라는 단어는 문맥상 명백히 달리 표시되지 않는 한 "및"을 포함함을 의도한다. "포함한다(include)"라는 표현은 "포함한다(comprise)"를 의미한다. 여기에 표시된 모든 백분율은 달리 표시되지 않는 한 원자 백분율(atomic percentage)이다. 여기에서 언급된 모든 특허들 및 공개문헌들은, 달리 표시되지 않는 한, 그 전부가 여기에 인용되어 통합된다. 상충되는 경우에는, 용어의 설명을 포함하여 본 명세서가 우선될 것이다. 여기에 언급된 물질들, 방법들 및 실시예들은 예시적인 것일 뿐이고, 한정의 의도는 아니다.

[0029] I. 금속 산화물 설페이트(sulfate) 물질들 일반 및 미합중국 특허공개 제2005/0242330A1호

[0030] 본 개시는, 통상 전자 응용에 유용한 금속 산화물 설페이트 무기 물질들의 용액 증착인, 무기 물질들의 용액 증착을 위한 방법의 구현예들에 관한 것이다. 이들 물질들의 구현예들은 미합중국 특허공개 제2005/0242330A1호에 설명되어 있다. 공개된 상기 출원의 특정 부분, 문단 0009 내지 문단 014가 아래에 부연된다. 부연된 이 본문에서 도면에 대한 참조부호는 미합중국 특허공개 제2005/0242330A1호에 공개된 도면들을 참조한다.

[0031] 도 1은 유전 전구체 물질의 제조 공정의 일 구현예를 나타낸다. 일반적으로, 공정(10)은 금속-함유 양이온과 같은 제 1 반응물(12)을 제공하는 단계, 다원자(polyatomic) 음이온과 같은 제 2 반응물(14)을 제공하는 단계, 및 그런 후 상기 다원자 음이온과 상기 금속-함유 양이온을 반응시키는 단계를 포함한다. 상기 금속-함유 양이온 및 상기 다원자 음이온은 함께 반응하였을 때 수용액과 같은 용액으로 될 수 있다. 일 구현예에서, 상기 금속-함유 양이온은 하프늄 옥시 염화물($HfOCl_2(aq)$)와 같은 하프늄 옥시 할로겐화물의 수용액을 이용하여 제공될 수 있다. 설페이트(SO_4^{2-})와 같은 상기 다원자 음이온은 황산($H_2SO_4(aq)$)과 같은 수용액을 이용하여 제공될 수 있다. 이들 두 반응물들은 원하는 물질들을 만들기에 적합한 공정들과 상대적인 양들을 이용하여 함께 혼합될 수 있다.

[0032] 상기 반응은 전구체 용액(16)을 생성할 수 있다. 전구체 용액(16)은 기판에 적용함으로써와 같이 원하는 대로 즉시 사용될 수 있다. 선택적으로, 전구체 용액(16)은 적어도 부분적으로 탈수된(dehydrated) 후 적용될 수 있다. 그런 후 위에서 주어진 예에서, 상기 전구체 용액은 하프늄 옥시-히드록시 설페이트($HfO_{2-x-z/2}(OH)_z(SO_4)_x$)를 형성할 수 있다. 본 화학식에서의 변수들에 있어서, x 및 z는 고정되거나 변화할 수 있으며, 어떤 값이든 가질 수 있다. 예를 들면, x의 값은 통상 약 0.1 내지 약 1.9이고, z의 값은 0.0 내지 약 2.0이다. 일 구현예에 대하여, 이 값들은 x=0.5이고 z=0이었다. 히드록시 기는 금속-함유 양이온의 일부일 수 있고, 이 화합물은 하프늄 옥시-히드록시 설페이트($HfO_{2-x-z/2}(OH)_z(SO_4)_x$)를 포함할 수 있다.

[0033] 다른 구현예들에서, 상기 다원자 음이온은 하나 또는 그 이상의 설페이트(SO_4^{2-}), 보레이트(BO_3^{3-}), 포스페이트(PO_4^{3-}), 텅스테이트(WO_4^{2-}) 및 실리케이트(SiO_4^{4-})를 포함할 수 있다. 상기 금속-함유 양이온은 금속 아산화물(suboxide)을 포함할 수 있고, 하나 또는 그 이상의 하프늄(Hf^{4+}), 티타늄(Ti^{4+}), 지르코늄(Zr^{4+}), 세륨

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(Ce^{4+}), 주석 (Sn^{4+}), 탄탈륨 (Ta^{5+}), 니오븀 (Nb^{4+}), 이트륨 (Y^{3+}), 몰리브데늄 (Mo^{4+}), 텅스텐 (W^{6+}), 알루미늄 (Al^{3+}), 갈륨 (Ga^{3+}), 아연 (Zn^{2+}), 크로뮴 (Cr^{3+}), 철 (Fe^{3+}), 비스무트 (Bi^{3+}), 란탄회귤(lanthanides), 하프늄 옥시-히드록사이드 ($HfO_y(OH)_z^{(4-2y-z)+}$), 지르코늄 옥시-히드록사이드 ($ZrO_y(OH)_z^{(4-2y-z)+}$), 티타늄 옥시-히드록사이드 ($TiO_y(OH)_z^{(4-2y-z)+}$), 탄탈륨 옥시-히드록사이드 ($TaO_y(OH)_z^{(5-2y-z)+}$), 이트륨 옥시-히드록사이드 ($YO_y(OH)_z^{(3-2y-z)+}$), 니오븀 옥시-히드록사이드 ($NbO_y(OH)_z^{(4-2y-z)+}$), 몰리브데늄 옥시-히드록사이드 ($MoO_y(OH)_z^{(4-2y-z)+}$), 텅스텐 옥시-히드록사이드 ($WO_y(OH)_z^{(6-2y-z)+}$), 알루미늄 옥시-히드록사이드 ($AlO_y(OH)_z^{(3-2y-z)+}$), 갈륨 옥시-히드록사이드 ($GaO_y(OH)_z^{(3-2y-z)+}$), 아연 옥시-히드록사이드 ($ZnO_y(OH)_z^{(2-2y-z)+}$), 크로뮴 옥시-히드록사이드 ($CrO_y(OH)_z^{(3-2y-z)+}$), 철 옥시-히드록사이드 ($FeO_y(OH)_z^{(3-2y-z)+}$), 비스무트 옥시-히드록사이드 ($BiO_y(OH)_z^{(3-2y-z)+}$), 및 란탄 계열의 옥시-히드록사이드들을 포함할 수 있다. y의 값은 상기 금속 양이온의 전하와 상기 금속 양이온에 결합된 히드록사이드 및 다른 다원자 음이온의 양과 관련된다.

[0034] 여기에 개시된 다원자 음이온들 및 금속-함유 양이온들을 이용하는 방법의 구현예들은 착화합물을 형성하기 위한 유기물질의 이용을 필요로 하지 않는, 즉, 음이온 및 양이온의 공급원이 유기물질을 포함하지 않는 유전 전구체 물질의 형성을 가져올 수도 있다. 그러나, 특정 구현예에 대하여 원하거나 필요한 경우에는 유기물질이 사용될 수 있다. 예를 들면, 에탄올과 같이 착화합물을 형성하지 않는(non-complexing) 유기물질이 전구체 용액의 부분적 용매로서 사용될 수 있다. 만일 전구체 물질에 착화합물을 형성하는(complexing) 유기물질이 포함되어 있지 않다면, 일단 상기 전구체 용액이 기판에 적용되면 통상 상기 전구체 용액은 유기 물질들을 분해/연소시키기 위해 400 ℃ 또는 그 이상의 온도에서 가열되거나 어닐링될 필요가 없다. 가열 및/또는 건조로 인한 전구체 용액의 증합은 다결정질 물질(polycrystalline material)이 아닌 비결정질막의 형성을 가져오고 그에 의하여 기판 위에 유전 물질의 용액-기반-응용을 가능하게 한다.

[0035] 일반적으로, 본 공정에서 개시된 구현예들은 공기 내의 대기압과 같은 주위 환경 조건에서 수행될 수 있다. 따라서, 진공 공정은 불필요하다. 그러나, 원한다면 진공 공정이 이용될 수 있다. 상기 공정은 주위 환경보다 높은 온도에서, 예를 들면 약 80 ℃ 내지 약 850 ℃의 범위, 통상 80 ℃ 내지 높아야 350 ℃의 온도 범위에서, 그리고 좀층 높아야 100 ℃의 온도에서 수행될 수 있다. 이들 저압 및 저온 공정 단계들은 개시된 공정들에 대하여 요구되는 에너지를 감소시킬 수 있다. 유전막의 처리에 유용한 낮은 온도로 인하여, 상기 막들은 플라스틱 기판들과 같은 저온 기판들 위에 처리되거나 또는 저온 기판들에 용액으로서 적용될 수 있다. 제조된 상기 결정질이 아닌 비정질(amorphous)의 유전 전구체(dielectric precursor) 용액은 웨이퍼 위와 같은 기판 위에 전구체 용액의 콘포말(conformal)한 도포성을 가능하게 한다. 상기 용액은 마스킹 또는 식각 단계들이 사용되지 않도록, 잉크젯 프린팅을 이용함에 의해서와 같이, 소정의 특정한 패턴으로 적용될 수도 있다. 따라서, 본 개시의 공정은 기판들 위에 포토리소그래피 공정을 수행하는 동안 물질의 형성 및 제거를 위해 사용될 수 있는 유해하거나 또는 독성을 갖는 물질들의 사용을 제거하거나 감소시킬 수 있다. 그러므로, 본 공정은 알려진 공정들에 비하여 시간의 측면에서 효율적이고, 환경적으로도 친환경적(green)이다. 게다가, 본 개시의 예시적 일 구현예에서 사용된 하프늄 옥사이드 및 설페이트 물질들은 독성 물질들이 아닐 수 있다.

[0036] 본 개시의 공정에 사용되는 물질들의 예는 하프늄 옥시 히드록시 설페이트류 ($HfO_{2-x-y/2}(OH)_x(SO_4)_y$), 하프늄 옥시 히드록시 텅스테이트류 ($HfO_{2-x-y/2}(OH)_x(WO_4)_y$), 하프늄 옥시 히드록시 보레이트류 ($HfO_{2-x-y/2}(OH)_x(BO_3)_y$), 하프늄 옥시 히드록시 포스페이트류 ($HfO_{2-x-y/2}OH_x(PO_4)_y$), 및 하프늄 옥시 히드록시 실리케이트류 ($HfO_{2-x-y/2}OH_x(SiO_4)_y$)를 포함하는 화합물들의 군에 속하는 화합물들을 포함한다. 이들 물질들은 80 ℃ 정도의 낮은 온도에서 증합될 수 있고, 약 740 ℃까지, 심지어는 1,200 ℃ 정도의 높은 온도에서도 비결정질을 유지할 수 있다. 물질의 증합은 가열 속도를 조절함으로써, 공-용매(co-solvent)를 사용함으로써, 다른 적절한 방법들에 의하여 및 이러한 방법들의 모든 조합들 및 어떤 조합들에 의하여 제어될 수 있다. 본 개시의 비결정질 막들은 조직(grain) 경계에서의 결함 형성을 감소시킬 수 있고, 비정질-결정질(amorphous-to-crystalline) 전이에서 크랙이 형성되는 것을 감소시킬 수 있다. 게다가, 본 개시의 유전막들은 상당히 높은 유전 상수, 즉, 유기 화합물들의 유전 상수보다 더 높은 유전 상수를 가질 수 있다. 잉크젯 프린팅 응용과 같은 용액-기반 처리에 의하여 고품질의 유전체를 형성할 수 있는 능력은 저렴한 가격의, 전계 효과 트랜지스터들 또는 캐패시터들과 같은 전자 부품의 형성을 가능하게 한다.

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[0037] 도 2는 유전 물질을 형성하기 위하여 전구체 용액(16)을 적용하기 위한 공정의 일 구현예를 개념적으로 나타낸다. 하프늄 옥시 설페이트와 같은 전구체 용액(16)이 적용자(applicator) (20)에 의하여 웨이퍼와 같은 기판(18)에 적용될 수 있다. 일 구현예에서, 적용자(20)는 노즐들(22)을 갖는 잉크젯 프린터를 포함할수 있다. 전구체 수용액(16)은 상기 잉크젯 프린터의 노즐들(22)을 통하여 분출된다. 다른 구현예들에서, 적용자(20)는 상기 전구체 용액의 적용 방법이 스핀-코팅, 딥(dip)-코팅, 또는 스프레이-코팅을 포함할 수 있도록 각각 스핀-코터, 딥-코터, 또는 스프레이-코터를 포함할 수 있다. 전구체 용액(16)의 비결정질의 용액-기반 성질들로 인하여 전구체 용액(16)은 적용되었을 때 우수한 콘포말(conformal) 도포성을 가능하게 할 수 있다. 일단 기판 표면에 또는 상기 기판 위에 증착된 막 또는 막들에 적용되면 상기 전구체 용액 내의 수분 함량을 재기하거나 감소시키기 위하여 상기 전구체 용액은 히터(24)로 가열함으로써 또는 다른 탈수(dehydration) 장치에 의하는 것과 같이 탈수될 수 있다. 상기 탈수 단계는 웨이퍼(18) 위에 하프늄 옥시 설페이트 박막과 같은 비결정질 유전물질(26)의 침전물 가져올 수 있다.

[0038] 도 3은 유전 물질 전구체 용액(16) (도 1 참조)의 일 구현예에 있어서, 특히, 황산(H_2SO_4)과 하프늄 옥시 클로라이드($HfOCl_2$)의 반응에 있어서, 상이한 전구체 농도들에 따른 가능한 용액 농도들을 나타내는 그래프이다. 더욱 구체적으로, 도 3은 전체 하프늄 농도(몰 농도(M))에 대한 전체 설페이트 농도(M)의 그래프를 나타낸다. 영역(28)은 투명한 용액, 즉, 시각적으로 감지할 수 있는 침전물이 그 안에 없는 용액을 나타내고, 영역(28)은 과량 황산(H_2SO_4)의 영역이다. 영역(30)은 투명한 용액, 즉, 시각적으로 감지할 수 있는 침전물이 그 안에 없는 용액을 나타낸다. 영역(30)은 과량 하프늄 옥시 클로라이드($HfOCl_2$)의 영역이다. 선분(32)은 황산과 하프늄 옥시 클로라이드가 일 대 일의 비율(1:1의 양론비)로 각각 존재하는 양론(stoichiometric) 선을 나타낸다. 영역(34)은 침전 영역, 즉, 시각적으로 감지할 수 있는 침전물이 그 안에 있는 용액을 나타낸다. 따라서, 영역(34) 또는 그의 일부는 잉크젯 프린팅 응용에 의하여 매끈하고도 실질적인 결함이 없는 막들을 형성하기에 가장 적합한 것은 아닌 용액들을 나타낼 수 있지만, 그의 사용이 배제되는 것은 아니다. 따라서, 전구체 용액(16) (도 2 참조)이 잉크젯 프린터 응용 장치(20) (도 2 참조)를 통해 적용될 때, 제 1 반응물 및 제 2 반응물의 농도가 영역(28) 또는 영역(30)의 어느 하나 안에 있고, 고체 영역(34) 안에 있지 않는 것이 바람직하다. 영역(34)의 용액에 존재하는 고체물은 노즐들(22)을 막거나, 매끈하지 않은 막을 형성할 수 있거나, 또는 바람직하지 않은 전구체 용액 적용을 가져올 수 있다. 다시 말하면, 상기 영역들(28 및 30)의 용액은 잉크젯 프린트헤드를 통해 또는 드롭퍼(dropper) 방법에 의하여 적용될 수 있는 가능한 "잉크" 전구체 용액을 나타낼 수 있다.

[0039] II. 일반 논의

[0040] 새로운 박막 유전체들 및 나노적층체들(nanolaminates)은 매끈하고 조밀한 막의 용액 증착을 이용하여, 통상 수용액 증착을 이용하여 개발되어 왔다. 용액 증착 기술들은 스핀 코팅 및 잉크젯 프린팅을 포함한다. 용액 증착에 이어서 적당한 열처리가 후속될 수 있다($T < 325℃$).

[0041] 본 발명의 개시에 따라 분말 및 막으로서 제조된 물질 모두의 화학을 정의하기 위해 다양한 분석 기술들이 사용되어 왔다. 상기 막의 품질과 기능성은 X-선 반사도(reflectivity), 전자 현미경, 및 전자 소자들에서의 성능에 의하여 평가되었다. 유전 특성들이 작동 구현예들에 대하여 결정되었으며, 약 8 내지 약 12의 범위를 커버하는 유전율(permittivity); 적어도 6 $MVcm^{-1}$까지의 항복 전계(breakdown field); 및 1 $MV\ cm^{-1}$의 전계 강도에서 1 $nA\ cm^{-2}$ 에 가까운 누설 전류를 포함한다. 상기 막질의 표면의 매끈함 및 기공이 없는 특성은 적어도 약 2 나노미터의 얇은 개별층들을 갖는 독특한 나노적층된(nanolaminated) 구조물의 제조를 용이하게 한다. 비교적 높은 유전율 막들은 박막 금속-절연체-금속(MIM: metal-insulator-metal) 캐패시터들 및 박막 트랜지스터들(TFTs)에서 높은 항복 강도와 낮은 누설 전류를 제공하면서 본 발명의 개시된 구현예들을 이용하여 실현될 수 있다. 절연막들의 예외적인 특성들도 독특한 나노적층 구조물의 제조를 가능하게 한다.

[0042] 박막 유전체로서 사용되기 위하여는 비결정질 물질들이 바람직한데, 그들은 조직(grain) 경계를 갖지 않고, 따라서 결정질과 관련된 거칠(roughness)과 전하 전도의 여지가 적다. 지르코늄과 하프늄의 수많은 산화물들, 예를 들면, 단순한 이성분계(binary), 실리케이트류, 및 알루미네이트류가 고유전율(high-permittivity) 유전체 응용의 후보들로 검증되어 왔다. 다성분 물질들에서, 순수한 이성분 산화물들에 비하여 더욱 강건한 항복(breakdown) 특성을 만들기 위하여, 유전율을 희생할 수 있음에도 불구하고 결정화가 저해될 수 있다. 이들 유전막들은 종종 다양한 유기-금속 또는 금속-염 전구체들과, 원자층 증착(ALD: atomic layer deposition), 화학기상증착(CVD: chemica vapor deposition), 졸-겔 처리, 또는 이들의 조합과 같은 기술들을 이용하여 형성된다. 그러나, 용액 증착 방법에 의하여 조밀하면서도 비결정질인 유용한 유전막을 제조하는 것은 증착 및 후속 공정

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모두가 수행되는 동안 결정화와 크래킹(cracking)을 저해할 것이 요구될 수 있다.

[0043] 본 발명의 개시된 어떤 구현예들은 금속 산화막의 개발에 관한 것이다. 금속 산화물들은 각각 $HfO_{2-x}(SO_4)_x$ 및 $ZrO_{2-x}(SO_4)_x$ (여기서, $0.1 \leq x \leq 1.5$)로 나타내어지는 화학식을 갖는 하프늄 및 지르코늄 설페이트계를 참조하여 여기에 일반적으로 예시된다. 이들 화합물들은 여기에 HafSOx 및 ZircSOx의 약어로 각각 지칭될 것이다. 이들계의 화학과 물리적 성질을 정의하기 위하여, HafSOx 및 그의 도핑된 유사체(analog)를, 즉, La-치환된 유도체 HafSOx:La와 같은 유사체를 분말 및 박막으로 제조하였다. 캐패시터들과 TFT들을 제조함으로써 HafSOx, ZircSOx 및 선택된 유도체들의 박막 유전 특성들을 평가하였다. 이들 분석들은 매우 높은 품질의 조밀한 막이 제조될 수 있음을 나타내었다. 혼합 HafSOx/ZircSOx 나노적층체의 막 두께 및 제조가 스핀-코팅 공정에 의하여 이제 조절될 수 있다.

[0044] 수많은 상(相)들 및 결정 구조들이 HfO_2-SO_3-H_2O 및 ZrO_2-SO_3-H_2O 계의 검증으로부터 보고되어왔다. 여러 구조들이 금속 원자, 설페이트 기 및 물의 응축과 관련된 구조적 차원(dimensionality)과 수화도의 변화를 보이는 화학식 $Hf(SO_4)_2 \cdot nH_2O$ 또는 $Zr(SO_4)_2 \cdot nH_2O$의 단순한 수화물들로 특성화된다. 설페이트에 비하여 금속이 풍부한 물질들이 일려져 있으며, $Zr_2(OH)_2(SO_4)_3 \cdot 4H_2O$; $Hf(OH)_2SO_4$, $Zr(OH)_2SO_4$와 이들의 수화물들; $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13} \cdot 33H_2O$ 및 $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$; 및 $Zr_3O_5SO_4$와 그의 수화물을 포함한다. 이러한 구조들 모두는 수소 결합의 변화 또는 탈수화로 인하여 실온과 약간의 가열조건에서 공기와 접촉할 때 모두 불안정한 것으로 보인다($Zr_3O_5SO_4$는 예외일 수 있다). 이것은 비결정질 막을 개발하기 위해 사용될 수 있는 탈수화 및 응축 공정을 가능하게 한다.

[0045] (변수 x로 나타낸) 하프늄에 대한 설페이트의 선택된 분율을 갖는 수용액으로부터 시작하여 HafSOx 침전물 기열에 의하여 유발되었다. 도 1은 공기로 건조된 HafSOx 침전물의 TGA(thermogravimetric analysis) 결과이다. TGA는 샘플의 무게(질량) 변화를 온도의 함수로 측정하기 위해 사용되는 열분석 기술이다. 공기로 건조된 HafSOx 침전물의 가열은 세 영역에서의 질량 손실을 가져온다. 다른 HafSOx 유도체들에 대하여도 유사한 특성들이 관찰되었다. 약 200 ℃의 온도 아래에서의 큰 질량 손실은 포함되었던 물의 손실에 기인한다. 약 200 ℃ 내지 약 700 ℃의 온도 범위에서의 질량 손실은 주로 물보다 더욱 강하게 결합된 히드록시 종의 제거에 기인한다. 약 700 ℃를 넘어서 시작되는 급격한 질량 손실은 $SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$에 따른 설페이트 분해에 기인한다. 탈수된 HafSOx 분말이 700 ℃와 950 ℃ 사이에서 HfO_2로 완전히 전환된다고 가정할 때, 상기 설페이트 분율은 질량 손실로부터 계산될 수 있다. 샘플의 질량 손실의 결정은 모액(mother solution)에서 설페이트의 레벨을 증가시키는 것이 침전물에서의 설페이트의 레벨의 증가를 가져옴을 밝혔다. 특히, 탈수된 화학식 $HfO_{1.54}(SO_4)_{0.46}$ 및 $HfO_{1.29}(SO_4)_{0.71}$ 각각에 대하여 하프늄에 대한 설페이트의 비율은 약 46%에서 약 71%까지 변화하였다. 설페이트 공급원으로서 $H_2SO_4(aq)$가 사용되든 $(NH_4)_2SO_4(aq)$가 사용되든, 동일한 최대 설페이트 조성이 침전되었고, 설페이트 레벨 < 46%인 생성물은 검출되지 않았다. 모든 샘플들에 대하여, 열중량 측정 프로파일에서 일부 변화가 관찰되었지만 720 ℃ 이상에서 설페이트 손실의 시작이 발생하였다. 이러한 가열 곡선들의 도함수(derivative)들에 대한 정의 가능한 값으로서의 피크 위치들은 테스트된 샘플들에 대하여 793 ℃와 817 ℃ 사이에서 분해됨을 나타낸다. 설페이트 공급원으로서 $H_2SO_4(aq)$을 사용하고 최대 설페이트 함량을 갖는 샘플들에 대하여 가장 높은 분해 온도가 관찰되었다.

[0046] 다시 도 1을 참조하면, 최대 설페이트 함량을 갖는 샘플들이 TGA 측정에 앞서 가열되었다. 수분과 관련된 질량 손실들이 감소되었고, 계산된 설페이트 함량들은 예열된 샘플들과 보통의 샘플들 모두가 비슷하였다. 이 70 내지 70%의 설페이트 함량은 보고된 결정들 $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$ 및 $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13} \cdot 33H_2O$의 조성들과 유사하다. TGA 연구로부터 Ahmed, Fjelvag, 및 Kjekhus는 그들의 연구에서의 Hf 및 Zr 디설페이트들에 대한 온도보다 더 높은 온도 및 다른 데서 보고된 염기성 설페이트들 $Hf(OH)_2SO_4 \cdot H_2O$ 및 $Zr_3O_5SO_4$에 대한 온도보다 더 높은 온도에서 $Hf_{18}O_{23}(SO_4)_{13}$ 및 $Zr_{18}O_{23}(SO_4)_{13}$에 대하여 설페이트 분해가 일어남을 발견하였다. 향상된 열적 안정성 외에, 약 13:18의 설페이트-금속 비율은 이 계에 특별한 안정성을 보여준다. 따라서, 이 조성물은 용액처리 및 가열이 필요한 목적에 대하여 적합할 수 있다.

[0047] 설페이트 $La_2O_2SO_4$는 1,300 ℃보다 큰 분해 온도를 갖는다. 란탄(La)은 빈성된 탈수 성질 및 열적 성질들, 한 예로서 열적 안정성과 같은 변성된 물성을 갖는 추가적인 화합물을 만들기 위해 HafSOx 모액에 첨가되었다. 혼

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합금속계인 $Hf_{1-c}La_cO_{2-x-z/2}(SO_4)_z$ (HafSOx:La)는 이러한 화합물을 예시한다. 이러한 화합물을 제조하기 위하여, 전구체 물질과 23% La (총 금속)을 포함하는 용액을 가열하여 침전물을 형성하였다. 회학 분석 결과 생성물에 3%의 La 만이 발견되는 것으로 나타났다. TGA로부터 금속에 대한 설페이트의 비율이 71%임이 입증되었고, 820 ℃에서의 (도함수 피크로서) 분해되는 것이 최대 설페이트 함량과 일치하는 것으로 발견되었다. 그런 후 32% La을 포함하는 구성 종의 염 용액에 $NH_3(aq)$를 첨가함으로써 공침전(co-precipitation)을 유발하였다. 생성물의 회학 조성을 분석한 결과, 모액에 존재하는 것과 동일한 La 분율인 것으로 밝혀졌다. 본 화학식에 대한 열분해는 도평되지 않은 HafSOx와 현저하게 상이하였다. 비록 가열 특성들이 덜 급격하였지만 설페이트에 기인한 질량 손실은 700 ℃ 위에서 현저하였고, 2 ℃(분)$^{-1}$의 더 느린 승온 속도로 가열하였을 때에도 1,000 ℃까지 가열하면서 질량이 일정하게 달성되지 않았다. 이 가열 속도에 대하여, (도함수 피크로서) 분해는, 비록 가열 조건에 달려있기는 하지만, 약 870 ℃에서 일어난다. 산화물의 완전한 분해는 1,500 ℃까지 가열함으로써 달성되었는데, 건조된 침전물에 대하여 화학식 $Hf_{0.62}La_{0.38}O_{1.48}(SO_4)_{0.36}$이 수득되었다.

[0048] 침전된 HafSOx 분말에 대하여 XRD 데이터를 수집하여 결정상에 대한 온도 범위를 입증하였다. 공기 건조 후, 최대 설페이트 함량과 설페이트 공급원으로서 $H_2SO_4(aq)$를 갖는 샘플들에 대하여 복잡한 회절 패턴이 기록되었고, 다른 샘플들은 회절이 없거나 확산되는 것을 보였다. HafSOx(x=0.7)에 대한 XRD 데이터를 도 2에 나타내었다. 공기 건조된 샘플들을 약 100 ℃ 내지 약 700 ℃ 사이의 온도에서 1시간 동안 건조시킨 후, 상기 물질은 비결정질이 되었다. 모노리딕 HfO_2의 결정성 피크 특성이 750 ℃ 이상에서 1시간 동안 가열한 후 관찰되었다. TGA에 의하여 설페이트 손실의 개시가 720 ℃에서 일어나므로, 결정화는 설페이트 손실과 일치하는 것으로 밝혀졌다. 3% La을 포함하면, 1,000 ℃의 온도까지도 유사한 회절 프로파일이 생성된다.

[0049] 도 3은 HafSOx:32% La에 대한 XRD 데이터를 나타낸다. 침전된 물질과 700 ℃에서 가열된 것 모두 X-선 비결정질이다. 비치환된 HafSOx에서와 같이, 감지할만한 결정상은 설페이트가 분해되기 시작하는 온도 구간인 700 ℃와 750 ℃ (1시간 가열) 사이에서 형성된다. 그러나 32% La의 치환으로는 모노리딕 HfO_2는 감지되는 상이 아니다. 오히려, 회절 프로파일은 입방계 (또는 정방정계) HfO_2와 일치한다. HfO_2의 상은 종종 탄탄계 원자들 포함함으로써 안정화된다. 적절한 상 다이어그램으로 고려하면 예측할 수 있는 바와 같이, 고온으로 가열하면 $Hf_2La_2O_7$과 모노리딕 HfO_2가 생성될 수 있다. 중간 온도 산화물 상들은, 900 ℃에서 10 내지 37%의 탄탄이 입방계 지르코니아를 안정화시키고 1,050 ℃에서 상분리가 일어남을 발견한 Zhang, Kershaw, 및 Dwight의 ZrO_2-La_2O_3 시스템에 관한 업적과 일관된다.

[0050] 재료들을 특성화하기 위하여 약 200 나노미터 내지 약 300 나노미터의 두께를 갖는 HafSOx 및 HafSOx:La 박막들이 제조되었다. 상기 막들에 대한 조성들은 Hf, La, Cl 및 S의 상대적인 농도에 기초하여 EMPA로 결정되었다. 이 방법에 따르면 산소 레벨이 덜 정확하므로, 발수된 화학식으로 표현하였다. 325 ℃에서 (5분간) 가열된 대표적인 두 HafSOx 막들은 하프늄에 대한 설페이트의 비율이 각각 67%와 85%로 나타난 $HfO_{0.985}(SO_4)_{0.67}Cl_{0.69}$ 및 $HfO_{0.915}(SO_4)_{0.85}Cl_{0.47}$로 결정되었다. 상기 85% 설페이트막은 650 ℃로 (5분간) 더 가열되어 $HfO_{1.275}(SO4)_{0.71}Cl_{0.09}$으로 결정되었다. 또한, 330 ℃에서 (5분간) 가열된 상기 HafSOx:La 막은 $Hf_{0.76}La_{0.24}O_{0.79}(SO_4)_{0.90}Cl_{0.39}$인 것으로 결정되었다. 650 ℃로 가열된 HafSOx에 대하여, 설페이트 비율은 71%로 감소하였으며, 이는 최대 설페이트로 가열 침전된 HafSOxjc 대한 조성과 일치한다. HafSOx:La에 대하여, La의 측정된 분율(24%)은 전구체 용액에서의 La 농도 23%와 잘 맞는다.

[0051] 선택된 온도에서 5분 동안 가열한 후 HafSOx(x~0.67 및 0.85)와 HafSOx:La 막들에 대한 투과 푸리에 변환 적외선 (FTIR: transmission Fourier transform infrared) 분석 결과들이 수집되었다. 주요한 두 개의 작용기를 감지하기 위하여 FTIR 스펙트럼들이 사용되었다. 3000 내지 3600 cm^{-1} 범위에서의 흡수는 히드록시기에 기인하고, 1000 내지 1200^{-1} 범위에서의 흡수는 설페이트 기에 기인한다. 가열과 함께, 히드록시기 흡수는 약 325 ℃ 내지 약 600 ℃의 범위에 걸쳐서 감소하는 반면, 설페이트 스트레치(stretch)는 HafSOx 막에 대하여는 약 650 ℃ 내지 700 ℃ 사이에서, HafSOx:La 막에 대하여는 약 700 ℃ 내지 750 ℃ 사이에서 거의 제거된다. (설페이트 흡수에 대한 프로파일은 기판으로부터의 SiO_2가 유사한 에너지를 흡수하기 때문에 약간 왜곡되지만, 스펙트럼들은 정성적으로 정확하다)

[0052] 도 4 및 도 5에 각각 보인 바와 같이, HafSOx(x~0.67 및 0.85) 및 HafSOx:24% La 막들에 대하여 각각 표시된

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온도에서 5분간 가열한 후 박막 XRD 데이터가 수집되었다. 두 HafSOx 조성물 모두에 대하여, 막들은 약 325 ℃ 내지 약 650 ℃까지 X-선 비결정질이다. 모노리딕 HfO_2는 약 700 ℃ 또는 그 이상에서 감지된다. HafSOx:La 막들은 약 330 ℃ 내지 약 700 ℃에서 비결정질인 반면, 입방게 상은 약 750 ℃ 내지 약 1000 ℃에서 감지된다. 상기 입방게 상은 1,100 ℃에서 모노리딕 HfO_2와 $Hf_2La_2O_7$으로의 분리가 시작되기 때문에 의판상 불안정하다. HafSOx 및 HafSOx:La 막들에 대하여, 설페이트의 손실은 산화를 결정화와 직접 상관될 수 있으며, 이는 분말 거동과 일관된다.

[0053] HafSOx, ZircSOx 및 이들의 유도체들의 막들은 유전체로서 사용되기 위한 스핀-코팅에 의하여 증착되었다. 전계 항복 강도뿐만 아니라 1 kHz에서의 손실 탄젠트와 유전율의 파라미터들을 결정하기 위하여 MIM 캐패시터들을 테스트하였다. "항복"은 전계 말도가 10 μA cm^{-2}를 넘는 전계로서 정의된다. HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, 및 ZircSOx:Ca에 대하여 유사한 테스트들이 수행되었다. 도 6은 알루미늄 점 몬택들이 0.011 cm^2의 민적을 나타내는 HafSOx 유전막에 대한 유전 항복 특성을 나타낸다. HafSOx 및 ZircSOx 막들은 4 내지 6 MV cm^{-1}의 항복 전계를 가졌다. ZircSOx:Ca에 대한 항복 전계는 3.6 MV cm^{-1}이었다. 가해진 1 MV cm^{-1}의 전계에서, 여섯 변형 물질 모두가 50 nA cm^{-2} 미만의 누설 전류를 보였으며, 많은 조성물들에 대하여 10 nA cm^{-2} 미만의 누설 전류가 관찰되었다. 모든 변형 물질들에 대하여 약 9 내지 약 12의 유전율 값들과 손실 탄젠트 < 1%가 측정되었다.

[0054] HafSOx:La 또는 ZircSOx:La를 게이트 유전체로서 이용하고, 아연 인듐 산화물 또는 아연 주석 산화물을 채널로서 이용하여 전계효과 트렌지스터(FET: field-effect transistor)를 제조하였다. 전류 변조(modulation)가 달성되었는데, 드레인-소오스 전압을 증가시킴에 따라 드레인-소오스 전류가 포화되었으며, 10^6보다 큰 온-투-오프 비율(on-to-off ratio)을 제공하고, pA cm^{-2}의 범위의 값을 갖는 게이트 누설 전류를 제공한다. 이러한 결과들은 HafSOx:La과 ZircSOx:La 막들이 소자 집적에 대하여 충분히 강건하고, 유전체/채널 계면의 품질의 요건도 만족됨을 나타낸다.

[0055] 새로운 종류의 비결정질 다성분 산화물 유전막으로서, HafSOx, ZircSOx 및 이들의 유도체들은 다른 혼합 시스템, 특히 $(MO_2)_{1-x}(Al_2O_3)_x$ 및 $(MO_2)_{1-x}(SiO_2)_x$ (여기서, M = Hf 또는 Zr)로 나타내어지는 알루미네이트들 및 실리케이트들과 비교될 수 있다. 이들 시스템들 각각에 대한 다양한 막 조성물들이 통상의 기상 기술들에 의하여 증착되었다. (유전체 응용에서 통상적인 조성으로서) 20 내지 50 몰%의 Al_2O_3 또는 SiO_2를 갖는 Hf 또는 Zr 알루미네이트와 실리케이트들의 경우에 있어서, 결정화는 통상 약 800 ℃ 내지 1,000 ℃에서 상 분정(phase segregation)과 함께 일어난다. 테스트된 HafSOx 분말 및 막들에 대하여, 결정화는 설페이트가 분해됨에 따라 약 700 ℃에서 일어났다. 유전체로서, 이들 알루미네이트들과 실리케이트들은 HafSOx 및 ZircSOx에 대한 8 내지 12의 값들과 비교해 볼 때 10 내지 15의 유전율 값을 보인다. 이들 새로운 종류의 산화물 설페이트 물질들은 비결정질, 상간 온도, 중간 유전율 유전체로 고려될 수 있다.

[0056] 주사 전자 현미경(SEM: scanning electron microscopy) 및 반사 X-선(XRR: X-ray reflectivity)을 이용하여 막의 성질을 더 검사하였다. HafSOx 및 HafSOx:La 막들에 대한 SEM 이미지들을 도 7 및 도 8에 나타내었다. 이들 이미지들은 유전체 테스트를 위해 전형적으로 사용된 것과 같은 약 150 나노미터 내지 약 300 나노미터의 범위의 두께들을 갖는 막들의 매끈한 표면과 조밀하고 균일한 단면을 나타낸다. 도 7은 그 위에 Ta 금속의 506-nm 층(712) 및 160 nm의 HafSOx 막(714)이 증착된 SiO_2 기판(710)을 나타낸다. 도 8은 그 위에 Ta 금속의 512-nm 층(812) 및 192 nm의 HafSOx/La 막(814)이 증착된 SiO_2 기판(810)을 나타낸다.

[0057] 더 얇은 막 형성을 위한 재현성의 엄격한 측정으로서 HafSOx/ZircSOx의 반복 기조를 갖는 다층 구조물들이 적층되었고 XRR로 분석되었다. 도 9는 XRR 스캔의 한 간섭 패턴을 나타낸다. 반복되는 이중층의 두께를 찾기 위해 정상파 하모닉스를 나타내는 피크 정점의 위치가 사용되었다. HafSOx와 ZircSOx의 두께를 독립적으로 규칙적으로 변화시키면서, 개별 층들의 두께가 결정되었다. 나노적층체 스택 내에서, 약 3 나노미터 정도로 얇은 단일층이 측정되었다. 회절 패턴에서 고차 반사가 관찰됨에 따라, 각 이중층은 조도(roughness)를 포함하여 0.5 미만의 변동성(variability)으로 증착되었다.

[0058] Si CMOS 기술에서 소자 크기의 축소는 유전체로서 얇고, 누설 전류가 높은 SiO_2의 교체의 필요성을 가져왔다. 교체되는 유전체들은 높은 유전율을 보여야 하고, 더 작은 누설 전류로 동일한 소자 캐패시턴스를 보이기 위해

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더 두꺼운 층을 가능하게 하여야 한다. HfO_2 및 ZrO_2는 이들의 바람직한 유전 특성 및 열적 특성으로 인하여 대체 게이트 유전체로서 상당한 주목을 끌어왔다. HfO_2 및 ZrO_2 유전체에 대한 도전의 하나는 매끈하고, 조밀하며, 핀-홀이 없고, 13 nm 이하의 두께를 갖는 초박막(ultra-thin films)을 만드는 것이다. 이전의 초박막들은 원자층 증착(ALD: atomic layer deposition)을 이용하여 형성되었다. ALD의 일부 유망한 결과들에도 불구하고, 이 방법은 긴 증착 시간(1 Å/분)과 함께 진공을 이용할 것이 요구되기 때문에 비용이 높고 생산성이 낮았다. 이로 인하여 HfO_2와 ZrO_2의 용액 기반 증착의 일부 연구가 촉발되었다. 현재까지 이들 막들은 ALD 막들과 동일한 균일성과 조밀성에 도달하지 못하였다.

[0059] 교환 반응을 이용하여, ALD 품질에 필적하고 DRAM (dynamic random access memory) 및 Si CMOS (complementary metal-oxide semiconductor) 기술에 사용하기에 적합한 $M(OH)_x$ 및 MO_x 초박막을 제조할 수 있다. 개시된 구현예들에 대하여, 상기 막들은 스핀-코팅을 이용하여 무기 응축을 통해 겔페이트 형태로 증착된다. 예를 들면, 반-고체 막이 $MO_x \cdot HCl \cdot H_2SO_4$ 조성으로 형성될 수 있다. 상기 겔페이트는 수산화나트륨 수용액을 이용하여 이온 교환으로 제거된다.

[0060] $$MO_x \cdot HCl \cdot H_2SO_4 + OH^-(aq) \rightarrow M(OH)_{2x} + Cl^-(aq) + SO_4^{2-}(aq)$$

[0061] 결과로서 얻어지는 히드록소(hydroxo) 및/또는 산화물 막들은 매끈하고, 조밀하며 핀홀이 없다. 예를 들면, 약 2 나노미터의 두께를 갖는 HfO_2 막들이 HafSOx 막들로부터 제조될 수 있다. 교환된 막들은 약 800 °C의 온도까지 약 10 초 내지 10 분 동안 열처리될 수 있고, 그 결과, 막의 표면 조도가 약 0.1 나노미터가 된다. 이러한 막의 특성들은 값비싼 원자층 증착 방법을 저비용 스핀-온 또는 분무(misting) 기술로 대체하면서 CMOS 및 관련 기술 분야에서 금속-유전체 게이트에 대한 요건들을 만족한다.

[0062] 증착된 반-고체 수화 히드록소 막들은 막의 모폴로지(morphology)를 붕괴시키지 않으면서 음이온 교환을 가능하게 한다. 예를 들면, SO_4^{2-}, WO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-}, VO_4^{3-}, AlO_4^{5-}, GaO_4^{5-}과 같은 옥소 음이온들과 이들의 프로톤화된 형태들, 예를 들면, HPO_4^{2-}, $H_2PO_4^-$ 및 할로겐들 F^-, Cl^-, Br^-, 및 I^-는, 예를 들면, Na_2SO_4(aq)와 같은 금속염 조(槽)에 상기 막들을 넣음으로써 선택적으로 교환될 수 있다. 이것은 전자 분야 용융 및 이온 교환 크로마토그레피 및 여과와 같은 다른 분야 응용에 대하여 막 성능을 최적화하기 위한 기회들을 제공한다.

[0063] 산화물 막들의 일부 구현예들에 대하여, 착제(complex) 조성물, 예를 들면, 둘 또는 그 이상의 금속 원자들을 제공하기 위해 기판에 직접 적용될 수 있는 단일-공급원 전구체 현탁액(liquid suspensions)을 제조하기는 어렵다. 다음의 방법들은 소자 응용을 위해 적합한 품질을 갖는 막 증착을 위한 단일-공급원 전구체로서의 그러한 현탁액들의 제조와 그들의 사용을 가능하게 한다.

[0064] 다음은 전구체 수용액의 합성과 상기 전구체를 이용하여 금속 산화물 막을 증착하기 위한 일반적인 방법을 설명한다. 상기 전구체 수용액은 비-수계 극성 용매 내에서 가수분해에 의하여 응축되고 이어서 증착을 위한 수성(aqueous) 환경으로 전환되는 폴리머 또는 올리고머 금속-히드록소 화합물들을 포함한다는 점에서 구분된다. 바람직한 박막 전기 및 광학 특성들 및 처리 온도들은 해로운 유기 오염물 없이 금속 수산화물들을 조밀한 고체 산화물들로 응축시킴으로써 달성된다. 합성 방법의 개시된 구현예들은 1) 극성 용매 내에 금속 염을 용해; 2) 가수분해 및 응축; 3) 용매 증발; 4) H_2O 내에 용해; 및 5) 용액 증착 및 경화의 일반 절차들을 따른다.

[0065] 금속 양이온(M^{n+})과 하나 또는 그 이상의 음이온들(X^{b-})을 포함하는 하나 또는 그 이상의 가용 염들은, 지방족 알코올류 또는 니트릴류, 특히 (탄소수 10 또는 그 이하의) 저알킬(lower alkyl) 알코올류 및 니트릴류와 같은, 예를 들면, 메탄올, 에탄올, 아세토니트릴 또는 이들의 혼합물과 같이 착화합물을 형성하지 않는, 비-수계 극성 용매에 용해된다. 많은 용매 시스템들이 가능하다. 특정 응용을 위해 적합한 용매들이 의도된 용액-상 반응과 양립할 수 있는 끓는점(통상 150 °C 미만), 저 유독성, 및 산-염기 및 산화환원 특성들을 고려하여 선택될 수 있다. 금속 공급원들은 단순 이온 또는 분자염($Zn(NO_3)_2$, $SnCl_4$ 등); 옥사 또는 히드록시염($ZrO(NO_3)_2$, ZnOHCl 등); 또는 잠재적인 유기염들($Fe(CH_3CO_2)_2$, $Cu(CHOO)_2$ 등)을 포함할 수 있다. 금속 양이온들의 적어도 하나는 3+보다 큰 형식 전하를 가져야 하고, 그러한 이온들(M^{n+}, 여기서 n>3)의 총 농도는 목적 산화물 내의 금속 양이온들의 50 몰%보다 커야 한다. 동시에, 소정량의 H_2O가 위에서 설명한 금속염들의 수화물로서, 순수한 액체로서, 또는 아래에 상설하는 멈기성 용액으로서 상기 용액 내에 도입된다. 상기 물의 양은 선택된 양이온들에 의

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하여 결정되며, 물의 통상적인 양은 비-수계 극성 용매의 20 몰%를 넘지 않을 것이다.

[0066] 그런 후, 상기 용액의 pH는 적절한 염기를 첨가함으로써 또는 산화-환원 메커니즘을 통해 자유 프로톤들의 반응에 의하여 초기 pH에 비하여 증가될 수 있다. 증가된 pH는 산성(a>3) 양이온들에 의하여 결합된 H_2O 리간드들의 가수분해와 그 결과로서 생성되는 히드록소-양이온들의 응축을 촉진한다. 최종 용액 pH는 사용된 금속 양이온들에 달려있지만 약 2 내지 약 8의 범위에 통상 있게 될 것이다. 이는 다음 기술들 중의 하나 또는 그들의 어떠한 또는 모든 조합들을 이용하여 달성될 수 있다.

[0067] a) NH_4OH, $(NH_4)_3PO_4$, CsOH 또는 유사한 화합물들을 함유하는 염기성 수용액의 첨가. 후속 공정에서 분해 또는 증발시키기 위하여 특정 화합물들(NH_4OH)이 선택될 수 있다. 달수에 이어서 고유한 모폴로지, 광학적 또는 전기적 특성들을 달성하기 위해 최종 산화물 막의 일부를 이루도록 의도된다면 다른 양이온들(예를 들면, Cs) 또는 다원자 음이온들(예를 들면, PO_4^{-3})이 사용될 수 있다.

[0068] b) 최종 산화막에 유사한 목적으로 포함시키기 위해 CaO 또는 SrO와 같은 염기성 산화물을 소량 첨가 또는 용해.

[0069] c) H_2O 내에 염기성 용액을 형성하는 NH_3 또는 다른 기체 화합물의 첨가.

[0070] d) H_2에 대한 직접 환원을 통해 또는 NO_3^-의 환원과 같이 다른 양성자 소비성 산화-환원 과정의 일부로서 양성자들을 소비할 수 있는, Zn, Al 또는 Fe와 같은 양전성(electropositive) 금속 환원제의 첨가. 결과로서 일어지는 양성자 종들은 그 이후 최종 산화막 내에 포함된다.

[0071] e) 최종 산화막 내에 포함되지 않으면서 양성자들을 소비하거나 상대 이온들을 분해하기 위한 유사한 목적으로 가용 염으로서 또는 액상의 H_2O_2, N_2H_4, 또는 H_2CO와 같은 수용액 또는 기상의 산화제 또는 환원제를 첨가.

[0072] 상기 용액들은 원하는 최종 조성에 따라 열 가수분해 및 응축을 촉진하기 위해 실온, 가열, 또는 용매열(solvothermal) 조건에서 교반될 수 있다. 적절한 반응 시간이 경과한 후에 상기 용액은 하나 또는 그 이상의 가용 올리고머 또는 폴리머 금속-히드록소 양이온 종을 포함할 것이다. 이들 종들은 사실상 호모 또는 헤테로-금속 종이다. H_2O에 비하여 비-수계 용매의 감소된 극성 및 크기가 입체 장애(steric) 효과 또는 변형된 전하-차폐(charge-screening) 성질들을 통하여 추가적인 응축 및 회전 과정을 방해할 수 있는 반면, 응축의 정도는 사용될 수 있는 H_2O(수성(aquo)- 또는 히드록소- 리간드들)의 제한된 몰비에 의하여 제한된다.

[0073] 가용한 금속 종들은 상기 비-수계 용매를 증발시킴으로써 분리된다. 분리된 금속-히드록소 화합물들은 솔벤트, 상대 이온, 및 가수 분해 비율(hydrolysis ratio) 등과 같은 특정 고려사항들에 따라 결정질 또는 비결정질 고체 또는 겔을 형성할 수 있다.

[0074] 산화물 막을 위한 전구체 용액들은 상기 분리된 고체를 H_2O에 녹이거나 분산시킴으로써 재조된다. 결과로서 얻어지는 졸 또는 용액은 균일하고, 열역학적으로 안정할 수도 있고, 그렇지 않을 수도 있다.

[0075] 전구체 용액들은 패터닝된 또는 블랭킷 액상 막을 형성하기 위해 프린팅, 스핀, 스프레이, 또는 딥-코팅을 포함하는 적합한 어떠한 기술이든 이용하여 기판에 적용된다. 액상 막은 약 100 ℃ 내지 600 ℃의 온도에서 약 5 내지 240 분 동안 대기 조건 하에서 열적으로 경화된다. 원하는 화학 또는 광전자 특성에 적합하도록 산소 양론 또는 양이온 산화 상태를 변화시키기 위해 진공 또는 형성 기체(forming gas) (예를 들면, H_2 및 흐르는 N_2 또는 Ar) 어닐링이 사용될 수 있다.

[0076] 여기에 설명한 막들의 '배끈함과 높은 원자 밀도는 용액 공정을 통해 순수한 무기 나노적층체들의 제조를 가능하게 한다. 이들 막들은 이하에서 더욱 상세하게 논의하는 바와 같이, 넓은 응용범위로의 개발을 위한 새로운 플랫폼을 나타낸다.

[0077] III. 응용들

[0078] 당 기술분야에서 통상의 지식을 가진 자는 HafSOx 및 ZircSOx 화합물들과 이러한 화합물들을 포함하는 막들이 수많은 상이한 소자들을 만들기 위해 사용될 수 있고, 그러한 화합물들을 이용하는 수많은 공정들의 실행에 사용될 수 있음을 이해할 것이다. 금속-유기 전구체들이 무기 산화물들의 용액-기반 증착에 광범위하게 채용되어 왔다. 유기 모이이티의 존재는 고온 소각(burnout) 단계를 필요로 하고, 이는 상당한 부피 변화와 일반적으로

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결정화를 가져오고 또한 "머드 크래킹(mud cracking)" 현상을 가져온다. 비결정질 HafSOx 및 ZircSOx 막들을 형성하기 위해 적절한 무기 조성물들과 본 발명에 개시된 구현예들을 사용함으로써 이들 문제점들이 제거되며, 단순한 탈수 및 중합은 막질 보존으로 이어진다. 상의 안정성을 이해하기 위하여, 대표적인 HafSOx 및 HafSOx:La 분말과 막들이 다양한 온도에서 특성화되었다. HafSOx 및 ZircSOx에 기초한 박막들은 상기 막들의 품질과 유용성을 검증하기 위하여 다양한 구성으로 증착되었다. 캐패시터 유전체를 제조하기 위해 여러 유도체들이 사용되었다. HafSOx:La 및 ZircSOx:La를 사용하여 FET 소자들의 게이트 유전체를 형성하였다. HafSOx 및 ZircSOx의 나노적층체의 층들은 주목할만한 매끈함을 2개의 원자층 이내로 재현성있게 시현하였다. 무엇보다도, HafSOx, ZircSOx 및 이들의 유도체들을 포함하는 막들의 종류는 전기 절연체, 보호 장벽, 광학 코팅, 및/또는 포토리소그래피를 위한 무기 폴리머로서 유용하다.

[0079] A. 레지스트, 임프린트 리소그래피 및 프린팅을 위한 패턴된 막들

[0080] 포토리소그래피는 마스크 위의 기하학적인 형태를 실리콘웨이퍼 또는 다른 반도체의 표면에 전사하기 위하여 널리 사용된다. 지난 40년간, 포토리소그래피 공정은 마이크로 전자산업에서 소자 구조물의 치수 제어 및 분해능 개선의 구동력이었다. 이러한 발전들은 고성능 개인용 컴퓨터, 휴대 전화, CD 플레이어, 및 이제 우리 삶의 필수적인 부분으로 자리잡은 다른 수많은 진보된 전자 제품들을 가능하게했다. 이들 제품들을 가능하게 하였던 포토리소그래피에서의 발전은 주로 짧은-파장으로 노광하는 도구의 개발과 폴리머 레지스트들의 해상도 및 피처(feature)-크기 능력을 비상하게 확장하는 데 중심을 두어왔다. 그러나, 더욱 작은 피처를 및 소자-수율 개선을 위한 탐색이 계속됨에 따라 폴리머계 레지스트 기술의 한계와 비효율성이 점차 더욱 명백해지고 있다.

[0081] 리소그래피를 통해 구현된 가장 작은 피처 크기는 무기 물질들의 전자빔 기록에 의하여 제조되었다. 그러나, 제조 환경에서 사용되기 위한 일관성 이상의 관심을 받기에는 이러한 피처들을 제조하기 위한 빔-도스 에너지는 과도하게 너무 높았다.

[0082] 여기에 설명된 막들의 증착 및 처리가 이루어지는 동안, 막들의 수화 레벨을 조절하는 것이 가능한데, 이는 적층된 막들의 상호확산(interdiffusion)과 그 결과 얻어지는 물리적 및 화학적 특성의 조절을 위한 방법을 제공한다. 이러한 조절된 상호확산은 그 결과로서 얻어진 물질 용해도에 있어서의 유도된 변성과 함께 막들의 높은 품질과 결합되어 새로운 리소그래피 패터닝 방법을 개발하기 위하여 사용되었다. 이러한 방법론은 두 개의 구별되는 막들을 적층하는 단계와 반응시키는 단계를 수반하며, 이중층 확산(bilayer diffusion)으로 지칭된다. 또한, 퍼옥사이드(O_2^{2-})와 같은 작은 배위종들은 추가적인, 새로운 리소그래피 패터닝 방법을 제공하기 위해 수계 무기 현탁액들과 막들에 통합될 수 있다. 이 기술에서, 막들에 에너지(에를 들면, 빛, 전자빔, 열)가 적용될 수 있으며, 상기 막의 용해도를 변화시키는 응축 반응을 유도하고, 그에 의하여 리소그래피 패터닝을 가능하게 한다.

[0083] 포지티브 또는 네거티브 포토레지스트를 이용하여 패턴들이 형성될 수 있다. 이 공정은 실리콘 기판(1012), 실리카층(1014) 및 레지스트층(1016)을 갖는 적층체 구조물(1010)을 참조하여 도 10에 개념적으로 도시된다. 포지티브 레지스트에 있어서, 상기 레지스트층(1016)은 UV광과 같은 에너지 공급원에 노출되고, 그 아래에 있는 물질들은 제거되게 된다. 이들 레지스트들에 있어서, UV 광에의 노출은 현상액(developer)에 더욱 잘 용해되게 되도록 상기 레지스트층(1016)의 화학 구조를 변화시킨다. 그런 후, 노출된 상기 레지스트층(1016)은 아래에 있는 원래의 물질 영역을 남긴 채 현상액에 의하여 제거된다. 다시 말해, "보이는 것은 무엇이든 간다." 따라서, 상기 마스크(1018)은 웨이퍼 상에 남게 될 패턴의 복사본을 정확히 포함한다.

[0084] 네거티브 레지스트들은 정반대의 방식으로 거동한다. UV 광에 대한 노출은 상기 네거티브 레지스트의 중합을 가져오고, 따라서, 더욱 용해되기 어렵게 된다. 그 결과 상기 네거티브 레지스트(1020)는 노출된 곳이면 어디나 표면 위에 남게 되고, 현상액은 노출되지 않은 부분 만을 제거한다. 따라서, 네거티브 포토레지스트를 위해 사용된 마스크들은 전사될 패턴의 역상(사진의 "네거티브")을 담는다.

[0085] 전자 제품 제조를 위해 현재 사용되는 레지스트 물질들은 유기 폴리머들이다. 이들 폴리머들은 패턴 해상도를 제한하는 코일링(coiling)과 모폴로지를 보인다. 본 발명의 무기 박막들은 새로운 레지스트 기술을 위한 기초를 형성한다. 여기서, 네거티브 레지스트들은 반고체 형태의 상기 무기막들을 빛 또는 전자빔들에 노출시키고, 그에 의하여 용해를 잃도록 함으로써, 특히 탈수 과정 동안 몰을 잃게 함으로써 구현될 수 있다. 이는 막을 경화시키고, 이들이 산에 녹지 않도록 한다.

[0086] 포지티브 레지스트의 일 구현예는 이중층 시스템을 이용하여 제조될 수 있다. 상기 이중층의 제1층은 하프늄 옥사이드 설페이트(HafSOx) 막 위에 증착된 포름산 구리 막을 포함한다. 상기 포름산 구리 막은 산에 용해될

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수 있고, 도핑되지 않은 HafSOx 막은 산에 불용성이다. 상기 이중층을 마스크를 통해 빛에 노출시키거나 포커스를 맞춘 전자빔에 노출시키는 것은 노출된 영역에서 상기 두 막의 상호확산을 가져오고, 그에 의하여 이전의 도핑되지 않았던 HafSOx 막을 용해될 수 있게 만든다.

[0087] 본 공정의 일 구현예가 도 11에 개념적으로 도시되어 있다. 도 11을 참조하면, 적절한 물질을 스핀 코팅 또는 잉크젯 코팅함으로써, 작업 소자를 정의하기 위해 요구되는 바와 같이 원하는 순서 및 두께로 적층체 구조물(1110)이 먼저 형성된다. 더욱 구체적으로, 기판 물질(1112)이 먼저 선택된다. 당 기술 분야에서 통상의 지식을 가진 자는 수많은 기판 물질의 무엇이든 본 발명의 이 구현예를 실행하기 위해 잠재적으로 사용될 수 있음을 이해할 것이다. 오직 예로서, 한정함이 없이, 적합한 기판은 반도체 물질들, 금속, 유리, 고분자 물질 및 이들의 조합을 포함한다. 그로써 레지스트 기술은 반도체 제조에서 수많은 응용에 유용할 수 있다. 일단 적합한 기판(1112)이 선택되면, HafSOx의 제1층(1114)이 상기 기판(1112) 위에 용액 증착된다. 그런 후, Cu:ZircSOx의 층(1116)과 같은 제2층이 층(1114) 위에 용액 증착된다. 상기 적층체 구조물(1110)은 그 후 마스크를 통해 전자빔 또는 빛과 같은 에너지 공급원에 조사된다. 마스크를 통해 빛 또는 전자빔에 조사되면, 상기 두 막들은 노출된 영역에서 상호확산되어, 이전에는 도핑되지 않았던 HafSOx 막을 가용하게 하여 적층체 구조물(1120)이 만들어진다. 그런 후, 노출되었던 상기 구조물(1120)은 현상된다. 이전에는 도핑되지 않았던 HafSOx 막은 가용하며, 따라서, 적층체 구조물(1130)에 표시된 바와 같이 제거된다.

[0088] 가요성 또는 유리 기판 위에, 구조물(1130)로 도시된 패턴은 임프린트 리소그래피를 위한 또는 그라비어 프린팅과 같은 일반화된 프린팅 공정을 위한 마스터 플레이트로 간주될 수 있다. 이러한 방식으로 HafSOx의 경화되고 패턴된 물질을 형성하는 것은 유체 제어 및 수송을 위한 소자의 제조에서 마이크로- 및 나노-채널 어레이를 개발하기 위한 수단들을 제공할 수도 있다. 그러한 소자들은 의료 진단, 잉크 수송 및 화학 합성에 응용될 수 있다.

[0089] 이중층 공정의 다른 구현예가 도 12에 도시된다. 상기 공정은 선택된 기판(1210) 위에 패턴된 산화물을 제조한다. 상기 기판은, 예를 들면, 유리, 반도체 웨이퍼, 금속, 금속 합금, 플라스틱, 또는 이들의 조합일 수 있다. 상기 공정의 첫 번째 단계는 고체 산 또는 염기, 예를 들면, 금속 Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, 또는 Lu의 하나 또는 그 이상을 포함하는 수화된 설페이트, 포스페이트, 나이트레이트, 실리케이트, 알루미네이트, 보레이트 또는 이들의 혼합물들의 박막(약 1 nm 내지 약 100 nm)을 증착하는 단계를 수반한다. 또한, 상기 고체 산/염기는 NH_3, OH, F, Cl, Br, I의 하나 또는 그 이상을 포함할 수 있다. 상기 고체 산/염기는 스핀 코팅 또는 프린팅을 통해 증착되는 것이 바람직하고, 물리 및 기상 증착은 추가적인 옵션이다. 하나의 예로서, 상기 고체 산은 $HfOCl_2$ 및 H_2SO_4(aq)의 수용액으로부터 스핀 코팅을 통해 증착될 수 있다. 상기 고체 산은 약 50 ℃에서 약 2분 동안 가열함으로써와 같이, 충분히 가열되어 구조적으로 강직한 막(1212)을 만든다. 프린팅 방식의 작업에서, 상기 기판(1210)은 가열된(약 25 내지 300 ℃) 평판(platen) 위에 위치되어질 수 있고, 예를 들면, 포름산 구리와 같은 산화물 전구체(1214)를 포함하는 잉크가 잉크젯 헤드를 통해 수송함으로써 또는 상기 전구체(1214)를 포함하는 템플릿과 상기 기판(1210)을 접촉시킴으로써 원하는 패턴으로 적용될 수 있다. 상기 템플릿은 그라비어 프린터, 활판(letterpress), 또는 마이크로콘택(microcontact)의 일부를 포함한다. 가열 조건에서(약 250 ℃보다 높은) 상기 전구체(1214)는 산화물로 분해되고, 이어서 상기 고체 산과 반응 및 상호확산하여 쉽게 세정 또는 식각되어 패턴(1218)을 드러낼 수 있는 생성물(1219)을 형성한다. 상기 산화물 전구체는 미세한 산화물 마이크로- 또는 나노-입자를 포함하는 페이스트 또는 현탁액 잉크에 의하여 대체될 수 있다. 가열과 함께 또는 가열 없이 미세한 입자들을 적용하는 것은 식각되어 패턴을 드러낼 수 있는 생성물을 형성하는 직접 반응을 가져오게 된다.

[0090] 도 13에, 선택된 기판(1310) 위에 패터닝된 산화물을 제조하기 위한 선택적인 구현예를 나타내었다. 초기 단계는 상기 기판 위에 고체 산(1312) 또는 염기를 증착하는 단계를 수반한다. 그런 후, 상기 산화물 전구체(1314)는 스핀 코팅, 프린팅, 화학 기상 증착 또는 물리 기상 증착을 통해 블랭킷 코팅으로서 적용된다. 그런 후, 광 마스크를 통해 빛과 같은 에너지 공급원에 노출시킴으로써 활성화된 전구체(1316)의 패턴이 형성된다. 적절한 광원은 무엇보다도, 필터링되지 않은 중수소 램프 또는 193 nm에서 빛을 만드는 광원을 포함한다. 선택적으로, 포커스를 맞춘 레이저 또는 전자빔으로 직접 기록함에 의하여 활성 전구체(1316)의 패턴이 형성된다. 그런 후, 만일 필요하다면, 상기 활성화되고 패터닝된 구조물(1316)은 두 층들의 상호확산을 촉진하기 위해 약 125 ℃ 내지 약 350 ℃의 온도로 가열될 수 있다. 그런 후, 상기 노출된 영역들은 원하는 패턴(1318)을 생성하기 위해 식각될 수 있다. 노출 감도를 계산하기 위한 절차로서 상기 고체 산 위에 산화물 전구체의 매우 얇은(약 2 nm) 막을 사용하는 것이 수반된다. 그런 후, 상기 전구체층은 산화물 나노입자들의 용액 캐스팅에 의하여,

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또는 화학 기상 증착 또는 물리 기상 증착과 같은 적절한 어버한 방법에 의해서든 증착된 산화물의 층으로 덮여진다. 상기 층들은 전구체 박막의 노출에 이어 상호확산된다.

[0091] 위에서 설명한 공정들은 포지티브 레지스트 기술에 관련된다. 고체 산/염기 및 전구체들은 물용성 생성물을 생성하게 선택하는 것도 가능하다. 이들 생성물들은 적어도 두 가지 방법으로 포지티브 이미지들을 생성하기 위해 사용될 수 있다. 하나의 구현예에서, 상기 두 층들은 하나의 불용성 층을 형성하기 위해 완전히 상호확산된다. 프린팅 또는 노출 및 현상에 이어서, 상기 막의 가용한(soluble) 부분들은 세정 또는 식각되어 포지티브 패턴을 드러낸다. 다른 접근에서는, 상호확산이 전구체와 고체 산/염기 사이에서만 일어나, 얇은 불용성의 장벽층을 생성한다. 그 후, 이 장벽층은 포지티브 이미지를 생성하기 위한 막의 스택의 식각을 조절하기 위해 사용된다. 상기 장벽층은 감광성이다. 그것은, 빛에 노출시키기 전에, 그렇지 않았다면 접촉과 함께 즉시 상호확산하였을 상기 전구체와 상기 고체 산/염기 층 사이의 반응을 방해한다. 일단 상기 장벽층이 감광되면, 그것은 반응성 산화물이 된다. 상기 장벽이 "깨어지고", 그런 후 상기 상부 층은 하부 층과 상호확산할 수 있다.

[0092] 광에 기반을 두든 임프린팅에 기반을 두든, 차세대 패터닝은 전자빔 리소그래피에 의하여 통상 제조되는 마스크 또는 템플릿들을 사용한다. 이들 템플릿들 또는 마스크들의 많은 것들은 하드마스크 HSQ (hydrogen silsesquioxane)으로 제조되고 있다. HSQ 마스크들은 다양한 전자, 데이터 저장, 및 미세전자기계 소자들의 제조에 널리 사용된다. HSQ는 또한 임프린트 리소그래피를 위한 하드 마스터/템플릿으로서 개발되고 있다.

[0093] 마스크들 및 템플릿들은 도 14에 나타낸 단일층 공정에서 여기서 설명된 막들을 이용하여 제조될 수 있다. 상기 공정의 제 1 단계는 기판(1412) 위에 무기 전구체(1410)의 박막(약 1 nm 내지 약 100 nm)을 증착하는 단계를 수반한다. 상기 무기 전구체(1410)는 퍼옥사이드 또는 유사한 배위 음이온과 함께 있는 고체 산 또는 염기, 예를 들면, 금속 Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, 또는 Lu의 하나 또는 그 이상을 포함하는 수화된 설페이트, 포스페이트, 나이트레이트, 실리케이트, 알루미네이트, 보레이트 또는 이들의 혼합물일 수 있다. 또한, 상기 고체 산/염기와 퍼옥사이드 혼합물은 NH_3, OH, F, Cl, Br, I의 하나 또는 그 이상을 포함할 수 있다. 상기 고체 산/염기는 스핀 코팅, 액체 미스팅(misting) 또는 프린팅을 통해 증착되는 것이 바람직하고, 물리 및 기상 증착은 추가적인 옵션이다. 하나의 예로서, 상기 고체 산은 $HfOCl_2$, H_2SO_4(aq), 및 H_2O_2(aq)의 수용액으로부터 스핀 코팅을 통해 증착될 수 있다. 상기 고체 산은 약 50 ℃ 내지 약 125 ℃의 온도에서 약 10초 내지 약 10분 동안의 시간 동안 가열함으로써와 같이, 충분히 가열되어 구조적으로 강직한 막을 만든다. 그런 후, 상기 막은 광 마스크를 통해 또는 정의된 레이저 또는 전자빔을 통해 노출되고, 노출된 영역에서 응축을 유발한다. 노출된 영역(1414)들의 용해도는 노출되지 않은 영역들에 비하여 감소되고, 따라서 상기 노출되지 않은 영역들은 산 또는 염기에 선택적으로 식각될 수 있다. 사용될 수 있는 산 또는 염기들의 예는, 무엇보다도, 염산, 황산, 과산화수소, 수산화나트륨, 및 테셔리메틸 암모늄 히드록사이드를 포함한다. 통상, 사용되는 산 또는 염기들의 농도는 약 0.1 M 내지 약 1 M의 범위 내이다. 그런 후, 약 100 ℃보다 높은 온도에서의 선택적인 열경화에 이어서 상기 막은 수성 산 또는 염기 내에서 노출되지 않은 영역들을 식각하기 위해 현상된다. 이 공정은 막 내에 네거티브-톤의 이미지를 생성한다. 적용된 막을 필드(field) 노출 시키기 전에 더 높은 온도로 예열함으로써, 포지티브-톤 이미지를 구현하도록 차별적인(differential) 식각 속도가 유발될 수 있다. 도 15는 열적으로 예열된 단일층 막에 대한 차별적인 식각 속도를 설명한다. 상기 그래프는 노출된 영역이 노출되지 않은 영역에 비하여 초기시간 이후에 더 빨리 식각되도록 열처리가 식각 속도에 영향을 미치는 것을 설명한다.

[0094] 또 다른 구현예에서, HafSOx 막은 수산화나트륨과 과산화수소의 혼합물로 처리되어, 음이온 교환 및 $M(OH)_x/H_2O_2$ 막의 형성을 가져온다. 선택적으로, $M(OH)_x/H_2O_2$ 막을 형성하기 위하여, 이전에 제조한 $M(OH)_x$ 막을 과산화수소에 적실 수 있다. 결과로서 얻어지는 $M(OH)_x/H_2O_2$ 막은, 그런 후, 빛 또는 전자빔에 노출됨으로써 패터닝된다. 이들 기술들은 폴리머 레지스트 없이 복합 MO_x 막의 단순한 직접 패터닝하기 위한 수단들을 제공한다. 예를 들면, HfO_2 막들은 Si CMOS 회로 및 프린트된 전자공학 응용에서 하이 k 유전체로서 사용되기 위해 직접 패터닝될 수 있다. 또 다른 예에서, 패터닝된 TiO_2 막은 H_2O_2 내에서 $Ti(OH)_4$를 용액 증착함으로써 형성된 $Ti(OH)_x/H_2O_2$ 막으로부터 제조될 수 있다.

[0095] 이들 방법들은 실질적으로 2-층 구현예들에서 사용된 확산을 제거하고, 노출 도스를 낮추며, 라인-에지 조도와 임계 차수(critical dimension)를 개선한다. 도 16은 전자빔이 0 $\mu C/cm^2$ 보다 크고 적어도 400 $\mu C/cm^2$까지의 범위의 도스 레벨을 갖는 단일층, 네거티브 톤 공정을 통해 패터닝된 HafSOx 막의 AFM(atomic force

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microscope) 이미지이다. 상기 이미지의 오른쪽의 나노미터 스케일은 상기 막 내부로 식각된 피처들의 높이를 나타낸다. 도 16에 나타낸 바와 같이, 피처들은 2 $\mu C/cm^2$라는 낮은 도스 레벨로 전자빔 노출을 통해 기록되었다. 이 도스 레벨은 알려진 최고의 화학 증폭된 폴리머 레지스트들에 필적할만하며, 무기 레지스트에 대하여 이전에 입증된 것보다 1000 배나 낮다. 피처들은 약 20 nm 미만의 해상도로 제조될 수 있다. 또한, 상기 막들은 HSQ에 대하여 증명된 것보다 거의 하나의 차수(an order of magnitude)만큼 작은 3 nm 미만으로 구조적 집적도(integrity)(예를 들면, 매끈하고, 조밀하고, 핀홀이 없는)를 증명한다.

[0096] 무기 물질의 침공 및 고온 처리 단계들뿐만 아니라 폴리머 레지스트와 관련된 막의 적용, 가열, 및 식각 단계들이 패터닝 과정에서 제거되었다.

[0097] 결과로서 얻어지는 막은 전자 소자의 기능적인 부품, 아래에 있는 기판의 후속 패터닝을 위한 하드 마스크, 또는 임프린팅을 위한 템플릿일 수 있다. 전자빔 노출을 제외하고, 모든 처리는 공기 중의 보통의 환경에서 수행된다. 여러 처리 단계들의 제거를 고려할 때, 개시된 기술은 소자 제조 수율을 개선하고 제조 비용을 낮추기 위한 새로운 방법을 제공한다. 수성 화학의 독특한 사용에 따르면, 상기 공정은 또한 환경 친화적이며, 세정된 생성물들은 완전히 회수되어 재생될 수 있다. 상기 기술은 많은 고급 기술들에 응용성을 갖는다. 그의 사용은 여기에 설명한 시스템에만 한정되지 않는다.

[0098] B. 핫 엠보싱(hot embossing) 리소그래피

[0099] 핫 엠보싱 리소그래피는 HafSOx, ZircSOx 및 관련 물질에 패턴을 생성하기 위한 다른 방법이다. 도 17에 개념적으로 도시한 본 방법은 유기 폴리머로 패턴을 생성하기 위해 매우 널리 적용되어 왔다. HafSOx 및 관련 조성물의 반고체 형태는 유기 폴리머들에 비하여 훨씬 더 높은 기계적 강도, 화학적 안정성 및 고유한 전기적 및 광학적 특성을 갖는 무기 물질의 패터닝할 기회를 제공한다.

[0100] 도 17을 참조하면, HafSOx 또는 관련된 무기 물질은, 유기 폴리머 대신, HafSOx 층(1714)을 형성하기 위해 적합한 기판(1712) 위에 스핀 코팅 또는 잉크젯 프린팅에 의하는 것과 같이 용액 증착된다. 기판(1712)과 HafSOx 층(1714)은 적층체 구조물(1710)을 정의한다. 나노미터, 마이크로 미터 또는 밀리미터 크기 스케일과 같은, 원하는 크기의 스케일의 단위 피처들을 갖는 스탬프(1716)가 상기 반고체 HafSOx 또는 관련된 막의 층(1714)에 프레스되어 스탬프된 층(1718)을 형성한다. 스탬프된 층(1718) 및 기판(1712)은, 그런 후, 가열되어 HafSOx를 경화시킨다. 그런 다음, 상기 스탬프가 제거되어 패터닝된 적층체 구조물(1720)에 패터닝된 HafSOx 물질을 정의한다.

[0101] C. 측정 장치

[0102] 위에서 설명한 이중층 포지티브 레지스트 기술을 위해 개발된 화학은 전자 현미경과 같이 적합한 분야에서 측정을 표준화하는 데 사용하기 위한 도 18에 도시한 바와 같은 물리적 자의 제조하기 위해 사용될 수도 있다. 본 응용에서, 교호하는 산-가용성 층들(1812)과 산-불용성 층들(1814)의 나노 적층체(1810)가 증착된다. 상기 산-가용성 층들은 하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 $(MO_{2-x-z/2}(OH)_z(SO_4)_x)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 $(MO_{2-x-z/2}(OH)_z(WO_4)_x)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 $(MO_{2-3x/2-z/2}(OH)_z(BO_3)_x)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 $(MO_{2-3x/2-z/2}(OH)_z(PO_4)_x)$ 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 $(MO_{2-2x-z/2}(OH)_z(SiO_4)_x)$ 화합물의 용액 증착에 의하여 형성된다. 통상 이 층은 구리로 도핑된다. 상기 산-불용성 층들은 하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 $(MO_{2-x-z/2}(OH)_z(SO_4)_x)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 $(MO_{2-x-z/2}(OH)_z(WO_4)_x)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 $(MO_{2-3x/2-z/2}(OH)_z(BO_3)_x)$ 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 $(MO_{2-3x/2-z/2}(OH)_z(PO_4)_x)$ 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 $(MO_{2-2x-z/2}(OH)_z(SiO_4)_x)$ 화합물의 용액 증착에 의하여 형성된다(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음).

[0103] 상기 층들(1812 및 1814)의 특징은 반사 X-선에 의하는 것과 같이, 정확하게 결정된다. 그런 후, 상기 산-가용성 층들(1812)은 식각되어 전자 현미경에서 목적물을 정확하게 측정하는 데 2차적인 척도로서 사용될 수 있는 평거-타임 패턴(1820)을 드러낸다.

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[0104] D. 부식 장벽

[0105] 금속 또는 합금 또는 세라믹과 같은 적절한 기판 위에 전구체 액체가 코팅되어 부식 장벽을 형성할 수 있다. 또한, 상기 액체는 몰드 내에 위치하거나 또는 흔히 사용되는 섬유 내부로 인입될 수도 있다. 상기 액체는 공기 중에서 가수분해, 이널링 또는 열분해를 포함하는 적합한 어떠한 공정에 의하여든 고체, 안정한 형태로 전환된다. 통상, 이것은 적어도 수 초동안, 더욱 전형적으로는 적어도 수 분동안 보통 100 °C 이상의 온도와 같이 원하는 결과를 얻기 위해 유효한 온도로, 시간 동안 가열할 것이 요구된다.

[0106] 상기 막들의 원자적으로 조밀한 성질로 인하여, 잠재적인 응용은 다른 많은 것들뿐만 아니라, 금속 및 금속/세라믹-계 열 보호(thermal protection) 시스템, 유기계 디스플레이 및 전자 제품, 태양 전지, 고 방사율(emissivity) 코팅, 산화물계 세라믹 매트릭스 시스템에 대한 계면 코팅, 인광체(phosphor) 위의 보호 코팅, 금속- 및 세라믹계 시스템에 대한 주변적 장벽 코팅, 복합체 및 섬유 레이저용 섬유, 용해 금속 처리에서의 부식 방지, 단열용 모노리딕 물질 및 축매 담체에 대한 얼, 부식 및 산화 방지를 포함하지만 여기에 한정되는 것은 아니다. 상기 막들을 적층할 수 있는 능력은 다른 층과 관련하여 한 층에서 결함의 위치를 무작위화(randomize)할 기회를 제공하여 개선된 부식 보호를 제공한다.

[0107] E. 광학 코팅

[0108] 상기 전구체 액체들은 반사 방지 코팅, 유전체 거울(dielectric mirror), X-선 거울, 간섭 필터, 회절 격자, 도파로(waveguide), 광면 코팅 및 내-스크래치 표면을 만들기 위해 적절한 광학 기판 위에 개별 층들로서 및 다층 형식으로 코팅될 수 있다. 적어도 두 개의 물질 조성물을 교호 적층함으로써 다층 주기성이 달성된다. 단층 주기성은 포토리소그래피 공정에 대하여 설명한 바와 같이 식각에 의하여 달성될 수 있다. 비결정질적인 성질, 층들 사이의 명확한 계면, 및 유전 상수를 조절하는 능력은 이론적 한계에 가까운 성능을 구현하기 위한 공정을 제공한다.

[0109] 선택적으로 증착되거나 식각된 다층 또는 단일층 구성에서, 주기적인 구조물은 회절 응용에 적합하다. 보이드 및/또는 단일 또는 다중 물질들의 조합은 구조물을 정의할 수 있다. 보이드 공간의 사용은 주어진 구조물 내에서 물리적 성질의 큰 대비를 가능하게 한다. 기능적인 특성들은 보이드 공간의 사용에 의하여 개선되거나 구현될 수 있다. 광학 격자도 유사하게 정의될 수 있다.

[0110] 실질적으로 매끈한 표면 막들은 여기에 개시된 방법의 구현예들에 따라 증착될 수 있기 때문에, 더 큰 정도의 조도(roughness)를 보이는 금속, 세라믹, 및 플라스틱과 같은 기판 층들을 평탄화하기 위해 막들이 사용될 수 있다.

[0111] F. 발광막

[0112] 물질은 수많은 발광 과정들에서 에너지를 흡수하고 광자를 방출할 수 있다. 발광 현상은 지배적인 상(또는 호스트) 만을 수반할 수도 있고, 또는 첨가된 원소들을 포함할 수도 있다. 단일 물질은 수많은 발광 첨기제에 대하여 호스트로서 작용할 수 있다. 개시된 막 조성물들의 많은 수는 시각적으로 투명하고, 투명성이 스펙트럼의 자외선 부분으로 잠재적으로 연장되고 있다. 이러한 물질들은 발광 호스트 물질로서 잠재적으로 기능한다. 이들 물질들은 조명 및 디스플레이 응용을 위해 관심이 있는 발광막을 가져오기 위하여, 예를 들면, Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+} 및 이들의 조합을 포함하는 통상의 발광성 이온들로 선택적으로 도핑될 수 있으나 여기에 한정되지 않는다.

[0113] G. 프린트된 전자 제품

[0114] 제조업자들은 종래의 기상 증착 및 리소그래피 공정의 한계를 제거한 새롭고, 효율적인 제조 방법들을 찾고 있다. 프린팅 및 관련 마스크리스(maskless) 기술들은 백-플레인(back-plane) 전자공학에 있어서, 제조 효율의 개선을 구현하기 위한 길로서 널리 간주되고 있다.

[0115] 개시된 용액-처리된 박막들은 대부분의 발전된 기상 처리 방법에 의하여 달성되는 것들과 유사한 모폴로지 및 소자-기능적 특성들을 보인다. 개시된 조성물의 용액들은 마이크로콘택, 그라비어, 잉크젯 프린터 또는 다른 적합한 수단들에 의해서와 같이 임프린트될 수 있다. 결과로서 얻어지는 임프린트된 용액들은 약 20 nA/cm^2 미만의 유전체 누설 전류 밀도를 갖고, 약 10 cm^2/Vs의 소자 이동도를 보이는 안정한 무기 트랜지스터 어레이들을 제조하기 위해 사용될 수 있다. 유전체 및 반도체 잉크들은 또한 약 100 nA/cm^2 미만의 유전체 누설 전류 밀도

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와 약 1 cm^2/Vs의 이동도를 갖는 트랜지스터 어레이를 제조하기 위해 유리 기판 위에 프린트될 수 있다. MIM 캐패시터 어레이들은 약 5보다 큰 상대 유전 상수 및 약 50 nA/cm^2 미만의 누설 전류 밀도로 제조될 수 있다.

실 시 예

[0153] 실시예들

[0154] 본 발명의 작동 및/또는 가상의 구현예들의 특정한 특징들을 예시하기 위하여 다음 실시예들이 제공된다. 당 기술분야에서 통상의 지식을 가진 자는 본 발명의 범위가 이들 실시예에서 언급된 특정한 특징들에 한정되지 않음을 이해할 것이다.

[0155] 실시예 1

[0156] 본 실시예는 벌크 침전물을 위한 또는 박막 전구체들로서 사용하기 위한 공급원으로서 용액들을 제조하기 위해 사용된 일반적인 방법을 설명한다. 다음 시약들이 사용되었다. $HfOCl_2 \cdot 8H_2O$ (Alfa Aesar, 99+% (1.5%Zr 제외)); $ZrOCl_2 \cdot 8H_2O$ (Wah Chang 분광 등급(spectrographic grade)); $La_2(SO_4)_3$ (Alfa Aesar, 99.9%); $La(NO_3)_3 \cdot 6H_2O$ (Johnson Matthey, 99.9%); $Ce_2(SO_4)_3 \cdot 8H_2O$ (Strem, 99%); CaO (Alfa Aesar, 99.95%); $(NH_4)_2SO_4$ (Mallinkrodt AR); H_2SO_4(aq) (EM Science, GR ACS, 95-98%); 및 NH_3(aq) (EM Science, GR ACS, 28-30%). 모든 용액들은 $HfOCl_2$ 또는 $ZrOCl_2$를 약 0.8 M의 총 금속 농도를 위하여 필요한 만큼의 $La_2(SO_4)_3$, $Ce_2(SO_4)_3$, 또는 CaO와 결합하고, 이어서 약 0.5 M의 총 금속 농도를 위하여 설페이트 용액을 첨가함으로써 제조되었다. 이들 용액들은 열-유발된 침전 및 스핀-코팅 유전막들에 대하여 직접 사용되었다. 히드록사이드 침전 반응 또는 나노적층체 증착을 위해 전구체로서 작용하는 데 필요한 바에 따라 추가적인 변경이 이루어졌다.

[0157] 실시예 2

[0158] 본 실시예는 실시예 1에 따라 제조된 용액들로부터의 벌크 침전을 위해 사용된 일반적인 방법을 설명한다. 침전은 끓는 수조에 용액의 튜브를 40분간 침지시킴으로써 유발되었다. 히드록사이드-유발된 침전에 대하여, $HfOCl_2$ 및 $La_2(SO_4)_3$는 23% La(금속 백분율)이 되도록 혼합되고, 이어서 $La(NO_3)_3$ 및 $(NH_4)_2SO_4$의 용액들을 첨가함으로써 약 0.39 M의 하프늄 농도([Hf]), 약 0.18 M의 란탄 농도([La]), 및 약 0.42 M의 설페이트 농도($[SO_4]$)를 제공하였다. 그런 후, (총 금속과 관련하여) 1.9 몰 당량의 포화 NH_3(aq)가 신속히 첨가되고, 그 결과로서 얻어지는 혼합물을 1분 동안 교반하였다. 모든 침전물들은 석션이 달린 종이 여과 및 여러 차례 탈이온수로 세척함에 의하여 상청액(supernatant)으로부터 분리되었다. 여과물은 1일 동안 실온에서 건조되었다. 이어서 샘플들을 주위 공기에서 알루미나 도가니에 넣고 약 100 °C에서 약 1,500 °C의 온도로 약 1 시간 내지 약 4 시간 동안 가열하였다. Siemens D5000 회절계로 Cu Kα 방사선을 이용하여 XRD 데이터를 수집하였다. 열중량분석 데이터는 Shimadzu TGA-50을 이용하여 N_2(g)를 흘리면서 Pt 도가니에서 샘플들(10-20 mg)을 통상 10 °C $분^{-1}$의 속도로 가열하고 최고 온도에서 15분 동안 유지함으로써 수집하였다. 유도 결합 플라스마 원자 발광 분석(ICPAES: inductively coupled plasma atomic emission spectroscopy)이 Jobin Yvon JY2000 분석 설정으로 수행되었다. 샘플들을 침지 밤(digestion bomb)에 넣고 수 시간 동안 200 °C에서 용해시키고 측정 가능한 수준으로 희석하였다.

[0159] 실시예 3

[0160] 본 실시예는 실시예 1에 따라 제조된 용액들을 이용하여 박막을 증착하기 위해 사용되는 일반적인 방법을 설명한다. HafSOx, ZircSOx 및 La, Ca 또는 Ca 첨가된 유도체들의 박막이 3,000 rpm으로 30초 동안 스핀코팅에 의하여 Si 기판 위에 증착되고, 즉시 이어서 135 °C에서 1.5 내지 2 분 동안 열판 증착을 하였다(1.5초 내지 약 2 분 동안 325 °C 오븐 표면 위에서 추가적인 가열이 특정 도함수에 대하여 필요할 수 있다). 이 공정은 원하는 증착 막 두께가 얻어질 때까지 반복되었다. 325 °C에서의 최종 오븐 어닐링은 5 내지 10분 동안 사용되었다.

[0161] 나노 적층체 막들을 위한 전구체들이 $HfOCl_2$ 또는 $ZrOCl_2$에 H_2SO_4를 금속에 대하여 46% 설페이트가 되도록 첨가함으로써 제조되었다. 용액은 금속 농도가 0.03 내지 0.13 M로 희석되었다. HafSOx와 ZircSOx의 교호하는 층들이 유전막에 대하여 설명한 바와 동일한 방식으로 증착되었다.

[0162] 상기 실리콘 기판은 SiO_2 또는 Ta 금속의 표면을 가졌다. 유전 테스트를 위하여 500-나노미터 Ta 표면이 이용

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되었다. 모든 다른 목적으로는 200-나노미터 SiO_2 표면이 사용되었다. 상기 표면들은 45℃의 (Decon Labs, Contrad 70) 용액 내에서 45분간 초음파 세척을 한 후 증착하기 전에 Millipore 물로서 완전히 표면을 세정함으로써 증착을 위한 준비를 하였다.

[0163] XRD 데이터는 50 kV 및 270 mA에서 회전 음극으로부터 생성된 Cu Kα 방사선을 채용한 Rigaku RAPID 회절계로 수집되었다. 회절된 빔이 이미지 판에 수집되는 동안 입사빔의 각도는 7.6° 이었다. Cu Kα 방사선으로 XRR 데이터가 수집되었다. 낮은 각도 반사가 10° (2Θ)까지 0.005° 단위로 수집되었다. 투과 FTIR 데이터가 코팅되지 않은 기판을 레퍼런스로 하여 Nicolet 5PC 스펙트로미터를 이용하여 수집되었다. EMPA가 수집되었다.

[0164] 증착된 유전체 위의 Al의 원형 콘택(1.2 mm 직경)들을 열적으로 증발시킴으로써 MIM 캐패시터 구조물들이 완성되었다. 유전 상수 및 손실 탄젠트의 파라미터들을 얻었다. 하부-게이트 트랜지스터 구조물도 활성 영역의 가열 없이 무기 채널 물질들을 스퍼터링함으로써 제조되었다. 이어서 ZTO-채널 소자들이 325 ℃로 1 시간 동안 가열되었다. 알루미늄 소오스 및 드레인 콘택들이 열적으로 증발되었다. 트랜지스터 특성화가 수행되었다.

[0165] 실시예 4

[0166] 본 실시예는 매끈하고, 조밀하며 핀홀이 없는 약 2 nm만큼 얇은 초박(ultra-thin) 나노적층체 막을 제조하기 위한 일반적인 방법을 설명한다. 미합중국 특허공개 제2005/0242330A1호에 설명된 바와 같이 $HfOCl_2 \cdot 8H_2O$ 또는 $ZrOCl_2 \cdot 8H_2O$, H_2O_2 (30%) 및 H_2SO_4(aq)를 포함하는 전구체 용액이 준비되었다. 상기 전구체 용액은 약 0.05 M 내지 0.4 M와 금속 이온 농도 및 금속에 대하여 70% H_2O_2 및 50% 설페이트를 포함하였다. 금속 이온 농도에서의 상기 차이는 코팅당 두께의 변화를 3 nm에서 25 nm로 변화시키는 것을 가능하게 하였다. 실리카 기판 위에 열성장 SiO_2의 박막이 증착되었다. 기판은 45 ℃에서 60 분간 Contrad-70 용액으로 초음파 조를 이용함으로써 세정되고, 이어서 탈이온수로 헹구어졌다. 스핀 코터를 이용하여 3000 rpm의 스핀 속도로 30초 동안 막이 증착되고, 이어서 125 ℃에서 1 내지 2 분 동안 열판(hotplate) 중합이 후속되었다. 스핀-코팅과 중합 단계는 원하는 두께에 도달할 때까지 반복되었다. 원하는 두께에 도달한 후, 일부 막들은 결정화 온도까지 가열되었다. 다른 막들은 0.1 M 내지 0.5 M NaOH 조에서 1 내지 2분 동안 1차 처리되고, 그런 후, 열처리되기 전에 탈이온수 조에서 1 내지 2 분 동안 세정되었다.

[0167] X-선 회절(XRD) 분석을 이용한 박막 특성화가 Cu Kα 방사선을 채용한 Rigaku R-axis RAPID로 수행되었다. Veeco NP-20 SiN 탐침 및 1.15 Hz의 스캔 주파수를 갖고 접촉 모드로 동작하는 Digital Instruments Nanoscope III Mulitmode AFM으로 원자력 현미경(AFM: atomic force microscopy) 측정을 수행하였다. Bruker Discover D8을 이용하여 반사 X-선 측정이 수행되었고, 상기 막의 표면과 계면 조도를 결정하기 위해 사용되었다. 4개의 튜닝가능한 파장 분산 분광기로 장착한 Cameca SX-50 전자 마이크로탐침 상에서 조성 분석이 얻어졌다. O, Cl, Na, S, 및 Si의 Kα 세기와 Zr 및 Hf의 Lα 세기를 모니터하기 위해 12, 16 및 22 kV의 가속 전압들이 사용되었고 5 점에 걸쳐 평균을 내었다. 분석을 위해 사용된 스탠다드는 MgO, Hf, Zr, FeS_2 (pyrite), $Ca_5(PO_4)_3Cl$ (apatite), Si, and Si_3AlNaO_8 (albite)이었다. Probe for Windows 자동화 및 분석 패키지를 이용하여 원본 세기(raw intensity)에 대한 수정이 이루어졌다. StrataGEM 조성 분석 소프트웨어 패키지를 사용하여 실험으로 구한 K-비율들과 모사된 값들을 비교함으로써 박막 기하구조를 수정하였다.

[0168] 비결정질이고, 원자 수준에서 평탄하고, 조밀하고, 핀홀이 없는 박막들이 증착된대로의(as-deposited) 막들과 교환된 막들에 대하여 스핀 코팅을 통해 증착되었다. 도 19는 약 0.1 nm의 조도를 갖는, 교환되지 않은 HafSOx 막의 AFM 이미지이다. 도 20은 HafSOx의 이온 교환과 650 ℃에서의 열처리 다음의 HfO_2 막의 TEM 이미지이다. 교환되지 않은 막들은 Zr에 대하여는 600 ℃까지, Hf에 대하여는 650 ℃까지 매끈하고 비결정질로 남았다. 그러나, 이들 온도보다 높게 가열한 후에는, 막들이 결정화되고 표면에 화산과 같은 피처들을 형성하면서 거칠게 되었다. 도 21은 실리카 위에 증착된 HfO_2 막의 AFM 이미지이다. 상기 HfO_2 막은 HafSOx의 열분해에 의하여 형성되었다. 결과로서 얻어지는 막은 약 5 nm의 조도를 가졌고, 화산과 같은 피크들을 가져왔다. 이들 피처들은 SO_3의 손실에 의하여 야기되었을 것으로 유력하게 추정되었다. 이것은 700 ℃를 넘는 온도에서 설페이트 분해(SO_3 (g) → SO_2 (g) + ½O_2 (g))가 잃어나는 Hf 설페이트 분말의 열질량 분석에 의하여 뒷받침된다. 화산 현상을 없애기 위하여, 막들은 0.1 내지 0.5 M NaOH(aq) 조 내에서 1분 내지 2분 동안 처리되고, 가열하기 전에 막으로부터 SO_4^{2-} 및 Cl^- 음이온들이 제거된다. 이전부터 NaOH는 히드록시 음이온을 지르코늄 염의 다른 음이온과 효과적으로 교환하는 것으로 알려져왔다. 상기 NaOH 처리는 40 내지 40%의 두께 감소를 가져오지만(2 내지

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15 nm의 두께의 층을 가져옴), 상기 처리는 지르코니아와 하프니아 대하여 각각 500 ℃와 550 ℃ 이하로 가열할 때 막의 매끈함(smoothness) (~1Å) 또는 비결정질 성질에는 영향이 거의 없다.

[0169] 도 22는 실리카 위에 증착되고, 이어서 0.1 M NaOH로 처리되고 450 ℃에서 10분간 가열된 $HafSO_x$ 막의 AFM 이미지이다. 결과로서 얻어지는 막은 약 0.1 nm의 조도를 가졌다. 이들 온도 위로 가열된 막들은 결정화되었지만 850 ℃까지의 온도에서는 매끈함을 유지하였다.

[0170] 도 23은 실리카 위에 증착되고, 이어서 0.1 M NaOH로 처리되고 650 ℃에서 10분간 가열된 HfO_2 막을 나타낸다. 결과로서 얻어지는 결정화된 막은 약 0.2 nm의 조도로 매끈하게 유지되었다.

[0171] X-선 회절 그래프에서(도 24 내지 도 27) 결정화 온도의 감소가 관찰되었다. 도 24 내지 도 27에서, 기판의 피크들은 소프트웨어에 의하여 제거되었다. "*"는 주요 정방정계(tetragonal) 상의 피크들을 나타낸다. 도 24는 700 ℃에서 정방정계와 단사정계(monoclinic) 상의 혼합물로 결정화된 처리되지 않은 HfO_2 막의 XRD 그래프이다. HfO_2 그래프는 단사정계 상에 대한 기준 그래프이다. 대조적으로, 도 25는 550 ℃에서 단사정계 상에서만 결정화된 0.1 M NaOH로 처리된 하프니아 막의 XRD 그래프이다. HfO_2 그래프는 단사정계 상에 대한 기준 그래프이다. 도 26은 650 ℃에서 단사정계와 정방정계 상이 혼합되어 결정화된, 처리되지 않은 지르코니아 막의 XRD 그래프이다. ZrO_2 그래프는 단사정계 상에 대한 기준 그래프이다. 도 27에서 보는 바와 같이, 0.13 M NaOH 처리된 지르코니아 막들은 500 ℃에서 정방정계에서만 결정화되었다. 계속 가열하면, 막은 단사정계와 정방정계 상 모두로 발전되었다. HfO_2와 ZrO_2의 정방정계 상들은 이전의 박막 연구에서 관찰되었다. 더 낮은 결정화 온도, 결정화 및 두께 손실은 NaOH 처리가 박막으로부터 용이온(SO_4^{2-} 및 Cl^-)을 제거함을 가리켰다.

[0172] 0.4 M Hf 용액으로부터 증착되고 350 ℃까지 5분 동안 가열된 막의 전자 탐침 미세 분석(EPMA: electron probe microanalysis)은 $HfO_{1.32}(SO_4)_{0.61}Cl_{0.15}$의 조성을 가지왔다. 상기 막 내의 염소는 급속한 열 탈수의 결과로 동적 트랩핑된 결과였다. NaOH(aq) 조 내에서의 처리된 막들은 측정 가능한 황의 레벨을 갖지 않았고(0.01 원자 퍼센트 미만), 0.3 원자 퍼센트 미만의 Cl이 관찰되었다. 이것은 황과 염소가 모두 NaOH(aq) 조 내에서 상기 막으로부터 제거되었음을 확인하였다. EMPA는 또한 상기 처리 후에 상기 막에 남은 잔류 나트륨은 0.3 원자 퍼센트 미만임을 확인하였다.

[0173] 실시예 5

[0174] 위에서 설명한 접근방법들의 구체적인 구현예들에서, 수화된 인듐 및 갈륨 나이트레이트 염들($In(NO_3)_3 \cdot 0.5H_2O$ 및 $Ga(NO_3)_3 \cdot 8.5H_2O$)을 메탄올(CH_3OH) 내에 용해시켰다. 최종 농도는 [In] = 0.288 M, [Ga] = 0.170 M이었다. 그런 후, 아연 분말을 상기 용액에 첨가하고, 플라스크를 밀봉하였다. 아연의 최종 농도는 0.2 M이었다. 1일 내지 7일의 기간에 걸쳐 반응시키고, 상기 분말은 서서히 산화되고 용해되어 전체 금속 이온 농도를 0.658 M까지 변화시켰다. 상기 메탄올 용액을 공기 중에 노출시키고, 실온에서 증발할 수 있도록 하였다. 그런 후, 상기 용액 내에 잔존하는 고체 잔사물을 H_2O에 용해시켜 총 금속 농도를 0.395 M로 하였다. 이 전구체 용액은 도전성 백 콘택(back contact)을 갖는 SiO_2 기판 위에 스핀-코팅되고, 450 ℃에서 1 시간 내지 4 시간 동안 이닐링되었다. 어닐링에 이어서, 투명하고 비결정질인 $InGa_{0.6}Zn_{0.7}O_{3.15}$ 반도체 막을 도 28의 SEM 이미지에 나타낸 바와 같이 수득하였다. 알루미늄 소오스 및 드레인 콘택들은 박막 트랜지스터(TFT)를 제조하기 위해 섀도우 마스크를 통해 산화물 반도체 막 위로 열 증발되었다. 이들 TFT들의 전계 효과 이동도는 8 $cm^2 V^{-1} s^{-1}$을 넘는 것으로 나타났다.

[0175] 실시예 6

[0176] 본 실시예는 이중층 무기 리소그래피 공정의 두 개의 일반적인 방법들을 설명한다. 하나의 작동 구현예에서, 약 30 nm 내지 약 60 nm의 두께를 갖는 $HafSO_x$ 막이 SiO_2/Si 기판 위에 용액 증착되었다. 상기 기판은 약 50 ℃로 설정된 열판(hot-plate)의 직접 위에 위치되고, 상기 막에 구조적 집적도들 부여하기 위해 가열되었다. 결과로서 얻어지는 막은 산에 불용성이었다. 그런 후, 상기 기판을 잉크젯 프린터의 가열된 평판(platen) (약 50 ℃ 내지 200 ℃) 위에 위치되고, 열 잉크젯 헤드를 통해서 기판 위에 포름산 구리의 선들이 프린트되었다. 포름산 구리는 가열됨에 따라 분해되고 $HafSO_x$ 막 내부로 확산되어 상기 막을 가용성으로 만들었다. 물로 세정한 후에, 약 300 ℃로 추가 가열하고, 묽은 산 내에서 현상한 결과, 도 29에 나타낸 바와 같이, 그려진 선들은

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명백히 뚜렷하였다.

[0177] 다른 작동 구현예에서, 패턴이 역시 포토리소그래피를 통해 생성되었다. 도 30에 나타낸 패턴의 후속적인 상호확산 및 현상을 위해, 여과되지 않은 중수소 램프를 이용하여 $HfO_{2-x}(SO_4)_x$ 이중층을 심자외선 광에 노출하여 포름산 구리의 분해를 촉진하였다. 피처 크기는 전자빔 기록(writing)에 따라 약 22 nm로 감소되었다. 상기 상호확산 과정은 패턴과 목적물을 나노스케일로 그리도록 전자빔 에너지를 통해 공간적으로 제어될 수 있다. 고해상도의 패턴들이 150 $\mu C/cm^2$ 근처의 전하 도스 레벨에서 생성되었는데, 많은 폴리머 레지스트들의 그것과 유사한 민감도를 나타낸다. 도 31 및 32는 약 200 $\mu C/cm2$의 도스 레벨에서의 전자빔 기록에 의해 생성된 두 패턴들이다. 도 31에서, 전자 현미경으로 측정한 바와 같이 상기 선의 간격은 500 nm이다.

[0178] 실시예 7

[0179] 본 실시예는 단일층 무기막을 패터닝하기 위한 일반적인 방법들을 설명한다. 피복시이드 또는 관련된 배위종들을 포함하는 단일 무기막은 적절한 기판 위에 스핀-캐스트(spin-cast), 액체 분무(misted), 또는 잉크젯 프린트된다. 상기 막은 100 °C 미만의 중간 정도의 온도에서 가열되어 막의 구조적 집적도를 제공한다. 그런 후, 상기 막은 패턴 또는 다른 바람직한 막 피처들을 정의하기 위해, 포토마스크를 통해 고에너지 광에 노출되거나, 공간 광 고폴레이션을 통한 마스크리스 패턴, 정의된 레이저 빔, 또는 전자빔에 노출된다. 도 33 및 또 34는 사진 공정으로 패터닝된 막들의 두 예들을 나타낸다. 도 33은 패터닝된 $ZrO_{2-x}(SO_4)_x$ 막이다. 도 34는 패터닝된 TiO_2 막이다. 상기 TiO_2 막은 약 15 내지 50 nm 두께이었다. 여과되지 않은 중수소 램프를 이용하여 패터닝하였고, 이어서 0.1 내지 0.2 M HCl로 60초 미만 동안 식각하였다. 도 35 내지 도 37은 전자빔에 의하여 패터닝된 $HfO_{2-x}(SO_4)_x$ 막들이다. 상기 막들은 약 30 내지 60 nm 두께이었다. 이들은 200 $\mu C/cm^2$의 도스 레벨로 전자빔을 이용하여 패터닝되었고, 이어서 5 내지 12 M HCl로 1 내지 4분 동안 식각되었다.

[0180] 개시된 본 발명의 원리가 적용될 수 있는 가능한 많은 구현예들의 관점에서, 예시된 구현예들은 단지 본 발명의 바람직한 실시예일 뿐이고, 본 발명의 범위를 한정하는 것으로 받아들여서는 안된다. 오히려, 본 발명의 범위는 첨부된 청구항들에 의하여 정의된다. 따라서, 우리는 이들 청구항들의 범위와 정신의 범위 내에 들어오는 모든 것을 우리의 발명으로 청구한다.

도면의 간단한 설명

[0116] 도 1은 다양한 전처리들과 함께 샘플들을 $N_2(g)$를 흘리면서 10°C $분^{-1}$의 속도로 가열하면서 HafSOx (x = 0.70)에 대한 열질량 분석(TGA: thermogravimetric analysis) (온도에 따른 상대 습도) 결과를 제공한다.

[0117] 도 2는 표시된 것을 제외하고는 언급된 온도로 공기 중에서 1 시간 동안 가열한 후의 HafSOx 분말에 대한 XRD 패턴이다.

[0118] 도 3은 표시된 것을 제외하고는 언급된 온도로 1 시간 동안 가열한 후의 HafSOx:32% La 분말에 대한 XRD 패턴이다.

[0119] 도 4는 공기 중에서 주어진 온도로 5 분 동안 가열한 후의 HafSOx 막에 대한 XRD 패턴으로, 31.8° 와 45.6° 에서의 매우 작은 피처(feature)들은 기판에 기인한 것이다.

[0120] 도 5는 언급된 온도로 공기 중에서 5 분 동안 가열한 후의 HafSOx:24% La 박막에 대한 XRD 패턴이다.

[0121] 도 6은 HafSOx 막에 대한 유전 함복 특성을 도시한다.

[0122] 도 7은 이산화실리콘 기판 위의 탄탈륨(Ta) 금속 위에 증착된 HafSOx의 일 구현예를 나타낸 SEM이다.

[0123] 도 8은 Ta위에 증착된 HafSOx:24% La에 대한 SEM이다.

[0124] 도 9는 이중층이 17.6 nm의 두께를 갖는 14 개의 교호층들(7개의 이중층들)을 포함하는 HafSOx/ZircSOx 다층 박막에 대한 XRR 패턴이다.

[0125] 도 10은 포지티브 또는 네거티브 포토레지스트 절차들을 나타낸 개념도이다.

[0126] 도 11은 이중층 시스템을 이용하는 포지티브 레지스트를 도시한 개념도로서 도시된 구현예가 하프늄 산화물 설페이트 (HafSOx) 막 위에 증착된 Cu-도핑된 지르코늄 산화물 설페이트 (Cu:ZircSOx) 막을 포함한다

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[0127] 도 12는 기판 위에 패터닝된 산화물을 생성하기 위한 이중층 공정을 나타낸 개념도이다.

[0128] 도 13은 기판 위에 패터닝된 산화물을 생성하기 위한 이중층 공정을 나타낸 개념도이다.

[0129] 도 14는 기판 위에 패터닝된 막을 생성하기 위한 단일층 공정을 나타낸 개념도이다.

[0130] 도 15는 열적으로 전처리된, 단일층 막에 대한 식각 시간에 따른 두께의 그래프이다.

[0131] 도 16은 전자빔에 의하여 패터닝된 막이다.

[0132] 도 17은 유기 고분자에 비하여 훨씬 더 높은 기계적 강도, 화학적 안정성 및 고유의 전기 및 광학적 특성을 갖는 여기에 개시된 화합물들의 반-고체 형태로 사용되기 위한 핫 엠보싱 리소그래피를 도시한 개념도이다.

[0133] 도 18은 전자 현미경과 같은 응용 분야에서 표준화 측정으로 사용되기 위한 물리적 자의 한 제조 방법을 도시한 개념도이다.

[0134] 도 19는 실리카 위에 증착된, 교환되지 않은 HafSOx 막의 AFM 이미지이다.

[0135] 도 20은 HafSOx의 이온 교환과 850 ℃에서의 열처리 후의 HfO_2의 TEM 이미지이다.

[0136] 도 21은 700 ℃ 이상으로 가열된 후 HafSOx 열분해로부터 형성되고 실리카 위에 증착된 HfO_2 막의 AFM 이미지이다.

[0137] 도 22는 0.1 M NaOH로 처리되고, 450 ℃로 10 분 동안 가열된, 실리카 위에 증착된 HafSOx 막의 AFM 이미지이다.

[0138] 도 23은 0.1 M NaOH로 처리되고, 650 ℃로 10 분 동안 가열된, 실리카 위에 증착된 HfO_2 막의 AFM 이미지이다.

[0139] 도 24는 처리되지 않은 하프니아 막의 XRD 그래프를 제공한다.

[0140] 도 25는 처리된 하프니아 막의 XRD 그래프를 제공한다.

[0141] 도 26은 처리되지 않은 지르코니아 막의 XRD 그래프를 제공한다.

[0142] 도 27은 처리된 지르코니아 막의 XRD 그래프를 제공한다.

[0143] 도 28은 실리카 위에 증착된 안듐 갈륨 아연 산화물 반도체 막의 SEM 이미지이다.

[0144] 도 29는 무기 확산-반응과 잉크젯 프린팅을 통해 생성된 선형 패턴이다.

[0145] 도 30은 이중층 막을 UV 광에 노출시킴으로써 생성된 패턴이다.

[0146] 도 31은 전자빔 기록에 의하여 패터닝된 막이다.

[0147] 도 32는 전자빔 기록에 의하여 패터닝된 막이다.

[0148] 도 33은 사진적으로 패터닝된 막이다.

[0149] 도 34는 사진적으로 패터닝된 막이다.

[0150] 도 35는 전자빔에 의하여 패터닝된 $HfO_{2-x}(SO_4)_x$ 막이다.

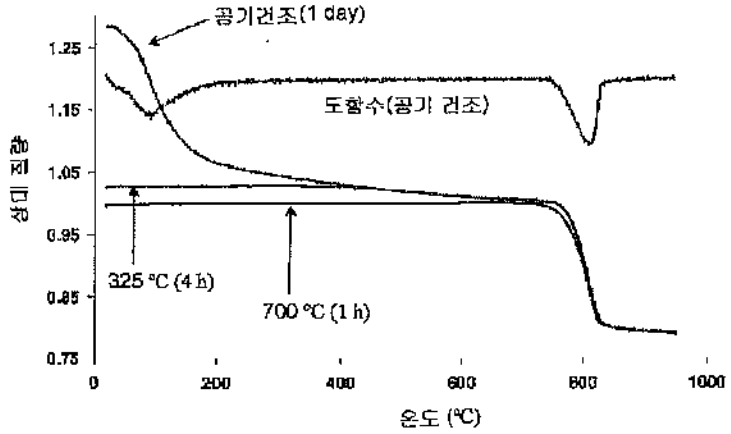
[0151] 도 36은 전자빔에 의하여 패터닝된 $HfO_{2-x}(SO_4)_x$ 막이다.

[0152] 도 37은 전자빔에 의하여 패터닝된 $HfO_{2-x}(SO_4)_x$ 막이다.

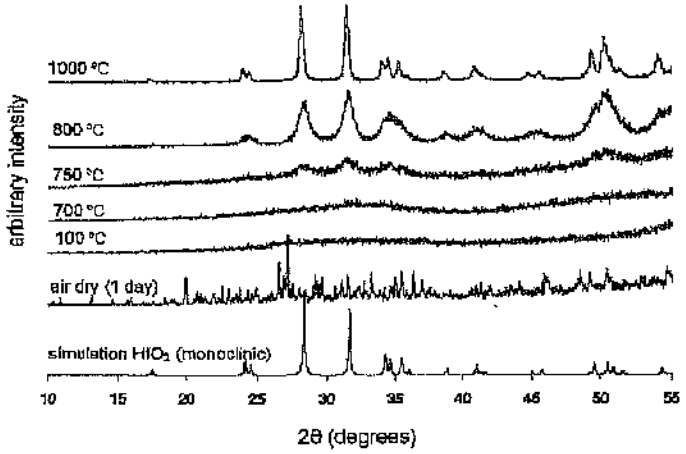
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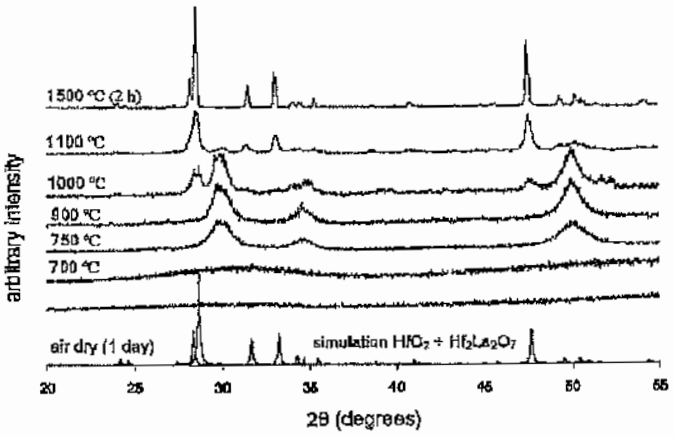


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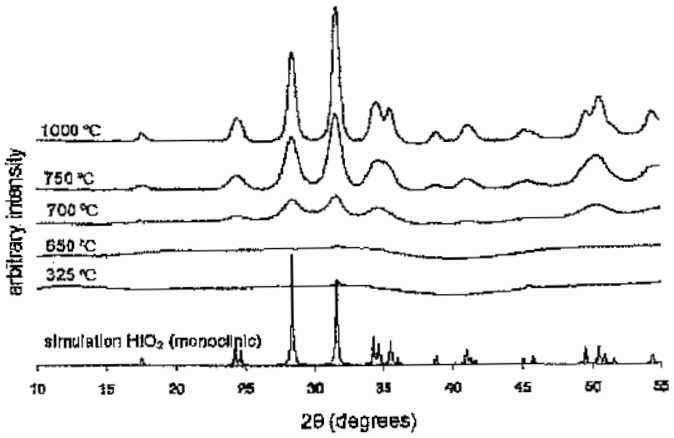


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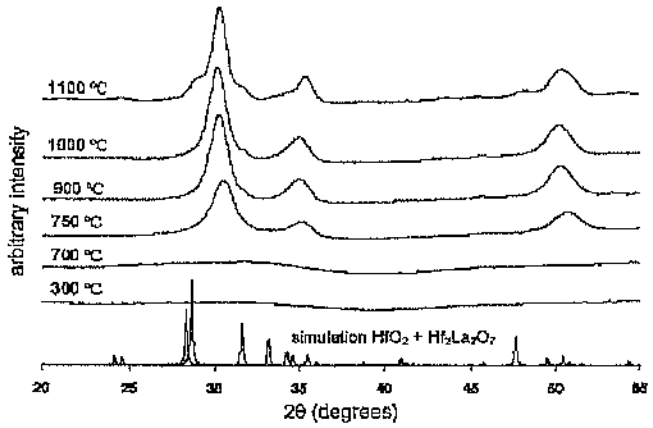


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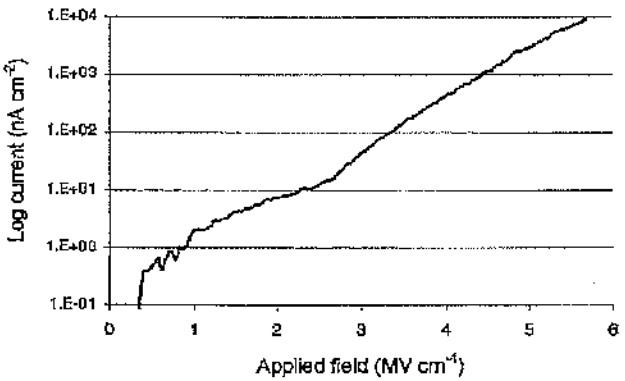


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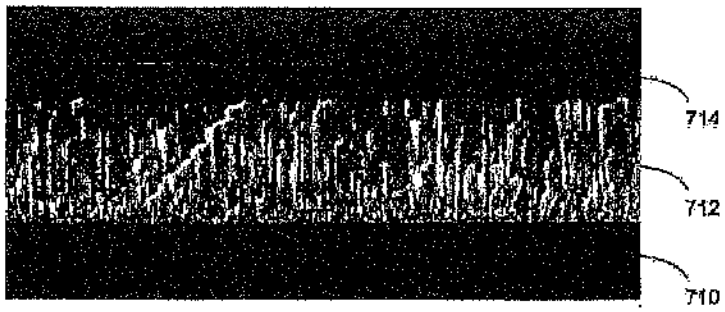
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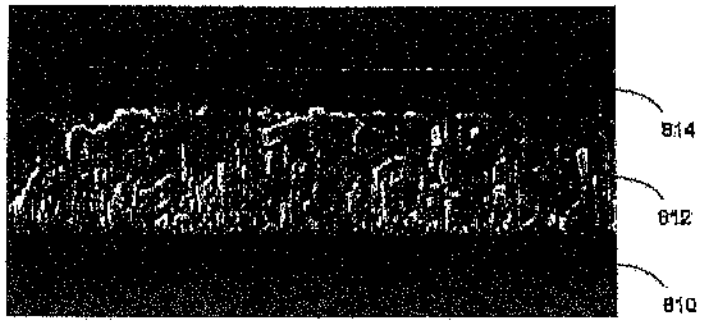


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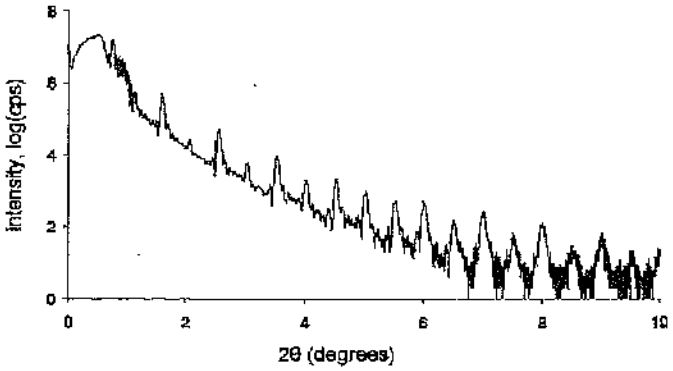


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도면8

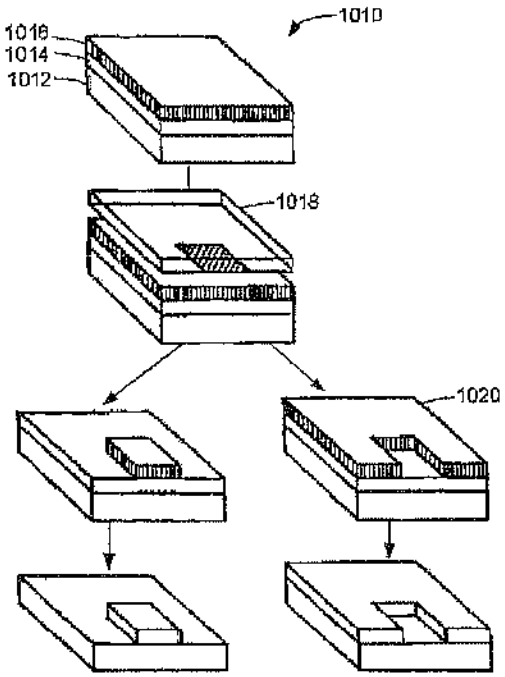


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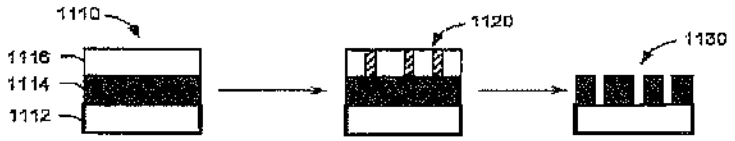


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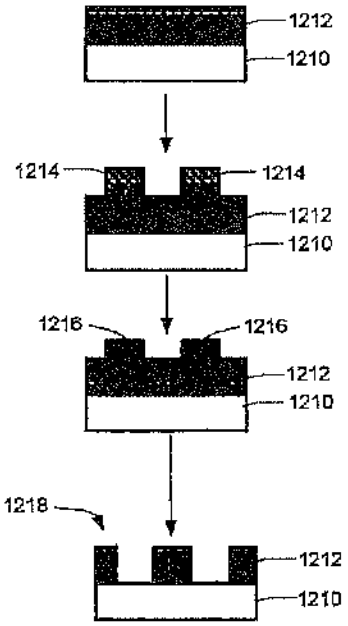
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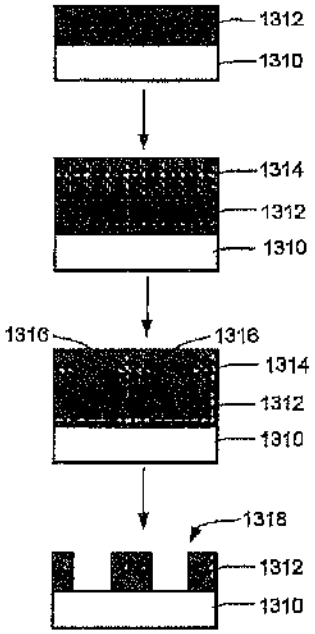
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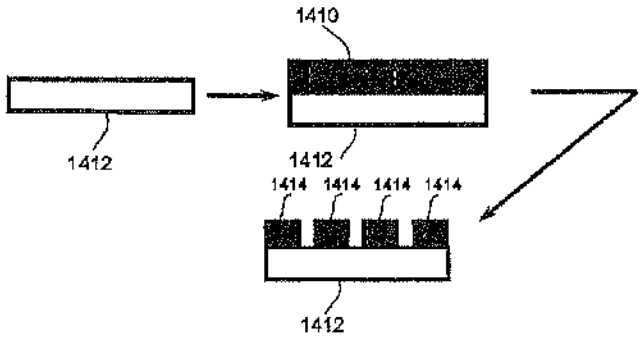


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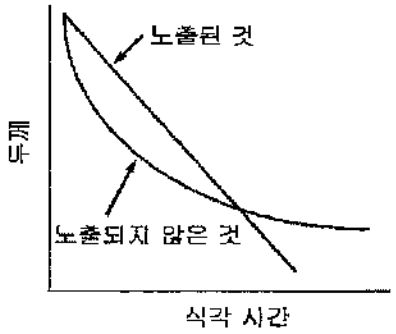


Lam Research Ex. 1004 - Page 333 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

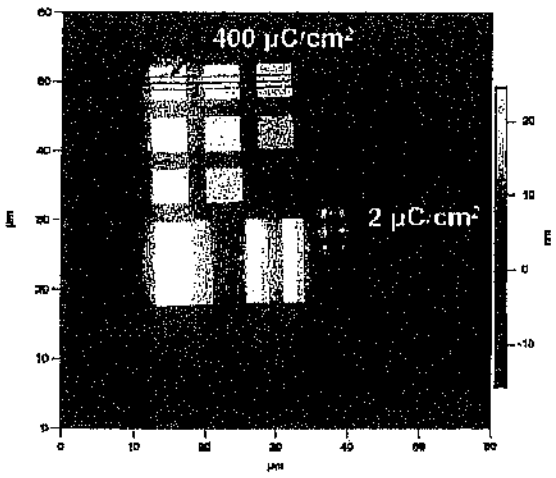
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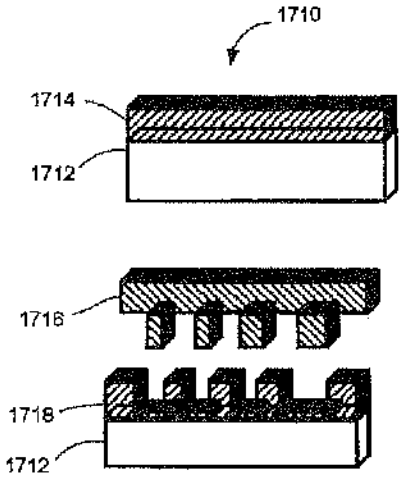
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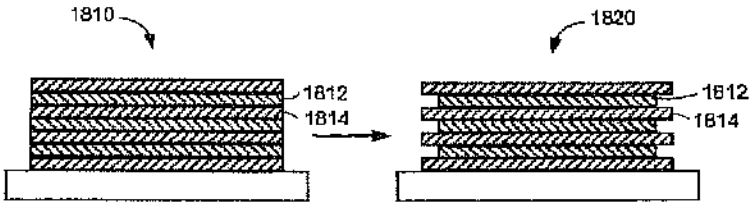
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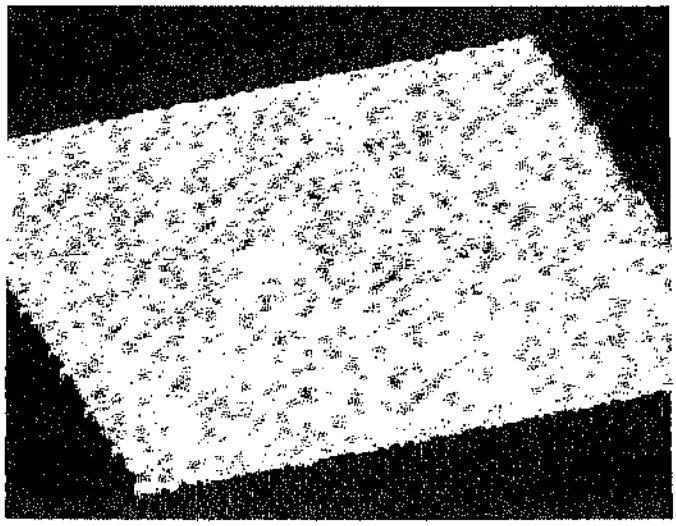


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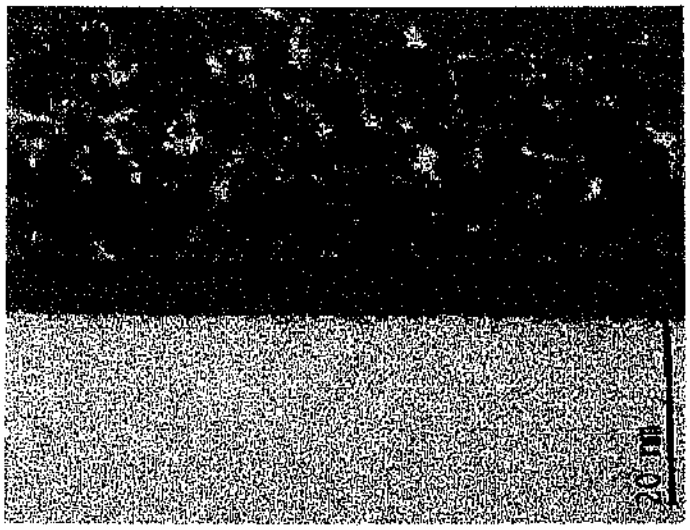


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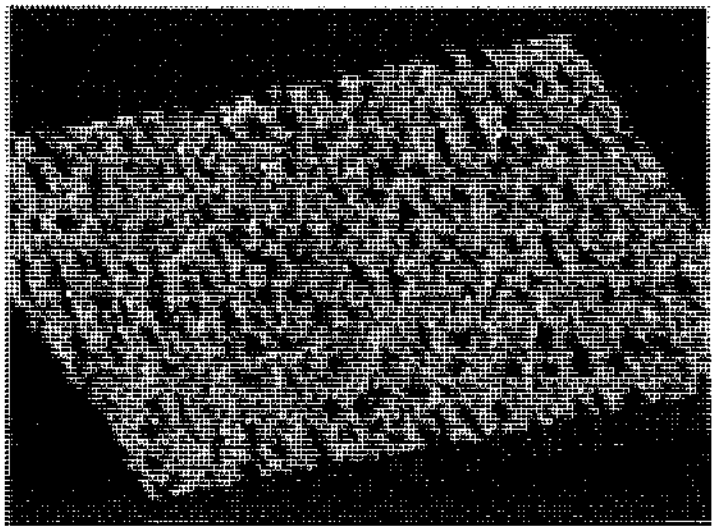
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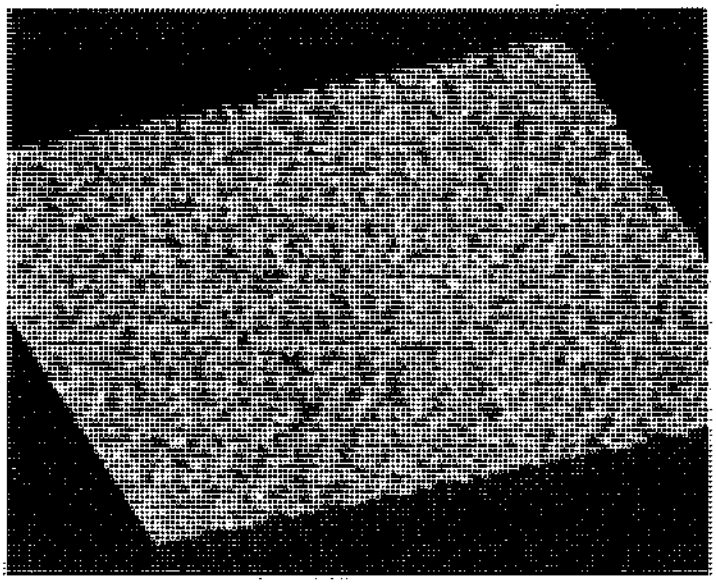
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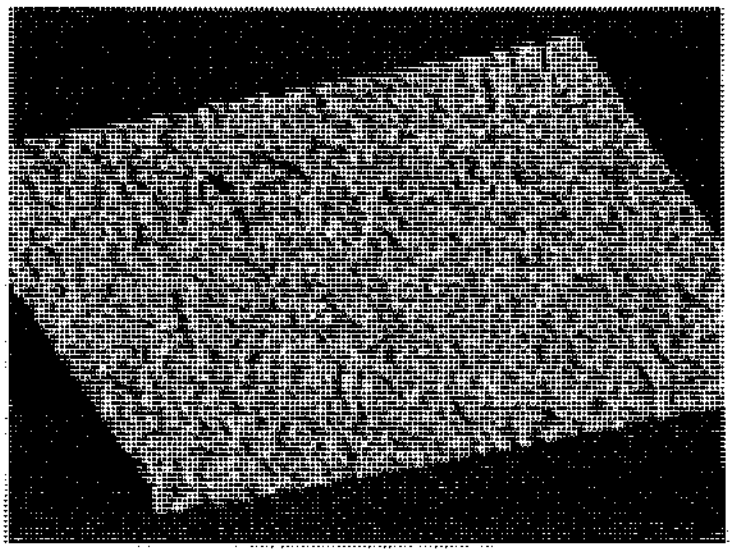
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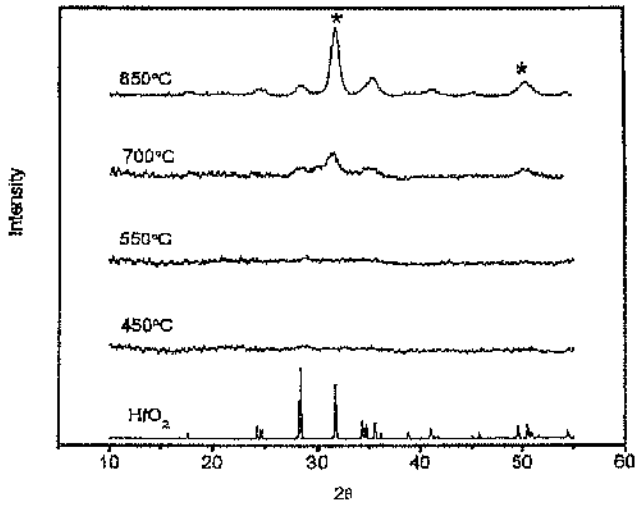
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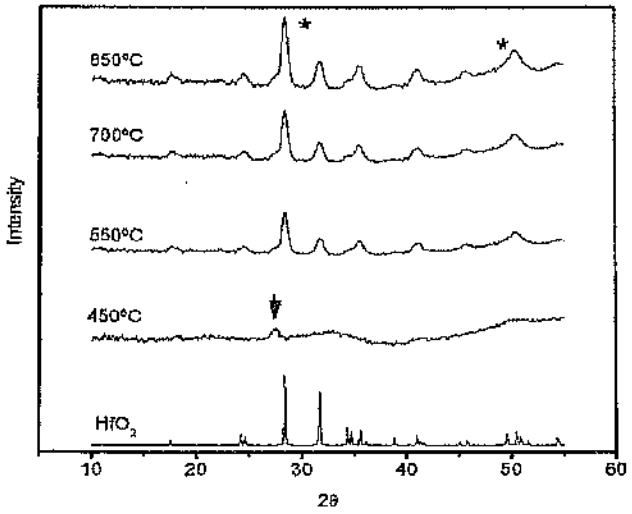
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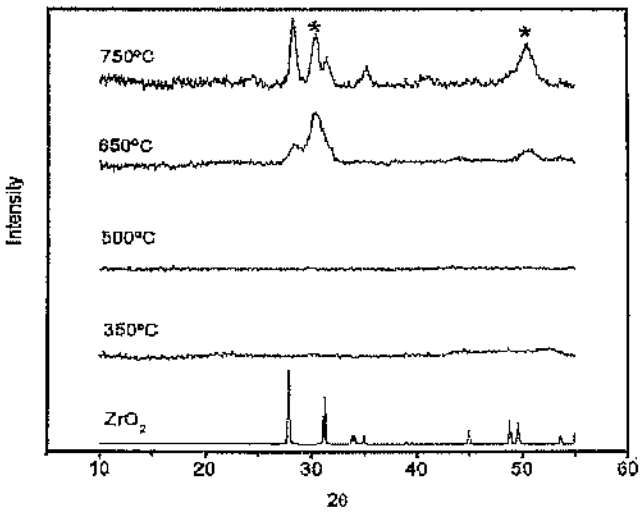
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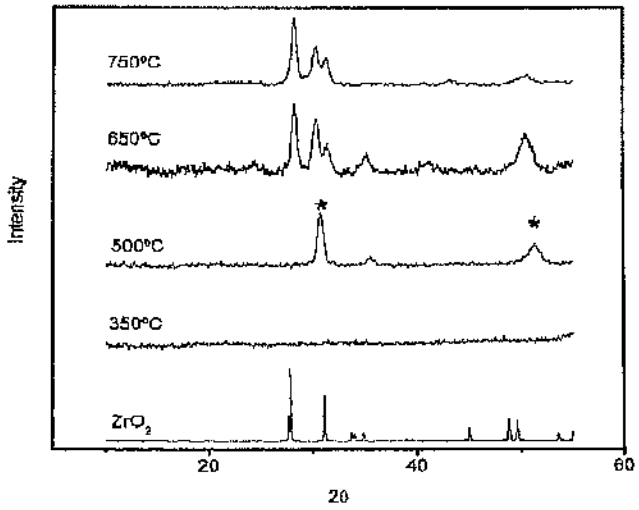
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650°C
700°C
550°C
450°C
HfO2
Intensity
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20
30
40
50
60
2θ

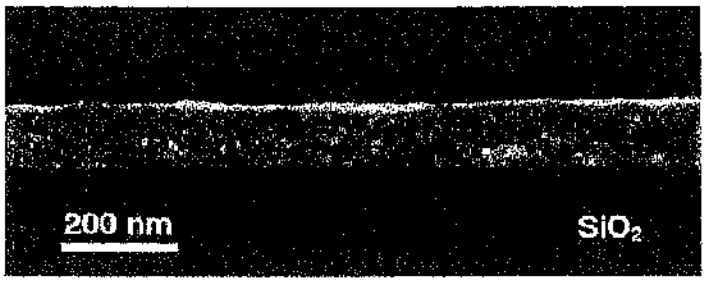
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ZrO2
Intensity
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40
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2θ

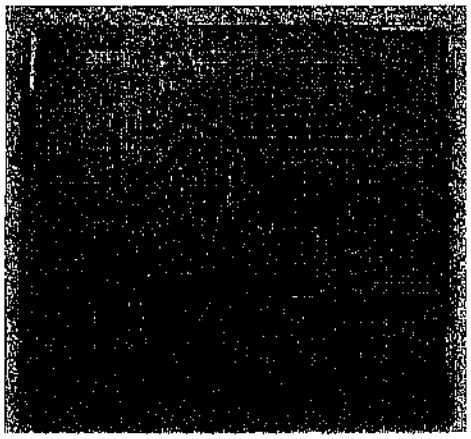
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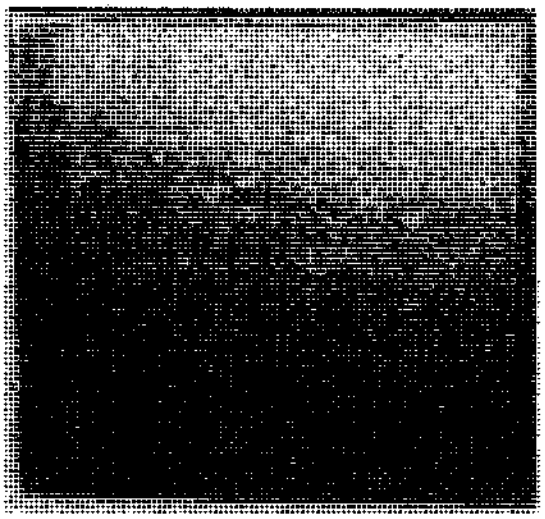
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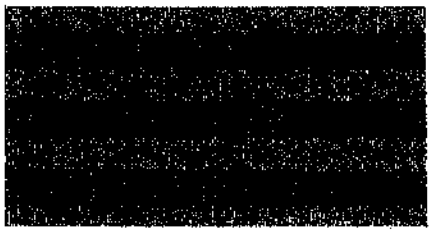
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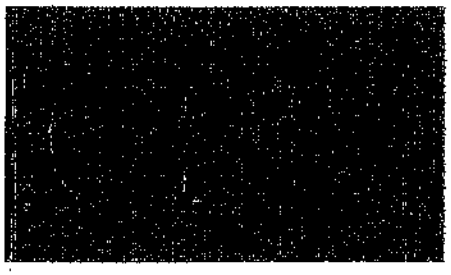
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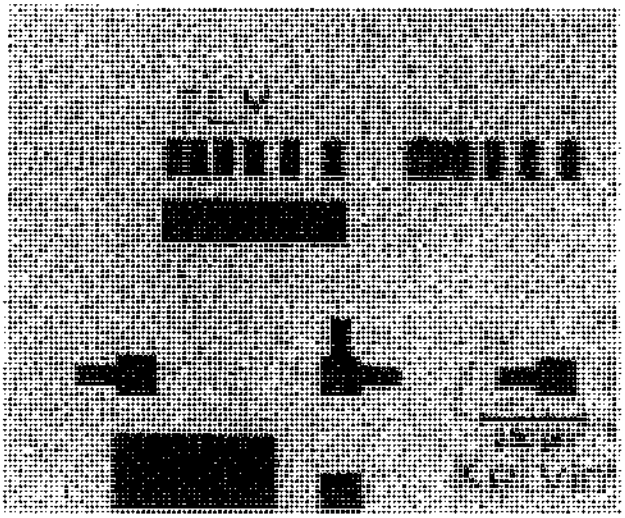
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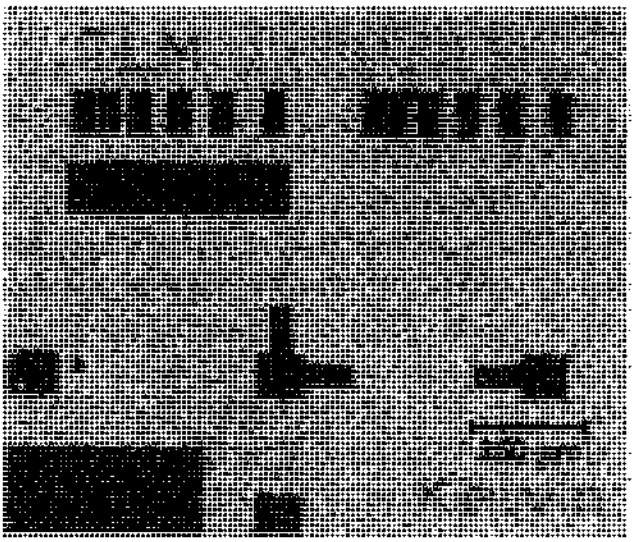
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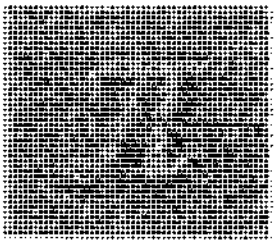
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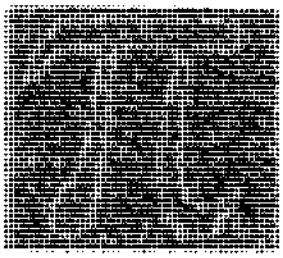
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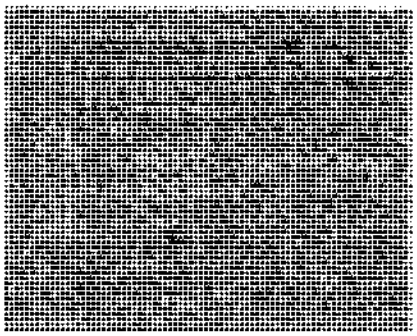
도면35



도면36



도면37



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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to the identity of the inventor (Rule 4.17(i)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*
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(54) Title: PATTERNED CERAMIC FILMS AND METHOD FOR PRODUCING THE SAME

(57) Abstract: A patterned ceramic film (10) is useful as ion-conducting ceramics, electrodes, hard ceramic coatings, transparent conducting oxides, transparent semiconducting oxides, ferroelectric oxides, and dielectric oxides. The ceramic film (10) may be produced from a liquid precursor solution.

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PATTERNED CERAMIC FILMS AND METHOD FOR PRODUCING THE SAME

BACKGROUND

Fuel cells use an electrochemical energy conversion of fuel (including but not limited to hydrogen, propane, methane, carbon monoxide, and the like) and oxidant(s) into electricity and heat. It is anticipated that fuel cells may be able to replace primary and secondary batteries as a portable power supply. In fuel cells, the fuel (usually containing a source of hydrogen) is oxidized typically with a source of oxygen to produce (primarily) water and carbon dioxide. The oxidation reaction at the anode, which liberates electrons, in combination with the reduction reaction at the cathode, which consumes electrons, results in a useful electrical voltage and current through the load.

As such, fuel cells provide a direct current (DC) voltage that may be used to power motors, lights, electrical appliances, etc. A solid oxide fuel cell (SOFC) is one type of fuel cell that may be useful in portable applications. The material properties, which are generally desirable for obtaining high performing fuel cell devices, also make fabrication of those fuel cell devices a significant challenge.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings, like reference numerals correspond to similar, though not necessarily identical components. For the sake of brevity, reference numerals having a previously described function may not necessarily be described in connection with subsequent drawings in which they appear.

Fig. 1A is a perspective front view of an embodiment of the present invention, showing an embodiment of a liquid film deposited on an embodiment of a substrate;

Fig. 1B is a view similar to Fig. 1A, showing an embodiment of a mask on a predetermined portion of an embodiment of the liquid film;

Fig. 1C is a view similar to Fig. 1A, showing an embodiment of a patterned liquid film;

Fig. 2A is a perspective front view of an alternate embodiment of the present invention, showing an embodiment of a liquid film deposited on an embodiment of a substrate;

Fig. 2B is a view similar to Fig. 2A, showing an embodiment of a mask on a predetermined portion of an embodiment of the liquid film;

Fig. 2C is a view similar to Fig. 2A, showing an embodiment of the patterned liquid film;

Fig. 3 is a scanning electron micrograph (SEM) at 35X magnification showing a top view of an embodiment of a patterned ceramic film according to an embodiment of the present invention; and

Fig. 4 is a schematic view of an embodiment of the fuel cell according to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

It was discovered that novel patterned ceramic films may be made relatively simply, quickly, and efficiently through use of a liquid precursor solution in conjunction with patterning and heating techniques. These patterned ceramic films may be used in various applications, including ion-conducting ceramics, patterned electrodes in fuel cells, hard ceramic coatings, transparent conducting oxides, and transparent semiconducting oxides.

Referring now to Fig. 1A, an embodiment for making a patterned ceramic film includes the step of depositing a liquid precursor solution onto a substrate 14 to form a liquid film 12.

It is to be understood that any suitable material may be chosen for the substrate 14. In an embodiment, the substrate 14 is single crystal silicon, polycrystalline silicon, silicon oxide containing dielectric substrates, alumina, sapphire, ceramic, and/or mixtures thereof. In an alternate embodiment of the present invention, a silicon wafer is the substrate 14 of choice.

In an embodiment, the liquid precursor solution is made by dissolving one or more metal salts in a photoresist. It is to be understood that any suitable metal salt(s) (non-limitative examples of the salt component of the metal salt(s) include nitrates, sulfates, and/or chlorides) may be chosen that do not overly contaminate the patterned ceramic film as observed by desired electrical, chemical, and/or mechanical performance, and/or reliability. In an embodiment, the metal salts are cerium nitrate and/or samarium nitrate.

Many metal salts are soluble in water. Therefore, dissolution of the metal salts would be easily achieved if a water-soluble photoresist were used. However, most photoresists are not water-soluble. It is to be understood that the photoresist may act as a carrier for the metal salt(s).

It is to be understood that some standard photoresists used in photolithography may, in some instances, not be suitable in embodiment(s) of the method. It is to be understood that replacing the photoresists useful for embodiments of the present invention with conventional photoresists may, in some instances, not result in a suitable ceramic film after heating. Without being bound to any theory, it is believed that a desirable photoresist will possess functional groups capable of stabilizing the metal cation to promote a substantially homogeneous liquid precursor solution. One non-limitative example of a suitable photoresist is one which has ketone groups on the ends of the repeat unit which may act to coordinate the metal cation. A non-limitative example of photoresists suitable for embodiments of the present invention include diacrylates. In an embodiment, the photoresist is tetra-ethlyene glycol diacrylate, polyvinylphenol (PVP), poly(4-vinylphenol), poly(4-hydroxystyrene), and/or any DNQ (diazonaphthoquinone)-Novolak based resist.

It is to be understood that the amount of metal salt(s) used depends upon the chosen metal salt and its solubility. In an embodiment, the concentration of metal salt to photoresist may be up to about 5 moles of metal per liter of photoresist.

It is to be understood that the liquid precursor solution is a true solution of the metal salts substantially fully dissolved in the photoresist. In order to obtain a fully miscible liquid precursor solution, the solution may be mixed until substantially all of the solids are dissolved into the photoresist. A fully miscible solution generally has no powder particles therein. Such a fully miscible solution may be advantageous for many reasons, for example, when the line-widths to be patterned are equal to or smaller than the size of the powder particles.

Generally, the time it takes to substantially fully dissolve the metal salts into the photoresist depends on the materials used. In an embodiment of the present invention, the total dissolution time is about two hours. If the metal salts are not substantially completely dissolved, the resulting liquid film 12 may possess undesirable heterogeneous properties.

In an embodiment of the present invention, one or more additives may optionally be mixed into the liquid precursor solution before it is deposited on the substrate 14. The addition of additives may assist in the thermal and ultraviolet curing of the liquid precursor solution after it is applied to the substrate 14. It is to be understood that any suitable additives may be chosen. In an embodiment, suitable photoinitiator additives include, but are not limited to 2,5 dimethyl 2,5-di-t-butylperoxy hexane (commercially available under the tradename LUPEROX 101 from ATOFINA Chemicals Inc. in Philadelphia, Pennsylvania), alpha, alpha-dimethoxy-alpha-phenylacetophenone (commercially available under the tradename IRGACURE 651 from Ciba Specialty Chemicals in Terrytown, New York), and/or mixtures thereof.

In an embodiment of the present invention, the liquid precursor solution is deposited onto the substrate 14 using deposition techniques including, but not limited to, spin coating, screen printing, dip coating, meniscus coating, and spray

coating. Spin coating generally forms very thin film thicknesses and small, intricate geometries. In an embodiment, the thin film thicknesses are less than or equal to about 1 μm. Screen printing generally forms thicker film thicknesses and larger geometries. In an alternate embodiment, the thicker film thicknesses are greater than or equal to about 10 μm.

In an embodiment, the liquid film 12 ranges in thickness from about 0.05 μm to about 0.5 μm. In an alternate embodiment, the liquid film 12 has a thickness of about 0.25 μm.

It is to be understood that a thicker liquid film 12 according to an embodiment of the present invention may be formed by depositing multiple layers 12 of the liquid precursor solution onto the substrate 14.

Now referring to Fig. 1B, the method of the embodiment of the present invention further includes the step of patterning the liquid film 12. It is to be understood that liquid film 12 may be patterned into any suitable shape, size and/or configuration.

Any applicable negative or positive photolithography technique may be selected to pattern the liquid film 12.

In an embodiment, patterning includes the step of masking a portion of the liquid film 12. A mask 16 is placed over the liquid film 12 such that one portion 22 of the liquid film 12 is masked and another portion 24 of the liquid film 12 is unmasked.

The patterning step further includes the step of exposing the liquid film 12, with the mask 16 thereon, to a light source 18. It is to be understood that any suitable light source 18 may be used. In an embodiment of the present invention, a UV lamp (365 nm 200 W/lin. in) is exposed to the liquid film 12. The light source 18 cures either the masked 22 or the unmasked 24 portion of the liquid film 12 (depending upon whether positive or negative photolithography is used).

Fig. 1B shows a non-limitative example of an embodiment of the present invention whereby a positive photolithography technique is used. With this

technique, the masked portion 22 of the liquid film 12 is cured, and the unmasked portion 24 of the liquid film 12 is uncured.

In an embodiment of the present invention, after the liquid film 12 is exposed to the light source 18, the method may further optionally include the step of baking the liquid film 12. It is to be understood that this post-exposure bake may be a low temperature bake. In an embodiment, the bake temperature ranges between about 50°C and about 250°C. In an alternate embodiment, the bake temperature is about 100°C.

Referring now to Fig. 1C, in an embodiment of the method of the present invention, the patterning step further includes the step of removing the uncured portion of the liquid film 12, leaving the patterned liquid film 20. It is to be understood that removal of the uncured portion of the liquid film 12 may be accomplished by any suitable means, including but not limited to solvent stripping. In an embodiment, removal occurs by dissolving the uncured portion of the liquid film 12 in isopropyl alcohol.

In an embodiment, the method includes the step of heating the patterned liquid film 20 to drive off the organics that remain from the liquid precursor solution. It is to be understood that any suitable heat treatment may be chosen. In an embodiment, the patterned liquid film 20 is fired at temperatures ranging between about 550°C and about 600°C. In a further embodiment, the firing temperature ranges between about 540°C and about 1050°C. It is to be understood that, in some instances, higher temperatures may aid in removing contamination, and/or achieving the desired morphology or phase of the patterned ceramic film 10.

It is to be understood that the line width W of the patterned liquid film 20 may be any suitable width; however in an embodiment, the width ranges between about 0.5 μm to about 2 mm.

Embodiment(s) of the patterned ceramic film 10 may have thicknesses ranging between about 0.2 μm and about 0.3 μm. It is to be understood that

patterned ceramic films 10 having thicknesses in this range are substantially crack free.

Referring now to Figs. 2A through 2C, an embodiment for making a patterned ceramic film 10 includes the steps as described hereinabove in relation to Figs. 1A through 1C. In contrast, however, referring particularly to Fig. 2B, the patterning step uses a negative photolithography technique. A mask 16 is placed over a portion of the liquid film 12 such that a portion 22 of the liquid film 12 is masked and a portion 24 of the liquid film 12 is unmasked.

In this embodiment using negative photolithography, the masked portion 22 is uncured, and the unmasked portion 24 of the liquid film 12 is cured.

Referring now to Fig. 2C, the method of the embodiment of the present invention further includes the step of removing the uncured portion 24 of the liquid film 12. Fig. 2C shows an alternate embodiment of the present invention wherein the patterned liquid film 20' is a reverse configuration of the mask 16 used (shown in Fig. 2B).

To further illustrate, the following example is given. It is to be understood that this example is provided for illustrative purposes and is not to be construed as limiting the scope of the claimed subject matter.

EXAMPLE

6.94 g of cerium nitrate and 1.78 g of samarium nitrate were added to 40 cc of tetra-ethylene glycol diacrylate to form the liquid precursor solution. 5 cc of LUPEROX™ photoinitiator and 5% by weight of IRGACURE 651 were added to the liquid precursor solution to assist in thermal and ultraviolet curing. The solution was mixed for about 2 hours so that the mixture was completely dissolved and a clear solution was obtained.

The liquid precursor solution was then spin coated onto a silicon wafer. Shadow masking and ultraviolet exposure were used to pattern the liquid film. After exposure, the uncured portion of the patterned liquid film was removed with isopropyl alcohol. The patterned liquid film was then fired at about 540°C to

remove the organic portion of the liquid precursor solution and to leave the desired samarium doped ceria (SDC) patterned ceramic film. This SDC patterned film may be suitable for use as an anode in a fuel cell (for example, in a solid oxide fuel cell (SOFC)).

Referring now to Fig. 3, a SEM at 35X magnification of a top view of the resultant SDC patterned ceramic film is shown.

It is to be understood that the embodiments of the patterned ceramic films may be used in a variety of applications, including, but not limited to, ion-conducting ceramics (for example, electrolytes), hard ceramic coatings, transparent conducting oxides (a non-limitative embodiment of which is indium tin oxide) and transparent semiconducting oxides (a non-limitative example of which is zinc oxide), ferroelectric oxides (a non-limitative example of which is lead zirconate titanate), dielectric oxides (non-limitative examples of which include aluminum oxides and zirconium oxides), and as anodes and cathodes. The electrolytes, anodes and cathodes may be suitable for use in fuel cells.

Referring now to Fig. 4, in an embodiment of the present invention, a fuel cell 100 includes at least one electrode 26, 30 in electrochemical contact with an electrolyte 28. It is to be understood that the electrode 26, 30 may be an anode 26 or a cathode 30. It is to be further understood that the electrolyte 28, the anode 26, and/or the cathode 30 may be a patterned ceramic film 10 according to embodiment(s) of the present invention.

Fig. 4 is a simplified schematic diagram of a dual chamber fuel cell 100. It is to be understood that fuel cell 100 may also be a single chamber fuel cell.

Further, it is to be understood that the fuel cell 100 may be one of solid oxide fuel cells, proton conducting ceramic fuel cells, Polymer Electrolyte Membrane (PEM) fuel cells, molten carbonate fuel cells, solid acid fuel cells, and Direct Methanol PEM fuel cells.

In the fuel cell 100 embodiments of the present invention, oxidants 34 are carried to the cathode 30, and reactants 32 are carried to the anode 26. In an embodiment, the reactants 32 are fuels, and the oxidants 34 are one of oxygen, air,

and mixtures thereof. It is to be understood that any suitable fuel/reactant 32 may be used with the fuel cell 100. In an embodiment, the fuel/reactant 32 is selected from at least one of hydrogen, methane, ethane, propane, butane, pentane, methanol, ethanol, higher straight chain or mixed hydrocarbons, for example, natural gas or gasoline (low sulfur hydrocarbons may be desirable, e.g. low sulfur gasoline, low sulfur kerosene, low sulfur diesel), and mixtures thereof. In an alternate embodiment, the fuel/reactant 32 is selected from the group consisting of butane, propane, methane, pentane, and mixtures thereof. Suitable fuels may be chosen for their suitability for internal direct reformation, suitable vapor pressure within the operating temperature range of interest, and like parameters.

It is to be understood that if fuel cell 100 is a single chamber fuel cell, a gaseous mixture of reactant 32 and oxidant 34 may be directed toward the anode 26 and/or the cathode 30.

An embodiment of a method of using fuel cell 100 includes the step of operatively connecting the fuel cell 100 to electrical load L and/or to electrical storage device S. The electrical load L may include many devices, including, but not limited to any or all of computers, portable electronic appliances (e.g. portable digital assistants (PDAs), portable power tools, etc.), and communication devices, portable or otherwise, both consumer and military. The electrical storage device S may include, as non-limitative examples, any or all of capacitors, batteries, and power conditioning devices. Some exemplary power conditioning devices include uninterruptible power supplies, DC/AC converters, DC voltage converters, voltage regulators, current limiters, etc.

It is also contemplated that the fuel cell 100 may, in some instances, be suitable for use in the transportation industry, e.g. to power automobiles, and in the utilities industry, e.g. within power plants.

An embodiment of a method of using a patterned ceramic film 10 includes the step of operatively disposing the patterned ceramic film 10 in a device. It is to be understood that any suitable device may be chosen such that the patterned ceramic film 10 is adapted to be used as an ion-conducting ceramic, an electrode,

hard ceramic coatings, transparent conducting oxides, transparent semiconducting oxides, ferroelectric oxides, and/or dielectric oxides.

Embodiments of the present invention may provide many advantages, examples of which include, but are not limited to the following. Embodiments of the present invention may advantageously provide a method of making patterned ceramic films while generally avoiding having to pattern the hard and brittle ceramic film. Further, embodiments of the patterned ceramic film 10 may be advantageously used as ion-conducting ceramics, electrodes, hard ceramic coatings, transparent conducting oxides, transparent semiconducting oxides, ferroelectric oxides, and/or dielectric oxides.

While several embodiments of the present invention have been described in detail, it will be apparent to those skilled in the art that the disclosed embodiments may be modified. Therefore, the foregoing description is to be considered exemplary rather than limiting, and the true scope is that defined in the following claims.

What is claimed is:

1. A method of making a patterned ceramic film (10), comprising:

depositing a liquid precursor solution onto a substrate (14), thereby forming a liquid film (12), the liquid precursor solution having at least one soluble metal salt dissolved into a photoresist;

patterning the liquid film (12); and

heating the patterned liquid film (20, 20'), thereby producing the patterned ceramic film (10);

wherein the patterned ceramic film (10) is adapted for use as at least one of ion-conducting ceramics, electrodes, hard ceramic coatings, transparent conducting oxides, transparent semiconducting oxides, ferroelectric oxides, and dielectric oxides.

2. The method as defined in claim 1 wherein the at least one soluble metal salt includes a metal cation and a salt anion, and wherein the salt anion comprises nitrates, sulfates, chlorides, and/or mixtures thereof.

3. The method as defined in at least one of claims 1 through 2 wherein the at least one soluble metal salt is substantially completely dissolved into the photoresist, wherein the liquid precursor solution is substantially fully miscible.

4. The method as defined in at least one of claims 1 through 3 wherein at least one additive is mixed into the liquid precursor solution.

5. The method as defined in at least one of claims 1 through 4 wherein the photoresist is at least one of diacrylates, polyvinylphenol (PVP), poly(4-vinylphenol), poly(4-hydroxystyrene), DNQ (diazonaphthoquinone)-Novolaks, and mixtures thereof.

6. The method as defined in at least one of claims 1 through 5 wherein patterning comprises:

masking a predetermined portion of the liquid film (12), wherein the liquid film (12) has a masked portion (22) and an unmasked portion (24);

exposing the liquid film (12) to a light source (18), whereby one of the masked portion (22) and the unmasked portion (24) is cured; and

removing the uncured portion.

7. The method as defined in at least one of claims 1 through 6, further comprising baking the exposed liquid film (12) at a temperature ranging between about 50°C and about 250°C before removing the uncured portion.

8. The method as defined in at least one of claims 1 through 7 wherein the removing is accomplished by solvent stripping.

9. The method as defined in at least one of claims 1 through 8 wherein heating is accomplished by firing the patterned liquid film (20, 20') at a temperature ranging between about 540°C and about 1050°C.

10. The method as defined in at least one of claims 1 through 9 wherein the substrate (14) is silicon, single crystal silicon, polycrystalline silicon, silicon oxide containing dielectric substrates, alumina, sapphire, ceramic, and/or mixtures thereof.

11. The method as defined in at least one of claims 1 through 10 wherein the patterned ceramic film (10) has a line width (W), the line width (W) ranging between about 0.5 μm to about 2 mm.

12. A fuel cell (100), comprising:

at least one electrode (26, 30) operatively disposed in the fuel cell (100); and

an electrolyte (28) in electrochemical contact with the at least one electrode (26, 30);

wherein at least one of the electrode (26, 30) and the electrolyte (28) comprises a patterned ceramic film (10) produced by the process comprising:

depositing a liquid precursor solution onto a substrate (14), thereby forming a liquid film (12), the liquid precursor solution having at least one soluble metal salt dissolved into a photoresist;

patterning the liquid film (12); and

heating the patterned liquid film (20, 20'), thereby producing the patterned ceramic film (10).

13. The fuel cell as defined in claim 12 wherein the electrode (26, 30) is an anode (26) or a cathode (30).

14. An electronic device (L, S), comprising:

a load (L); and

the fuel cell (100) of at least one of claims 12 and 13 connected to the load (L).

15. A method of using a patterned ceramic film (10), the patterned ceramic film (10) having been formed by a process comprising:

depositing a liquid precursor solution onto a substrate (14), thereby forming a liquid film (12), the liquid precursor solution having at least one soluble metal salt dissolved into a photoresist;

patterning the liquid film (12); and

heating the patterned liquid film (20, 20'), thereby producing the patterned ceramic film (10);

wherein the method of using the patterned ceramic film (10) comprises operatively disposing the patterned ceramic film (10) in a device (L, S), wherein the patterned ceramic film (10) comprises at least one of an ion-conducting ceramics, electrodes, hard ceramic coatings, transparent conducting oxides, transparent semiconducting oxides, ferroelectric oxides, and dielectric oxides.

16. A method of using a fuel cell (100), comprising:

operatively connecting the fuel cell (100) to a load (L), wherein the fuel cell (100) comprises at least one of an electrode (26, 30) and an electrolyte (28) comprising a patterned ceramic film (10) formed by a process comprising:

depositing a liquid precursor solution onto a substrate (14), thereby forming a liquid film (12), the liquid precursor solution having at least one soluble metal salt dissolved into a photoresist;

patterning the liquid film (12); and

heating the patterned liquid film (20, 20'), thereby producing the patterned ceramic film (10).

17. A ceramic film (10), comprising:

a metal-organic liquid precursor solution having a pattern; and

means for converting the precursor solution into the ceramic film (10) having the pattern therein, wherein the ceramic film is adapted for use as at least one of ion-conducting ceramics, electrodes, hard ceramic coatings, transparent conducting oxides, transparent semiconducting oxides, ferroelectric oxides, and dielectric oxides.

18. A method of making a patterned ceramic film (10), comprising:

depositing a liquid precursor solution onto a substrate (14), thereby forming a liquid film (12), the liquid precursor solution having at least one soluble metal salt dissolved into a photoresist, wherein the at least one soluble metal salt is

substantially completely dissolved into the photoresist, and wherein the liquid precursor solution is substantially fully miscible;

patterning the liquid film (12), wherein patterning comprises:

masking a predetermined portion of the liquid film (12), wherein the liquid film (12) has a masked portion (22) and an unmasked portion (24);

exposing the liquid film (12) to a light source (18), whereby one of the masked portion (22) and the unmasked portion (24) is cured; and

removing the uncured portion; and

firing the patterned liquid film (20, 20') at a temperature sufficient to substantially drive off organic materials, thereby rendering the patterned ceramic film (10);

wherein the patterned ceramic film (10) is adapted for use as at least one of ion-conducting ceramics, electrodes, hard ceramic coatings, transparent conducting oxides, transparent semiconducting oxides, ferroelectric oxides, and dielectric oxides.

19. The method as defined in claim 18 wherein the liquid film (12) ranges in thickness between about 0.05 μm and about 0.5 μm.

20. The method as defined in at least one of claims 18 through 19 wherein the patterned ceramic film (10) has a thickness ranging between about 0.2 μm and about 0.3 μm.

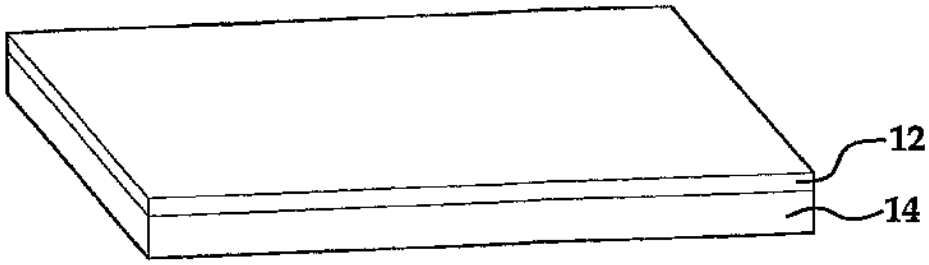


FIG. 1A

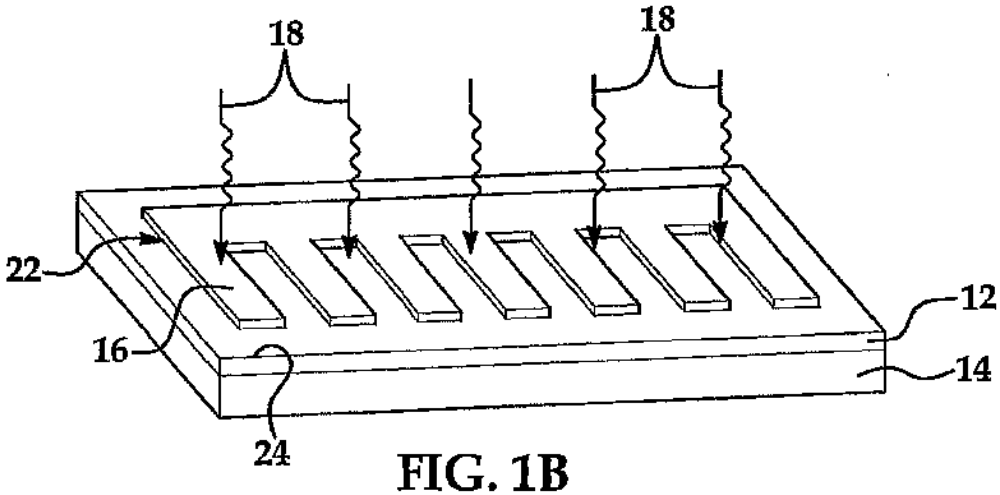


FIG. 1B

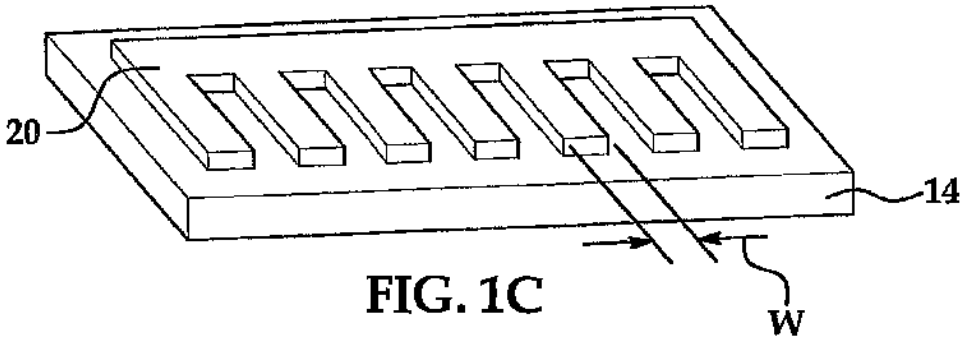


FIG. 1C

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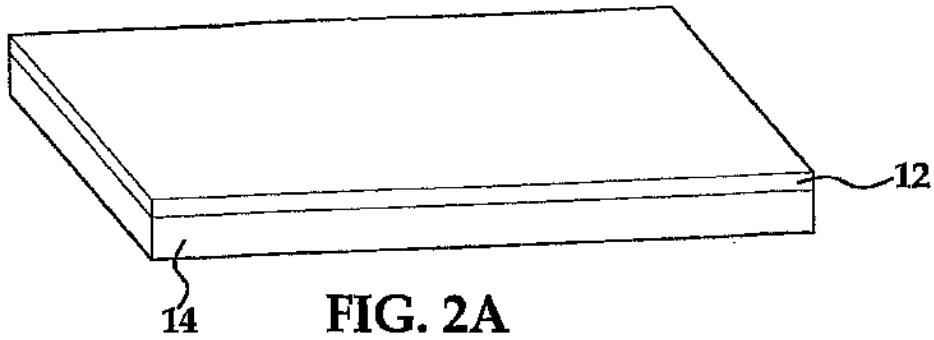


FIG. 2A

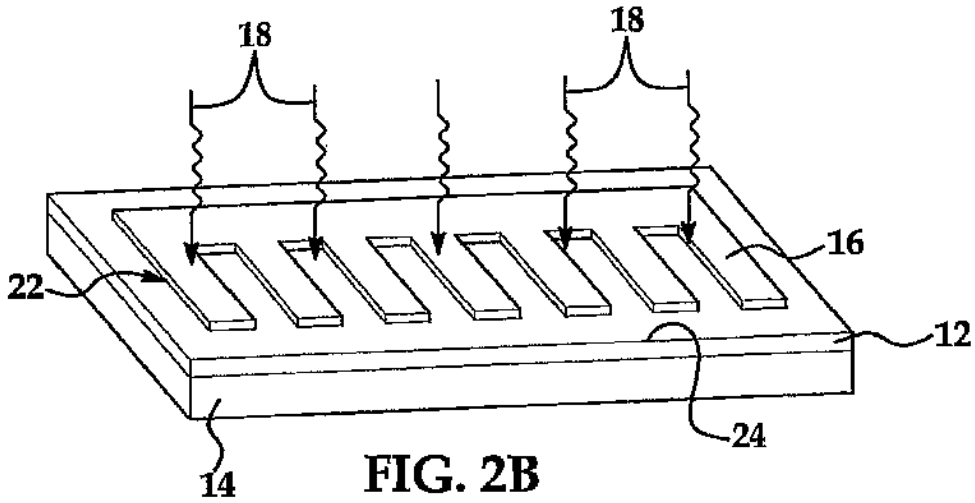


FIG. 2B

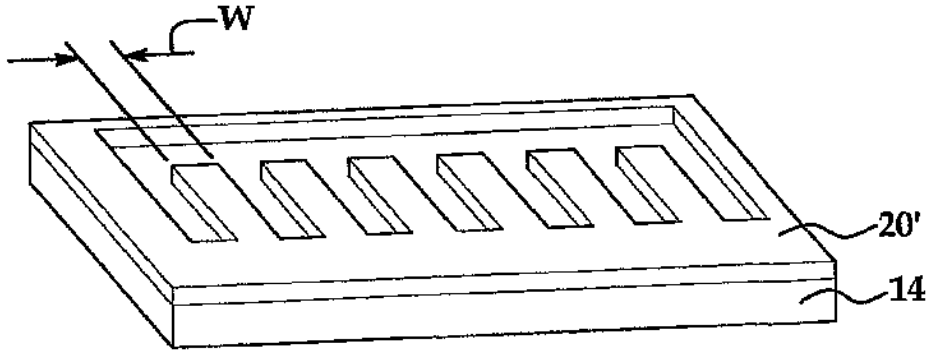


FIG. 2C

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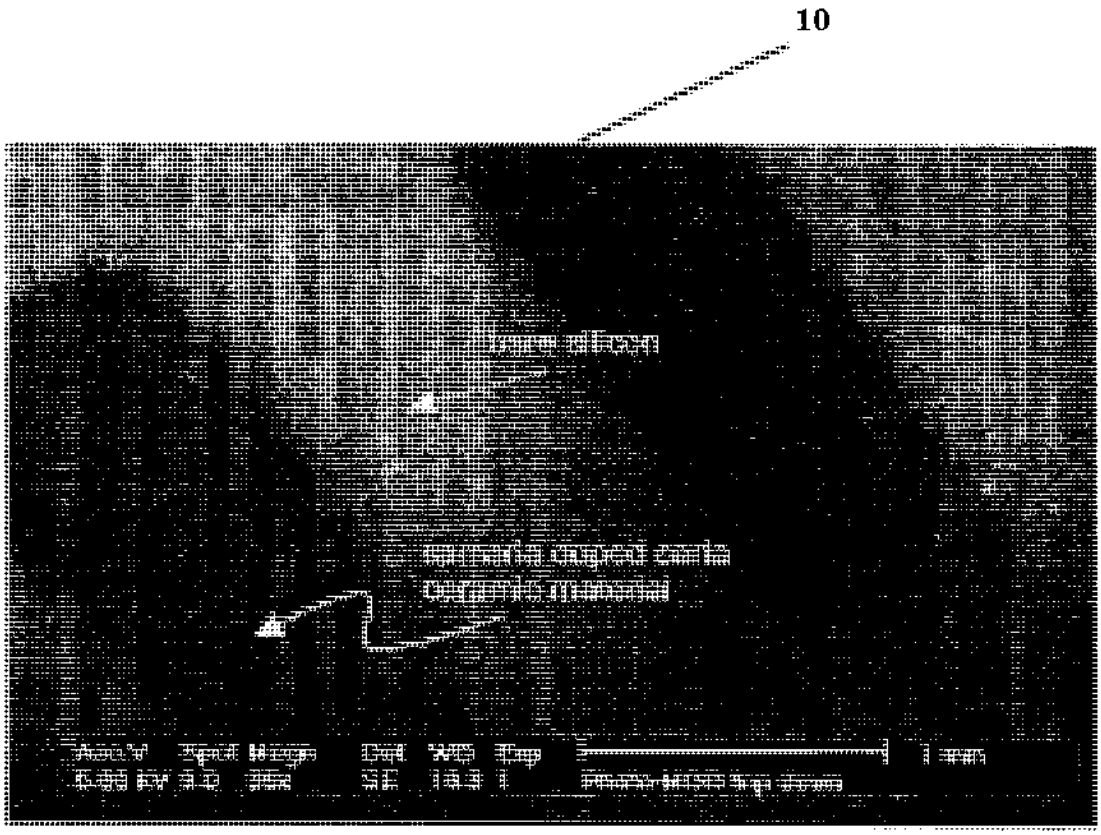


FIG. 3

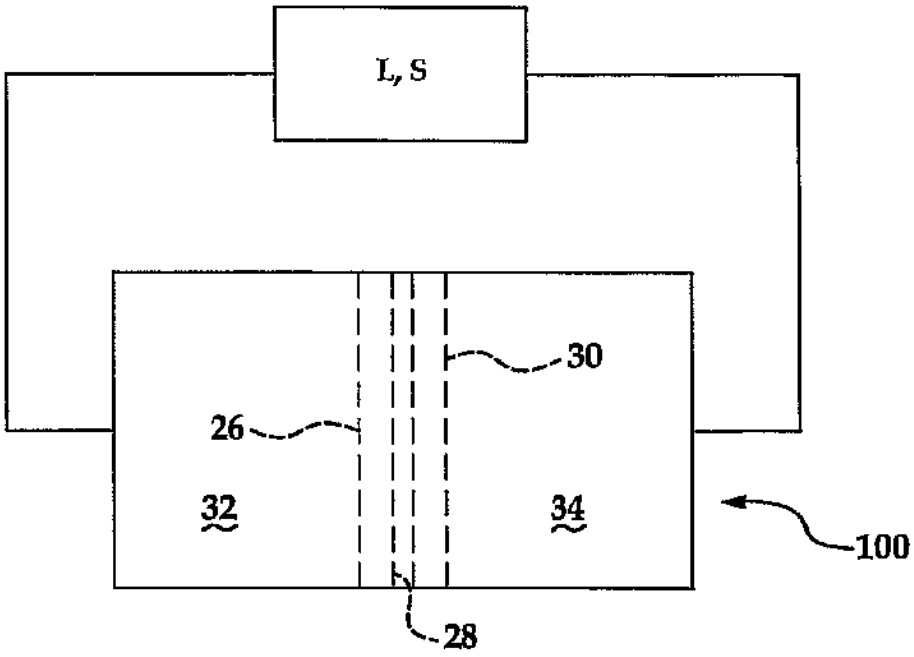


FIG. 4

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Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
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Attorney Docket Number:	5063.02US02
Receipt Date:	10-JUL-2013
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Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1781
Examiner Name	Nicole T. Gugliotta
Attorney Docket Number	5063.02-US-02

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Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1781
Examiner Name	Nicole T. Gugliotta
Attorney Docket Number	5063.02-US-02

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1781
Examiner Name	Nicole T. Gugliotta
Attorney Docket Number	5063.02-US-02

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☒ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☐ Fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☐ None

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Peter S. Dardi/	Date (YYYY-MM-DD)	2013-07-30
Name/Print	Peter S. Dardi, Ph.D.	Registration Number	39650

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No documents available for this priority number.

Espacenet

Bibliographic data: JPH03148659 (A) — 1991-06-25

IONIZING RADIATION SENSITIVE NEGATIVE TYPE RESIST MATERIAL COMPOSITION

Inventor(s): NAMIKI TAKAHISA; SAITO KAZUMASA; OIKAWA AKIRA; WATABE KEIJI ± (NAMIKI TAKAHISA, ; SAITO KAZUMASA, ; OIKAWA AKIRA, ; WATABE KEIJI)

Applicant(s): FUJITSU LTD ± (FUJITSU LTD)

Classification: - **international:** ***G03F7/038; H01L21/027;*** (IPC1-7): G03F7/038; H01L21/027
- **cooperative:**

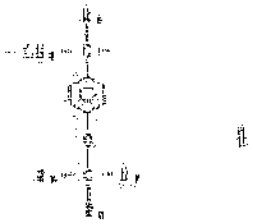
Application number: JP19890287444 19891106

Priority number (s): JP19890287444 19891106

Abstract of JPH03148659 (A)

PURPOSE:To enhance the sensitivity, definition and dry etching resistance of the resist by incorporating a specific copolymer into the compsn. CONSTITUTION:The copolymer which contains 10 to 85% repeating unit of formula I and 15 to 90% repeating unit of formula II and has 2,000 to 1,000,000 weight average mol. wt. is incorporated into this compsn. In the formula, R1 denotes halogen or 1 to 12C alkyl halide; R2, R3 denote H, halogen, 1 to 12C alkyl halide; R4, R8 denote H or 1 to 3C alkyl; R5 denote H or 1 to 12C alkyl; R6, R7 denote 1 to 12C alkyl. Copolymers of alkyl chloride and para-t-butoxy styrene, etc., are usable as the above-mentioned copolymer.





Last updated: 13.03.2013 Worldwide Database 5.8.8.7; 92p

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⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　平3－148659

⑤1Int.Cl.⁵	識別記号	庁内整理番号	⑬公開　平成3年(1991)6月25日
G 03 F 7/038	501	7124－2H	
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H 01 L 21/027			
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審査請求　未請求　請求項の数 1　（全4頁）

⑤4発明の名称　電離放射線感応性ネガ型レジスト材料組成物

⑳特　願　平1－287444
㉒出　願　平1(1989)11月6日

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⑦4代理人　弁理士　青木　朗　外4名

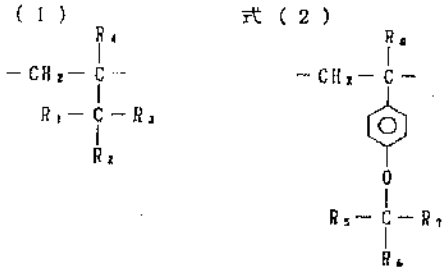
明　細　書

1. 発明の名称

電離放射線感応性ネガ型レジスト材料組成物

2. 特許請求の範囲

式（1）　式（2）



（式中、R_1はハロゲン、または炭素数1～12のモノもしくはポリハロゲン化アルキル基を表わし、R_2, R_3は、それぞれ水素、ハロゲン、または炭素数1～12のモノもしくはポリハロゲン化アルキル基を表わし、R_4, R_8は、それぞれ水素、または炭素数1～3のアルキル基を表わし、R_5は水素、または炭素数1～12のアルキル基を表わし、R_6, R_7は、それぞれ炭素数1～12のアルキル基を表わす）で示される繰り返し単位を含み、その全数に対して式（1）の繰り返し単位の数が10～85%、式（2）の繰り返し単位の数が15～90%であり、かつ重量平均分子量が2,000～1,000,000である共重合体を含む、ことを特徴とする、電離放射線感応性ネガ型レジスト材料組成物。

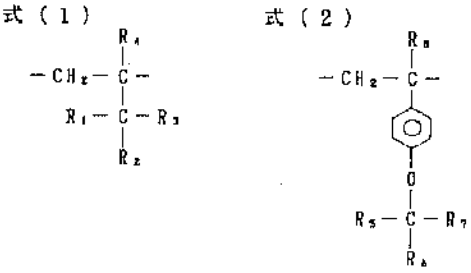
3. 発明の詳細な説明

〔概　要〕

電離放射線感応性ネガ型レジスト材料に関し、

解像性、感度およびドライエッチング耐性の高い電離放射線感応性ネガ型レジスト材料を提供することを目的とし、

式（1）　式（2）



（式中、R_1はハロゲン、または炭素数1～12のモノもしくはポリハロゲン化アルキル基を表わし、

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R_2, R_3 は、それぞれ水素、ハロゲン、または炭素数1～12のモノもしくはポリハロゲン化アルキル基を表わし、R_4, R_6 は、それぞれ水素、または炭素数1～3のアルキル基を表わし、R_5 は水素、または炭素数1～12のアルキル基を表わし、R_7, R_7 は、それぞれ炭素数1～12のアルキル基を表わす）で示される繰り返し単位を含み、その全数に対して式（1）の繰り返し単位の数が10～85%、式（2）の繰り返し単位の数が15～90%であり、かつ重量平均分子量が 2,000～ 1,000,000 であるように構成する。

〔産業上の利用分野〕

本発明は電離放射線感応性ネガ型レジスト材料組成物に関する。

〔従来の技術およびその課題〕

近年、半導体装置などの高集積化にともない、配線はますます微細化されている。最新64MbitのD-RAM の最小線幅は0.7 μm程度で、今後さらに配線は細くなる傾向にある。それに伴い、レジスト材料もこのような微細な配線パターンの解像ができる高解像性のものが望まれており、また生産量をあげるために高感度のものが必要とされている。また、レジストとしてはドライエッチング耐性に優れていることも重要な条件である。

ドライエッチング耐性の優れたものとして、特にポリスチレン系のものが知られているが、ポリスチレンはそれ自体電離放射線に対して非常に感度が低く、そのままではレジストとしては用いられない。そこで不飽和基などの反応性の高い基を導入して感度を向上させるという方法が採られている。しかし、その感度が電離放射線によって起こる架橋反応のみに依存しているので、一般に低感度である場合が多い。さらに感度を上げるために不飽和基を増やすと、未露光部にまで架橋反応が起こってコントラストを低下させ、かえって解像性を低くする場合もある。

また、解像性の高いものとして、一般に化学増幅系レジストと呼ばれるものが知られている。これは、レジストに酸発生剤を含むものであって、電離放射線を照射して、酸を発生させ、発生した酸が触媒的に作用して、ポリマーを架橋または分解するものである。これはポリマーに酸発生剤を加える必要がある。

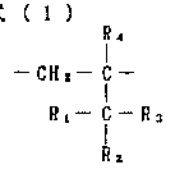
〔発明の解決すべき課題〕

本発明は、従来のレジストとは異なって、反応性の高い官能基を導入することもなく、また、酸発生剤を加えずにポリマー分子自身が酸発生剤に対応する部分を含み、これが酸を発生して架橋反応を起こし、高感度化を達成し、かつ解像性に優れたドライエッチング耐性も高い電離放線感応性ネガ型レジストを提供することを目的とする。

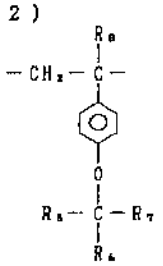
〔課題を解決するための手段〕

本発明の上記課題は、

式（1）



式（2）



（式中、R_1 はハロゲン、または炭素数1～12のモノもしくはポリハロゲン化アルキル基を表わし、R_2, R_3 は、それぞれ水素、ハロゲン、または炭素数1～12のモノもしくはポリハロゲン化アルキル基を表わし、R_4, R_6 は、それぞれ水素、または炭素数1～3のアルキル基を表わし、R_5 は水素、または炭素数1～12のアルキル基を表わし、R_7, R_7 は、それぞれ炭素数1～12のアルキル基を表わす）で示される繰り返し単位を含み、その全数に対して式（1）の繰り返し単位の数が10～85%、式（2）の繰り返し単位の数が15～90%であり、かつ重量平均分子量が 2,000～ 1,000,000 であるレジストによって達成することができる。

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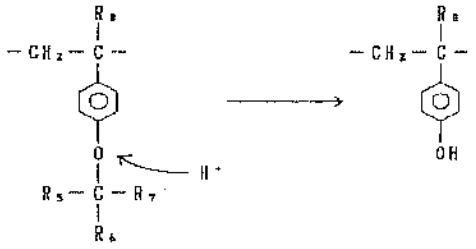
〔作　用〕

レジストに電離放射線を照射するとポリマー同士で架橋反応が起こり、分子量が増大して現像液に不溶化するが、分子量が最初から大きいと、少しの架橋反応で分子量が不溶化に充分な値に達する。従って分子量が高いほど電離放射線の照射量が少なくて済む、即ち感度が高いことになる。しかし分子量が高いと現像液に浸した際に膨潤という現象が起こる。これはレジストでパターンを作成した際にそのパターンが現像液を吸って膨らむ現象で、甚だしい場合にはそれぞれのパターンがくっついてしまう場合もあり、解像性を低下させる重要な原因とされている。ポリマーの分子量が高いほど膨潤も大きくなるので、レジストに使用するポリマーの分子量には感度と解像性の点から最適値が存在する。

本発明のポリマーは重量平均分子量が 1,000,000 を超えると、解像性が低下し、 2,000未満では電離放射線感度が低下する。

本発明のポリマーは、式〔１〕で示される繰り返し単位のR_1, R_2 またはR_3 に含まれるハロゲンが、電離放射線の照射によってはずれてラジカルとなり、はずれた部分において相互に架橋して高分子量化する。これによって照射された領域は、有機溶媒に対する溶解度が減少するので、現像されてパターンを形成する。

さらに、注目すべきことは、このとき発生したハロゲンラジカルが、レジスト中に残存する有機溶媒から水素を引き抜いてハロゲン化水素になる。こうして生成したハロゲン化水素は、繰り返し単位（２）の中のターシャルブトキシ基を攻撃する。このためターシャルブトキシ基は下式のように、はずれ、水酸基となる。



こうして、ポリマーの極性が変化し、無極性溶媒に対する溶解度がますます低下する。即ち本発明になるポリマーは、感度が架橋反応のみならず同時に発生するハロゲン化水素による加水分解に起因するポリマー自身の極性の変化にも依存していることが大きな特徴である。またこのハロゲン化水素は触媒的に使用されるため、１分子のハロゲン化水素が多くのターシャルブトキシ基を攻撃することが可能である。

従って、ポリマー中の繰り返し単位の全数に対して、繰り返し単位（１）の数が、10%未満では発生するハロゲンラジカルの量が不足し、85%を超えると、ハロゲンが遊離して大量のハロゲン化水素を発生しても、繰り返し単位（２）の数が少ないので加水分解されるアルコキシ基が少ないため、電離放射線照射前後のポリマーの極性の変化が小さくなり単に架橋反応にのみ感度が依存してしまうことになる。従って感度は大して上がらず、既存のレジスト材料となんら違いがなくなる。

繰り返し単位（１）中のR_1 ～R_3 の炭素数が12より多い場合、一方においてモノマの分子量が大きくなり、他方においてポリマーの分子量に上限があるので、重合したポリマー中の繰り返し単位（１）の数を所望の10%より少なくする必要がおき、また炭素鎖が長すぎるので、立体障害によって重合が困難となり、ポリマーの分子量が 2,000 未満になることがおきる。

繰り返し単位（２）中のR_5 ～R_7 の炭素数が12より多い場合も、上記と同じ欠点を生じ、さらに、立体障害によってアルコキシ基の酸素原子がブロックされて加水分解が困難となる。

また、R_1, R_2 の炭素数が３より多いと、立体障害の原因となり、またこれらの炭素数を３以下に限定することによって、R_1 ～R_3 およびR_5 ～R_7 の炭素数を12までと多くすることができる。

〔実施例〕

〔合成例１〕

アリルクロライド7.9 g（0.1 mol）と、PTBST（パラターシャルブトキシスチレン、北興化学工

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業）17g（0.1mol）を、水素化カルシウムで充分乾燥後さらに金属ナトリウム存在下で蒸留したＴＨＦ 100mlに混合し、精製窒素気流下で、これに重合開始剤としてノルマルブチルリチウム１gを加え、−78℃で３時間反応させた。その後反応溶液を大量のメタノール中に注ぎ、アリルクロライドとPTBST の共重合体を析出させた。こうして得られたポリマー２gを、さらにベンゼン−メタノールで５回精製した。その結果、最終的に得られたポリマーの重量平均分子量は1.5×10⁴、分散度は1.12、収率は95.0%であった。元素分析の結果によると、このポリマー分子中の（１）式で表される繰り返し単位と（２）式で表される繰り返し単位の比は、ほぼ１：１であった。

（合成例２）

３，４−ジクロロ−２−メチル−１−ブテン14.2g（0.1mol）と、PTBST(北興化学工業）17g（0.1mol）を、（合成例１）と全く同じように共重合させた。その結果、最終的に得られたポリマーの重量平均分子量は2.7×10⁴、分散度は1.07、収率は92.5%であった。また、このポリマー分子中の（１）式で表される繰り返し単位と（２）式で表される繰り返し単位の比は、やはりほぼ１：１であった。

（実施例１）

（合成例１）により得られたポリマー１gをMIBK（メチルイソブチルケトン）５gに溶解してレジスト溶液を作り、スピンコートによりシリコンウェハに膜厚が1μmになるように塗布し、80℃で20分間プリベークし、電子線を照射し、MIBKで30秒間現像し、IPA(イソプロパノール）で30秒間洗浄した。このようにして電子線感度を測定したところ残膜率90%のところで21μC／cdであった。また最小0.3μmのパターンを解像することができた。またＸ線マスク（大日本印刷、ミクロ製品研究所製）を介してPdLα線（4.37Å）を45mJ／cdの露光量で照射した。このようにして得られたパターンを走査型電子顕微鏡で観察したところ、0.4μmのラインアンドスペースを解像できた。

（実施例２）

（実施例１）と同様にして（合成例２）で作製したポリマーの電子線感度を測定したところ15μC／cdで、最小0.3μmのラインパターンが解像できた。Ｘ線感度は40mJ／cdだった。

〔発明の効果〕

本発明によれば、感度、解像性ともに優れ、またドライエッチング耐性も高い電離放射線感応性ネガ型レジストを提供できる。

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Lam Research Ex. 1004 - Page 374　Lam Research Corp. v. Inpria Corp.　IPR2024-00033 - U.S. Patent No. 9,823,564

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PHOTOSENSITIVE RESIN COMPOSITION FOR LIGHT SHIELDING FILM, METHOD FOR FABRICATING LIGHT SHIELDING FILM, TRANSFER MATERIAL, AND METHOD FOR MANUFACTURING TRANSFER MATERIAL

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Classification: - international: ***B05D1/26; G02B5/20; G03F7/004; G03F7/038***
- cooperative:

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Abstract of JP2006284947 (A)

PROBLEM TO BE SOLVED: To provide a photosensitive resin composition for a light shielding film, with which high black density is obtained in a thin film state, which is excellent in a light shielding property and in a heat curing property after exposure, and with which high resolution image can be formed. ; SOLUTION: The photosensitive resin composition for the light shielding film contains metal particles and/or metal compound particles as a black colorant, together with a binder resin, a photo-acid generator and a cross-linking agent. ; COPYRIGHT: (C)2007,JPO&INPIT

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最終頁に続く

(54)【発明の名称】遮光膜用感光性樹脂組成物、遮光膜の作製方法、転写材料及びその製造方法

(57)【要約】
【課題】　薄膜で高い黒濃度を得、遮光性に優れると共に、露光後の加熱硬化性に優れ、高解像度の像の形成が可能な遮光膜用感光性樹脂組成物を提供する。
【解決手段】　バインダー樹脂、光酸発生剤及び架橋剤と共に、黒色剤として金属粒子及び／又は金属化合物粒子を含有している。
【選択図】　なし

【特許請求の範囲】
【請求項1】
バインダー樹脂と、光を吸収して酸を発生する光酸発生剤と、前記光酸発生剤の作用により架橋する架橋剤と、金属粒子及び／又は金属化合物粒子とを含有することを特徴とする遮光膜用感光性樹脂組成物。
【請求項2】
顔料を更に含む請求項１に記載の遮光膜用感光性樹脂組成物。
【請求項3】
前記顔料がカーボンブラック又は黒鉛である請求項２に記載の遮光膜用感光性樹脂組成物。
【請求項4】
膜厚１．０μｍの遮光膜を形成した際の光学濃度が４．０以上である請求項１～３のいずれか１項に記載の遮光膜用感光性樹脂組成物。
【請求項5】
表示装置を構成する遮光膜の形成に用いられる請求項１～４のいずれか１項に記載の遮光膜用感光性樹脂組成物。
【請求項6】
仮支持体上に、少なくとも１層の、バインダー樹脂と、光を吸収して酸を発生する光酸発生剤と、前記光酸発生剤の作用により架橋する架橋剤と、金属粒子及び／又は金属化合物粒子とを含有する感光性樹脂層を有することを特徴とする転写材料。
【請求項7】
遮光膜の形成に用いられる請求項６に記載の転写材料。
【請求項8】
表示装置を構成する遮光膜の形成に用いられる請求項６又は７に記載の転写材料。
【請求項9】
基板上に、請求項１～５のいずれか１項に記載の遮光膜用感光性樹脂組成物を塗布し、乾燥させて感光性樹脂層を形成する工程と、
形成された前記感光性樹脂層をパターン状に露光する工程と、
形成された前記感光性樹脂層を加熱する工程と、
少なくとも前記露光後の前記感光性樹脂層を現像して未露光部を除去する工程と、
を含むことを特徴とする遮光膜の作製方法。
【請求項10】
前記塗布は、スリット状ノズルを有する塗布装置を用いて行なう請求項９に記載の遮光膜の作製方法。
【請求項11】
請求項６～８のいずれか１項に記載の転写材料を用いて、仮支持体上の少なくとも１層の感光性樹脂層を基板に転写する工程と、
転写された前記感光性樹脂層をパターン状に露光する工程と、
転写された前記感光性樹脂層を加熱する工程と、
少なくとも前記露光後の前記感光性樹脂層を現像して未露光部を除去する工程と、
を含むことを特徴とする遮光膜の作製方法。
【請求項12】
請求項６～８のいずれか１項に記載の転写材料の製造方法であって、
仮支持体上に、スリット状ノズルを有する塗布装置を用いた塗布により感光性樹脂層を塗設することを特徴とする転写材料の製造方法。

【発明の詳細な説明】
【技術分野】
【0001】
本発明は、遮光性の膜形成に好適な遮光膜用感光性樹脂組成物、並びにこれを用いた遮光膜の作製方法、転写材料及びその製造方法に関する。

【背景技術】
【0002】
近年、例えば液晶表示素子や固体撮像素子として組み合わせ、カラー画像を得ることを目的としたカラーフィルタが注目を浴びている。このカラーフィルタは、二種以上の画素（Ｒ（赤）、Ｇ（緑）、Ｂ（青）、遮光膜（ブラックマトリクスなど）や、透明部分、透明画素などが組み合わされてなるカラー画像層で構成される。
【0003】
カラーフィルタの製造方法としては、従来は、カラーフィルタを設置する対象面に着色剤を含有する感光性樹脂溶液を塗布し、その塗布膜をパターン状に露光して画素層を形成し、次いでその画素層の上に、他の色の着色剤を含有する感光性樹脂溶液を塗布し、この塗布膜をパターン状に露光して最初の画素層と着色の異なる画素層を形成する工程を繰り返し行なう方法が一般的に利用されてきた。
【0004】
これに対し、別に用意した支持体シート（仮支持体）の上に、着色剤を含有する感光性樹脂溶液を塗布して着色感光性樹脂層を形成して構成された、色が異なる複数枚の感光性転写シート（転写材料）を用意し、まず一枚の感光性転写シートをカラーフィルタ設置対象面に載せて着色感光性樹脂層を転写し、これをパターン状に露光して画素層を形成し、次いでその画素層を覆うようにして更に、他の色の感光性転写シートを重ねて着色感光性樹脂層を転写し、これをパターン状に露光して最初の画素層と着色の異なる画素層を形成する工程を繰り返し行なう方法が提案され、近年ではかかる方法の利用が増えている。この方法による場合、高い均質性と高精度の膜厚均一性を有する着色感光性樹脂層で構成された画素層を形成することができる。
【0005】
上記のいずれの方法でも、カラーフィルタを構成する着色画素の作製には、画素形成用のパターン状に切り抜かれたフォトマスクを用い、その開口部分を通過させて感光性樹脂層を露光し、その露光部分を硬化させ、次いで未露光部（未硬化部）を現像液で現像処理して除去する方法が利用される。
【0006】
しかしながら、従来の転写材料の場合、感光性樹脂層は、光重合開始剤、光重合性モノマー、アクリル系重合バインダー、光重合禁止剤、顔料等を含んでラジカル重合系に構成されており、このような感光性樹脂層を有する面を露光すると、感光性樹脂層の深さ方向（厚み方向）で深さに伴なう光の減衰により反応率が異なり、層表面から離れたガラス等の基板側、具体的には基板と感光性樹脂層との界面付近では著しく反応率が低下してほとんど重合硬化しないため、現像処理した際に細線画像にサイドエッチが入りやすく、細線ができない、あるいは現像ラチチュードが狭いという問題があった。
特に、遮光膜（ブラックマトリクスなど）の用途では高い遮光性能が要求されるが、黒濃度が高くなるほど層厚に伴なう光の減衰は大きくなり、サイドエッチの発生や現像ラチチュードの低下はより顕著となる。
【0007】
かかる問題に対して、バインダー、光酸発生剤、及び光酸発生剤の作用により架橋する架橋剤（メラミン系樹脂など）等を含む感光性樹脂組成物が提案されている（例えば、特許文献１参照）。これは、光を受けて光酸発生剤から生成する酸（$I \rightarrow I^- + H^+$）の触媒作用によって酸反応性分子（架橋剤）から架橋体を生成して重合硬化するものである（ＰＡＧ；Photo Acid Generator）。
【0008】
この場合、感光性樹脂層の黒濃度が高いときには、やはり露光時に発生する酸の発生量は層表面付近で多く、層表面から離れた基板との界面付近では少なくなるため、さらに加熱処理を施すことによって酸の拡散を促進し、層表面から厚み方向に向かって架橋反応が促され、基板との界面近傍に至るまで感光性樹脂層の重合硬化を良好に行なうことができる。
【特許文献1】

特開２００２－３５１０７５号公報
【発明の開示】
【発明が解決しようとする課題】
【0009】
しかしながら、酸の触媒作用を利用したＰＡＧでは、加熱処理により拡散（加熱拡散）する酸（H^+）は、層の厚み方向のみならず、あらゆる方向（厚み方向である縦方向に対する横方向など）に拡散していくため、高濃度で高硬度の膜が得られても細線を形成するのは難しい。また、現像ラチチュードの点でも不充分である。結果的に、ボケた画像しか得られない。特に高い黒濃度の膜に構成しようとする場合には、感光性樹脂層はある程度の厚みが必要であり、充分な重合硬化性を得るには露光後の加熱に長時間を要するばかりか、加熱時間が長くなると層内に酸が広く拡散し、ボケの程度も悪化してしまう。
【0010】
本発明は、上記に鑑みなされたものであり、薄膜で高い黒濃度が得られ、遮光性に優れると共に、短時間での加熱硬化性に優れ、高解像度の像を形成することができる遮光膜用感光性樹脂組成物、薄膜で黒濃度が高く、遮光性及び短時間での加熱硬化性に優れた膜の形成を可能とする転写材料及びその製造方法、並びに、薄膜で黒濃度が高く遮光性能に優れた遮光膜を高解像度に形成し得、加熱拡散による硬化をより短い時間で行ない得る遮光膜の作製方法を提供することを目的とし、該目的を達成することを課題とする。
【課題を解決するための手段】
【0011】
本発明は、前記ＰＡＧを利用して高解像度で高濃度の黒パターンを形成する場合において、高濃度化と光酸発生剤から生成する酸の層厚方向以外の方向への拡散の抑制には、金属系粒子が有効であるとの知見を得、かかる知見に基づいて達成されたものである。
前記課題を達成するための具体的手段は以下の通りである。
【0012】
＜１＞　バインダー樹脂と、光を吸収して酸を発生する光酸発生剤と、前記光酸発生剤の作用により架橋する架橋剤と、金属粒子及び／又は金属化合物粒子とを含有することを特徴とする遮光膜用感光性樹脂組成物である。
＜２＞　顔料を更に含む前記＜１＞に記載の遮光膜用感光性樹脂組成物である。
【0013】
＜３＞　前記顔料がカーボンブラック又は黒鉛である前記＜２＞に記載の遮光膜用感光性樹脂組成物である。
＜４＞　膜厚１．０μｍの遮光膜を形成した際の光学濃度が４．０以上である前記＜１＞～＜３＞のいずれか１つに記載の遮光膜用感光性樹脂組成物である。
＜５＞　表示装置を構成する遮光膜の形成に用いられる前記＜１＞～＜４＞のいずれか１つに記載の遮光膜用感光性樹脂組成物である。
【0014】
＜６＞　仮支持体上に、少なくとも１層の、バインダー樹脂と、光を吸収して酸を発生する光酸発生剤と、前記光酸発生剤の作用により架橋する架橋剤と、金属粒子及び／又は金属化合物粒子とを含有する感光性樹脂層を有することを特徴とする転写材料である。
＜７＞　遮光膜の形成に用いられる前記＜６＞に記載の転写材料である。
＜８＞　表示装置を構成する遮光膜の形成に用いられる前記＜６＞又は＜７＞に記載の転写材料である。
【0015】
＜９＞　基板上に、前記＜１＞～＜５＞のいずれか１つに記載の遮光膜用感光性樹脂組成物を塗布し、乾燥させて感光性樹脂層を形成する工程と、形成された前記感光性樹脂層をパターン状に露光する工程と、形成された前記感光性樹脂層を加熱する工程と、少なくとも前記露光後の前記感光性樹脂層を現像して未露光部を除去する工程とを含むことを特徴とする遮光膜の作製方法である。
＜１０＞　前記塗布は、スリット状ノズルを有する塗布装置を用いて行なう前記＜９＞

に記載の遮光膜の作製方法である。
【0016】
＜１１＞　前記＜６＞～＜８＞のいずれか１つに記載の転写材料を用いて、仮支持体上の少なくとも１層の感光性樹脂層を基板に転写する工程と、転写された前記感光性樹脂層をパターン状に露光する工程と、転写された前記感光性樹脂層を加熱する工程と、少なくとも前記露光後の前記感光性樹脂層を現像して未露光部を除去する工程とを含むことを特徴とする遮光膜の作製方法である。
＜１２＞　前記＜６＞～＜８＞のいずれか１つに記載の転写材料の製造方法であって、仮支持体上に、スリット状ノズルを有する塗布装置を用いた塗布により感光性樹脂層を塗設することを特徴とする転写材料の製造方法である。
【発明の効果】
【0017】
本発明によれば、薄膜で高い黒濃度が得られ、遮光性に優れると共に、短時間での加熱硬化性に優れ、高解像度の像を形成することができる遮光膜用感光性樹脂組成物、薄膜で黒濃度が高く、遮光性及び短時間での加熱硬化性に優れた膜の形成を可能とする転写材料及びその製造方法、並びに、薄膜で黒濃度が高く遮光性能に優れた遮光膜を高解像度に形成し得、加熱拡散による硬化をより短い時間で行ない得る遮光膜の作製方法を提供することができる。
【発明を実施するための最良の形態】
【0018】
以下、本発明の遮光膜用感光性樹脂組成物、遮光膜の作製方法、並びに転写材料及びその製造方法について詳細に説明する。
【0019】
＜遮光膜用感光性樹脂組成物＞
本発明の遮光膜用感光性樹脂組成物は、バインダー樹脂と、光酸発生剤と、架橋剤と、金属粒子及び／又は金属化合物粒子とを少なくとも含んでなり、必要に応じて、着色剤や界面活性剤等のその他の成分を用いて構成することができる。
【0020】
本発明の遮光膜用感光性樹脂組成物においては、光を受けて光酸発生剤から生成する酸（H^+）の触媒作用によって後述のバインダー樹脂と架橋剤（例えば酸架橋性のメチロール化メラミン樹脂）との間で架橋反応を起こさせると共に、さらに加熱処理を加えることにより酸の拡散を促進させることで、層の表面から基板界面付近の層深部に向かって架橋反応が促され、表面から厚み方向の層深部に至る感光性樹脂層が充分に重合硬化する（ＰＡＧ）。そのため、黒濃度が高濃度であっても基板界面まで充分に架橋反応させ得ると共に、現像の許容度が広く、一方で成分の混合、塗布、乾燥工程での架橋反応は抑えられ、露光部と未露光部の現像液に対する溶解性のコントラストを充分に大きくとることができる。したがって、薄膜で高濃度、高精細な遮光膜（ブラックマトリックスなど）を得ることができる。
さらに、本発明の遮光膜用感光性樹脂組成物は、後述するように、金属粒子や金属化合物粒子を黒色剤として含み、薄膜で高濃度が得られるので、前記ＰＡＧによる場合に、酸の拡散は薄い層中で起こることから加熱拡散による硬化を短時間で行なえると共にパターンの線太りも生じ難い。したがって、薄膜で高濃度を有しかつ高解像度の遮光膜（ブラックマトリックスなど）が得られる。
【0021】
－バインダー樹脂－
本発明の遮光膜用感光性樹脂組成物は、バインダー樹脂の少なくとも１種を含有する。このバインダー樹脂は、パターン露光で後述の光酸発生剤から生成する酸の触媒作用で後述の架橋剤と架橋体（ポリマー）をつくって硬化させるものである。
【0022】
バインダー樹脂としては、例えば、（メタ）アクリル系樹脂、ポリエステル樹脂、ビニ

ル系樹脂、ノボラック樹脂（フェノールノボラック樹脂、クレゾールノボラック樹脂等）、ポリヒドロキシスチレン等の公知のバインダー樹脂の中から適宜選択することができる。

【0023】

本発明では特に、（メタ）アクリル系のモノマーの共重合によって得られるビニル系共重合体が好ましく、メタクリル酸アルキルエステル、アクリル酸アルキルエステル、又はカルボキシル基含有モノマーを構成単位として含む共重合体がより好ましい。柔軟さを付与する点で、（メタ）アクリル系が好ましく、弱アルカリ現像適正の付与の点で、カルボキシル基を含有することが好ましい。

なお、（メタ）アクリルは、アクリル又はメタクリルの両方をとり得ることを示す。以下同様である。

【0024】

上記の中でも、特にメタクリル酸メチル及びベンジルメタクリレートの少なくとも１つを含む共重合体が好ましい。メタクリル酸メチル及びベンジルメタクリレートの少なくとも１つを含む共重合体には、メタクリル酸メチルを含む共重合体、ベンジルメタクリレートを含む共重合体、メタクリル酸メチル及びベンジルメタクリレートを含む共重合体等が挙げられる。

【0025】

前記メタクリル酸メチルを含む共重合体には、メタクリル酸／メタクリル酸メチル共重合体（共重合比：１４～１７．６モル％／８２．４～８６モル％、重量平均分子量２０，０００～１４０，０００）、メタクリル酸／メタクリル酸メチル／エチルアクリレート共重合体（共重合比：５～１０モル％／７０～６０モル％／２５～３０モル％、重量平均分子量２０，０００～１４０，０００）等が挙げられる。

【0026】

前記ベンジルメタクリレートを含む共重合体には、メタクリル酸／ベンジルメタクリレート共重合体（共重合比：２５～３７モル％／７５～６３モル％、重量平均分子量２０，０００～１５０，０００）、メタクリル酸／ベンジルメタクリレート／スチレン共重合体（共重合比：２０モル％／１７．８モル％／６２．２モル％、重量平均分子量２０，０００～１４０，０００）等が挙げられる。

【0027】

前記メタクリル酸メチル及びベンジルメタクリレートを含む共重合体には、メタクリル酸／メタクリル酸メチル／ベンジルメタクリレート共重合体（共重合比：１４．６～２７．２モル％／７９．１～３２．７モル％／１６．３～４０モル％、重量平均分子量２０，０００～１５０，０００）、メタクリル酸／メタクリル酸メチル／ベンジルメタクリレート／２－エチルヘキシルアクリレート共重合体（共重合比：１０～１５モル％／７０～６５モル％／１０モル％／１０モル％、重量平均分子量２０，０００～１５０，０００）等が挙げられる。

【0028】

従来より市販のネガ型レジスト組成物によく使用されているクレゾールノボラック樹脂やポリヒドロキシスチレン及びその誘導体は露光後、ベーク後に着色してしまうが、このような露光後、ベーク処理時での着色が少なく、光透過率が低下しない点で、上記したメタクリル酸／ベンジルメタクリレート共重合体、メタクリル酸／メタクリル酸メチル／ベンジルメタクリレート共重合体等が特に好ましい。

【0029】

前記バインダー樹脂の遮光膜用感光性樹脂組成物における含有量としては、該組成物の全固形分に対して、１０～９０質量％が好ましく、２０～７０質量％がより好ましい。

【0030】

－光酸発生剤－

本発明の遮光膜用感光性樹脂組成物は、光酸発生剤の少なくとも１種を含有する。この光酸発生剤は、パターン状に露光した際に酸（H^+）を発生し、架橋反応による重合硬化

を促進させるものである。

【0031】

光の照射により酸を発生する光酸発生剤には、有機ハロゲン化合物、オニウム塩、スルホン酸エステル等が挙げられる。これらの中では、有機ハロゲン化合物が好ましく、特にハロメチル化トリアジン化合物、ハロメチル化オキサジアゾール化合物が好ましい。

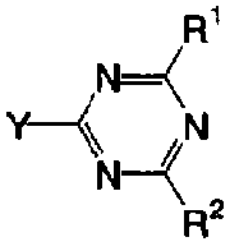
【0032】

前記ハロメチル化トリアジン化合物としては、下記一般式（１）で表される化合物が挙げられる。但し、本発明においては、これらに限定されるものではない。

【0033】

【化1】

(1)



【0034】

前記一般式（１）中、R^1及びR^2は、各々独立にハロメチル基を表し、Ｙは炭素数５以上の有機基を表す。

【0035】

前記ハロメチル基としては、例えば、トリクロロメチル基、トリブロモメチル基、ジクロロメチル基、ジブロモメチル基などが挙げられ、前記炭素数５以上の有機基としては、例えば、置換基を有していてもよい、フェニル基、ナフチル基、スチリル基、スチリルフェニル基、フリルビニル基、四級化アミノエチルアミノ基などが挙げられる。

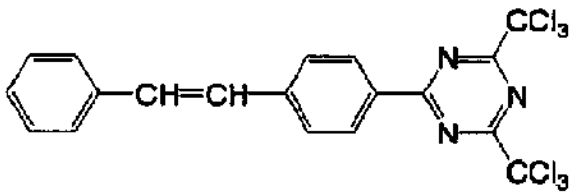
【0036】

以下、ハロメチル化トリアジン化合物の具体例〔例示化合物（２）～（２３）〕を列挙する。

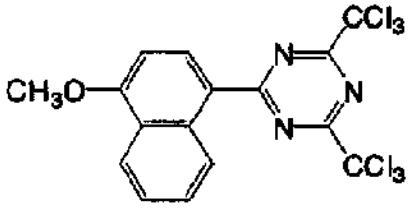
【0037】

【化2】

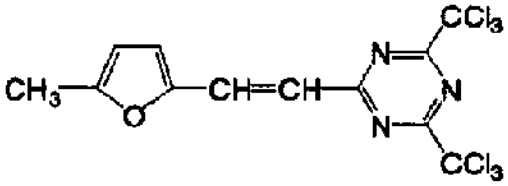
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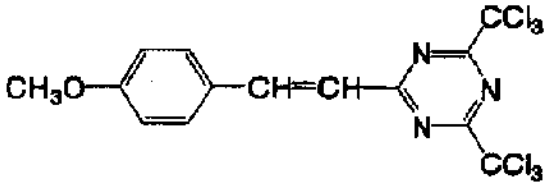
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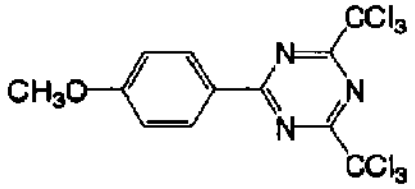
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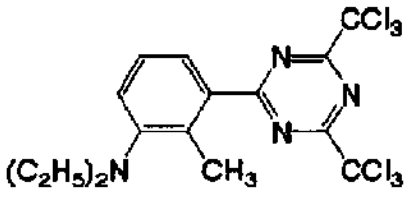
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(6)



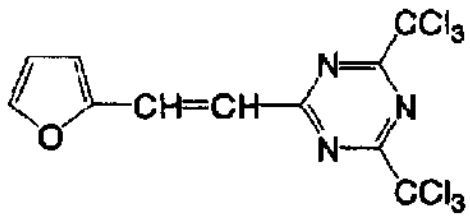
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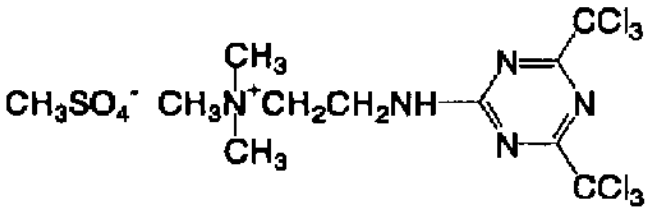
【0038】

【化3】

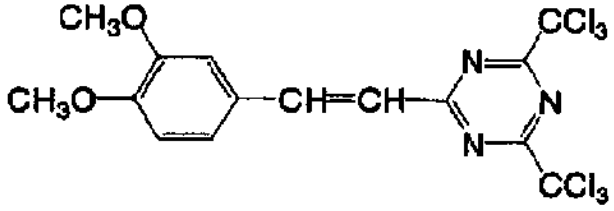
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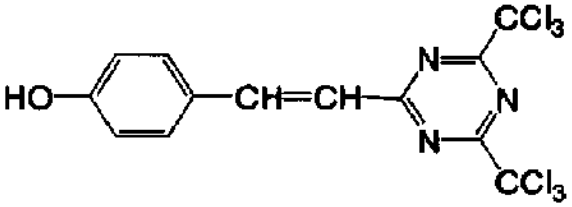
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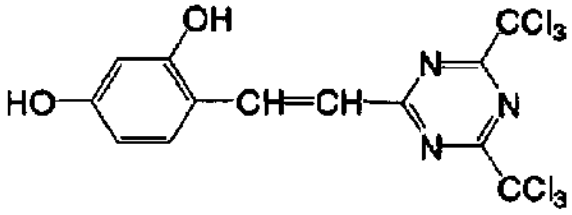
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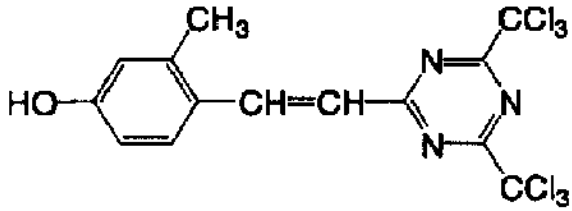
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(12)



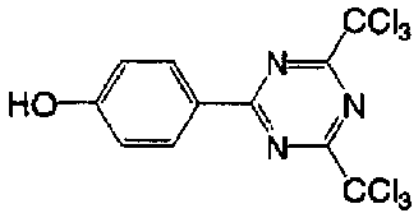
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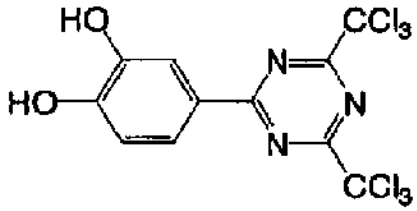
【0039】

【化4】

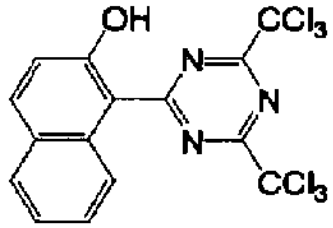
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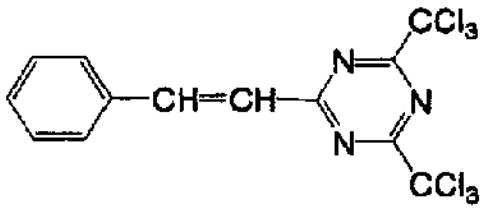
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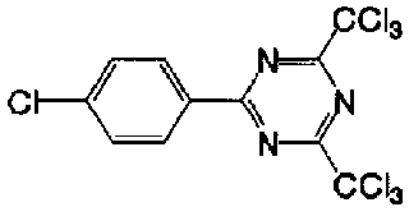
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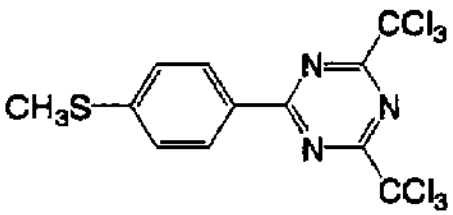
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(18)



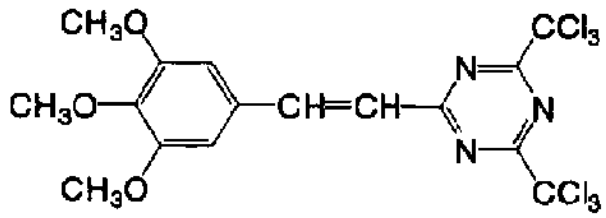
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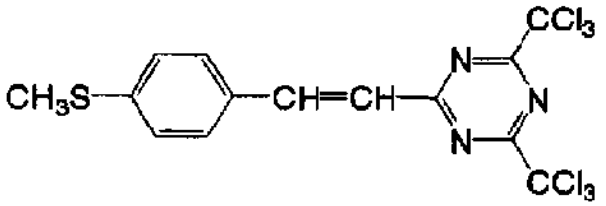
【0040】

【化5】

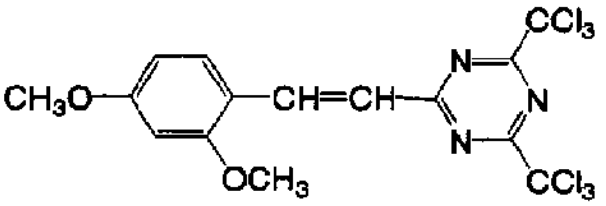
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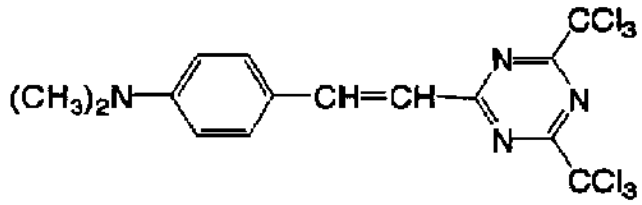
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(22)

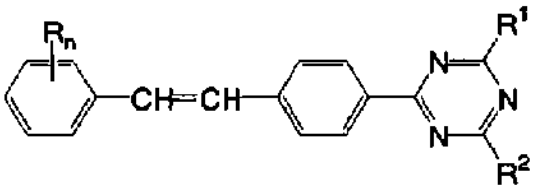


(23)



【0041】
前記一般式（１）で表されるハロメチル化トリアジン化合物の中でも、好ましいものは下記一般式（２４）、（２５）、又は（２６）で表される化合物である。
【0042】
【化6】

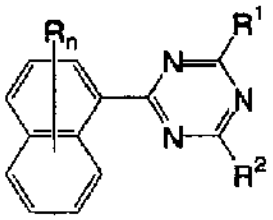
(24)



【0043】
前記一般式（２４）中のR^1及びR^2は、各々独立にハロメチル基を表し、Ｒは炭素数１～４のアルキル基又は炭素数１～４のアルコキシ基を表す。ｎは、Ｒの個数を表すものであり、０～３の整数である。
【0044】

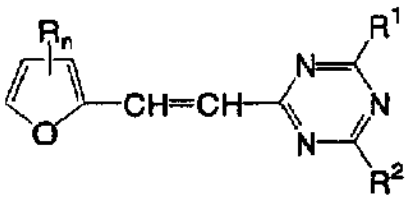
【化7】

(25)



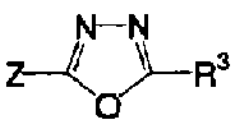
【0045】
前記一般式（２５）中のR¹及びR²は、各々独立にハロメチル基を表し、Rは炭素数１～４のアルキル基又は炭素数１～４のアルコキシ基を表す。nは、Rの個数を表すものであり、０～３の整数である。
【0046】
【化8】

(26)



【0047】
前記一般式（２６）中のR¹及びR²は、各々独立にハロメチル基を表し、Rは炭素数１～４のアルキル基を表す。nは、Rの個数を表すものであり、０～１の整数である。
【0048】
上記の一般式（２４）～（２６）で表される化合物の中でも、好ましいものは各々の一般式において、R¹及びR²がトリクロロメチル基であって、Rが炭素数１～２のアルキル基であって、更に一般式（２４）及び（２５）ではnが0～２の整数、一般式（２６）では0～１の整数である化合物である。
【0049】
前記ハロメチル化オキサジアゾール化合物としては、下記一般式（２７）で表される化合物が挙げられる。
【0050】
【化9】

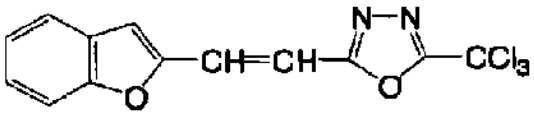
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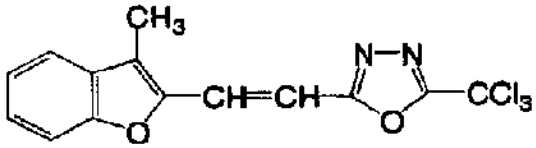
【0051】
前記一般式（２７）中、R³はハロメチル基を表し、Zは置換基を有していてもよいベンゾフリル基又はベンゾフリルビニル基を表す。
【0052】
以下、ハロメチル化オキサジアゾール化合物の具体例〔例示化合物（２８）～（４５）〕を列挙する。
【0053】

【化10】

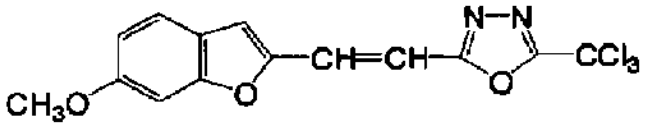
(28)



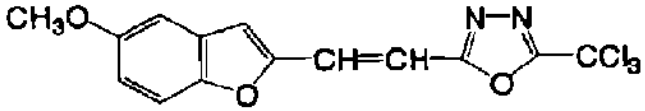
(29)



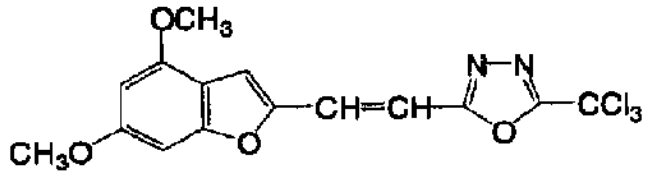
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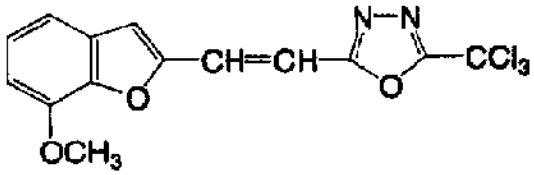
(31)



(32)



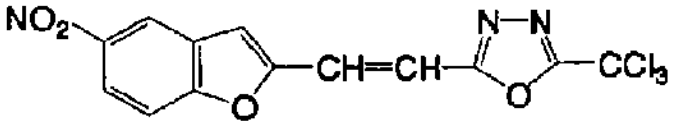
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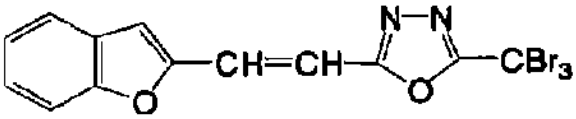
【0054】

【化11】

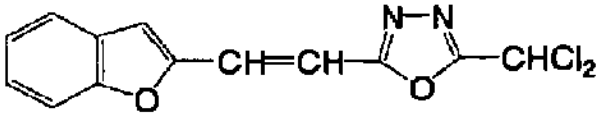
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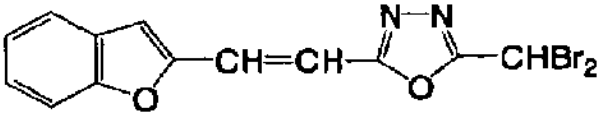
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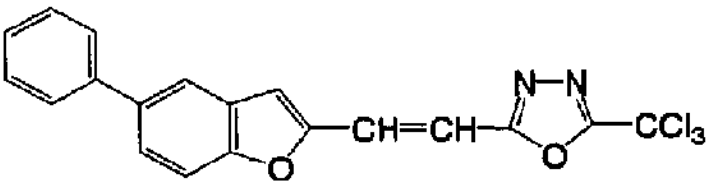
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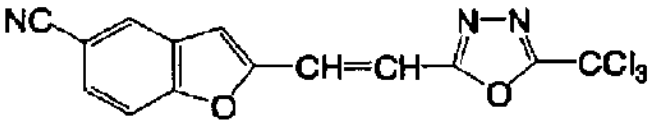
(37)



(38)



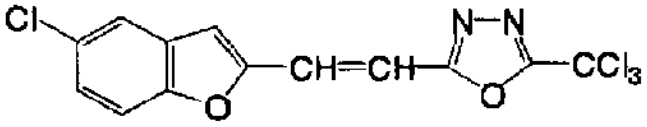
(39)



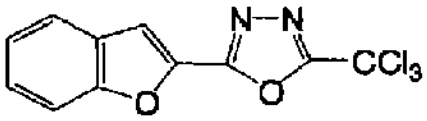
【0055】

【化12】

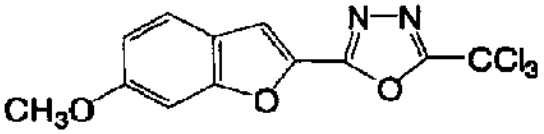
(40)



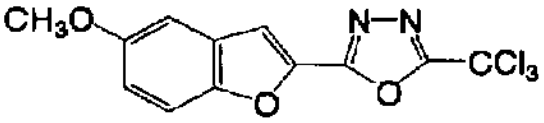
(41)



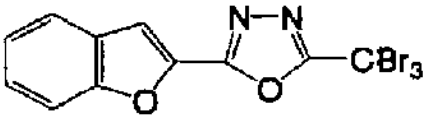
(42)



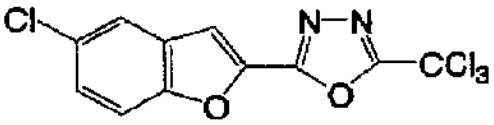
(43)



(44)



(45)



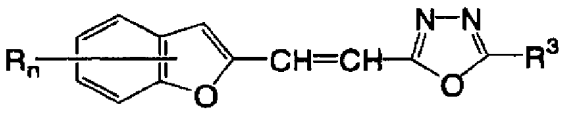
【0056】

前記一般式（２７）で表されるハロメチル化オキサジアゾール化合物の中でも、好ましいのは下記一般式（４６）で表される化合物である。

【0057】

【化13】

(46)



【0058】
前記一般式（４６）中のR^{3}はハロメチル基を表し、Ｒは炭素数１～４のアルキル基又は炭素数１～４のアルコキシ基を表す。ｎは、Ｒの個数を表すものであり、０～２の整数である。更に好ましいのは、R^{3}がトリクロロメチル基であって、Ｒが炭素数１～２のアルキル基又はアルコキシ基であって、ｎが０～１の整数である化合物である。
【0059】
光酸発生剤の遮光膜用感光性樹脂組成物中における含有量としては、該組成物の固形分に対して、０．０５～１５質量％、好ましくは５～１５質量％である。光酸発生剤の量が前記範囲であると、露光により充分な酸を発生してバインダー樹脂と後述の架橋剤との架橋反応が良好に行なえ、現像後の残膜率が高く、耐熱性、耐薬品性等を具えた画像を形成することができる。
【0060】
－架橋剤－
本発明の遮光膜用感光性樹脂組成物は、架橋剤の少なくとも１種を含有する。この架橋剤は、露光時に前記光酸発生剤から生成する酸の触媒作用により架橋反応を起こして硬化する作用を有する。すなわち、既述のバインダー樹脂との間で架橋反応して架橋体を形成し、露光部を硬化して画像化することができる。
【0061】
架橋剤としては、架橋性基を少なくとも１種含む置換基（以下、「架橋性置換基」と称する。）を有する化合物が挙げられる。
【0062】
前記架橋性置換基の具体例としては、下記（ｉ）～（vi）が挙げられる。
（ｉ）ヒドロキシアルキル基、アルコキシアルキル基、アセトキシアルキル基等のヒドロキシアルキル基又はその誘導体；
（ii）ホルミル基、カルボキシアルキル基等のカルボニル基又はその誘導体；
（iii）ジメチルアミノメチル基、ジエチルアミノメチル基、ジメチロールアミノメチル基、ジエチロールアミノメチル基、モルホリノメチル基等の含窒素基含有置換基；
（iv）グリシジルエーテル基、グリシジルエステル基、グリシジルアミノ基等のグリシジル基含有置換基；
（ｖ）ベンジルオキシメチル基、ベンゾイロキシメチル基等のアリルオキシアルキル基やアラルキルオキシアルキル基等の芳香族誘導体；
（vi）ビニル基、イソプロペニル基等の重合性多重結合含有置換基；
等を挙げることができる。
上記のうち、本発明における架橋剤の架橋性置換基としては、ヒドロキシアルキル基、アルコキシアルキル基等が好ましく、特にアルコキシメチル基が好ましい。
【0063】
前記架橋性置換基を有する架橋剤としては、例えば、
（ｉ）メチロール基含有メラミン化合物、メチロール基含有ベンゾグアナミン化合物、メチロール基含有ウレア化合物、メチロール基含有グリコールウリル化合物、メチロール基含有フェノール化合物等のメチロール基含有化合物；
（ii）アルコキシアルキル基含有メラミン化合物、アルコキシアルキル基含有ベンゾグアナミン化合物、アルコキシアルキル基含有ウレア化合物、アルコキシアルキル基含有グリ

コールウリル化合物、アルコキシアルキル基含有フェノール化合物等のアルコキシアルキル基含有化合物；
（iii）カルボキシメチル基含有メラミン化合物、カルボキシメチル基含有ベンゾグアナミン化合物、カルボキシメチル基含有ウレア化合物、カルボキシメチル基含有グリコールウリル化合物、カルボキシメチル基含有フェノール化合物等のカルボキシメチル基含有化合物；
（iv）ビスフェノールA系エポキシ化合物、ビスフェノールF系エポキシ化合物、ビスフェノールS系エポキシ化合物、ノボラック樹脂系エポキシ化合物、レゾール樹脂系エポキシ化合物、ポリ（ヒドロキシスチレン）系エポキシ化合物等のエポキシ化合物；等を挙げることができる。

【0064】

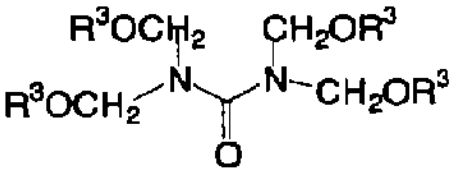
上記の架橋剤の中でも、アルコキシメチル化ウレア化合物又はその樹脂、アルコキシメチル化グリコールウリル化合物又はその樹脂が好ましい。

特に好ましい架橋剤として、下記一般式（４７）で表されるアルコキシメチル化ウレア化合物、又は下記一般式（４８）で表されるアルコキシメチル化グリコールウリル化合物を挙げることができる。

【0065】

【化14】

(47)



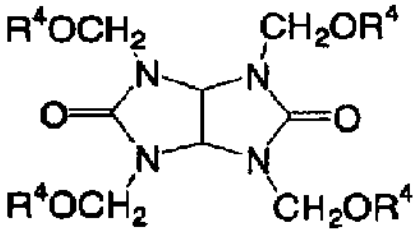
【0066】

前記一般式（４７）中のR^3は、炭素数１～４のアルキル基を表す。

【0067】

【化15】

(48)



【0068】

前記一般式（４７）中のR^4は、炭素数１～４のアルキル基を表す。

【0069】

前記一般式（４７）、（４８）において、R^3又はR^4で表されるアルキル基としては、メチル基、エチル基、プロピル基、ブチル基等を挙げることができる。

【0070】

上記のアルコキシメチル化ウレア化合物、アルコキシメチル化グリコールウリル化合物は、例えば、尿素化合物やグリコールウリル化合物とホルマリンとを縮合反応させてメチロール基を導入した後、更にメチルアルコール、エチルアルコール、プロピルアルコール、ブチルアルコール等の低級アルコール類でエーテル化し、次いで反応液を冷却して析出

する化合物又はその樹脂を回収することで得られる。また、ＣＹＭＥＬ（商品名；三井サイアナミッド社製）、ニカラッド（三和ケミカル社製）等の市販品として入手することもできる。

【0071】

架橋剤としては、メラミン、ベンゾグアナミン、グリコールウリル、又は尿素にホルムアルデヒドを作用させた化合物、又はそれらのアルキル変性化合物、エポキシ化合物、レゾール化合物等が有効であり、その具体例には以下のものが挙げられる。

【0072】

具体的な例として、三井サイアナミド社製のサイメル（登録商標）３００、同３０１、同３０３、同３５０、同７３６、同７３８、同３７０、同７７１、同３２５、同３２７、同７０３、同７０１、同２６６、同２６７、同２８５、同２３２、同２３５、同２３８、同１１４１、同２７２、同２５４、同２０２、同１１５６、同１１５８は、メラミンにホルムアルデヒドを作用させた化合物又はそのアルキル変性物の例である。また、サイメル（登録商標）１１２３、同１１２５、同１１２８は、ベンゾグアナミンにホルムアルデヒドを作用させた化合物又はそのアルキル変性物の例である。また、サイメル（登録商標）１１７０、同１１７１、同１１７４、同１１７２は、グリコールウリルにホルムアルデヒドを作用させた化合物又はそのアルキル変性物の例である。更に、尿素にホルムアルデヒドを作用させた化合物又はそのアルキル変性物の例として、三井サイアナミド社製のＵＦＲ（登録商標）６５、同３００を挙げることができる。

【0073】

また、前記エポキシ化合物の例としては、ノボラックエポキシ樹脂（東都化成社製のＹＤＰＮ－６３８、同７０１、同７０２、同７０３、同７０４等）、アミンエポキシ樹脂（東都化成社製のＹＨ－４３４等）、ビスフェノールＡエポキシ樹脂、ソルビトール（ポリ）グリシジルエーテル、（ポリ）グリセロール（ポリ）グリシジルエーテル、ペンタエリスリトール（ポリ）グリシジルエーテル、トリグリシジルトリスヒドロキシエチルイソシアヌレート、アリルグリシジルエーテル、エチルヘキシルグリシジルエーテル、フェニルグリシジルエーテル、フェノールグリシジルエーテル、ラウリルアルコールグリシジルエーテル、アジピン酸グリシジルエーテル、フタル酸グリシジルエーテル、ジブロモフェニルグリシジルエーテル、ジブロモネオペンチルグリコールジグリシジルエーテル、グリシジルフタルイミド、（ポリ）エチレングリコールグリシジルエーテル、ポリプロピレングリコールジグリシジルエーテル、ネオペンチルグリコールジグリシジルエーテル、グリセリンポリグリシジルエーテル、トリメチロールプロパンポリグリシジルエーテル、ブチルグリシジルエーテル、等を挙げることができる。

【0074】

特に好ましい化合物として、分子中に$-N(CH_2OR)_2$基を有する化合物（Ｒは水素原子又はアルキル基を表す。）が挙げられる。詳しくは、尿素あるいはメラミンにホルムアルデヒドを作用させた化合物又はそのアルキル変性物が特に好ましい。

【0075】

また、前記レゾール化合物の例としては、群栄化学社製のＰＰ－３０００ｓ、ＰＰ－３０００Ａ、ＲＰ－２９７８、ＳＰ－１９７４、ＳＰ－１９７５、ＳＰ－１９７６、ＳＰ－１９７７、ＲＰ－３９７３等が挙げられる。

【0076】

架橋剤の遮光膜用感光性樹脂組成物中における含有量としては、前記バインダー樹脂の量に対して、５～７０質量％が好ましく、１０～４０質量％がより好ましい。

【0077】

－金属粒子及び／又は金属化合物粒子－

本発明の遮光膜用感光性樹脂組成物は、金属粒子及び金属化合物粒子よりなる群より選択される少なくとも１種（以下、「本発明に係る金属粒子」ともいう。）を含有する。遮光用の黒色材料として本発明に係る金属粒子を選択的に用いるので、高い黒濃度が得られ、薄い形態で高度の遮光性が得られると共に、薄い形態に構成されるので、ＰＡＧによる

場合の加熱時の酸の拡散に伴なうパターンの線太りを防止することができ、加熱拡散による硬化時間の短縮も図れる。
　なお、本発明に係る金属粒子には、後述の複合粒子、コア・シェル複合粒子が含まれる。
【0078】
〈金属粒子〉
　金属粒子としては、長周期周期表（ＩＵＰＡＣ　１９９１）の例えば、元素周期表の第３周期、第４周期、第５周期、及び第６周期からなる群から選ばれる金属を主成分として含むことが好ましく、また、第２族、第８族、第９族、第１０族、第１１族、第１２族、第１３族、及び第１４族からなる群から選ばれる金属を主成分として含むことが好ましい。これらの金属のうち、本発明に係る金属粒子としては第４周期、第５周期、又は第６周期の金属であって、第２族、第１０族、第１１族、第１２族、又は第１４族の金属がさらに好ましい。
【0079】
　本発明における金属粒子は、球状、立方体を含む正側面体状などのほか、縦、横、高さの比の少なくとも１つが異なる形状異方性の形（例えば、形状異方性を有する球状、あんパン状、ジャガイモ状、棒状（針状、円柱形、直方体等の角柱形、ラグビーボール型等）、平板状（鱗片状、楕円板状、板状）、繊維状、金平糖状、コイル状等）のいずれであってもよい。
　また、後述する金属化合物粒子、複合粒子、コアシエル複合粒子の場合も同様である。
【0080】
　前記金属粒子として好ましい例は、銅、銀、金、白金、パラジウム、ニッケル、錫、コバルト、ロジウム、イリジウム、鉄、ルテニウム、カルシウム、オスミウム、マンガン、モリブデン、タングステン、ニオブ、タンテル、チタン、ビスマス、アンチモン、鉛、又はこれらの合金、から選ばれる少なくとも一種を挙げることができる。さらに好ましい金属は、銅、銀、金、白金、パラジウム、ニッケル、錫、コバルト、ロジウム、イリジウム又はこれらの合金、より好ましい金属は、銅、銀、金、白金、錫又はこれらの合金から選ばれる少なくとも一種である。これらのうち、金、銀、銅、錫が好ましく、とりわけ銀が好ましい。銀としては、棒状をした銀やコロイド銀も好適である。金属粒子の製造には、前記金属を２種以上組合せてもよく、合金として用いることも可能である。

　また、金属化合物と金属との複合微粒子として用いることもできる。
【0081】
〈金属化合物粒子〉
　金属化合物粒子は、前記金属と金属以外の他の元素との化合物の粒子であり、「金属と他の元素との化合物」としては、金属の酸化物、硫化物、硫酸塩、炭酸塩などがある。このうち、硫化物が色調や微粒子形成のしやすさから特に好ましい。これら金属化合物の例としては、酸化銅(II)、硫化鉄、硫化銀、硫化銅(II)、チタンブラックなどが挙げられるが、硫化銀は色調、微粒子形成のしやすさや安定性の観点から特に好ましい。
【0082】
〈複合粒子〉
　本発明においては、前記金属粒子と前記金属化合物粒子とを用い、これらが結合して１つの粒子になった複合粒子も用いることができる。複合粒子の形状には特に制限はない。例えば、粒子の内部と表面で組成の異なるもの、２種類の粒子が合一したもの等を挙げることができる。また、金属化合物と金属は、それぞれ１種でも２種以上であってもよい。金属化合物と金属との複合粒子の具体例としては、銀と硫化銀との複合粒子、銀と酸化銅(II)との複合粒子などがある。
【0083】
〈コア・シェル複合粒子〉
　本発明においては、コア・シェル型の複合粒子（コア・シェル複合粒子）も用いること

ができる。コア・シェル型の複合粒子とは、コア材料の表面をシェル材料でコートしたものである。

【0084】

前記コア材料をコートするシェル材料としては、例えば、Ｓｉ、Ｇｅ、ＡｌＳｂ、ＩｎＰ、Ｇａ、Ａｓ、ＧａＰ、ＺｎＳ、ＺｎＳｅ、ＺｎＴｅ、ＣｄＳ、ＣｄＳｅ、ＣｄＴｅ、ＰｂＳ、ＰｂＳｅ、ＰｂＴｅ、Ｓｅ、Ｔｅ、ＣｕＣｌ、ＣｕＢｒ、ＣｕＩ、ＴｌＣｌ、ＴｌＢｒ、ＴｌＩ、及びこれらの固溶体、又はこれらを９０ｍｏｌ％以上含む固溶体から選ばれる少なくとも一種の半導体、あるいは銅、銀、金、白金、パラジウム、ニッケル、錫、コバルト、ロジウム、イリジウム、鉄、ルテニウム、オスミウム、マンガン、モリブデン、タングステン、ニオブ、タンテル、チタン、ビスマス、アンチモン、鉛、又はこれらの合金から選ばれる少なくとも一種の金属を用いることができる。

【0085】

好ましいシェル材料としては、銅、銀、金、パラジウム、ニッケル、錫、ビスマス、アンモチン、鉛、又はこれらの合金から選ばれる少なくとも１種を挙げることができる。

前記シェル材料は、反射率を低下させる目的で屈折率の調整剤としても好適に用いられる。

【0086】

また、コア・シェル複合粒子を構成するコア材料としては、例えば、銅、銀、金、パラジウム、又はこれらの合金から選ばれる少なくとも一種の金属を用いることができる。

【0087】

コアシェル構造を有するコア・シェル複合粒子の作製方法には、特に制限はなく、代表的な方法として以下の方法が挙げられる。

（１）公知の方法で作製した金属粒子の表面に、酸化、硫化などにより、金属化合物のシェルを形成する方法であり、例えば、金属粒子を水などの分散媒に分散させて、硫化ナトリウムや硫化アンモニウムなどの硫化物を添加する方法がある。この方法により粒子の表面が硫化されてコアシェル複合粒子が形成される。

この場合、用いる金属粒子は、気相法、液相法などの公知の方法で作製することができる。金属粒子の作製方法については、例えば「超微粒子の技術と応用における最新動向II」（住べテクノリサーチ（株）、２００２年発行）に記載されている。

（２）金属粒子を作製する過程で連続的に表面に金属化合物のシェルを形成する方法であり、例えば、金属塩溶液に還元剤を添加して、金属イオンの一部を還元して金属粒子を作製し、次いで硫化物を添加して、作製した金属粒子の周囲に金属硫化物を形成する方法がある。

【0088】

～金属粒子の作製～

金属粒子は市販のものを用いることができる他、金属イオンの化学的還元法、無電解メッキ法、金属の蒸発法等により調製することが可能である。

形状異方性の形に構成された粒子の場合、特に棒状の銀粒子（銀ロッド）の場合は、球形銀粒子を種粒子としてその後、銀塩をさらに添加し、CTAB（セチルトリメチルアンモニウムブロマイド）等の界面活性剤存在下、アスコルビン酸など比較的還元力の弱い還元剤を用いることにより銀ロッドやワイヤーが得られる。これは、Ａｄｖ．Ｍａｔｅｒ．２００２，１４，８０－８２に記載がある。また、同様の記載がＭａｔｅｒ．Ｃｈｅｍ．Ｐｈｙｓ．２００４，８４，１９７－２０４、Ａｄｖ．Ｆｕｎｃｔ．Ｍａｔｅｒ．２００４，１４，１８３－１８９にもなされている。また、電気分解を用いた方法として、Ｍａｔｅｒ．Ｌｅｔｔ．２００１，４９，９１－９５に記載の方法、マイクロ波を照射することにより銀ロッドを生成する方法として、Ｊ．Ｍａｔｅｒ．Ｒｅｓ．２００４，１９，４６９－４７３に記載の方法がある。逆ミセルと超音波の併用した例として、Ｊ．Ｐｈｙｓ．Ｃｈｅｍ．Ｂ，２００３，１０７，３６７９－３６８３が挙げられる。

金に関しても同様に、Ｊ．Ｐｈｙｓ．Ｃｈｅｍ．Ｂ　１９９９，１０３、３０７３－３０７７及びＬａｎｇｍｕｉｒ１９９９，１５，７０１－７０９、Ｊ．Ａｍ．Ｃｈｅｍ．Ｓ

ｏｃ．２００２，１２４，１４３１６－１４３１７に記載されている。
ロッド状の粒子の形成方法は上記の方法を改良（添加量調整、ＰＨ制御）しても調製できる。
【0089】
～粒子径～
本発明に係る金属粒子（複合粒子、コア・シェル複合粒子を含む。）が真球もしくは球形である場合、その粒子径としては、２～６００ｎｍが好ましく、１０～３００ｎｍがより好ましい。
【0090】
また、形状異方性の粒子である場合、粒子径は三軸径とする。すなわち、１個の金属粒子がちょうど（きっちりと）収まる箱（直方体）を考え、この箱の長さＬ、幅ｂ、高さ又は厚みｔをもってこの金属粒子の寸法と定義する仕方である。金属粒子を箱に収める場合、いくつかの仕方があるが、本発明では以下の方法を採用する。
まず、平面上に金属粒子を、最も重心が低くて安定に静止するように置く。次に、平面に対し直角に立てた２枚の平行な平板により金属粒子を挟み、その平板間隔が最も短くなる位置の平板間隔を「幅ｂ」とする。次に、前記幅ｂを決する２枚の平板に対し直角で前記平面に対しても直角の２枚の平行な平板により金属粒子を挟み、この２枚の平板間隔を「長さＬ」とする。最後に金属粒子の最も高い位置に接触するように天板を前記平面に平行に載せ、天板と平面との間隔を高さ又は厚みｔとする（この方法により平面、各２枚の平板及び天板によって画される直方体が形成される。）。また、金属粒子の三軸径ｂ、Ｌ及びｔの最も長いものに該当する軸を「長軸」と定義し、長軸方向における長さを「長軸長」と、また、長軸に平行な光を金属粒子に照射して得られる投影面積を真円換算した場合の直径を「短軸長」と定義する。
【0091】
～アスペクト比～
本発明に係る金属粒子（複合粒子、コア・シェル複合粒子を含む。）のアスペクト比とは、金属粒子又は金属化合物粒子の、上記のように定義した長軸長を短軸長で割った値を意味し、１００個の金属粒子について測定した値の平均値と定義する。なお、粒子の投影面積は電子顕微鏡写真上での面積を測定し、撮影倍率を補正することにより得られる。
【0092】
粒子のアスペクト比（粒子の長軸長／粒子の短軸長の比）は、2以上であることが好ましく、4以上であることがより好ましい。アスペクト比の上限は、１００程度である。この範囲では、黒色粒子が得られ易く、大きすぎて可視光域の吸収が小さくなることもなく、高解像化に効果的である。さらに好ましくは、４～８０であり、最も好ましくは１０～６０である。粒子の短軸長は、４～５０ｎｍが好ましく、１５～５０ｎｍがより好ましく、１５～３０ｎｍが最も好ましい。粒子の長軸長（最大長）は、１０～１０００ｎｍが好ましく、１００～１０００ｎｍがより好ましく、４００～８００ｎｍが更に好ましく、可視光波長より短いことが最も好ましい。
【0093】
また、粒子径と形状の異なる粒子を混合することによって、吸収スペクトル制御でき、色相を無彩色に近づけることもできる。
【0094】
～粒度分布～
粒度分布は、長軸長の平均粒径の、粒度分布幅Ｄ９０／Ｄ１０が2以上２０未満であることが好ましい。ここで、Ｄ９０は粒子の９０％が見出される最大直径であり、Ｄ１０は粒子の１０％が見出される最大直径である。粒度分布は、色調の観点から、より好ましくは2以上１５以下であり、さらに好ましくは4以上１０以下である。粒度分布が前記範囲であると、粗大粒子による散乱による濁りが生じるのを防止できる。
【0095】
「金属粒子及び／又は金属化合物粒子」の遮光膜用感光性樹脂組成物中における含有量

としては、用いる粒子の種類や性状により異なるが、２～４０体積％が好ましく、５～３０体積％がより好ましい。

【0096】

着色剤

本発明の遮光膜用感光性樹脂組成物は、前記金属粒子及び／又は金属化合物粒子と共に、さらに顔料及び／又は染料を併用して好適に構成することができる。

【0097】

前記顔料としては、例えば、硫酸バリウム、硫酸鉛、酸化チタン、黄色鉛、ベンガラ、酸化クロム、カーボンブラック等の無機顔料、アントラキノン系顔料、ペリレン系顔料、ジスアゾ顔料、フタロシアニン顔料、イソインドリン顔料、ジオキサジン顔料、キナクリドン顔料、ペリノン系顔料、トリフェニルメタン系顔料、チオインジゴ顔料等の有機顔料などが挙げられる。これらは、１種単独で又は２種以上を混合して用いることができる。

前記顔料の中でも、アントラキノン系顔料、フタロシアニン顔料、ジオキサジン顔料、カーボンブラックが特に好ましい。

【0098】

以下、具体的にカラーインデックス（Ｃ．Ｉ．）ナンバーで示す。

Ｃ．Ｉ．赤：９，９７，１２２，１２３，１４９，１６８，１７７，１８０，１９２，２１５，２１６，２１７，２２０，２２３，２２４，２２６，２２７，２２８，２４０；

Ｃ．Ｉ．青：１５、１５：６、２２、６０、６４；

Ｃ．Ｉ．緑：７，３６；

Ｃ．Ｉ．黒：７；

Ｃ．Ｉ．黄色：１２，２０，２４，８６，９３，１０９，１１０，１１７，１２５，１３７，１３８，１４７，１４８，１５３，１５４，１６６，１６８；

Ｃ．Ｉ．オレンジ：３６，４３，５１，５５，５９，６１；

Ｃ．Ｉ．バイオレット：１９，２３，２９，３０，３７，４０，５０；

Ｃ．Ｉ．茶：２３，２５，２６；

【0099】

顔料の平均粒径は０．００５～３μｍの範囲にあるのが好ましい。より好ましくは０．０１～１μｍである。この範囲の粒径にするには、ボールミル、サンドミル、ビーズミル、３本ロール、ペイントシェーカー、超音波などの分散処理が有効である。

【0100】

前記染料としては、例えば、クリスタルバイオレット、メチルバイオレット、エチルバイオレット、オイルブルー＃６０３、ビクトリアピュアーブルーＢＯＨ、マラカイトグリーン、ダイモンドグリーン等が挙げられる。

上記以外に、黒鉛も好適に用いることができる。

【0101】

なお、用途等に応じて、前記顔料及び染料は併用してもよく、また、顔料及び／又は染料は必ずしも含有する必要はない。

本発明においては、カーボンブラック及び／又は黒鉛を既述の本発明に係る金属粒子と共に併用する態様が最も好ましい。

【0102】

上記において、カーボンブラック等の炭素系の黒色顔料は、窒素ガス吸着法で測定した比表面積が５０m^2／ｇ以下のものが好ましい。中でも、５０～１０m^2／ｇの範囲内が好ましく、更に好ましくは３０～１５m^2／ｇの範囲内である。比表面積が前記範囲内であると、良好な遮光性能が得られると共に、分散時の分散安定性が良好である。

【0103】

着色剤（特にカーボンブラック、黒鉛）を併用する場合、着色剤の量としては、本発明に係る金属粒子の総量に対して、１０～９０体積％が好ましく、より好ましくは２０～５０体積％である。本発明に係る金属粒子と共に着色剤を併用することで、形成された遮光膜の反射率等をコントロールするのに有効であり、特に着色剤の量を前記範囲内とすると

、薄膜で高い遮光性を有すると同時に、光リークがなく表面の平坦性に優れた遮光膜を形成するのに効果的である。また、基板単独でも、また両面から偏光板で挟んでこの２枚の偏光板の偏光軸を直交したときにも光漏れがなく高い遮光性が得られ、高性能のカラーフィルタを得ることができ、高画質画像の表示が可能な液晶表示素子の製造に寄与する。また、工業的に有利な電着法によるカラーフィルタの製造において、遮光膜を背面露光法で形成する場合にも充分な増膜性、遮光性を得ることができる。

【0104】

－その他の成分－

本発明の遮光膜用感光性樹脂組成物には、種々の目的や用途に応じて、各種添加剤を含有することができる。添加剤としては、例えば、界面活性剤、密着促進剤、可塑剤等が挙げられる。

【0105】

前記界面活性剤は、遮光膜用感光性樹脂組成物を塗布液として用いる場合の塗布性、得られる塗膜の平滑性を向上させる目的で用いることができ、具体例として、ＢＭ－１０００（ＢＭ Ｃｈｅｍｉｅ社製）、メガファックスＦ１４２Ｄ、同Ｆ１７２、同Ｆ１７３、同Ｆ１８３、同F１７６ＰＦ、同Ｆ１７７ＰＦ（いずれも大日本インキ化学工業（株）製）、フロラードＦＣ－１３５、同ＦＣ－１７０Ｃ、フロラードＦＣ－４３０、同ＦＣ－４３１（いずれも住友スリーエム（株）製）、サーフロンＳ－１１２、同Ｓ－１１３、同Ｓ－１３１、同Ｓ－１４１、同Ｓ－１４５（いずれも旭硝子（株）製）、ＳＨ－２８ＰＡ、ＳＨ－１９０、ＳＨ－１９３、ＳＺ－６０３２、ＳＦ－８４２８、ＤＣ－５７、ＤＣ－１９０（いずれも東レ・シリコーン（株）製）の商品名で市販されている、フッ素系又はシリコン系界面活性剤が挙げられる。

【0106】

界面活性剤を含有する場合の含有量としては、遮光膜用感光性樹脂組成物の全固形分に対して、０．０５～１０質量％が好ましい。この範囲で含有すると、特に基板へのパターン密着性の点で有効である。更には、０．０８～５質量％の範囲が好ましく、０．１～３質量％の範囲が特に好ましい。

【0107】

本発明の遮光膜用感光性樹脂組成物は、例えばアセトン、メチルエチルケトン、メチルブチルケトン等のケトン、各種エーテル、エステルなどの有機溶剤を用いて塗布液として調製することができる。この塗布液は、塗布により被塗物となる仮支持体（シート等）や液晶表示素子などの表面に感光性樹脂層を形成するために好適に用いることができる（以下、この塗布液を「感光性樹脂層用塗布液」ということがある。）。この感光性樹脂層の厚みには特に制限はなく、適宜選択することができるが、０．２～１．３μｍが好適であり、０．３～０．８μｍがより好適である。この範囲の薄膜に構成しても高い黒濃度が得られる。

【0108】

すなわち、本発明の遮光膜用感光性樹脂組成物は、上記のような塗布による塗膜など、膜厚１．０μｍの遮光膜を形成した際に該遮光膜の光学濃度が４．０以上となるように構成された態様が好適である。カラーフィルタを構成する遮光膜（ブラックマトリクスなど）をはじめプルーフなどの印刷材料や、ＰＤＰ（Plasma Display Panel）用の隔壁材料、インクジェットインク、レジストインクなど、高度の遮光性能と薄膜形成性とが要求される用途においては、薄膜にしつつ高い黒濃度が得られることが重要であり、かかる場合に本発明の遮光膜用感光性樹脂組成物を好適に用いることができる。本発明の遮光膜用感光性樹脂組成物は、液晶表示装置等を構成するカラーフィルタの遮光膜（ブラックマトリクスなど）の形成に特に好適であり、ブラックマトリクスの形成に最適である。

【0109】

本発明の遮光膜用感光性樹脂組成物は、上記した塗布液の塗布による方法以外に、下記方法を適用して遮光膜を形成するようにすることもできる。

～インクジェット法～

インクジェット法を利用して、本発明の遮光膜用感光性樹脂組成物を吐出して遮光膜を形成することができる。これは、コストダウンの点で好ましい。このインクジェット法としては、エネルギー発生素子として電気熱変換体を用いたバブルジェット（登録商標）タイプ、あるいは圧電素子を用いたピエゾジェットタイプ等が使用可能であり、着色面積及び着色パターンは任意に設定することができる。インクジェット法には、インクが充分に拡散しにくい傾向があり、白抜けを生じて色ムラやコントラスト低下を招来する原因となりやすいが、この場合には有機溶剤に顔料を組成物（インク）全体の質量に対して少なくとも１０質量%以上の濃度で分散させたものに調製することが好ましい。詳細については、特開２００４－３２５７３６号公報の記載を参照できる。

【0110】

また、遮光膜用感光性樹脂組成物を吐出した際の濡れ広がりを制御し、濃度均一性に優れた遮光膜を作製するには、用いる溶剤種としてはインクジェット印刷における適性の表面張力が３５ｍＮ／ｍ以下で、かつ沸点が１３０℃以上のものが好ましい。表面張力が３５ｍＮ／ｍ以下であると吐出時のドット形状の安定性が良好であり、沸点が１３０℃以上であるとノズル近傍での乾燥性が抑えられ、ノズル詰まり等の吐出不良を回避することができる。濡れ広がりを制御することにより、着色画素を形成した際の混色、遮光膜中の白抜け等の欠陥のない、均一な高濃度で、膜形状が鮮明でエッヂのシャープな遮光膜が得られる。

【0111】

さらに、特開２００２－３７２６１５号公報に記載されているような、インキが瞬時に硬化し、顔料の分散安定性の確保や基材との密着性の確保も併せて向上させる手段を適用することによって、遮光膜を作製する際の生産性を向上させることも可能である。

【0112】

～印刷法～

印刷法を利用して、遮光膜を短時間に作製するようにすることができる。印刷法として、版胴と圧胴との間に透明基材を通して該透明基材に遮光パターンを印刷形成するにあたり、前記版胴は前記遮光パターンに対応する凸版の版面を備え、前記版面を構成する凸版部に、光膜用感光性樹脂組成物（転写インキ）を備えた転写シートから、前記凸版部に相対して遮光パターンとした凸版を備えた凸版体により遮光パターンで転写インキを転写して、前記版胴の版面に転写インキを遮光パターンに設け、遮光パターンに設けられた前記転写インキを、版胴の版面から前記透明基板に転写する方法がある。版胴の版面は撥インキ性を備えていることが良好である。版面における転写開始位置と転写終了位置とに粘着剤を塗布することが良好である。転写インキが版胴の版面で遮光パターンに設けられ、この転写インキを一度に透明基材に転写するため、印刷による遮光膜の作製に要する時間が短縮されると共に、透明基材に形成される遮光膜を形成する転写インキの見当ズレがなく、転写シートを用いた印刷手法により適正な遮光膜が得られる。そして、版胴の版面における凸版部の凸版が撥インキ性を備えれば、版面から透明基材への転写インキの転写が良好になると共に、版面の洗浄も容易になる。

【0113】

前記印刷方法のほか、版胴と圧胴との間に透明基材を通して該透明基材に遮光パターンを印刷形成するにあたり、前記版胴は前記遮光パターンに対応する凸版の版面を備え、前記版面を構成するセルに遮光膜用感光性樹脂組成物（黒インキ）をインキジェット供給手段にて充填し、前記版胴の版面に黒インキを遮光パターンにて設け、これを乾燥させた後、版胴の版面から前記透明基板に転写する印刷方法がある。この場合、版胴は凹版の版面を備え、版面を構成するセルに遮光膜用感光性樹脂組成物（黒インキ）をインキジェット供給手段にて充填し、前記版面に黒インキを遮光パターンにて設け、これを乾燥させた後、版胴の版面から前記透明基板に転写する構成とするので、工程時間が更に大幅に短縮されると共に見当ズレがなく、セル中でインキ形状が安定し、セル形状に透明基材側に転写できることから、遮光膜を精度よく形成できる。

【0114】

＜転写材料及びその製造方法＞
～転写材料～
本発明の転写材料は、仮支持体上に少なくとも１層の感光性樹脂層を設けて構成したものであり、更に必要に応じて中間層や熱可塑性樹脂層、保護フィルム等の他の層を設けて構成することもできる。
【0115】
前記感光性樹脂層は、バインダー樹脂と、光を吸収して酸を発生する光酸発生剤と、前記光酸発生剤の作用により架橋する架橋剤と、金属粒子及び／又は金属化合物粒子とを含んでなる層であり、これら各成分を含む態様で公知の方法により形成することができ、既述の本発明の遮光膜用感光性樹脂組成物を用いて（好ましくは塗布液の塗布により仮支持体（シート等）の表面に塗設することにより）最も好適に形成することができる。バインダー樹脂等の各成分の詳細については既述の通りである。
【0116】
本発明の転写材料を構成する感光性樹脂層の層厚は、用途や目的に応じて選択することができるが、ブラックマトリクス等の遮光膜などの薄膜が要求される用途では薄い程よく、０．２～１．３μｍの範囲とするのが好ましく、０．３～０．８μｍの範囲とするのがより好ましい。この感光性樹脂層は被転写体に転写されて黒色画像（例えばブラックマトリクス）を構成するものであり、前記範囲の薄い層に構成しても高い黒濃度、遮光性を満足することができる。
【0117】
次に、本発明の転写材料を構成する仮支持体並びに他の層について述べる。
－仮支持体－
仮支持体には、プラスチックスフィルムが好ましい。例えば、ポリエチレンテレフタレート、ポリエチレンナフタレート、セルローストリアセテート、セルロースアセテートブチレート、セルロースアセテートプロピオネート、ポリカーボネート、ポリスチレン、ポリエチレン等のフィルムを挙げることができる。中でも、ポリエチレンテレフタレートフィルムが好ましく、特に２軸延伸、熱固定されたポリエチレンテレフタレートフィルムが、安定性、強靭さなどの点から特に好ましい。
【0118】
仮支持体の厚さには特に制限はないが、５～２００μｍの範囲が一般的であり、特に１０～１５０μの範囲が取扱い易さ、汎用性などの点で好ましい。
【0119】
－熱可塑性樹脂層－
熱可塑性樹脂層は、アルカリ可溶性の熱可塑性樹脂層であって、この層を構成する樹脂は、実質的な軟化点が８０℃以下であることが好ましい。
軟化点が８０℃以下のアルカリ可溶性の熱可塑性樹脂としては、エチレンとアクリル酸エステル共重合体とのケン化物、スチレンと（メタ）アクリル酸エステル共重合体とのケン化物、ビニルトルエンと（メタ）アクリル酸エステル共重合体とのケン化物、ポリ（メタ）アクリル酸エステル、及び（メタ）アクリル酸ブチルと酢酸ビニル等の（メタ）アクリル酸エステル共重合体などとのケン化物、（メタ）アクリル酸とエチレン不飽和基含有モノマーとの共重合体から選ばれる少なくとも１つであることが好ましい。さらに、「プラスチック性能便覧」（日本プラスチック工業連盟、全日本プラスチック成形工業連合会編著、工業調査会、１９６８年１０月２５日発行）による、軟化点が約８０℃以下の有機高分子のうちアルカリ水溶液に可溶なものを使用することができる。
【0120】
また、軟化点が８０℃以上の有機高分子物質を、その有機高分子物質中に該有機高分子物質と相溶性のある各種可塑剤を添加することで実質的な軟化点を８０℃以下に下げて用いることも可能である。また、仮支持体との接着力を調節するために、有機高分子物質中に実質的な軟化点が８０℃を越えない範囲で各種のポリマーや過冷却物質、密着改良剤あるいは界面活性剤、離型剤等を加えることも可能である。

【0121】
特に特開平７－２８２３２号公報に記載の、（Ａ）重量平均分子量５万～５０万かつガラス転移温度Ｔｇ＝０～１４０℃のアルカリ可溶な熱可塑性樹脂と、（Ｂ）重量平均分子量３千～３万かつＴｇ＝３０～１７０℃のアルカリ可溶な熱可塑性樹脂とを、（Ａ）／（Ｂ）比＝５／９５～９５／５［質量比］の範囲で混合したものが好適である。前記（Ａ）の特に好ましい例は、メタクリル酸／２－エチルヘキシルメタクリレート／ベンジルメタクリレート／メチルメタクリレート共重合体（共重合モル比：５／１０／３０／５５、質量平均分子量：１０万、Ｔｇ：約７０℃）である。前記（Ｂ）の特に好ましい例は、スチレン／アクリル酸共重合体（共重合組成モル比：６５／３５、質量平均分子量：１万、Ｔｇ：約１００℃）である。また、前記（Ａ）／（Ｂ）比の特に好ましい範囲は、３０／７０～６０／４０である。
【0122】
前記可塑剤の好ましい具体例としては、ポリプロピレングリコール、ポリエチレングリコール、ジオクチルフタレート、ジヘプチルフタレート、ジブチルフタレート、トリクレジルホスフェート、クレジルジフェニルホスフェート、ビフェニルジフェニルホスフェート、ポリエチレングリコールモノ（メタ）アクリレート、ポリエチレングリコールジ（メタ）アクリレート、ポリプロピレングリコールモノ（メタ）アクリレート、ポリプロピレングリコールジ（メタ）アクリレート、エポキシ樹脂とポリエチレングリコールモノ（メタ）アクリレートとの付加反応生成物、有機ジイソシアナートとポリエチレングリコールモノ（メタ）アクリレートとの付加反応生成物、有機ジイソシアナートとポリプロピレングリコールモノ（メタ）アクリレートとの付加反応生成物、ビスフェノールＡ－ポリエチレンオキシド付加物のジ（メタ）アクリレートを挙げることができる。
【0123】
可塑剤の量は、熱可塑性樹脂層を構成する熱可塑性樹脂の量（好ましくは前記熱可塑性樹脂（Ａ）及び（Ｂ）の合計量）に対して、好ましくは０～２００％［質量比］であり、より好ましくは２０～１００％［質量比］である。
また、可塑剤の特に好ましい例は、ビスフェノールＡ、１モルにエチレンオキシドを合計で１０モル付加し、両末端アルコールをメタクリルエステル化した化合物である。可塑剤の特に好ましい添加量は、熱可塑性樹脂の量（好ましくは前記熱可塑性樹脂（Ａ）及び（Ｂ）の合計量）の３０～６０質量％である。
【0124】
熱可塑性樹脂層は、上記の各成分を溶剤に均一に溶解してなる塗布液の塗布、乾燥により塗設できる。前記溶剤の好ましい例は、メトキシプロピレングリコールアセテート、２－ヒドロキシプロピン酸エチル、３－メトキシプロピオン酸メチル、３－エトキシプロピオン酸エチル、乳酸メチル、乳酸エチル、シクロヘキサノン、メチルイソブチルケトン等の高沸点溶剤及びこれら高沸点溶剤の混合物、メチルエチルケトンやアセトン等の低沸点溶剤及びこれら低沸点溶剤の混合物である。高沸点溶剤と低沸点溶剤との質量組成比は、塗布乾燥速度が良好で乾燥ムラ防止の点で、１／９９～９９／１から好適に選択できる。好ましくは高沸点溶剤／低沸点溶剤の質量比が９０／１０～１０／９０の範囲であり、８０／２０～２０／８０の範囲が最も好ましい。
【0125】
熱可塑性樹脂層は、仮支持体上に、一般に知られた塗布方法、例えばディップコート法、エアーナイフコート法、カーテンコート法、ワイヤーバーコート法、グラビアコート法、エクストルージョンコート法、スリットコート法などにより、前記熱可塑性樹脂等を含む塗布液（以下、「熱可塑性樹脂層用塗布液」ということがある。）を塗布し、乾燥させることにより形成することができる。
【0126】
熱可塑性樹脂層の層厚は、感光性樹脂層を転写する際に被転写面に存在する０．５μｍ以上の凹凸を完全に吸収する観点から、１μｍ以上が好ましい。また、上限については、塗布製造適性の制限から約１００μｍ以下が一般的であり、約５０μｍ以下が好ましく、

約２０μｍ以下が特に好ましい。

【0127】

中間層

中間層（分離層ともいう。）としては、熱可塑性樹脂層と感光性樹脂層との間で互いに成分が混じり合うのを防止する目的で設けられる。

中間層は、水またはアルカリ水溶液に分散または溶解し、中間層と接して設けられる熱可塑性樹脂層用塗布液中の有機溶剤に不溶もしくは難溶であればよく、公知のもので構成できる。

例えば、特開昭４６－２１２１７公報や特公昭５６－４０８２４公報に記載のポリビニルエーテル／無水マレイン酸重合体、カルボキシアルキルセルロースの水溶性塩、水溶性セルロースエーテル類、カルボキシアルキル澱粉の塩、水塩、ポリビニルアルコール、ポリビニルピロリドン、各種のポリアクリルアミド類、各種の水溶性ポリアミド、ポリアクリル酸の水溶性塩、ゼラチン、エチレンオキサイド重合体、各種の澱粉およびその類似物からなる群の水溶性塩、スチレン／マレイン酸の共重合体、及びマレイネート樹脂、並びにこれら２種以上を組合せたものを挙げることができる。

【0128】

特に、１）水溶性ポリビニルブチラール単独や、２）ポリビニルアルコールとポリビニルピロリドンとの組合せが好ましい。

ポリビニルアルコールは、鹸化率が８０モル%以上であるものが好ましく、ポリビニルピロリドンの含有率は中間層固形分の１～７５質量%が一般的であり、１～６０質量%が好ましく、特に好ましくは１０～５０質量%である。この範囲とすると、感光性樹脂層との接着性が充分に得られ、感光性樹脂層用塗布液に対する耐溶剤性を損なうこともない。

【0129】

中間層の層厚は、約０．１～５μｍが好適であり、特に０．５～２μｍが好ましい。この範囲とすると、感光性樹脂層用塗布液に対する耐溶剤性を有し、塗布速度の任意選択と乾燥を制限なく行なうことができる。

【0130】

中間層用塗布液の溶媒は水単独か、水と混和性の有機溶剤と水との混合物から選ばれる。下層となる熱可塑性樹脂層との接着性を高めるために、熱可塑性樹脂層を若干膨潤させ得るように選択するのが好ましい。好ましい溶媒の例としては水／メタノール、水／エタノール、水／プロパノール、水／メトキシエタノール、水／メトキシプロパノール、水／アセトンなどを挙げることができる。水とこれらの有機溶剤の組成比は質量比で９９／１～５０／５０の範囲から選択できる。この範囲とすることで、溶剤の添加効果が得られると共に、水溶性樹脂の充分な溶解性を得ることができる。

【0131】

中間層は、熱可塑性樹脂層上に一般に知られた塗布方法、例えば、ディップコート法、エアーナイフコート法、カーテンコート法、ワイヤーバーコート法、グラビアコート法、エクストルージョンコート法、スリットコート法などにより、中間層用塗布液を塗布することによって形成することができる。

【0132】

－保護フィルム－

保護フィルムは、転写材料を保存する際の、感光性樹脂層への不純物の付着や損傷を避けるために設けることが好ましく、薄い保護フィルムが好ましい。

保護フィルムは、仮支持体と同一か又は類似の材料からなるものでもよいが、使用時には感光性樹脂層から容易に分離可能なもので構成する必要がある。

【0133】

また、保護フィルムは、感光性樹脂層と接触する面の平滑性が重要であり、約０．０１μｍ程度の突起があると感光性樹脂層への損傷となるので問題になりやすい。そのため、保護フィルムとする材料としては、例えば、シリコン紙、ポリオレフィンもしくはポリテトラフルオルエチレンシートが好ましい。特に好ましくは、ポリプロピレンフィルムまた

はポリエチレンフィルムである。

【0134】

保護フィルムの厚みは、１～１００μｍが好適であり、３～５０μｍが好ましく、特に好ましくは５～２０μｍである。この範囲であると、強度を維持でき、感光性樹脂層との間の接着性も維持できる。

【0135】

～転写材料の製造方法～

本発明の転写材料は、例えば、好ましくは帯電防止層と接着性表面とを有する仮支持体の前記接着性表面上に、熱可塑性樹脂層用塗布液を塗布し、乾燥させることにより、アルカリ可溶性の熱可塑性樹脂層を塗設し、その後この熱可塑性樹脂層上に該層を溶解しないがある程度膨潤させる溶媒を用いてなる中間層用塗布液を塗布し、乾燥させて中間層を積層した後、更に該中間層を溶解しない溶剤を用いて調製された感光性樹脂層用塗布液を塗布し、乾燥させて感光性樹脂層を積層する。その後、保護フィルムを感光性樹脂層上にラミネートして作製できる。

上記の各層を形成するための塗布液は、既述のように一般に知られた塗布方法により塗布することができる。

【0136】

上記のうち、本発明の転写材料の製造方法は、既述の本発明の転写材料を作製するものであって、仮支持体上への感光性樹脂層の塗設をスリット状ノズルを有する塗布装置を用いた塗布により行なうことを特徴するものである。すなわち、感光性樹脂層は、液を吐出する部分にスリット状の穴を有するスリット状ノズルを用いて行なうスリットコート法により形成される。スリット状ノズルを用いることによって、より均一厚の層形成が可能である。

【0137】

具体的には、特開２００４－８９８５１号公報、特開２００４－１７０４３号公報、特開２００３－１７００９８号公報、特開２００３－１６４７８７号公報、特開２００３－１０７６７号公報、特開２００２－７９１６３号公報、特開２００１－３１０１４７号公報等に記載のスリット状ノズル、及びスリットコーターが好適に用いられる。

【0138】

上記による以外に、仮支持体上に該仮支持体側から順に熱可塑性樹脂層及び中間層を設けた第１シートと、保護フィルム上に感光性樹脂層を設けた第２シートとを用意し、第１シートの中間層表面と感光性樹脂層の表面とが接するように貼り合せることによって作製することもできる。また更に、仮支持体上に熱可塑性樹脂層を設けた第１シートと、保護フィルム上に該保護フィルム側から順に感光性樹脂層及び中間層を設けた第２シートとを用意し、第１シートの中間層表面と第２シートの熱可塑性樹脂層の表面とが接するように貼り合せることによって作製することもできる。

【0139】

本発明の転写材料は、既述したように、金属粒子及び／又は金属化合物粒子を含有して薄膜で高い黒濃度を有し、遮光性に優れた感光性樹脂層を設けてなるものであるため、高度の遮光性が要求される用途に好適であり、特にブラックマトリクスなどに代表される遮光膜の形成に好適である。

【0140】

＜遮光膜の作製方法＞

本発明の遮光膜の作製方法は、既述の本発明の遮光膜用感光性樹脂組成物を基板上に直に塗布する方法（塗布法）、又は一旦既述の本発明の遮光膜用感光性樹脂組成物を用いて構成された転写材料の感光性樹脂層を基板上に転写する方法（転写法）により遮光膜を作製するものである。

【0141】

本発明の遮光膜の作製方法により作製される遮光膜は、本発明の遮光膜用感光性樹脂組成物を用いてなるので、薄膜で黒濃度が高く遮光性に優れる。そのため、ブラックマトリ

クスなど薄膜が求められる用途に好適であり、その場合には、０．２～１．３μｍの範囲が好適であり、０．３～０．８μｍの範囲がより好適である。

【0142】

本発明の第１の遮光膜の作製方法は、塗布法によるものである。すなわち、基板上に、既述の本発明の遮光膜用感光性樹脂組成物を塗布し、乾燥させて感光性樹脂層を形成する工程（塗布工程）と、塗布工程で形成された感光性樹脂層をパターン状に露光する工程（パターン露光工程）と、塗布工程で形成された感光性樹脂層を加熱する工程（加熱工程）と、少なくとも露光後の感光性樹脂層を現像して未露光部を除去する工程（現像工程）とで構成したものである。

【0143】

また、本発明の第２の遮光膜の作製方法は、転写法によるものである。すなわち、既述の本発明の転写材料を用いて、仮支持体上の少なくとも１層の感光性樹脂層を基板に転写する工程（転写工程）と、転写工程で転写された感光性樹脂層をパターン状に露光する工程（パターン露光工程）と、転写工程で転写された感光性樹脂層を加熱する工程（加熱工程）と、少なくとも露光後の感光性樹脂層を現像して未露光部を除去する工程（現像工程）とで構成したものである。

転写法におけるパターン露光工程、加熱工程、及び現像工程は、前記塗布法の場合と同様にして行なえる。

塗布工程又は転写工程の後、パターン露光工程と加熱工程とはいずれが前工程であってもよいし、同時工程であってもよく、また、加熱工程と現像工程とはいずれが前工程であってもよいし、同時工程であってもよい。

【0144】

以下、各工程について説明する。

－塗布工程－

塗布法における塗布工程では、被塗物である基板上に、既述の本発明の遮光膜用感光性樹脂組成物を塗布し、乾燥させて感光性樹脂層を形成する。塗布には、一般に知られた塗布方法、例えば、ディップコート法、エアーナイフコート法、カーテンコート法、ワイヤーバーコート法、グラビアコート法、エクストルージョンコート法、スリットコート法などを適用することができる。

【0145】

中でも、液を吐出する部分にスリット状の穴を有するスリット状ノズルを用いて行なうスリットコート法が好ましく、スリット状ノズルを有する塗布装置（スリットコーター）を用いて好適に塗布することができる。

塗布厚は、最終的に得られる遮光膜の膜厚が前記範囲となる範囲で適宜選択すればよい。

【0146】

前記基板には、透明基板が好適であり、例えば、表面に酸化ケイ素皮膜を有するソーダガラス板、低膨張ガラス、ノンアルカリガラス、石英ガラス板等の公知のガラス板、あるいはプラスチックスフィルム等を挙げることができる。また、基板は、予めカップリング処理を施しておくことにより、本発明の組成物、又は本発明の転写材料の感光性樹脂層との間の密着を良好にすることができる。カップリング処理としては、特開２０００－３９０３３記載の方法が好適に用いられる。

【0147】

－転写工程－

転写法における転写工程では、既述の本発明の転写材料を用いて、仮支持体上に設けられている少なくとも１層の感光性樹脂層を基板に転写する。

【0148】

基板への感光性樹脂層の転写は、基板の被転写面（先行パターンや薄膜が既に形成されているときはその形成面）を洗浄後、転写材料から保護フィルムを剥離除去し、基板の洗浄面と転写材料の露出した感光性樹脂層の表面とを、ラミネーターのヒートローラーによ

り加熱加圧下で貼り合せて積層体とし、この積層体から仮支持体を剥離して基板上に転写する。ラミネーターは、市販のラミネーターを適宜選択することができる。

【0149】

転写時のヒートローラーの温度は、５０℃～１５０℃が好ましく、圧着時の線圧は、５Ｋｇ／ｃｍ～２５Ｋｇ／ｃｍが好ましい。また、ラミネート速度は、搬送速度で０．２～１ｍ／分が好ましい。

特に好ましい条件としては、加圧と共に加熱可能な加熱圧着ロールを用い、加熱圧着ロール温度１３０～１４０℃、圧着時の線圧１０～１５Ｋｇ／ｃｍ、搬送速度１～３ｍ／分である。

【0150】

－パターン露光工程－

パターン露光工程では、塗布工程又は転写工程で形成された感光性樹脂層をパターン状に露光する。本工程は、後述の加熱工程の前工程として行なってもよいし、加熱工程の後工程として行なってもよく、また、加熱工程と同時に行なうようにすることもできる。

【0151】

露光は、形成された感光性樹脂層に、所定のパターンのマスクを介して光を照射することによって行なえ、後述の現像工程を経た際に所望のパターンが得られるように潜像を形成する。すなわち、露光領域では、光酸発生剤から酸（Ｈ＋）が生成され、酸の触媒作用によりバインダー樹脂と架橋剤との間で架橋反応して架橋体を形成し、パターン状に重合硬化する。

【0152】

光源としては、例えば、ｇ線（波長４３６ｎｍ）、ｉ線（波長３６５ｎｍ）、超高圧水銀灯、キセノン灯、カーボンアーク灯、アルゴンレーザー等の公知の光源からの連続状及び／又は輝線状の紫外線、ＫｒＦエキシマレーザー等の遠紫外線、シンクロトロン放射線等のＸ線、電子線等の荷電粒子線などが挙げられる。中でも、ｇ線、ｉ線、及びこれらを含む３００～４４０ｎｍの波長領域の紫外線が好ましい。特開平６－５９１１９号公報に記載のように、４００ｎｍ以上の波長の光透過率が２％以下である光学フィルター等を併用してもよい。

【0153】

－加熱工程－

加熱工程では、前記パターン露光工程でのパターン露光後あるいはパターン露光時に、加熱（ベーク）処理を行なう。パターン露光時に発生した酸の存在下で架橋反応が開始後、更にパターン露光された露光領域を加熱することによって酸の拡散を促進し、感光性樹脂層の表面近傍から厚み方向に向かって架橋反応が促され、膜深部まで感光性樹脂層の重合硬化を良好に行なう。本発明においては、形成された感光性樹脂層は薄膜に構成されるため、酸の不要な拡散（例えば厚み方向である縦方向に対する横方向などへの拡散）が抑えられ、パターンの線太りを防止して高解像度の細線を得ることができる。

【0154】

本工程は、上記のパターン露光工程の前工程として行なうことができ、パターン露光工程の後工程として行なうこともでき、パターン露光工程と同時（パターン露光前から加熱することを含む。）に行なうようにすることもできる。また、本工程は、後述の現像工程の前工程として行なってもよいし、現像工程の後工程として行なってもよく、また、現像工程と同時に行なうようにすることもできる。なお、感光性樹脂層は、現像後には感光性を消失しているが、本明細書中では説明の簡易化の観点から感光性樹脂層と記載することがある。

【0155】

ベーク処理の条件は、光酸発生剤、架橋剤等により異なるが、８０～１４０℃、好ましくは１００～１２０℃にて１５秒～３分、好ましくは１５秒～１分が公的である。

【0156】

－現像工程－

現像工程では、露光後及び、前工程に加熱工程を設けた場合には加熱後の感光性樹脂層を現像処理して未露光部を現像除去し、パターンを顕在化させる。現像は、弱アルカリ現像液を用い、温度２６～４０℃、ｐＨ９～１１の条件下で行なうのが好ましい。

【0157】

この現像工程は、主に感光性樹脂層の現像によるパターン化を施すために設けられるが、転写法における転写工程により感光性樹脂層を形成した場合には、感光性樹脂層と共に熱可塑性樹脂層及び中間層が積層された状態にあるため、熱可塑性樹脂層及び中間層を除去するための第１のアルカリ現像と、感光性樹脂層の未露光部を除去するための第２のアルカリ現像とで構成されるのが望ましい。

【0158】

この場合、第１のアルカリ現像は、弱アルカリ現像液を用い、温度２６～４０℃、ｐＨ９～１１の条件下で行ない、第２のアルカリ現像は、上記同様に弱アルカリ現像液を用いて温度２６～４０℃、ｐＨ９～１１の条件下で行なうのが好ましい。

【0159】

感光性樹脂層現像用の現像液としては、アルカリ性物質の希薄水溶液を用いることができ、これに更に水と混和性の有機溶剤を少量添加したものを用いてもよい。

適当なアルカリ性物質としては、アルカリ金属水酸化物類（例、水酸化ナトリウム、水酸化カリウム）、アルカリ金属炭酸塩類（例、炭酸ナトリウム、炭酸カリウム）、アルカリ金属重炭酸塩類（例、炭酸水素ナトリウム、炭酸水素カリウム）、アルカリ金属ケイ酸塩類（例、ケイ酸ナトリウム、ケイ酸カリウム）、アルカリ金属メタケイ酸塩類（例、メタケイ酸ナトリウム、メタケイ酸カリウム）、アンモニア、エチルアミン、ｎ－プロピルアミン、ジエチルアミン、トリエチルアミン、メチルジエチルアミン、ジメチルエタノールアミン、トリエタノールアミン、ジエタノールアミン、モノエタノールアミン、モルホリン、テトラアルキルアンモンニウムヒドロキシド類（例えばテトラメチルアンモニウムヒドロキシド、テトラエチルアンモニウムヒドロキシド）、ピロール、ピペリジン、１，８－ジアザビシクロ〔５，４，０〕－７－ウンデセン、１，５－ジアザビシクロ〔４，３，０〕－５－ノナン、又は燐酸三ナトリウム等を挙げることができる。

【0160】

水と混和性の有機溶剤としては、例えば、メタノール、エタノール、２－プロパノール、１－プロパノール、ブタノール、ジアセトンアルコール、エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、エチレングリコールモノ－ｎ－ブチルエーテル、ベンジルアルコール、アセトン、メチルエチルケトン、シクロヘキサノン、ε－カプロラクトン、γ－ブチロラクトン、ジメチルホルムアミド、ジメチルアセトアミド、ヘキサメチルホスホルアミド、乳酸エチル、乳酸メチル、ε－カプロラクタム、Ｎ－メチルピロリドン等を好適に挙げることができる。水と混和性の有機溶剤の濃度は、０．１～３０質量％が一般的である。

【0161】

また、現像液には、さらに公知のアニオン型もしくはノニオン型の界面活性剤を添加することができる。界面活性剤の濃度は、０．０１～１０質量％が好ましい。現像液は、浴液として、あるいは噴霧液として用いることができ、現像方法については、液盛り法、ディッピング法、揺動浸漬法、スプレイ法等を利用することができる。

【0162】

本工程は、前記加熱工程の前工程として行なってもよいし、加熱工程の後工程として行なってもよく、また、加熱工程と同時に行なってもよい。

【0163】

既述のように、本発明の遮光膜用感光性樹脂組成物を用いることによって、薄膜で高濃度を有し、かつ高解像度の遮光膜を得ることができる。特に、表示装置を構成する液晶表示素子（特にカラーフィルタ）のブラックマトリクス（ここでいうブラックマトリクスは、画素間に配置される黒色部であり、ストライプ状や格子状にものなどがある。）を得るのに有用である。また、本発明の転写材料及び遮光膜の作製方法による場合も同様である

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【0164】

ブラックマトリックスは、液晶表示を行なう液晶セルに対して着色された各画素毎に電圧印加を行なう必要から、遮光性のみならず、電気絶縁性を兼ね備える必要がある。具体的には、ブラックマトリックスの体積抵抗値は、１×１０^{9}Ω・ｃｍ以上に保持することが好ましい。ＩＰＳ方式では電界が液晶層面内方向にかかるが、対向基板のブラックマトリックスの電気抵抗が前記範囲にあると電界を正常に印加し得、液晶配向に乱れや表示ムラのない表示が可能となる。したがって、ＩＰＳ方式の液晶表示装置に用いるブラックマトリックスは、高い遮光性を有するだけでなく高い抵抗値を示す必要がある。体積抵抗値を前記範囲とするには、ブラックマトリックスを体積抵抗値１Ω・ｃｍ以上の粒子とポリマーとからなり、該ブラックマトリックスの表面粗度を１００オングストローム以下にすることが好ましい。

【0165】

ここで、体積抵抗値は、単位面積、単位長さ当たりの抵抗値を示し、ポリマー体積抵抗率の測定と同様に、ガードリング付きの三端子法でブラックマトリックスをなす遮光膜用感光性樹脂組成物の塗布膜の上下に設けられた電極面に所定の電圧を印加したときの電流値から求められる。また、基板上に形成された互いに対向する対向電極を遮光膜用感光性樹脂組成物で覆い、この対向電極間に所定の電圧を印加して電流値及び電極形状をもとに求めてもよい。

【0166】

また、ブラックマトリクスの電圧保持率は８０％以上が好ましく、より好ましくは９０％以上である。電圧保持率が前記範囲内であると、イオン性物質等の不純物が液晶中に溶出して液晶層へのイオン性物質が混入する等に伴なう白ムラ等の発生がなく、良好な表示画像が得られる。電圧保持率を８０％以上とするには、ブラックマトリクスの形成時に用いる光酸発生剤の量、加熱条件等を調整して架橋度を高めることが好ましい。電圧保持率を８０％以上とすることにより、特に高温高湿等の厳しい表示条件下での長時間表示であっても、焼付きや白ムラ等の表示不良の発生が防止され、表示品質に優れた液晶表示装置が可能となる。

【実施例】

【0167】

以下、実施例により本発明を説明するが、本発明はこれらの実施例に限定されるものではない。なお、実施例中の「部」は質量基準である。

【0168】

（実施例１）

（１）感光性転写シートの作製

厚さ１００μｍのポリエチレンテレフタレートフィルム（ＰＥＴ仮支持体）を用意し、このＰＥＴ仮支持体上に、下記組成よりなる塗布液を塗布し、乾燥させて、乾燥層厚が２０μｍの熱可塑性樹脂層を形成した。

【0169】

〈熱可塑性樹脂層溶液の組成〉

・メチルメタクリレート／２－エチルヘキシルアクリレート／ベンジルメタクリレート／メタクリル酸（＝５５／１１．７／４．５／２８．８〔モル比〕）共重合体
…１５部
（重量平均分子量９００００）

・ポリプロピレングリコールジアクリレート
（平均分子量８２２）　…　６．５部

・テトラエチレングリコールジメタクリレート　…　１．５部

・ｐ－トルエンスルホンアミド　…　０．５部

・ベンゾフェノン　…　１．０部

・メチルエチルケトン　…３０部

【0170】
次いで、上記より形成された熱可塑性樹脂層の上に、下記組成よりなる塗布液を塗布し、乾燥させて、乾燥層厚が１．６μｍの中間層を形成した。
【0171】
〈中間層用塗布液の組成〉
・ポリビニルアルコール
（ＰＶＡ　２０５、鹸化率８０％、（株）クラレ製）…　１３０部
・ポリビニルピロリドン　…　６０部
（ＧＡＦコーポレション製 ＰＶＰ Ｋ－９０）
・フッ素系界面活性剤
（サーフロンＳ－１３１、旭硝子（株）製）　…　１０部
・蒸留水　…３３５０部
【0172】
次いで、下記組成よりなる黒色感光性樹脂層用塗布液を調製し、この黒色感光性樹脂層用塗布液を中間層の上に更に塗布し、乾燥させて、乾燥層厚が０．６０μｍのＡｇ粒子含有の黒色感光性樹脂層を形成した。その後、黒色感光性樹脂層の表面に保護フィルムとしてポリプロピレンフィルムを貼り付けた。得られた黒色感光性樹脂層の透過光学濃度は１．０であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は６．７であった。
以上のようにして、ＰＥＴ仮支持体／熱可塑性樹脂層／中間層／黒色感光性樹脂層／保護フィルムの積層構造に構成された本発明の感光性転写シートを作製した。
【0173】
本実施例では、透過光学濃度を以下のようにして求めた。
分光光度計ＵＶ－２１００（島津製作所（株）製）を用いて、感光性転写シート（保護フィルムなし）の透過光学濃度（ＯＤ）を波長３５５ｎｍで測定すると共に、さらに黒色感光性樹脂層形成前の、熱可塑性樹脂層及び中間層が形成されたＰＥＴ仮支持体の透過光学濃度（OD^0）を同様の方法で測定し、得られたＯＤからOD^0を差し引いた値（透過ＯＤ；＝ＯＤ－OD^0）を透過光学濃度とした。
【0174】
〈黒色感光性樹脂層用塗布液の組成〉
・メタクリル酸／ベンジルメタクリレート共重合体　…　１９．９８部
（モル比：２８／７２、重量平均分子量：３００００）
・架橋剤（ＭＷ－３０Ｍ、三和ケミカル（株）製）　…　４．７６部
・Ａｇ粒子（平均粒子径８０ｎｍ）　…　５１．３部
・界面活性剤　…　０．１７部
（大日本インキ化学工業（株）製、Ｆ１７７Ｐ）
・光酸発生剤　…　２．３８部
（２，４－ビス（トリクロロ）－６，４－［４－Ｎ，Ｎ－ジエトキシカルボメチル）－３　ブロモフェニル　ｓ　トリアジン）
・メチルエチルケトン　…１０６．８０部
・プロピレングリコールモノメチルエーテルアセテート
…　４４．７０部
【0175】
（２）転写法による画像形成
上記より得た感光性転写シートから保護フィルムを剥がし、露出した黒色感光性樹脂層の表面を、厚さ１．１ｍｍのガラス基板の表面と接するようにラミネータ（Ｌａｍｉｃｌｌ型、（株）日立インダストリイズ製）を用いて１３０℃、０．２ｍ／ｍｉｎ、１０Ｋｇ／ｃｍの条件で貼り合せ、ＰＥＴ仮支持体を剥離して黒色感光性樹脂層を熱可塑性樹脂層及び中間層と共に転写し、光学濃度４．０の黒色感光性樹脂層が転写形成されたガラス基板を得た。

【0176】
続いて、この黒色感光性樹脂層の表面に、フォトマスクを介して４００ｍｊ／ｃｍ²にてパターン状に露光を行ない、露光を修了して１分経過した後、１４０℃に加熱されたホットプレート上にガラス基板面で接するようにして載置して１２秒間加熱処理（露光後ベーク）を行なった。
【0177】
露光後ベークの後、熱可塑性樹脂層及び中間層の除去用のアルカリ現像液Ｔ　ＰＤ２（富士写真フイルム（株）製）の１０倍希釈液（３３℃、ｐＨ－１０．７）を用いて熱可塑性樹脂層及び中間層を現像除去し、さらに水洗処理した後、続けて黒色感光性樹脂層の未露光部を、アルカリ現像液Ｔ　ＣＤ（富士写真フイルム（株）製）の５倍希釈液（３３℃、ｐＨ＝９．９）を用いて現像し、水洗処理を行なって、ガラス基板上に遮光性の黒色画像を形成した。
【0178】
（３）評価
下記のようにして測定、評価を行ない、測定、評価の結果を下記表１に示す。
－１．解像度－
上記より得た感光性転写シートを用い、前記同様にしてガラス基板上に黒色感光性樹脂層を転写形成し、形成された黒色感光性樹脂層を、５０μｍ～１μｍまで２μｍ間隔毎に狭くなるライン状のパターンを有するマスクを用いて、パターン露光した。その後、前記同様に現像処理を行ない、ラインが残っている部分のライン幅（μｍ）を光学顕微鏡を用いて計測し、これを解像度とした。値の小さい方が解像度に優れることを示す。
【0179】
－２．表示ムラ－
黒色画像が形成されたガラス基板に対し、下記のようにして着色画素を形成してカラーフィルタとし、レーザー顕微鏡等を用いた膜厚測定により突起の有無を評価した。ここでの突起は、画像表示した際に表示ムラを起こす一因となるものであり、着色画素を設けたときの着色画素と黒色画像との重なり部分が角状の突起となって起きるものである。
【0180】
〈カラーフィルタの作製〉
－感光性樹脂転写材料の作製－
厚さ７５μｍのポリエチレンテレフタレートフィルム仮支持体（ＰＥＴ仮支持体）の上に、スリット状ノズルを用いて、下記処方Ｈ１からなるクッション層用塗布液を塗布、乾燥させてクッション層を形成した。次に、このクッション層上に下記処方Ｐ１からなる中間層用塗布液を塗布、乾燥させて中間層（酸素遮断膜）を積層した。この中間層上に更に、下記表１に記載の組成よりなる着色感光性樹脂組成物Ｒ２を塗布、乾燥させて感光性樹脂層を積層した。このようにして、ＰＥＴ仮支持体の上に、乾燥膜厚が１４．６μｍの熱可塑性樹脂層と乾燥膜厚が１．６μｍの中間層と乾燥膜厚が２．４μｍの感光性樹脂層を設け、感光性樹脂層上には保護フィルム（厚さ１２μｍポリプロピレンフィルム）を圧着した。
【0181】

【表1】

着色感光性樹脂組成物	R1	G1	B1	R2	G2	B2
R顔料分散物1 (C. I. P. R. 254)	44	-	-	44	-	-
R顔料分散物2 (C. I. P. R. 177)	5.0	-	-	5.0	-	-
G顔料分散物1 (C. I. P. G. 36)	-	24	-	-	24	-
Y顔料分散物1 (C. I. P. Y. 150)	-	13	-	-	13	-
B顔料分散物1 (C. I. P. B. 15:6 + C. I. P. V. 23)	-	-	8.0	-	-	7.2
B顔料分散物2 (C. I. P. B. 15:6)	-	-	14.4	-	-	13
プロピレングリコールモノメチルエーテルアセテート	7.6	29	28	7.6	29	23
メチルエチルケトン	37	26	41	37	26	35
シクロヘキサノン	-	1.3	-	-	1.3	-
バインダー1	-	2.5	-	-	3	-
バインダー2	0.7	-	-	0.8	-	-
バインダー3	-	-	19	-	-	17
DPHA液	3.8	3.5	4.2	4.4	4.3	3.8
2-トリクロロメチル-5-(p-スチリルメチル)1, 3, 4-オキサジアゾール	0.12	0.1	0.17	0.14	0.15	0.15
2, 4-ビス(トリクロロメチル)-6-[4-(N, N-ジエトキシカルボニルメチル)-3-ブロモフェニル]-s-トリアジン	0.050	0.050	-	0.058	0.060	-
フェノチアジン	0.010	0.005	0.020	0.010	0.005	0.020
添加剤1	-	-	-	0.52	-	-
界面活性剤1	0.060	0.070	0.060	0.060	0.070	0.050

質量部

【0182】
上記のようにして、仮支持体と熱可塑性樹脂層と中間層（酸素遮断膜）と赤色の感光性樹脂層とが積層されて積層体に構成された感光性樹脂転写材料を作製した（以下、感光性樹脂転写材料Ｒ２と称する）。

【0183】
〔クッション層用塗布液の処方111〕
・メタノール　…１１．１部
・プロピレングリコールモノメチルエーテルアセテート　…　６．４部
・メチルエチルケトン　…５２．４部
・メチルメタクリレート／２　エチルヘキシルアクリレート／ベンジルメタクリレート／メタクリル酸共重合体　…　５．８３部
〔共重合比（モル比）－５５／１１．７／４．５／２８．８、重量平均分子量－１０万、Ｔｇ≒７０℃〕
・スチレン／アクリル酸共重合体　…１３．６部
〔共重合比（モル比）＝６３／３７、重量平均分子量＝１万、Ｔｇ≒１００℃〕
・ビスフェノールＡにペンタエチレングリコールモノメタクリートを２当量脱水縮合した化合物（新中村化学工業（株）製、２，２－ビス［４－（メタクリロキシポリエトキシ）フェニル］プロパン）　…　９．１部
・界面活性剤１　…　０．５４部

【0184】
＊界面活性剤１：
メガファックＦ－７８０－Ｆ（大日本インキ化学工業（株）製）
〔組成〕

・$C_8F_{17}CH_2CH_2OCOCH=CH_2$（４０部）とH（O（$CH_2$）$CHCH_2$）$_7$OCOCH－$CH_2$（５５部）とH（O$CH_2CH_2$）$_7$OCOCH－$CH_2$（５部）との共重合体（重量平均分子量３万）…３０部
・メチルイソブチルケトン…７０部

【0185】
〔中間層用塗布液の処方Ｐ１〕
・ポリビニルアルコール　…　２．１部
（ＰＶＡ－２０５（鹸化率－８８％）、（株）クラレ製）
・ポリビニルピロリドン　…　０．９５部
（ＰＶＰ、Ｋ　３０；ＧＡＦコーポレーション社製）
・メタノール　…４４部
・蒸留水　…５３部

【0186】
次に、得られた感光性樹脂転写材料Ｒ２の作製において用いた前記着色感光性樹脂組成物Ｒ２を、前記表１に記載の組成よりなる着色感光性樹脂組成物Ｇ２及びＢ２に代えたこと以外は、上記と同様の方法により、感光性樹脂転写材料Ｇ２及びＢ２を作製した。

【0187】
着色感光性樹脂組成物Ｒ２、Ｇ２及びＢ２の調製方法は、それぞれ前記表１中の着色感光性樹脂組成物Ｒ１、Ｇ１及びＢ１の調製方法に準ずるものとし、着色感光性樹脂組成物Ｒ１、Ｇ１及びＢ１の調製方法は後記する。なお、着色感光性樹脂組成物Ｒ２の調製は、着色感光性樹脂組成物Ｒ１の調製方法において、フェノチアジン等の添加後、界面活性剤１の添加前に、前記表１に記載の量の添加剤１をはかり取り、温度２４℃（±２℃）で混合して１５０ｒ．ｐ．ｍ．で２０分間撹拌するようにした。
※添加剤１：燐酸エステル系特殊活性剤（ＨＩＰＬＡＡＤ　ＥＤ１５２、楠本化成（株）製）

【0188】
－レッド（Ｒ）画素の形成－
前記感光性樹脂転写材料Ｒ２の保護フィルムを剥離後、露出した感光性樹脂層が、上記より遮光膜（遮光性の黒色画像）が形成されたガラス基板の表面と接するように重ね合わせ、ラミネータＬａｍｉｃｌｌ型〔（株）日立インダストリイズ製〕を用いて、ゴムローラ温度１３０℃、線圧１００Ｎ／ｃｍ、搬送速度２．２ｍ／分の条件にてラミネートした。次いで、ＰＥＴ仮支持体を剥離してガラス基板上に転写した。

【0189】
次に、超高圧水銀灯を有するプロキシミティー型露光機（日立電子エンジニアリング（株）製）を用い、マスク（画像パターンを有する石英露光マスク）と、該マスクと熱可塑性樹脂層とが向き合うように配置したガラス基板とを略平行に垂直に立てた状態で、マスク面と感光性樹脂層の中間層に接する側の表面との間の距離を２００μｍに設定し、マスクを介して熱可塑性樹脂層側から露光量４０ｍＪ／ｃｍ^{2}でパターン露光した。

【0190】
次に、トリエタノールアミン系現像液（２．５％のトリエタノールアミン、ノニオン界面活性剤、及びポリプロピレン系消泡剤含有；商品名：Ｔ－ＰＤ１、富士写真フイルム（株）製）にて３０℃で５０秒間、フラットノズル圧力０．０４ＭＰａでシャワー現像し、熱可塑性樹脂層と酸素遮断膜とを除去した。

【0191】
次に、炭酸Ｎａ系現像液（０．０６モル／リットルの炭酸水素ナトリウム、同濃度の炭酸ナトリウム、１％のジブチルナフタレンスルホン酸ナトリウム、アニオン界面活性剤、消泡剤、及び安定剤を含有；商品名：Ｔ－ＣＤ１、富士写真フイルム（株）製）を用いて、３５℃で３５秒間、コーン型ノズル圧力０．１５ＭＰａでシャワー現像し、パターン画素を得た。

【0192】

次に、洗浄剤（燐酸塩、珪酸塩、ノニオン界面活性剤、消泡剤、及び安定剤含有；商品名：Ｔ－ＳＤ１、富士写真フイルム（株）製）を用いて、３３℃で２０秒間、コーン型ノズル圧力０．０２ＭＰａでシャワーとナイロン毛を有す回転ブラシを用いて残渣除去を行なうことにより、レッド（Ｒ）画素を形成した。その後さらに、この基板に対し、Ｋ画像が形成されている側から超高圧水銀灯により５００ｍＪ／ｃｍ^{2}の光でポスト露光した後、２２０℃で１５分間熱処理した。

【0193】

Ｒ画素の厚みは２．０μｍであり、Ｃ．Ｉ．ピグメント・レッド（Ｃ．Ｉ．Ｐ．Ｒ．）２５４、Ｃ．Ｉ．Ｐ．Ｒ．１７７の塗布量はそれぞれ０．８８ｇ／ｍ^2、０．２２ｇ／ｍ^{2}であった。

その後、Ｒ画素が形成されたガラス基板を再び、上記のように洗浄剤を用いてブラシ洗浄し、純水でシャワー洗浄した後、シランカップリング液は使用せずに、基板予備加熱装置により１００℃で２分間加熱した。

【0194】

－グリーン（Ｇ）画素の形成－

次に、上記より得た感光性樹脂転写材料Ｇ２を用い、前記Ｒ画素の形成と同様の工程を行ない、ガラス基板の遮光膜及びＲ画素が形成されている側にグリーン画素（Ｇ画素）を形成した。但し、露光工程での露光量は４０ｍＪ／ｃｍ^2、炭酸Ｎａ系現像液によるシャワー現像は３４℃で４５秒間とし、熱処理は２２０℃で１５分間とした。

Ｇ画素の厚みは２．０μｍであり、Ｃ．Ｉ．ピグメント・グリーン（Ｃ．Ｉ．Ｐ．Ｇ．）３６、Ｃ．Ｉ．ピグメント・イエロー（Ｃ．Ｉ．Ｐ．Ｙ．）１５０の塗布量はそれぞれ１．１２ｇ／ｍ^2、０．４８ｇ／ｍ^{2}であった。

【0195】

その後、Ｒ画素及びＧ画素が形成されたガラス基板を再び、上記のように洗浄剤を用いてブラシ洗浄し、純水でシャワー洗浄した後、シランカップリング液は使用せずに、基板予備加熱装置により１００℃で２分間加熱した。

【0196】

－ブルー（Ｂ）画素の形成－

次に、上記より得た感光性樹脂転写材料Ｂ２を用い、前記Ｒ画素の形成と同様の工程を行ない、ガラス基板の遮光膜並びにＲ画素及びＧ画素が形成されている側にブルー画素（Ｂ画素）を形成した。但し、露光工程での露光量は３０ｍＪ／ｃｍ^2、炭酸Ｎａ系現像液によるシャワー現像は３６℃で４０秒間とした。

Ｂ画素の厚みは２．０μｍであり、Ｃ．Ｉ．ピグメント・ブルー（Ｃ．Ｉ．Ｐ．Ｂ．）１５：６、Ｃ．Ｉ．ピグメント・バイオレット（Ｃ．Ｉ．Ｐ．Ｖ．）２３の塗布量はそれぞれ０．６３ｇ／ｍ^2、０．０７ｇ／ｍ^{2}であった。

【0197】

その後、Ｒ、Ｇ、Ｂの各画素が形成されたガラス基板を２４０℃で５０分間ベークし、カラーフィルタを得た。

【0198】

（実施例２）

実施例１と同様にして、黒色感光性樹脂層用塗布液を調製した。次に、厚さ１．１ｍｍのガラス基板を用意し、このガラス基板上に、得られた黒色感光性樹脂層用塗布液を乾燥膜厚が０．６０μｍになるように、スリット＆スピンコーターを用いて塗布し、乾燥させて、黒色感光性樹脂層を塗設した。

ここで、黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は６．７であった。

【0199】

続いて、塗設した黒色感光性樹脂層の表面に、フォトマスクを介して４００ｍｊ／ｃｍ^{2}にてパターン状に露光を行ない、露光を修了して１分経過した後、１４０℃に加熱され

たホットプレート上にガラス基板面で接するようにして載置して１２秒間加熱処理（露光後ベーク）を行なった。

【0200】

露光後ベークの後、熱可塑性樹脂層及び中間層の除去用のアルカリ現像液Ｔ　ＰＤ２（富士写真フイルム（株）製）の１０倍希釈液（３３℃、ｐＨ－１０．７）を用いて熱可塑性樹脂層及び中間層を現像除去し、さらに水洗処理し、続けて黒色感光性樹脂層の未露光部を、アルカリ現像液Ｔ　ＣＤ（富士写真フイルム（株）製）の５倍希釈液（３３℃、ｐＨ－９．９）を用いて現像し、水洗処理を行なって、ガラス基板上に遮光性の黒色画像を形成した。その後、実施例１と同様の評価を行なった。但し、カラーフィルタの形成は以下のようにして行なった。

【0201】

〈カラーフィルタの作製（スリット＆スピンコーターによる塗布）〉

－レッド（Ｒ）画素の形成－

上記のように遮光膜（遮光性の黒色画像）が形成されたガラス基板の遮光膜形成面側に、スリット＆スピンコーターにて、前記表１に記載の組成よりなる着色感光性樹脂組成物Ｒ１を塗布した。引き続き、真空乾燥機ＶＣＤ（東京応化社製）を用いて３０秒間溶媒の一部を乾燥させて塗布膜の流動性をなくした後、ＥＢＲ（エッジ・ビード・リムーバー）にて基板周囲の不要な塗布液を除去し、１２０℃で３分間プリベークして膜厚２．４μｍの感光性樹脂層Ｒ１を形成した。

【0202】

次に、超高圧水銀灯を備えたプロキシミティー型露光機（日立電子エンジニアリング社製）を用い、マスク（画像パターンを有する石英露光マスク）と感光性樹脂層Ｒ１が設けられたガラス基板とを垂直に立てた状態で、マスク面と感光性樹脂層Ｒ１の表面との間の距離を２００μｍとし、露光量１５０ｍＪ／ｃｍ２でパターン露光した。

次に、純粋をシャワーノズルから噴霧し、感光性樹脂層Ｒ１の表面を均一に湿らせた後、ＫＯＨ系現像液ＣＤＫ－１（富士フイルムエレクトロニクスマテリアルズ（株）製；ＫＯＨ及びノニオン界面活性剤含有アルカリ現像液）を、フラットノズルから２３℃、ノズル圧力０．０４ＭＰａにて６０秒間噴射してシャワー現像し、レッドパターンを得た。続いて、ガラス基板のレッドパターンが形成された側に超純水を超高圧洗浄ノズルにより９．８ＭＰａの圧力で噴射して残渣を除去し、ガラス基板上にレッド（Ｒ）画素を形成した。その後、２２０℃で３０分間熱処理（ベーク）した。

【0203】

Ｒ画素の厚みは１．６μｍであり、Ｃ．Ｉ．ピグメント・レッド（Ｃ．Ｉ．Ｐ．Ｒ．）２５４、Ｃ．Ｉ．Ｐ．Ｒ．１７７の塗布量はそれぞれ０．８８ｇ／ｍ^2、０．２２ｇ／ｍ^{2}であった。

【0204】

グリーン（Ｇ）画像の形成

次に、前記遮光膜及びＲ画素が形成されたガラス基板に、前記表１に示す組成よりなる着色感光性樹脂組成物Ｇ１を用い、前記Ｒ画素の形成と同様にして塗布、露光、現像、及びベークを行ない、ガラス基板の遮光膜及びＲ画素が形成されている側にグリーン画素（Ｇ画素）を形成した。但し、露光工程での露光量は１５０ｍＪ／ｃｍ２とし、現像工程でのシャワー現像は２３℃で６０秒間とし、熱処理は２２０℃で３０分間とした。

【0205】

Ｇ画素の厚みは１．６μｍであり、Ｃ．Ｉ．ピグメント・グリーン（Ｃ．Ｉ．Ｐ．Ｇ．）３６、Ｃ．Ｉ．ピグメント・イエロー（Ｃ．Ｉ．Ｐ．Ｙ．）１５０の塗布量はそれぞれ１．１２ｇ／ｍ^2、０．４８ｇ／ｍ^{2}であった。

【0206】

－ブルー（Ｂ）画像の形成－

次に、前記遮光膜並びにＲ画素及びＧ画素が形成されたガラス基板に、前記表１に示す組成よりなる着色感光性樹脂組成物Ｂ１を用い、前記Ｒ画素の形成と同様にして塗布、露

光、現像、及びベークを行ない、ガラス基板の遮光膜並びにR画素及びG画素が形成されている側にブルー画素（B画素）を形成した。但し、露光工程での露光量は１５０ｍＪ／ｃｍ２とし、現像工程でのシャワー現像は２３℃で６０秒間とし、熱処理は２２０℃で３０分間とした。

【0207】

B画素の厚みは１．６μｍであり、Ｃ．Ｉ．ピグメント・ブルー（Ｃ．Ｉ．Ｐ．Ｂ．）１５：６及びＣ．Ｉ．ピグメント・バイオレット（Ｃ．Ｉ．Ｐ．Ｖ．）２３の塗布量はそれぞれ０．６３ｇ／ｍ２、０．０７ｇ／ｍ２であった。

【0208】

その後、R、G，Bの各画素が形成されたガラス基板を２４０℃で５０分間ベークし、カラーフィルタを得た。

【0209】

ここで、前記表１に記載の着色感光性樹脂組成物Ｒ１、Ｇ１及びＢ１の調製について説明する。

〈着色感光性樹脂組成物Ｒ１の調製〉

着色感光性樹脂組成物Ｒ１は、前記表１に記載の量のR顔料分散物１、R顔料分散物２、及びプロピレングリコールモノメチルエーテルアセテートをはかり取り、温度２４℃（±２℃）で混合して１５０ｒ．ｐ．ｍ．で１０分間撹拌し、次いで、前記表１に記載の量のメチルエチルケトン、バインダー２、ＤＰＨＡ液、２－トリクロロメチル－５－（ｐ－スチリルメチル）－１，３，４－オキサジアゾール、２，４－ビス（トリクロロメチル）－６－［４－（Ｎ，Ｎ－ジエトキシカルボニルメチル）－３－ブロモフェニル］－ｓ－トリアジン、及びフェノチアジンをはかり取り、温度２４℃（±２℃）でこの順に添加して１５０ｒ．ｐ．ｍ．で３０分間撹拌し、更に、前記表１に記載の量の界面活性剤１をはかり取り、温度２４℃（　２℃）で添加して３０ｒ．ｐ．ｍ．で３０分間撹拌し、ナイロンメッシュ＃２００で沪過することによって得た。

【0210】

なお、前記表１に記載の組成物Ｒ１中の各組成の詳細は以下の通りである。また、界面活性剤１の組成は既述の通りである。

＊R顔料分散物１の組成

・Ｃ．Ｉ．ピグメント・レッド２５４…８．０部

・５　［３　オキソ　２　［４　［３，５-ビス（３　ジエチルアミノプロピルアミノカルボニル）フェニル]アミノカルボニル］フェニルアゾ］－ブチロイルアミノベンズイミダゾロン…０．８部

・ポリマー〔ベンジルメタクリレート／メタクリル酸（－７２／２８[モル比]）のランダム共重合物（重量平均分子量３７，０００）〕…８．０部

・プロピレングリコールモノメチルエーテルアセテート…８３．２部

【0211】

＊R顔料分散物２の組成

・Ｃ．Ｉ．ピグメント・レッド１７７…１８部

・ポリマー〔ベンジルメタクリレート／メタクリル酸（－７２／２８[モル比]）のランダム共重合物（重量平均分子量３７，０００）〕…１２部

・プロピレングリコールモノメチルエーテルアセテート…７０部

＊バインダー２の組成

・ベンジルメタクリレート／メタクリル酸／メチルメタクリレート（－３８／２５／３７[モル比]）のランダム共重合物（重量平均分子量３０，０００）…２７部

・プロピレングリコールモノメチルエーテルアセテート…７３部

＊添加剤１：燐酸エステル系特殊活性剤（ＨＩＰＬＡＡＤ　ＥＤ１５２、楠本化成（株）製）

＊ＤＰＨＡ液の組成

・ジペンタエリスリトールヘキサアクリレート（商品名：ＫＡＹＡＲＡＤ　ＤＰＨＡ、

日本化薬（株）製）…７６部
・プロピレングリコールモノメチルエーテル…２４部
【0212】
〈着色感光性樹脂組成物Ｇ１の調製〉
着色感光性樹脂組成物Ｇ１は、前記表１に記載の量のＧ顔料分散物１、Ｙ顔料分散物１、及びプロピレングリコールモノメチルエーテルアセテートをはかり取り、温度２４℃（±２℃）で混合して１５０ｒ.ｐ.ｍ.で１０分間攪拌し、次いで、前記表１に記載の量のメチルエチルケトン、シクロヘキサノン、バインダー１、ＤＰＨＡ液、２－トリクロロメチル－５－（ｐ－スチリルメチル）－１，３，４－オキサジアゾール、２，４－ビス（トリクロロメチル）－６－［４－（Ｎ，Ｎ－ジエトキシカルボニルメチル）－３－ブロモフェニル］－ｓ－トリアジン、及びフェノチアジンをはかり取り、温度２４℃（±２℃）でこの順に添加して１５０ｒ.ｐ.ｍ.で３０分間攪拌し、更に、前記表１に記載の量の界面活性剤１をはかり取り、温度２４℃（±２℃）で添加して３０ｒ.ｐ.ｍ.で５分間攪拌し、ナイロンメッシュ＃２００で沪過することによって得た。
【0213】
なお、前記表１に記載の組成物Ｇ１中の各組成の詳細は以下の通りである。また、ＤＰＨＡ液及び界面活性剤１の組成については既述の通りである。
＊Ｇ顔料分散物１の組成
・Ｃ．Ｉ．ピグメント・グリーン３６…１８部
・ポリマー〔ベンジルメタクリレート／メタクリル酸（＝７２／２８[モル比]）のランダム共重合物（重量平均分子量３７，０００）〕…１２部
・シクロヘキサノン…３５部
・プロピレングリコールモノメチルエーテルアセテート…３５部
＊Ｙ顔料分散物１
商品名：ＣＦエローＥＸ３３９３（御国色素社製）
＊バインダー１
・ポリマー〔ベンジルメタクリレート／メタクリル酸（＝７８／２２[モル比]）のランダム共重合物（分子量４０，０００）〕…２７部
・プロピレングリコールモノメチルエーテルアセテート…７３部
【0214】
〈着色感光性樹脂組成物Ｂ１の調製〉
着色感光性樹脂組成物Ｂ１は、前記表１に記載の量のＢ顔料分散物１、Ｂ顔料分散物２、及びプロピレングリコールモノメチルエーテルアセテートをはかり取り、温度２４℃（±２℃）で混合して１５０ｒ.ｐ.ｍ.で１０分間攪拌し、次いで、前記表１に記載の量のメチルエチルケトン、バインダー３、ＤＰＨＡ液、２－トリクロロメチル－５－（ｐ－スチリルメチル）－１，３，４－オキサジアゾール、及びフェノチアジンをはかり取り、温度２５℃（±２℃）でこの順に添加して、温度４０℃（±２℃）で１５０ｒ.ｐ.ｍ.で３０分間攪拌し、更に、前記表１に記載の量の界面活性剤１をはかり取り、温度２４℃（±２℃）で添加して３０ｒ.ｐ.ｍ.で５分間攪拌し、ナイロンメッシュ＃２００で沪過することによって得た。
【0215】
なお、前記表１に記載の組成物Ｂ１中の各組成の詳細は以下の通りである。また、ＤＰＨＡ液及び界面活性剤１の組成については既述の通りである。
＊Ｂ顔料分散物１
商品名：ＣＦブルーＥＸ３３５７（御国色素社製）
＊Ｂ顔料分散物２
商品名：ＣＦブルーＥＸ３３８３（御国色素社製）
＊バインダー３の組成
・ベンジルメタクリレート／メタクリル酸／メチルメタクリレート（＝３６／２２／４２[モル比]）のランダム共重合物（重量平均分子量３０，０００）…２７部

・プロピレングリコールモノメチルエーテルアセテート…７３部

【0216】

（実施例３）

実施例２において、スリット＆スピンコーターを、スリット状ノズルを備えたガラス基板用コーターＭＨ－１６００（エフ・エー・エス・ジャパン社製）に代えたこと以外、実施例２と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚あたりの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は６．７であった。また、実施例１と同様の評価を行なった。但し、カラーフィルタの形成は以下のようにして行なった。

【0217】

〈カラーフィルターの作製（スリット状ノズルを用いた塗布による作製）〉

実施例２のカラーフィルタの作製において、スリット＆スピンコーターをスリット状ノズルを備えたガラス基板用コーターＭＨ－１６００（エフ・エー・エス・ジャパン社製）に代えたこと以外、実施例２と同様にして、上記より得た遮光膜（遮光性の黒色画像）が形成されたガラス基板に、カラーフィルタを形成した。

【0218】

（実施例４）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、Ａｇ粒子（平均粒子径８０ｎｍ）４１部及びカーボンブラック（ＣＢ）１．７６部（添加体積比（Ag／CB）＝８０／２０）に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を０．７０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚あたりの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は５．７であった。また、実施例１と同様の評価を行なった。

【0219】

（実施例５）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、Ａｇ粒子（平均粒子径８０ｎｍ）２５．７部及びカーボンブラック（ＣＢ）４．４部（添加体積比（Ag／CB）＝５０／５０）に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を０．９０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚あたりの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は４．４であった。また、実施例１と同様の評価を行なった。

【0220】

（実施例６）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、Ａｇ粒子（平均粒子径８０ｎｍ）１０．３部及びカーボンブラック（ＣＢ）７．０４部（添加体積比（Ag／CB）＝２０／８０）に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を１．００μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚あたりの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は４．０であった。また、実施例１と同様の評価を行なった。

【0221】

（実施例７）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、下記より得た銀／硫化銀コアシェル粒子（平均粒子径９０ｎｍ）５１．３部に代えると共

に、形成した黒色感光性樹脂層の乾燥層厚を０．８０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は３．９であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は４．９であった。また、実施例１と同様の評価を行なった。

【0222】

〈銀／硫化銀コアシェル粒子の作製〉

銀粒子のアセトン分散物（平均粒径３０ｎｍ、濃度２．５質量％）２００ｇにビニルピロリドン／酢酸ビニル共重合体（＝６０／４０［質量比］、重量平均分子量５０００）を０．９５ｇ添加して、３０分間撹拌した。次いで、これに濃度７．２質量％の硫化ナトリウム水溶液（２３℃）を、撹拌しながら金属の硫化率が３０％になるように添加し、添加終了後そのまま３０分間撹拌を行なって、硫化銀のシェルを持つ銀／硫化銀コアシェル粒子を得た。

ここで、硫化率とは、金属粒子が硫化されている割合で、硫化率０％は全く硫化されていない状態を、１００％は粒子全体が完全に硫化物になっている状態を表す。

【0223】

（実施例８）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、Ｓｎ粒子（平均粒子径３６ｎｍ、短軸２０ｎｍ、長軸５０ｎｍ）５１．３部に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を０．９０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は４．４であった。また、実施例１と同様の評価を行なった。

【0224】

（実施例９）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、Ａｇ粒子（平均粒子径１１７ｎｍ、短軸６０ｎｍ、長軸１８０ｎｍ）５１．３部に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を０．８０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は５．０であった。また、実施例１と同様の評価を行なった。

【0225】

（比較例１）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子（５１．３部）をカーボンブラック（２１．１７部）に代え、メタクリル酸／ベンジルメタクリレート共重合体をアクリル樹脂に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を１．５０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は３．５であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は２．３であった。また、実施例１と同様の評価を行なった。

【0226】

【表2】

	金属粒子		カーボンブラック	粒子径[nm]	短軸[nm]	長軸[nm]	膜厚[μm]	ベーク時間[秒]	透過光学濃度	単位体積あたりの透過光学濃度	解像度[μm]	突起の有無（表示ムラ）
	種	添加体積比	添加体積比									
実施例1	（転写法）	Ag粒子	100%	0%	80			0.60	12	4.0	6.7	6	無
実施例2	（塗布法）スリット&スピンコート	Ag粒子	100%	0%	80			0.60	12	4.0	6.7	6	無
実施例3	（塗布法）スリットコート	Ag粒子	100%	0%	80			0.60	12	4.0	6.7	6	無
実施例4	（転写法）	Ag粒子	80%	20%	80			0.70	12	4.0	5.7	6	無
実施例5	（転写法）	Ag粒子	50%	50%	80			0.90	12	4.0	4.4	6	無
実施例6	（転写法）	Ag粒子	20%	80%	80			1.00	12	4.0	4.0	6	無
実施例7	（転写法）	銀-硫化銀コアシェル	100%	0%	90			0.80	12	3.9	4.9	6	無
実施例8	（転写法）	Sn粒子	100%	0%	36	20	50	0.90	12	4.0	4.4	6	無
実施例9	（転写法）	Ag粒子	100%	0%	117	60	180	0.80	12	4.0	5.0	6	無
比較例1	（転写法）	—	0%	100%	—			1.50	30	3.5	2.3	20	有

※　添加体積比(%)の計算は、銀の比重を10．5とし、カーボンブラックの比重を1．8とし、その他を1．0として行なった。

【0227】

前記表２に示すように、実施例では、露光後ベークを短時間で行ないながら、高解像度の黒色画像を形成することができ、形成された黒色画像は４．０の高濃度を有し、単位体

積あたりの濃度も高めることができた。また、表示ムラもなく、良好な表示画像が得られた。

これに対し、金属粒子を用いずカーボンブラックのみ構成した比較例１では、黒色画像の濃度が低いばかりか、該濃度を得るのに厚膜となって、露光後ベークに長時間を要し、形成された黒色画像の解像度、表示ムラにも劣っていた。

【0228】

上記の実施例以外に、露光前に加熱（ベーク）を行なうようにした場合も同様であり、露光後現像した後に加熱（ベーク）を行なうようにした場合も同様である。

Ｆターム(参考)

2H025	AA02	AA04	AB11	AB13	AC01	AD01	BE00	BJ00	CB00	CC08
	CC17	CC20	EA04	FA12						
2H048	BA02	BA11	BA55	BA64	BA66	BB01	BB02	BB42	BB46	
4D075	AC02	AC43	AC92	BB20Z	BB26Z	BB40Y	BB42Y	BB46Y	CA48	CB07
	DA04	DA06	DB13	DB31	DB33	DB36	DB37	DB48	DC24	DC40
	EA45	EB14	EB19	EB22	EB32	EB35	EB45	EC01	EC07	EC10
	EC11	EC24	EC37							

Electronic Acknowledgement Receipt

EFS ID:	16454592
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	30-JUL-2013
Filing Date:	05-AUG-2010
Time Stamp:	15:28:45
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	US_IDS_Form__SB_08a.pdf	612050 71022a8dde23eda5932974dfb3b0f47c87ac9e8d	no	4

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2	Foreign Reference	JP03-148659.pdf	265902 83847f590789183931 50cebf675b2ef41dce0fa3	no	5
Warnings:					
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3	Foreign Reference	JP2006284947A.pdf	1667735 ee3e6f1f3f92a36d6de30a3201a23d9798555462	no	46
Warnings:					
Information:					
4	Non Patent Literature	JP_OA_20130611.pdf	326257 9334e7f9ae64bbbe1f6c601dda1c1602d6ca8b5f	no	5
Warnings:					
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		Total Files Size (in bytes):	2871944		

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02	1662

62274 7590 09/16/2013

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EXAMINER	
ROBINSON, CHANCEITY N	
ART UNIT	PAPER NUMBER
1722	

MAIL DATE	DELIVERY MODE
09/16/2013	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Examiner-Initiated Interview Summary	Application No.	Applicant(s)	
	12/850,867	STOWERS ET AL.	
	Examiner	Art Unit	
	CHANCEITY ROBINSON	1722	

All participants (applicant, applicant's representative, PTO personnel):

(1) *CHANCEITY ROBINSON*. (3)_____.

(2) *Peter Dardi*. (4)_____.

Date of Interview: *09/06/2013*.

Type: ☒ Telephonic ☐ Video Conference
☐ Personal [copy given to: ☐ applicant ☐ applicant's representative]

Exhibit shown or demonstration conducted: ☐ Yes ☒ No.
If Yes, brief description: _____.

Issues Discussed ☐101 ☐112 ☐102 ☐103 ☒Others
(For each of the checked box(es) above, please describe below the issue and detailed description of the discussion)

Claim(s) discussed: *1-30*.

Identification of prior art discussed: *none*.

Substance of Interview
(For each issue discussed, provide a detailed description and indicate if agreement was reached. Some topics may include: identification or clarification of a reference or a portion thereof, claim interpretation, proposed amendments, arguments of any applied references etc...)

Examiner called Applicant's representative, Peter Dardi to do a phone restriction over claims 1-30. Applicant's representative inform the examiner that he has to discuss it with his clients. The examiner stated she would just mail out the restriction. However, the examiner reviewed the case history for the application and found out that a phone restriction had already been made on this instant application. Examiner called Applicant's representative back and left a message on his voicemail stating she is withdrawning her restriction and accepting the previously made telephone restriction made between Nicole Gugliotta and Mengmeng Fahrni on Jan. 2012 .

Applicant recordation instructions: It is not necessary for applicant to provide a separate record of the substance of interview.

Examiner recordation instructions: Examiners must summarize the substance of any interview of record. A complete and proper recordation of the substance of an interview should include the items listed in MPEP 713.04 for complete and proper recordation including the identification of the general thrust of each argument or issue discussed, a general indication of any other pertinent matters discussed regarding patentability and the general results or outcome of the interview, to include an indication as to whether or not agreement was reached on the issues raised.

☐ Attachment

/Chanceity N Robinson/ Examiner, Art Unit 1722	

Office Action Summary	Application No. 12/850,867	Applicant(s) STOWERS ET AL.	
	Examiner CHANCEITY ROBINSON	Art Unit 1722	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *3* MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☐ Responsive to communication(s) filed on _____.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☒ An election was made by the applicant in response to a restriction requirement set forth during the interview on *01 January 2012*; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

5)☒ Claim(s) *1-30* is/are pending in the application.

5a) Of the above claim(s) *14-30* is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-13* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☒ The drawing(s) filed on *11/10/2010* is/are: a)☒ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some * c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)

2) ☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date *08/15/2011, 08/28/2012, 10/23/2012, 07/10/2013 & 07/30/2013*.

3) ☒ Interview Summary (PTO-413) Paper No(s)/Mail Date. *09/06/2013* .

4) ☐ Other: _____.

1. The present application is being examined under the pre-AIA first to invent provisions.

DETAILED ACTION

Election/Restrictions

2. Restriction to one of the following inventions is required under 35 U.S.C. 121:

I. Claims 1 - 13, drawn to a precursor solution, classified in class 430, subclass 270.1.

II. Claims 14 – 30 & 35 - 38, drawn to a method of patterning (use), classified in class 430, subclass 302.

III. Claims 31 - 34, drawn to a structure, classified in class 428, subclass 212.

The inventions are distinct, each from the other because of the following reasons:

Inventions I and III are related as mutually exclusive species in an intermediate-final product relationship. Distinctness is proven for claims in this relationship if the intermediate product is useful to make other than the final product, and the species are patentably distinct (MPEP § 806.05(j)). In the instant case, the intermediate product is deemed to be useful as to be used to any product containing the components of the precursor solution, and not necessarily one comprising a patterned surface on a substrate with an average line-roughness of less than 2.25 nm at a pitch of no more than 50 nm or features having an average width of less than about 30 nm. Therefore, the precursor solution can be useful to make a product other than the final structure (product). The inventions are deemed patentably distinct because there is nothing of record to show them to be obvious variants.

Inventions II and I are related as product and process of use. The inventions can be shown to be distinct if either or both of the following can be shown: (1) the process for using the product as claimed can be practiced with another materially different product or (2) the product as claimed can be used in a materially different process of using that product. See MPEP § 806.05(h). In the instant case, the method requires heating the substrate, removing the solvent, irradiating the surface for patterning, which are not required of the claims for the precursor solution. Therefore, the precursor solution of group I can be patterned using a different method, such as patterning by etching.

Inventions III and II are related as process of making and product made. The inventions are distinct if either or both of the following can be shown: (1) that the process as claimed can be used to make another and materially different product or (2) that the product as claimed can be made by another and materially different process (MPEP § 806.05(f)). In the instant case, the patterned surface of the final structure can be obtained by another materially different method, such as etching.

Restriction for examination purposes as indicated is proper because all these inventions listed in this action are independent or distinct for the reasons given above and there would be a serious search and examination burden if restriction were not required because one or more of the following reasons apply:

(a) the inventions have acquired a separate status in the art in view of their different classification;

b) the inventions have acquired a separate status in the art due to their recognized divergent subject matter;

(c) the inventions require a different field of search (for example, searching different classes/subclasses or electronic resources, or employing different search queries);

(d) the prior art applicable to one invention would not likely be applicable to another invention;

(e) the inventions are likely to raise different non-prior art issues under 35 U.S.C. 101 and/or 35 U.S.C. 112, first paragraph.

Applicant is advised that the reply to this requirement to be complete must include (i) an election of an invention to be examined even though the requirement may be traversed (37 CFR 1.143) **and (ii) identification of the claims encompassing the elected invention.**

The election of an invention may be made with or without traverse. To reserve a right to petition, the election must be made with traverse. If the reply does not distinctly and specifically point out supposed errors in the restriction requirement, the election shall be treated as an election without traverse. Traversal must be presented at the time of election in order to be considered timely. Failure to timely traverse the requirement will result in the loss of right to petition under 37 CFR 1.144. If claims are added after the election, applicant must indicate which of these claims are readable on the elected invention.

If claims are added after the election, applicant must indicate which of these claims are readable upon the elected invention.

Should applicant traverse on the ground that the inventions are not patentably distinct, applicant should submit evidence or identify such evidence now of record showing the inventions to be obvious variants or clearly admit on the record that this is the case. In either instance, if the examiner finds one of the inventions unpatentable over the prior art, the evidence or admission may be used in a rejection under 35 U.S.C. 103(a) of the other invention.

During a telephone conversation with Mengmeng Fahrni (Reg. No. 57,717) and Nicole Gugliotta in January 2012 a provisional election was made *with traverse* to prosecute the invention of Group I, claims 1 - 13. Affirmation of this election must be made by applicant in replying to this Office action. Claims 14 – 38 are withdrawn from further consideration by the examiner, 37 CFR 1.142(b), as being drawn to a non-elected invention.

Claim Rejections - 35 USC § 112

3. The following is a quotation of 35 U.S.C. 112(b):
(b) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.

The following is a quotation of 35 U.S.C. 112 (pre-AIA), second paragraph:
The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

4. Claims 1-10 are rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention. Claims 1-10 recite the term “the composition” or “the aqueous inorganic patterning composition”. However, there is no positive recitation of a composition or aqueous inorganic patterning composition recited by the instant claims. There is insufficient antecedent basis for these limitations in the claims.

5. Claim 10 is rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention. Claim 10 recites “… a combination thereof within an appropriate oxygenated ion.” However, the term “within an appropriate oxygenated ion” is indefinite and confusing claim language. Appropriate correction is required.

Claim Rejections - 35 USC § 103

6. The following is a quotation of pre-AIA 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained through the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

7. The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under pre-AIA 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.

2. Ascertaining the differences between the prior art and the claims at issue.

3. Resolving the level of ordinary skill in the pertinent art.

4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

8. Claims 1-5 and 7-10 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Jason Stowers, Douglas A. Keszler, "High resolution, high sensitivity inorganic resists", (2009) as evidenced by Nakamura (JP 2006/284947 A).

Regarding claims 1-5 and 7-10, Stowers et al. disclose an aqueous precursor solutions (aqueous inorganic patterning precursor solution) comprising $ZrOCl_2 \cdot 8H_20$, $HfOCl_2 \cdot H_20$, H_2SO_4, $H_20_2$and purified water (especially, please see 2. Experimental). Stowers et al. disclose that a final metal concentration is 0.5M and metal-to-sulfate ratios 1:05-0.7.

Stowers et al. do not explicitly disclose the molar concentration ratio of ligands to metal suboxide cations is at least about 2 or least about 5 or at least about 7 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours or 24 hours without additional mixing as instantly recited. It is noted that the term “about" is relative terminology. The molar concentration ratio is optimizable. In general, it is the exertion of creative capability for those skilled in the art to optimize or

adapt number-range of compositional ration. If the difference is only the number-range of the compositional ratio, it is obvious for those skilled in the art to optimize or adapt number-range of compositional ratio unless there are grounds which can suppose existence of non-obviousness except advantageous effects compared with the invention of Reference. Thus, in the invention of Stowers et al., the content of H202 is within optimal range which can be properly adjusted by those skilled in the art unless there are grounds which can suppose existence of non-obviousness except advantageous effects compared with the invention of Reference.

Therefore, it is discussed below whether or not the invention of this application has advantageous effects compared with the invention of Stowers et al. Since Stowers et al. disclose that peroxide inhibits condensation of metal oxides (please see page 732, lines 4-7 of left column.), it is obvious for those skilled in the art to predict function effects of stability with respect to phase separation in the invention of this application by increasing concentration ratio of peroxide.

With respect to the above, it is described in the specification that the increase in the radiation sensitive ligand concentration reduces agglomeration of the metal cations to stabilize, the precursor solution and thus the precursor solution can be stable relative to settling of solids without further stirring for at least two hours (please see from page 7, lines 30-31 to page 8, lines 1-2). However, the above matter does not specifically support in practical examples and quantitative function in the differences of the ratio of mole concentration cannot be understood. If the increase of stability in precursor solution is qualitative function, it is obvious for those skilled from indication of Stowers et

al. It is described in the specification that significantly increasing the radiation sensitive ligand concentration in the precursor solutions results in a coating material that has greater contrast following radiation exposure so that there are surprising added benefits where precursor solution stabilization further accomplishes improved patterning and shorter development times (please see page 8, lines 18-22 and page 13, lines 16-21).

However, it is technical common sense in filing time that the contrast to developer increases if stabilization in the precursor solution increases and thus unnecessary reaction of an unexposed area does not arise as evidenced by Nakamura (see entire reference). Thus, those skilled in the art can qualitatively predict the above advantages. Specific composition of the precursor solution is described in Example 1 and patterning by using the precursor solution is described in Example 3 and 4. However, it is not described in the specification that there are quantitative differences as to contrast and developing time in between a molar concentration ratio of ligands to metal suboxide cations of more than 2 (Hf based coating material) and less than 2 (Zr based coating material). Thus, special technical sense is not found as to a molar concentration ratio of ligands to metal suboxide cations of more than 2.

Therefore, it is not considered that the invention of this application has advantageous effects compared with the invention of Stowers et al. and thus the content of H_2O_2 in the invention of Stowers et al. is within optimal range which can be properly adjusted by those skilled in the art from indication of Stowers et al.

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide

cations to yield desired molar concentration ratio. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

9. Claim 6 is rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Jason Stowers, Douglas A. Keszler, "High resolution, high sensitivity inorganic resists", (2009) as evidenced by Nakamura (JP 2006/284947 A) as applied to claims 1-5 and 7-10 above, and further in view of Keszler et al. (WO 2009/120169 A1).

Regarding claim 6, Stowers et al. do not explicitly disclose the polyatomic anions comprise borate, phosphate, tungstate, silicate or combinations thereof as instantly recited. However, Keszler et al. teach a precursor solution (abstract and title and page 30, lines 10-17) comprising borate, phosphate and silicate and combinations thereof in view of aiding in coating, liquid misting, physical and vapor deposition and solubility. Keszler et al. and Stowers et al. are analogous art in the inorganic precursor solution. Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify the polyatomic anions of Stowers et al. to include borate, phosphate and silicate and combinations thereof in view of aiding in coating, liquid misting, physical and vapor deposition and solubility.

10. Claims 1-13 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Herman et al. (US 2005/0242330 A1) in view of Keszler et al. (KR2008/0090383; citations from corresponding US PGPUB 2011/0045406 A1).

Regarding claims 1 and 7-9, Herman et al. disclose an aqueous inorganic patterning precursor solution (dielectric material) comprising a meta containing cation a

polyatomic anion, wherein the metal containing cation includes one or more HfO^{2+}, ZrO^{2+}, etc and the polyatomic anion includes one or more of sulfate, borate and tungstate, and etc (figures, claims and [0009-0010 and 0014-0016]).

Herman et al. do not explicitly disclose the precursor solution comprises radiation sensitive ligands comprising peroxide groups as instantly recited. Also, Herman et al. do not explicitly disclose the molar concentration ratio of ligands to metal suboxide cations is at least about 2 or least about 5 or at least about 7 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours or 24 hours without additional mixing as instantly recited. It is noted that the term “about" is relative terminology. The molar concentration ratio is optimizable. Nonetheless, Keszler et al. teach a laminate structure comprising a layer comprising solid inorganic acid or base and peroxide (abstract, claims and [0018-0019 and 0065-0068]). The molar concentration of ligands to metal suboxide cations could have been easily selected by one of ordinary skill in the art to adjust the properties of the precursor solution. It would have been obvious to one of ordinary skill in the art at the time of the invention to include a ligand comprising peroxide group to the precursor solution of Herman et al. in view of aiding in bonding and oxidation.

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide cations to yield desired molar concentration ratio. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Further regards to claims 2 and 3, Herman et al. do not explicitly disclose the metal suboxide cation concentration from about 0.01 M to about 1.4M as instantly recited or polyatomic anion concentration about 0.75 to about 1.5 times the metal suboxide cation concentration as instantly recited. It is noted that the term “about" is relative terminology. The concentration is optimizable.

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the polyatomic anion and metal suboxide cations to yield desired concentration. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Further regards to claims 4, 5 and 6, Herman et al. teach HfO^{2+} and ZrO^{2+} as metal containing cations and sulfate, borate and tungstate as polyatomic inorganic anions (figures, claims and [0009-0010 and 0014-0016]).

Further regards to claim 10, Herman et al. teach metal such as HF and Zr (claims).

Regarding claims 11-13, Herman et al. do not explicitly disclose a method of formation of a radiation sensitive inorganic coating precursor solution as instantly recited. However, Keszler et al. teach a method for formation of an inorganic precursor composition combining a first aqueous solution comprising metal suboxide cations and a complexing solution comprising a ligand having peroxide group ([0064 and 0097] and, claims and figures examples).The first aqueous solution is mixed with the complexing solution to form a ligand-cation mixture prior to introduction of the inorganic anions

([0064 and 0097] and, claims and figures examples). The ligand-cation mixture solution is aged at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion ([0064 and 0097] and, claims and figures examples).

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to easily conceive the teaching of Keszler et al. to the method of patterning a dielectric material in Herman et al.

Double Patenting

11. The nonstatutory double patenting rejection is based on a judicially created doctrine grounded in public policy (a policy reflected in the statute) so as to prevent the unjustified or improper timewise extension of the "right to exclude" granted by a patent and to prevent possible harassment by multiple assignees. A nonstatutory double patenting rejection is appropriate where the claims at issue are not identical, but at least one examined application claim is not patentably distinct from the reference claim(s) because the examined application claim is either anticipated by, or would have been obvious over, the reference claim(s). See, e.g., *In re Berg*, 140 F.3d 1428, 46 USPQ2d 1226 (Fed. Cir. 1998); *In re Goodman*, 11 F.3d 1046, 29 USPQ2d 2010 (Fed. Cir. 1993); *In re Longi*, 759 F.2d 887, 225 USPQ 645 (Fed. Cir. 1985); *In re Van Ornum*, 686 F.2d 937, 214 USPQ 761 (CCPA 1982); *In re Vogel*, 422 F.2d 438, 164 USPQ 619 (CCPA 1970); and *In re Thorington*, 418 F.2d 528, 163 USPQ 644 (CCPA 1969).

A timely filed terminal disclaimer in compliance with 37 CFR 1.321(c) or 1.321(d) may be used to overcome an actual or provisional rejection based on a nonstatutory double patenting ground provided the reference application or patent either is shown to

be commonly owned with this application, or claims an invention made as a result of activities undertaken within the scope of a joint research agreement. A terminal disclaimer must be signed in compliance with 37 CFR 1.321(b).

The USPTO internet Web site contains terminal disclaimer forms which may be used. Please visit http://www.uspto.gov/forms/. The filing date of the application will determine what form should be used. A web-based eTerminal Disclaimer may be filled out completely online using web-screens. An eTerminal Disclaimer that meets all requirements is auto-processed and approved immediately upon submission. For more information about eTerminal Disclaimers, refer to http://www.uspto.gov/patents/process/file/efs/guidance/eTD-info-I.jsp.

Claims 1-13 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-23 of U.S. Patent No. 8,206,892. Although the claims at issue are not identical, they are not patentably distinct from each other because both the US Patent '892 and the instant claims have claims drawn to an aqueous inorganic patterning precursor solution. Both the US Patent ‘892 and the instant claims recite open claim language, “comprising”; therefore, other elements and steps may be added to their respective inventions. Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide cations to yield desired molar concentration ratio. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CHANCEITY ROBINSON whose telephone number is (571)270-3786. The examiner can normally be reached on Monday to Friday (with every other Friday off): 9:00 -6:00 pm eastern time.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Cynthia Kelly can be reached on (571)272-1526. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Chanceity N Robinson/
Examiner, Art Unit 1722

Examiner-Initiated Interview Summary	Application No.	Applicant(s)	
	12/850,867	STOWERS ET AL.	
	Examiner	Art Unit	
	CHANCEITY ROBINSON	1722	

All participants (applicant, applicant's representative, PTO personnel):

(1) *CHANCEITY ROBINSON*. (3)_____.

(2) *Peter Dardi*. (4)_____.

Date of Interview: *09/06/2013*.

Type: ☒ Telephonic ☐ Video Conference
☐ Personal [copy given to: ☐ applicant ☐ applicant's representative]

Exhibit shown or demonstration conducted: ☐ Yes ☒ No.
If Yes, brief description: _____.

Issues Discussed ☐101 ☐112 ☐102 ☐103 ☒Others
(For each of the checked box(es) above, please describe below the issue and detailed description of the discussion)

Claim(s) discussed: *1-30*.

Identification of prior art discussed: *none*.

Substance of Interview
(For each issue discussed, provide a detailed description and indicate if agreement was reached. Some topics may include: identification or clarification of a reference or a portion thereof, claim interpretation, proposed amendments, arguments of any applied references etc...)

Examiner called Applicant's representative, Peter Dardi to do a phone restriction over claims 1-30. Applicant's representative inform the examiner that he has to discuss it with his clients. The examiner stated she would just mail out the restriction. However, the examiner reviewed the case history for the application and found out that a phone restriction had already been made on this instant application. Examiner called Applicant's representative back and left a message on his voicemail stating she is withdrawning her restriction and accepting the previously made telephone restriction made between Nicole Gugliotta and Mengmeng Fahrni on Jan. 2012 .

Applicant recordation instructions: It is not necessary for applicant to provide a separate record of the substance of interview.

Examiner recordation instructions: Examiners must summarize the substance of any interview of record. A complete and proper recordation of the substance of an interview should include the items listed in MPEP 713.04 for complete and proper recordation including the identification of the general thrust of each argument or issue discussed, a general indication of any other pertinent matters discussed regarding patentability and the general results or outcome of the interview, to include an indication as to whether or not agreement was reached on the issues raised.

☐ Attachment

/Chanceity N Robinson/ Examiner, Art Unit 1722	

Notice of References Cited	Application/Control No. 12/850,867	Applicant(s)/Patent Under Reexamination STOWERS ET AL.	
	Examiner CHANCEITY ROBINSON	Art Unit 1722	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-2005/0242330	11-2005	Herman et al.	252/570
*	B	US-2011/0045406	02-2011	Keszler et al.	430/270.1
	C	US-			
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
*	N	WO 2009120169 A1	10-2009	World Intellect	KESZLER et al.	
*	O	JP 2006284947 A	10-2006	Japan	NAKAMURA, HIDEYUKI	
	P	KR 20080090383 A	10-2008	Korean	Keszler et al.	
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
*	U	Jason, Stowers. Douglas A Keszler, "High resolution, high sensitivity inorganic resists", Microelectronic Engineering, Vol. 86, NO. 4-6, 2009 pp. 730-733
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

(19) 대한민국특허청(KR)
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(11) 공개번호 10-2008-0090383
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(51) Int. Cl.
H01B 1/12 (2006.01)
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심사청구일자 2008년08월18일
번역문제출일자 2008년04월29일
(86) 국제출원번호 PCT/US2007/023084
국제출원일자 2007년10월31일
(87) 국제공개번호 WO 2008/082448
국제공개일자 2008년07월10일
(30) 우선권주장
60/856,070 2006년11월01일 미국(US)

(71) 출원인
더 스테이트 오브 오레곤 액팅 바이 엔드 쓰루 더 스테이트 보드 오브 하이어 에쥬케이션 온 비해프 오브 오레곤 스테이트 유니버시티
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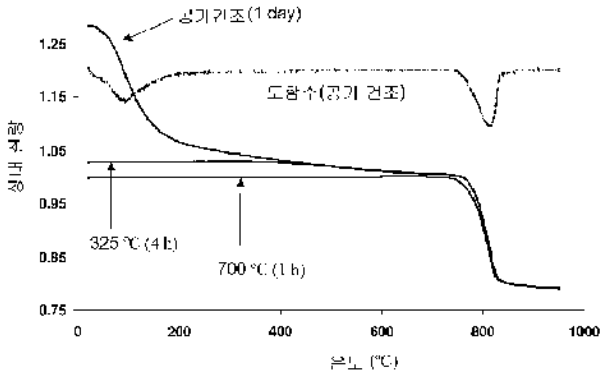
전체 청구항 수 : 총 27 항

(54) 용액 처리된 박막들 및 적층체들, 상기 박막들 및적층체들을 포함하는 장치들, 및 그들의 사용 방법 및 제조방법

(57) 요 약

하프늄 및/또는 지르코늄 옥시 히드록시 화합물들을 포함하는 박막 또는 적층체 구조물을 갖는 소자들 및 그러한 소자들의 제조 방법이 개시된다. 상기 하프늄 및 지르코늄 화합물들은 반응과 같은, 통상 다른 금속으로 도핑될 수 있다. 제조될 수 있는 전자 소자 또는 부품의 예는, 전연체, 트랜지스터 및 캐패시터를 포함하지만 여기에 한정되지 않는다. 포지티그 또는 네거티그 레지스트를 사용하여 소자를 패터닝하기 위한 방법이 설명된다. 시클 릴먼, 인프린트 리소그래피에 대하여 마스터 템플레이트가 사용될 수 있다. 부식 장벽을 갖는 소자를 제조하기 위한 방법의 구현예가 설명된다. 광학 시편과 코팅을 포함하는 광학 소자의 구현예들이 설명된다. 전사 엔니징을 이용하여 치수를 정확하게 측정하기 위한 것과 같은 물리적 자의 구현예가 설명된다.

대 표 도 - 도1



Lam Research Ex. 1004 - Page 442 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

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특허청구의 범위

청구항 1

하프늄 및/또는 지르코늄 옥시 하이드록시 실레이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 하이드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 하이드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 하이드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 하이드록시 실리케이트 ($MO_{2-x-z/2}(OH)_z(SiO_4)_x$) 화합물 중에서 적어도 하나를 포함하는 박막 또는 적층체 구조물을 포함하는 소자.

(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음)

청구항 2

제 1 항에 있어서,

상기 박막 또는 적층체가 약 9 내지 약 12의 범위에서 값을 갖는 유전율, 적어도 6 MV cm^{-1}까지의 항복 전계, 및 1 MV cm^{-1}의 전계 강도에서 거의 1 nA cm^{-2}의 누설 전류를 갖는 것을 특징으로 하는 소자.

청구항 3

제 1 항에 있어서,

상기 화합물이 란탄을 더 포함하고, 화학식 $M_{1-x}La_xO_{2-x-z/2}(SO_4)_z$ (MSOx:La)를 갖는 것을 특징으로 하는 소자.(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 약 3.8의 범위에서 어떤 값이든 가질 수 있음)

청구항 4

제 1 항에 있어서,

상기 화합물이 HafSOx, HafSOx/La, ZirSOx, ZirSOx:La, HafSOx:Ce, 또는 ZirSOx:Ca이고, 상기 소자가 50 nA cm^{-2} 미만의 누설 전류와 약 9 내지 약 12의 값을 갖는 유전율을 갖는 것을 특징으로 하는 소자.

청구항 5

제 1 항에 있어서,

상기 소자가 HafSOx:La 및/또는 ZirSOx:La을 게이트 유전체로서, 아연 인듐 산화물 및/또는 아연 주석 산화물을 채널로서 포함하는 전계효과 트랜지스터이고, 상기 트랜지스터가 10^6보다 큰 온-투-오프 비율(on-to-off ratio) 및 pA cm^{-2} 범위의 값을 갖는 게이트 누설 전류를 갖는 것을 특징으로 하는 소자.

청구항 6

제 1 항에 있어서,

광학 기판을 더 포함하고, 상기 박막 또는 적층체 구조물이 상기 광학 기판 위에 코팅을 형성하는 것을 특징으로 하는 소자.

청구항 7

제 6 항에 있어서,

상기 코팅이 반사-방지 코팅이고, 및/또는 상기 코팅이 가시광선 또는 자외선에 대하여 투명한 것을 특징으로 하는 소자.

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청구항 8

제 6 항에 있어서,

상기 광학 기판과 코팅이 유전체 거울(dielectric mirror), X-선 거울, 감쇠 필터, 회절 격자, 및/또는 도파관(waveguide)을 정의하는 것을 특징으로 하는 소자.

청구항 9

제 7 항에 있어서,

상기 코팅이 Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+} 및 이들의 조합으로부터 선택되는 발광성 이온을 포함하는 도핑된 발광층을 제공하기 위하여, 선택적으로 도핑된 것을 특징으로 하는 소자.

청구항 10

제 1 항에 있어서,

상기 소자가 임프린트 리소그래피를 위한 마스터 플레이트이고, 상기 박막 또는 적층체 구조물이 가요성 또는 유리 기판 위에 증착되고, 상기 박막 또는 적층체 구조물이 상기 기판 위에 증착된 HafSOx의 제1층과 ZirSOx:Cn을 포함하는 제2층을 포함하고, 상기 제1층 및 제2층을 포함하는 적층체 구조물이 에너지 공급원에 노출됨으로써 패터닝되는 것을 특징으로 하는 소자.

청구항 11

제 10 항에 있어서,

마스크를 통해 빛 또는 전자빔에 노출시키는 것이 상기 두 층들의 상호확산(interdiffuse)을 노출된 영역에서 일으키고, 그에 의하여 노출 이전에는 도포되어 있었던 HafSOx 층을 가용하게(soluble) 만들고, 가용하게 된 상기 HafSOx 층이 세정되어 상기 마스터 플레이트의 적어도 부분적인 트렌팅 구조물을 정의하는 것을 특징으로 하는 소자.

청구항 12

박막 또는 적층체 구조물을 제공하는 단계; 및

상기 구조물을 에너지 공급원에 노출시키는 단계;

를 포함하고,

상기 구조물은 기판과 상기 기판 위에 증착된 하나 또는 그 이상의 층들을 포함하고,

상기 하나 또는 그 이상의 층들의 적어도 하나는 하프늄 및/또는 지르코늄 옥시 하드록시 실페이트 ($MO_{x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 하드록시 텅스페이트 ($MO_{x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 하드록시 보레이트 ($MO_{x-(x/2+z/2)}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 하드록시 포스페이트 ($MO_{2-(2x/2+z/2)}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 하드록시 실리케이트 ($MO_{2-(4x/2+z/2)}(OH)_z(SiO_4)_x$) 화합물을 포함하는 소자의 제조 방법.

(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 3.5(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음)

청구항 13

제 12 항에 있어서,

상기 박막 또는 적층체 구조물은 기판, 패터닝을 위한 제1층, 및 하프늄 및/또는 지르코늄 옥시 하드록시 화합물을 포함하는 제2층을 포함하고, 상기 제2층은 포지티브 레지스트층으로서 에너지 공급원에 노출되고 상기 레지스트층 분절이 현상액에 녹을 수 있는 분절로 전환되고,

상기 구조물을 패터닝하기 위하여 상기 레지스트층을 현상액으로 처리함으로써 상기 에너지 공급원에 노출된 레

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지스트층 물질을 제거하는 단계를 더 포함하는 것을 특징으로 하는 방법.

청구항 14

제 12 항에 있어서,

상기 박막 또는 적층체 구조물은 기판, 패터닝을 위한 제1층, 및 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 제2층을 포함하고, 상기 제2층은 네거티브 레지스트층으로서 에너지 공급원에 노출되면 상기 레지스트층이 중합되고,

상기 에너지 공급원에 노출되지 않은 물질을 제거하기 위하여 현상물질(developer)로 상기 구조물을 처리함으로써 상기 구조물을 패터닝하는 단계를 더 포함하는 것을 특징으로 하는 방법.

청구항 15

제 13 항에 있어서,

상기 포지티브 레지스트가 이중층(bilayer)을 포함하고, 상기 이중층의 제2층이 불용성 하프늄 옥사이드 설페이트(HafSOx) 막 위에 증착되고 산에 녹을 수 있으며 Cu-도핑된 지르코늄 옥사이드 설페이트(ZircSOx:Cu) 막을 포함하고,

마스크를 통해 빛 또는 전자빔을 포함하는 에너지 공급원에 노출시키는 것이 상기 ZircSOx:Cu 막과 상기 HafSOx 막의 상호확산을 노출된 영역에서 일으키고, 그에 의하여 HafSOx 막을 가용하게 만드는 것을 특징으로 하는 방법.

청구항 16

제 12 항에 있어서,

상기 하프늄 및/또는 지르코늄 옥시 히드록시 화합물이 설페이트를 포함하고, 상기 설페이트가 염기성 수용액과의 이온 교환에 의하여 후속 제거되고, 상기 염기성 용액이 1족 금속 히드록사이드, 가용성 2족 금속 히드록사이드, 가용성 3족 금속 히드록사이드, 가용성 란탄계 히드록사이드, 암모늄 히드록사이드 및/또는 수성(aqueous) 3차 아민, 또는 이들의 조합을 포함하는 것을 특징으로 하는 방법.

청구항 17

제 12 항에 있어서,

반도체 물질, 금속, 유리, 실리카, 고분자 물질, 또는 이들의 조합을 포함하는 적절한 기판을 제공하는 단계;

상기 기판 위에 HafSOx의 제 1 막을 용액 증착하는 단계;

적층체 구조물을 형성하기 위하여, 상기 제 1 막 위에 ZircSOx:Cu의 제 2 막을 용액 증착하는 단계;

상기 HafSOx 막과 상기 ZircSOx:Cu 막이 노출된 영역에서 상호확산하고 그에 의하여 노출 이전에는 도핑되지 않았던 HafSOx 막을 가용하게 만들기 위해, 상기 적층체 구조물을 에너지 공급원에 노출시키는 단계; 및

HafSOx 막을 제거하기 위하여 상기 노출된 구조물을 현상하는 단계;

를 포함하는 것을 특징으로 하는 방법.

청구항 18

제 12 항에 있어서,

상기 박막 또는 적층체 구조물이 기판, 상기 기판 위에 증착된 불용성 하프늄 옥사이드 설페이트(HafSOx)의 제 1 층, 및 상기 제 1 층 위에 증착되고 포름산 구리염(copper formate)을 포함하는 제 2 층을 포함하고,

상기 포름산 구리염의 분해와 상기 HafSOx 층과의 상호확산을 유발하고 그에 의하여 가용성 생성물을 생성하고 상기 가용성 생성물을 제거하기 위해, 상기 제 1 층 및 제 2 층을 포함하는 상기 적층체 구조물이 약 50 ℃ 내지 약 200 ℃의 온도로 가열되는 것을 특징으로 하는 방법.

청구항 19

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제 12 항에 있어서,

상기 박막 또는 적층체 구조물이 기판 및 고체 무기 산 또는 염기를 포함하는 제 1 층을 포함하고, 상기 고체 무기 산 또는 염기가 21번 내지 78번 범위의 원자 번호를 갖는 금속을 포함하고, 상기 제 1 층이 과산화물 또는 다른 배위 음이온을 더 포함하며, 상기 제 1 층이 산 또는 염기에 가용하며,

구조적으로 단단한 막을 제조하기 위하여 약 50 ℃ 내지 약 125 ℃의 온도로 상기 제 1 층이 가열되고, 마스크를 통하여 레이저, 전자빔 및/또는 빛에 노출시키는 것이 상기 막의 노출된 영역이 노출되지 않은 영역에 비하여 더 낮은 용해도를 갖도록 하므로써 노출되지 않은 영역이 제거되고 상기 막에 패턴이 정의되는 것을 특징으로 하는 방법.

청구항 20

제 19 항에 있어서,

상기 막에 패턴을 정의하기 위하여 상기 막이 0 $\mu C/cm^2$ 보다 크고 적어도 400 $\mu C/cm^2$까지의 도스 레벨, 더욱 일반적으로는 약 2 $\mu C/cm^2$ 내지 약 400 $\mu C/cm^2$의 도스 레벨로 전자빔에 노출되는 것을 특징으로 하는 방법.

청구항 21

제 19 항에 있어서,

패터닝된 상기 막이 약 3 nm 미만의 구조적 집적도(integrity)를 보이는(demonstrate) 것을 특징으로 하는 방법.

청구항 22

제 12 항에 있어서,

상기 소자가 마이크로- 또는 나노-제닉 이레이를 포함하고, 상기 구조물이 기판, 제 1 층, 및 제 2 층을 포함하고, 상기 제 2 층은 금속 산화물 층이고, 상기 방법이

상기 구조물을 패터닝하는 단계; 및

상기 구조물을 패터닝함으로써 생성된 원하는 패턴을 갖는 내구성이 있는 물질을 형성하기 위하여 상기 구조물을 에너지 공급원에 노출시키는 단계;

를 더 포함하는 것을 특징으로 하는 방법.

청구항 23

제 22 항에 있어서,

스탬핑(stamping)된 층을 형성하기 위하여 준-고체(semi-solid) 하프늄 또는 지르코늄 화합물에 원하는 크기 스케일의 단위 지형물(feature)들을 스탬핑하는 단계를 더 포함하는 것을 특징으로 하는 방법.

청구항 24

상기 소자가 금속 및 금속/세라믹-계 열 보호(thermal protection) 시스템, 유기계 디스플레이 및 전자 제품, 태양 전지, 고 방사율(emissivity) 코팅, 산화물계 세라믹 매트릭스 시스템에 대한 재발 코팅, 인광체(phosphor) 위의 보호 코팅, 금속- 및 세라믹계 시스템에 대한 주변적 장벽 코팅, 복합체 및 섬유 레이저용 심유, 용해 금속 처리에서의 부식 방지, 반응용 모노리딕 물질 및 촉매 담체로부터 선택되며, 청구항 22의 방법에 의하여 제조되는 소자.

청구항 25

소자를 제공하는 단계;

하프늄 및/또는 지르코늄 옥시 하드록시 산페이트 $(MO_{2-x-2y}(OH)_{2x}(SO_4)_y)$ 화합물, 하프늄 및/또는 지르코늄 옥시 하드록시 텅스테이트 $(MO_{2-x-2y}((OH)_{2x}(WO_4)_y)$ 화합물, 하프늄 및/또는 지르코늄 옥시 하드록시 모레이트 $(MO_{2-2x}$

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$_{z/2}(OH)_z(BO_5)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) 화합물을 포함하는 금속 산화물층을 포함하는 소자 위에 적어도 하나의 부식 장벽을 형성하는 단계(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음); 및

상기 부식 장벽을 형성하기 위해 상기 화합물을 에너지 공급원에 노출시키는 단계;

를 포함하는 부식 장벽을 갖는 소자의 제조 방법.

청구항 26

하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_5)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) 화합물을 포함하는 조성물을 제공하는 단계(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음);

상기 화합물을 포함하는 용액을 형성하는 단계;

상기 용액을 섬유들(fibers) 내부로 인입시키는 단계; 및

상기 섬유들을 고체로 전환시켜 안정한 섬유로 만드는 단계;

를 포함하는 섬유의 제조 방법.

청구항 27

적어도 두 금속을 포함하는 금속 산화물 막의 제조 방법으로서,

용액을 제조하는 단계로서, 금속 양이온 및 하나 또는 그 이상의 음이온으로 필수적으로 구성되는 하나 또는 그 이상의 가용성 염을 착화합물을 형성하지 않는(non-complexing) 비수계 극성 용매에 용해시키는 단계를 포함하고, 금속 양이온들의 적어도 하나가 3+보다 큰 형식 전하를 갖고, 3+보다 큰 형식 전하를 갖는 금속 양이온들의 농도가 상기 금속 산화물 막 내의 금속 양이온들의 50 몰%를 초과하고, 상기 용매가 150 ℃ 미만의 끓는점을 갖는, 용액을 제조하는 단계;

상기 용액의 pH를 증가시키되, 상기 pH를 증가시키는 단계는 염기성 수용액을 첨가하는 단계, 가용성 염기 산화물을 소량 첨가하는 단계, 염기성 수용액을 형성할 수 있는 기체 화합물을 첨가하는 단계, 양성자를 소비할 수 있고 상기 막 내에 통합되는 양전성(electropositive) 금속을 첨가하는 단계, 양성자를 소비하거나 상대 이온(counter ion)을 분해하지만 상기 막 내에 통합되지 않는 수계 또는 기체 산화제를 첨가하는 단계, 또는 이들 단계들의 조합을 포함하는, 상기 용액의 pH를 증가시키는 단계;

상기 비수계 용매를 증발시킴으로써 고체를 제조하는 단계;

상기 고체를 물에 용해시키는 단계;

패터닝된 또는 블랭킷 액막을 형성하기 위해 상기 용해된 고체를 기판 위에 증착하는 단계; 및

상기 막을 열적으로 경화하는 단계;

를 포함하는 금속 산화물 막의 제조 방법.

명 세 서

기 술 분 야

<1> 본 개시는 전자 및 광학적 응용을 포함하는 목적들에 대하여 공간적으로-정의되는 구조물을 만드는 데 유용한

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무기 금속 산화물 물질을 포함하는 소자들 및 특성들의 구현예들 및 그들의 제조 방법 및 사용 방법의 구현예들에 관한 것이다.

<2> <관련 출원의 상호 참조>

<3> 본 출원은 2006년 11월 1일이 출원되었고, 그 전문가 여기에 인용되어 통합되는 미합중국 비정규출원 제60/856,670호의 선행 출원일의 이익을 주장한다.

<4> <정부 지원의 감사>

<5> 본 개시의 구현예들은 DARPA 보조금 번호 HR0011-06-1-0045의 인정 기금을 이용하여 개발되었다. 미합중국 정부는 본 발명의 특정 권리를 갖는다.

배경 기술

<6> 전자 소자들은 일반적으로 물질의 순차적인 증착 및 식각과 같은 반복적인 공정 단계들을 이용하여 제조된다. 무기 물질들을 포함하는 소자들에 있어서, 금속-유기 전구체들이 무기 산화물들의 용액-기반(solution-based) 증착에 대하여 널리 사용되어 왔다. 유기 모이어티(moiety)의 존재는 유기 물질의 제거를 위한 고온 소각(burnout) 단계가 필요하게 한다. 이 단계는 상당한 부피 변화, 결정화 및 "너드 크래킹(mud cracking)"이라고 하는 현상을 일으킬 수 있다. 이와 관련된 결함들이 이 물질들의 패턴으로서의 그리고 소자들 내에서의 성능을 저해한다.

<7> 전자 소자 응용에 있어서 용액 처리 물질을 위한 방법들이 특허받아 왔다. 예를 들면, Ostergard의 미합중국 특허 제6,946,677호 "Pre-Patterned Substrate for Organic Thin Film Transistor Structures and Circuits and Related Method for Making Same"은 원하는 회로구성을 기판의 표면에 형성하는 단계, 및 그에 의하여 유기박막 트랜지스터(OTFT: organic thin film transistor) 구조 및 상호 연결하는 도전성 경로들을 형성하기에 유용한 물질을 수용하기 위해 상기 영역을 에비-패터닝(pre-patterning)하는 단계를 설명한다. 상기 미합중국 특허 제6,946,677호에 따르면, OTFT 물질은 잉크젯 프린팅과 같은 프린팅 기술을 이용하여 에비-패터닝된 영역에 증착된다.

<8> Weng 등의 미합중국 특허 제6,927,108호는 트랜지스터를 형성하기 위한 박막 물질들의 용액 처리를 설명한다. 상기 미합중국 특허 제6,927,108호는 "트랜지스터 동작이 가능한 용액 처리된 박막 구조를 형성하기 위해 순차적으로 조직화된 도전성 용액-처리된 박막 물질 전구체들, 반도체 용액-처리된 박막 물질 활성 영역들, 및 유전 용액-처리된 박막 물질 층들"을 형성하는 단계를 설명한다.

<9> 미합중국 특허공개 제2005/0242330A1호는 전자 응용에 유용한 하프늄 및 지르코늄 화합물들에 관한 것으로서, 여기에 인용되어 통합된다. 미합중국 특허공개 제2005/0242330A1호는 발명자로서 Douglas Keszler 박사를 지명하고 있으며 그는 여기에 개시된 구현예들의 발명자이기도 하다.

발명의 상세한 설명

<10> 미합중국 특허공개 제2005/0242330A1호는 선행 기술의 결함을 해결하는 방식으로 무기 화합물의 용액 증착과 화합물을 개시한다. 여기 놀면, 본 발명에 따른 용액 증착은 금속-유기 증착 기술에 대하여 요구되는 유기 물질의 사용을 피할 수 있으며, 따라서 유기물질의 소각(burnout)을 피할 수 있고, 소각에 따라 관련되는 크래킹 문제를 피할 수 있다.

<11> 본 발명의 일 구현예는 하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) 화합물 중에서 적어도 하나를 포함하는 박막 또는 적층체 구조물을 포함하는, 전자 소자와 같은, 소자에 관한 것이다. 여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있다. x는 약 0.1 내지 약 3.5/(금속원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있다. 예를 들면, 옥시 히드록시 설페이트 화합물들과 같이 전하가 2인 다원자 이온에 대해서는 x는 약 0.1 내지 약 1.75의 범위 내에서 어떠한 값이든 가질 수 있다. z는 0.0 내지 약 3.8의 범위에서 어떤 값이든 가질 수 있다.

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<12> 특정 구현예들은 화학식 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$)를 갖는 하프늄 또는 지르코늄 옥시 히드록시 설페이트 화합물을 포함하는 박막 또는 적층체에 관한 것이다. (여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 1.75의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 약 3.8의 범위에서 어떤 값이든 가질 수 있음) 이들 화합물들은 HafSOx 및 ZircSOx로 불리기도 한다. 상기 하프늄 및 지르코늄 화합물들은 통상 칼슘, 세륨, 란탄, 또는 이들의 조합과 같은 다른 금속들로 도핑될 수도 있다. 특정 구현예들은 화학식 $M_{1-x}La_yO_{2-x-z/2-y/z}(OH)_z(SO_4)_x$ (MSOx:La)를 갖는 화합물을 제조하기 위해 도펀트로서 란탄을 사용하였다. 여기서, 조성과 양론은 위에서 언급한 바와 같다. 란탄-도핑된 화합물의 특정 예는 $Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$이다. 추가적인 예시적인 화합물들은 HafSOx:La, ZircSOx:La, HafSOx:Ce, 또는 ZircSOx:Ca를 포함한다. 특정 구현예에서, 설페이트는 수성 염기와의 이온 교환을 통해 후속적으로 제거되고, M(OH)x 또는 MOx 막을 가져오게 된다. 적합한 수성 염기들은, 무엇보다도, 1족 금속 히드록사이드들, 2족 금속 히드록사이드들, 3족 금속 히드록사이드들, 란탄화 히드록사이드들, 암모늄 히드록사이드, 및/또는 수성 3차 아민류를 포함한다.

<13> 특정 구현예들은 둘 또는 그 이상의 금속을 갖는 착체(complex) 조성물을 포함하는 얇은 산화물 막 또는 적층체들에 관한 것이다. 상기 금속 양이온들의 적어도 하나는 3+보다 큰 전하를 갖고, 3+보다 큰 전하를 갖는 양이온들의 총 농도는 목표 산화물 내의 금속 양이온들의 50 몰%를 넘는다. 용해된 염들과 소정량의 물을 포함하는 비-수계 용액이 제조된다. 물의 양은 비-수계 용매의 20 몰% 미만이다. 상기 용액의 pH는 염기를 첨가함에 의하여 또는 산화-환원 메커니즘을 통한 자유 양성자의 반응에 의하여 최초 용액에 비하여 증가된다. 최종 용액의 pH는 사용되는 금속 양이온에 의존하지만, 약 2 내지 9의 범위에 있을 것이다. 증가된 pH는 양이온에 결합된 물 분자들의 가수분해와 그 결과로서 얻어지는 이들 히드록소-양이온들의 응축을 가져온다. 상기 용매는 증발되고, 그 결과 고체는 물에 용해 또는 분산되게 되고 이어서 기판에 액체 막으로서 적용된다. 그런 후, 상기 액체 막은 100 ℃ 내지 600 ℃ 사이의 온도에서 약 5 분 내지 240 분 동안 열적으로 경화된다.

<14> 본 발명에 따라 제조될 수 있는 전자 소자들 또는 소자 부품들의 예는 전계 효과 트랜지스터에서 게이트 절연막과 같은 절연체류, 전계 효과 트랜지스터와 같은 트랜지스터류, 및 MIM 캐패시터와 같은 캐패시터류를 포함하지만 여기에 한정되지 않는다. 본 구현예에 따라 제조된 박막들 및 적층체들은 약 9 내지 약 12의 범위에서 유전율 값을 갖고, 적어도 3 MV cm^{-1}에서 약 6 MV cm^{-1}까지의 항복 전계를 갖고, 1 MV cm^{-1}의 전계 강도에서 거의 1 nA cm^{-2}의 누설 전류를 가졌다. ZircSOx:Ca를 이용하여 제조한 소자들은 약 3.6 MV cm^{-1}의 항복 전계, 약 50 nA cm^{-2} 미만, 더욱 전형적으로는 약 10 nA cm^{-2} 미만의 누설 전류를 가졌다.

<15> HafSOx:La 및/또는 ZircSOx:La를 게이트 유전체 물질로서 이용하여 전계 효과 트랜지스터들을 제조할 수 있다. 개시된 특정 구현예들은 채널로서 아연 인듐 산화물 및/또는 아연 주석 산화물을 사용하였다. 특정 전계 효과 트랜지스터들은 10^6보다 큰 온-투-오프 비율(on-to-off ratio), 및 nA cm^{-2}의 게이트 누설 전류를 가졌다.

<16> 본 발명의 또 다른 구현예는 포토레지스트를 이용하여 소자를 패터닝하는 방법에 관한 것이다. 본 방법의 특정 구현예는 먼저 패터닝될 구조물을 제공하는 단계를 포함한다. 상기 구조물은 통상 반도체 물질, 금속, 유리, 고분자 물질, 또는 이들의 조합과 같은 기판; 실리카와 같이, 패터닝을 위한 물질층; 및 레지스트 층을 포함한다. 상기 레지스트 층은 통상 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함한다. 상기 구조물은 전자빔 또는 빛, 특히 예를 들면 자외선 광과 같은 에너지 공급원에 노출된다. 그런 후, 상기 소자를 패터닝하기 위해 물질이 제거되거나 소자의 활성, 패터닝된 부품으로서 유지된다.

<17> 상기 레지스트는 포지티브 레지스트 또는 네거티브 레지스트일 수 있다. 예를 들면, 상기 방법은 상기 레지스트층을 에너지 공급원에 노출시켜 상기 레지스트 층 물질을 현상액(developer)에 용해될 수 있는 물질로 전환시키는 단계를 포함할 수 있다. 상기 현상액에 용해될 수 있는 물질은 그 후 현상액을 이용하여 제거된다. 적합한 현상액들은, 무엇보다도, 산, 염기, 및/또는 초음파 교반(ultrasonic agitation)을 포함할 수 있다. 다시 예로서, 상기 방법은 에너지 공급원에 노출된 레지스트층 물질을 제거하는 단계를 포함할 수 있다. 본 발명을 특정 작동 이론에 한정됨이 없이, 적어도 특정 구현예에 대하여, 에너지 공급원에 대한 노출은 레지스트 층의 중합을 일크길 수 있고, 에너지 공급원에 노출되기 전에 비하여 현상액에 상대적으로 덜 용해되게 만들 수 있다.

<18> 포지티브 레지스트의 한 구현예는 이중층을 포함한다. 상기 이중층의 제1층은 하프늄 옥사이드 설페이트(HafSOx) 막 위에 증착된 포름산 구리의 막을 포함한다. 상기 포름산 구리의 막은 산에 가용성이고, 도핑되지 않은 HafSOx 막은 산에 불용성이다. 상기 이중층을 마스크를 통해 빛에 노출시키거나 포커스를 맞춘 전자빔에

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노출시키는 것은 노출된 영역에서 두 막들이 상호확산하도록 하며, 그에 의하여 그 이전에 도핑되지 않았던 HafSOx 막을 가용성이 되게 한다.

<19> 레지스트를 제조하기 위한 이중층 공정의 다른 구현예는 고체 산 또는 염기의 제 1 층을 기판 위에 증착하는 단계를 포함하고, 상기 산 또는 염기는 하나 또는 그 이상의 금속 원자를 포함한다. 포름산 구리와 같은 산화물 전구체를 포함하는 현탁액을 상기 제 1 층 위에 원하는 패턴으로 적용한다. 가열 조건 하에서, 상기 전구체는 분해되어 옥사이드가 된다. 이어서 상기 산화물은 상기 제 1 층과 반응 및 상호확산하여 식각을 통해 패턴을 드러낼 수 있는 생성물을 형성한다. 선택적인 구현예는 산화물 입자를 가열과 함께, 또는 가열함이 없이 상기 제 1 층 위에 증착하고, 식각될 수 있는 생성물을 형성하는 직접 반응을 가져오는 단계를 포함한다. 추가적인 구현예는 산화물 전구체의 박층을 상기 제 1 층 위에 증착하는 단계를 포함한다. 그런 후, 포토마스크를 통해 빛에 노출시키거나 또는 포커스를 맞춘 레이저 또는 전자빔으로 직접 기록함으로써 활성화된 전구체의 패턴이 형성된다.

<20> 본 발명의 또 다른 구현예는 임프린트 리소그래피를 위한 마스터 플레이트에 관한 것이다. 상기 마스터 플레이트는 가요성 또는 유리 기판과 같은 기판을 포함하고, 박막 또는 적층체 구조물의 적어도 한 층이 적어도 하나의 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함한다. 마스터 플레이트의 특정 구현예는 상기 기판 위에 증착된 HafSOx의 층과 ZircSOx:Cu 층과 같은 제 2 층을 포함한다. 상기 마스터 플레이트는 노출된 영역에서 두 막들이 상호확산하도록 하기 위하여 마스크를 통해 빛 또는 전자빔에 노출시키는 것과 같이 에너지 공급원에 노출시킴으로써 패턴될 수 있다. 이것은 이전에 도핑되지 않았던 HafSOx 막이 가용성이 되어, 제거됨으로써 마스터 플레이트의 프린팅 피처들을 적어도 부분적으로 정의한다.

<21> 또 다른 구현예에서, 단일층 공정에서 본 발명의 막들을 이용하여 마스크 또는 템플릿을 제조할 수 있다. 고체 산 또는 염기와 같은, 무기 전구체의 박막이 퍼옥사이드 또는 유사한 음이온과 함께 기판 위에 증착된다. 상기 막은 구조적으로 강직한 막을 생성하기 위해 가열된다. 그런 후, 노출된 영역에서 응축/가교를 유발하기 위해 포토마스크를 통해 또는 레이저 또는 전자빔을 통해 노출된다. 노출된 영역의 용해도는 노출되지 않은 영역에 비하여 감소된다. 그런 후, 노출되지 않은 영역은 선택적으로 식각되어 막 내에 네거티브-톤의 이미지를 생성할 수 있다. 노출시키기 전에 상기 막을 더 높은 온도로 예열함으로써 포지티브-톤의 이미지들도 형성될 수 있다. 일부 구현예들에서, HafSOx와 같은 막을 수산화나트륨과 과산화수소의 혼합물로 처리함으로써 $M(OH)_x/H_2O_2$ 막이 형성된다. 그런 후, 그 결과로서 얻어지는 막은 빛에 또는 전자빔에 노출시킴으로써 패터닝된다.

<22> 기판, 패터닝을 위한 물질층, 및 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 금속 산화물층을 포함하는 패터닝될 구조물을 제공하는 단계를 포함하는 소자의 형성 방법이 또한 설명된다. 상기 구조물은 패터닝되고 그런 후 에너지 공급원에 노출되어, 상기 구조물을 패터닝함으로써 생성된 원하는 패턴을 갖는 내구성이 있는 물질을 형성한다. 상기 방법에 따라 제조된 소자의 일구현예는 마이크로- 또는 나노-채널 어레이와 같은 채널 어레이를 포함할 수 있다. 그러한 구현예들에 대하여, 상기 소자를 만들기 위한 방법은 반-고체 하프늄 또는 지르코늄 화합물에 원하는 크기 스케일의 단위 피처들을 스탬핑하여 스탬핑된 층을 형성하는 단계를 포함할 수 있다.

<23> 부식 장벽을 갖는 소자를 제조하기 위한 방법의 구현예도 설명된다. 상기 방법의 개시된 구현예들은 소자를 제공하는 단계 및 상기 소자 위에 적어도 하나의 부식 장벽을 형성하는 단계를 포함한다. 부식 장벽은 통상 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 금속 산화물층을 포함한다. 상기 방법은 부식 장벽을 형성하기 위해 상기 화합물을 에너지 공급원에 노출시키는 단계를 포함할 수도 있다. 그러한 소자들의 예는 금속 및 금속/세라믹-계 열 보호(thermal protection) 시스템, 유기계 디스플레이 및 전자 제품, 태양 전지, 고 방사율(emissivity) 코팅, 산화물계 세라믹 매트릭스 시스템에 대한 계면 코팅, 인광체(phosphor) 위의 보호 코팅, 금속- 및 세라믹계 시스템에 대한 주변적 장벽 코팅, 복합체 및 섬유 레이저용 섬유, 용해 금속 처리에서의 부식 방지, 단열용 모노리딕 물질 및 촉매 담체를 포함한다.

<24> 섬유를 형성하기 위한 방법의 구현예도 설명된다. 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 용액이 형성된다. 그런 후, 상기 용액은 섬유 내부로 인입된다. 상기 섬유는 가수분해, 어닐링, 공기 열분해 및 이들의 조합과 같이 적절한 어떠한 방법에 의해서든 고체, 안정한 형태로 전환될 수 있다.

<25> 광학 소자의 구현예들도 또한 설명된다. 상기 소자의 특히 개시된 구현예들은 광학 기판과, 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 기판 코팅을 포함한다. 상기 층은 반사방지 코팅일 수 있다. 상기 광학 기판 및 코팅은, 예를 들면, 유전체 거울(dielectric mirror), X-선 거울, 간섭 필터, 회절 격자, 및/또는 도파로(waveguide)를 정의할 수 있다. 상기 광학 소자는 시각적으로 투명하거나 또는 자외선 빛에 투명

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한 것과 같이 부동한 층을 포함할 수도 있다. 상기 층은 Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+} 및 이들의 조합으로부터 선택되는 발광 이온들을 갖는 도펀트 층을 제공하기 위해 선택적으로 도핑될 수 있다. 상기 층을 도핑하는 단계는 발광층을 형성하기 위해 사용될 수 있다.

<26> 물리적 자를 제조하기 위한 방법의 구현예들도 개시된다. 특정 구현예들은 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물의 용액 증착에 의하여 적어도 하나의 산-가용성 층을 형성하는 단계를 포함한다. 적어도 하나의 산-불용성 층이 상기 산-가용성 층에 인접하여 형성되고, 상기 산-불용성 층은 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물의 용액 증착에 의하여 형성된다. 이들 단계들의 반복은 교호하는 층들을 생성하고, 상기 방법은 교호하는 산-불용성 및 산-가용성 층들의 두께을 정확하게 결정하는 단계를 포함한다. 두께의 결정은 X-선 반사와 같이 적절한 어떠한 방법을 이용해서든 달성될 수 있다. 게다가, 적어도 하나의 층이 식각되어 측정하는 목적물에 대하여 손가락 모양의 2차 참조 패턴을 정의한다. 그러한 손자의 특정 구현예들은 전자 현미경을 이용하여 치수를 정확하게 측정하는 데 유용하다.

<27> 본 발명의 위에서의 그리고 다른 목적들, 피처들 및 장점들은 첨부된 도면을 참조하여 진행되는 다음의 상세한 설명으로부터 더욱 명백해질 것이다.

<28> 본 발명의 개시된 구현예들은 무기 물질들의 용액 증착(solution deposition)에 의하여 제조될 수 있는, 전자 소자들 또는 전자 소자들의 부품들을 포함하는 소자들에 관한 것이다. 본 개시서 전체적, 단수를 나타내는 "하나의(a, an)" 및 "상기"는 문맥상 명백히 달리 표시되지 않는 한 복수의 지시대상(referent)도 포함한다. 유사하게, "또는"이라는 단어는 문맥상 명백히 달리 표시되지 않는 한 "및"을 포함하는 의도한다. "포함한다(include)"라는 표현은 "포함하다(comprise)"를 의미한다. 여기에 표시된 모든 백분율은 달리 표시되지 않는 한 원자 백분율(atomic percentage)이다. 여기에서 언급된 모든 특허들 및 공개문헌들은, 달리 표시되지 않는 한, 그 전부가 여기에 인용되어 통합된다. 상충되는 경우에는, 용어의 설명을 포함하여 본 명세서가 우선될 것이다. 여기에 언급된 물질들, 방법들 및 실시예들은 예시적인 것일 뿐이고, 한정의 의도는 아니다.

<29> **I. 금속 산화물 설페이트(sulfate) 물질들 일반 및 미합중국 특허공개 제2005/0242330A1호**

<30> 본 개시는, 통상 전자 응용에 유용한 금속 산화물 설페이트 무기 물질들의 용액 증착, 무기 물질들의 용액 증착을 위한 방법의 구현예들에 관한 것이다. 이들 물질들의 구현예들은 미합중국 특허공개 제2005/0242330A1호에 설명되어 있다. 공개된 상기 출원의 특정 부분, 문단 0009 내지 문단 014가 아래에 부연된다. 부연된 이 문단에서 도면에 대한 참조부호는 미합중국 특허공개 제2005/0242330A1호에 공개된 도면들을 참조한다.

<31> 도 1은 유전 전구체 물질의 제조 공정의 일 구현예를 나타낸다. 일반적으로, 공정(10)은 금속-함유 양이온과 같은 제 1 반응물(12)을 제공하는 단계, 다원자(polyatomic) 음이온과 같은 제 2 반응물(14)을 제공하는 단계, 및 그런 후 상기 다원자 음이온과 상기 금속-함유 양이온을 반응시키는 단계를 포함한다. 상기 금속-함유 양이온 및 상기 다원자 음이온은 함께 반응하였을 때 수용액과 같은 용액으로 될 수 있다. 일 구현예에서, 상기 금속-함유 양이온은 하프늄 옥시 염화물($HfOCl_2(aq)$)와 같은 하프늄 옥시 할로겐화물의 수용액을 이용하여 제공될 수 있다. 설페이트(SO_4^{2-})와 같은 상기 다원자 음이온은 황산($H_2SO_4(aq)$)과 같은 수용액을 이용하여 제공될 수 있다. 이들 두 반응물들은 원하는 물질들을 만들기에 적합한 공정들과 상대적인 양들을 이용하여 함께 혼합될 수 있다.

<32> 상기 반응은 전구체 용액(16)을 생성할 수 있다. 전구체 용액(16)은 기판에 적용하므로써와 같이 원하는 대로 즉시 사용될 수 있다. 선택적으로, 전구체 용액(16)은 적어도 부분적으로 탈수화(dehydrated) 후 적용될 수 있다. 그런 후 위에서 주어진 예에서, 상기 전구체 용액은 하프늄 옥시-히드록시 설페이드($HfO_{2-z/2}(OH)_z(SO_4)_x$)를 형성할 수 있다. 본 화학식에서의 변수들에 있어서, x 및 z는 고정되거나 변화할 수 있으며, 어떤 값이든 가질 수 있다. 이를 들면, x의 값은 통상 약 0.1 내지 약 1.9이고, z의 값은 0.0 내지 약 2.0이다. 일 구현예에 대하여, 이 값들은 x=0.5이고 z=0이었다. 히드록시 기는 금속-함유 양이온의 일부인 수 있고, 이 화합물은 하프늄 옥시-히드록시 설페이드($HfO_{2-z/2}(OH)_z(SO_4)_x$)를 포함할 수 있다.

<33> 다른 구현예들에서, 상기 다원자 음이온은 하나 또는 그 이상의 설페이트(SO_4^{2-}), 보레이트(BO_3^{3-}), 포스페이트(PO_4^{3-}), 텅스테이트(WO_4^{2-}) 및 실리케이트(SiO_3^{4-})를 포함할 수 있다. 상기 금속-함유 양이온은 금속 아산화물(suboxide)을 포함할 수 있고, 하나 또는 그 이상의 하프늄 (Hf^{4+}), 티타늄 (Ti^{4+}), 지르코늄 (Zr^{4+}), 세륨

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(Ce^{4+}), 주석 (Sn^{4+}), 탄탈륨 (Ta^{5+}), 니오븀 (Nb^{4+}), 이트륨 (Y^{3+}), 몰리브데늄 (Mo^{4+}), 텅스텐 (W^{6+}), 알루미늄 (Al^{3+}), 갈륨 (Ga^{3+}), 아연 (Zn^{2+}), 크로뮴 (Cr^{3+}), 철 (Fe^{3+}), 비스무트 (Bi^{3+}), 란탄화물(lanthanides), 하프늄 옥시-히드록사이드 ($HfO_y(OH)_z^{(4-2y-z)+}$), 지르코늄 옥시-히드록사이드 ($ZrO_y(OH)_z^{(4-2y-z)+}$), 티타늄 옥시-히드록사이드 ($TiO_y(OH)_z^{(4-2y-z)+}$), 탄탈륨 옥시-히드록사이드 ($TaO_y(OH)_z^{(5-2y-z)+}$), 이트륨 옥시-히드록사이드 ($YO_y(OH)_z^{(3-2y-z)+}$), 니오븀 옥시-히드록사이드 ($NbO_y(OH)_z^{(4-2y-z)+}$), 몰리브데늄 옥시-히드록사이드 ($MoO_y(OH)_z^{(4-2y-z)+}$), 텅스텐 옥시-히드록사이드 ($WO_y(OH)_z^{(6-2y-z)+}$), 알루미늄 옥시-히드록사이드 ($AlO_y(OH)_z^{(3-2y-z)+}$), 갈륨 옥시-히드록사이드 ($GaO_y(OH)_z^{(3-2y-z)+}$), 아연 옥시-히드록사이드 ($ZnO_y(OH)_z^{(2-2y-z)+}$), 크로뮴 옥시-히드록사이드 ($CrO_y(OH)_z^{(3-2y-z)+}$), 철 옥시-히드록사이드 ($FeO_y(OH)_z^{(3-2y-z)+}$), 비스무트 옥시-히드록사이드 ($BiO_y(OH)_z^{(3-2y-z)+}$), 및 란탄 계열의 옥시-히드록사이드들을 포함할 수 있다. y의 값은 상기 금속 양이온의 전하와 상기 금속 양이온에 결합된 히드록사이드 및 다른 다원자 음이온의 양과 관련된다.

<34> 여기에 개시된 다원자 음이온들 및 금속-함유 양이온들을 이용하는 방법의 구현예들은 착화합물을 형성하기 위한 유기물질의 이용을 필요로 하지 않는, 즉, 음이온 및 양이온의 공급원이 유기물질을 포함하지 않는 유전 전구체 물질의 형성을 가져올 수도 있다. 그러나, 특정 구현예에 대하여 원하거나 필요한 경우에는 유기물질이 사용될 수 있다. 예를 들면, 에탄올과 같이 착화합물을 형성하지 않는(non-complexing) 유기물질이 전구체 용액의 부분적 용매로서 사용될 수 있다. 만일 전구체 물질에 착화합물을 형성하는(complexing) 유기물질이 포함되어 있지 않다면, 일단 상기 전구체 용액이 기판에 적용되면 통상 상기 전구체 용액은 유기 물질들을 분해/연소시키기 위해 400 ℃ 또는 그 이상의 온도에서 가열되거나 어닐링될 필요가 없다. 가열 및/또는 건조로 인한 전구체 용액의 중합은 다결정질 물질(polycrystalline material)이 아닌 비결정질막의 형성을 가져오고 그에 의하여 기판 위에 유전 물질의 용액-기반-응용을 가능하게 한다.

<35> 일반적으로, 본 공정에서 개시된 구현예들은 공기 내의 대기압과 같은 주위 환경 조건에서 수행될 수 있다. 따라서, 진공 공정은 불필요하다. 그러나, 원한다면 진공 공정이 이용될 수 있다. 상기 공정은 주위 환경보다 높은 온도에서, 예를 들면 약 80 ℃ 내지 약 850 ℃의 범위, 통상 80 ℃ 내지 높아야 350 ℃의 온도 범위에서, 그리고 종종 높아야 100 ℃의 온도에서 수행될 수 있다. 이들 저압 및 저온 공정 단계들은 개시된 공정들에 대하여 요구되는 에너지를 감소시킬 수 있다. 유전막의 처리에 유용한 낮은 온도로 인하여, 상기 막들은 플라스틱 기판들과 같은 저온 기판들 위에 처리되거나 또는 저온 기판들에 용액으로서 적용될 수 있다. 제조된 상기 결정질이 아닌 비정질(amorphous)의 유전 전구체(dielectric precursor) 용액은 웨이퍼 위와 같은 기판 위에 전구체 용액의 콘포말(conformal)한 도포성을 가능하게 한다. 상기 용액은 마스킹 또는 식각 단계들이 사용되지 않도록, 잉크젯 프린팅을 이용함에 의해서와 같이, 소정의 특정한 패턴으로 적용될 수도 있다. 따라서, 본 개시의 공정은 기판들 위에 포토리소그래피 공정을 수행하는 동안 물질의 형성 및 제거를 위해 사용될 수 있는 유해하거나 또는 독성을 갖는 물질들의 사용을 제거하거나 감소시킬 수 있다. 그러므로, 본 공정은 알려진 공정들에 비하여 시간의 측면에서 효율적이고, 환경적으로도 친환경적(green)이다. 게다가, 본 개시의 예시적 일 구현예에서 사용된 하프늄 옥사이드 및 설페이트 물질들은 독성 물질들이 아닐 수 있다.

<36> 본 개시의 공정에 사용되는 물질들의 예는 하프늄 옥시 히드록시 설페이트류($HfO_{2-x-z/2}(OH)_z(SO_4)_x$), 하프늄 옥시 히드록시 텅스테이트류($HfO_{2-x-z/2}(OH)_z(WO_4)_x$), 하프늄 옥시 히드록시 보레이트류($HfO_{2-x-z/2}(OH)_z(BO_3)_x$), 하프늄 옥시 히드록시 포스페이트류($HfO_{2-x-z/2}OH_z(PO_4)_x$), 및 하프늄 옥시 히드록시 실리케이트류($HfO_{2-x-z/2}OH_z(SiO_4)_x$)를 포함하는 화합물들의 군에 속하는 화합물들을 포함한다. 이들 물질들은 80 ℃ 정도의 낮은 온도에서 중합될 수 있고, 약 740 ℃까지, 심지어는 1,200 ℃ 정도의 높은 온도에서도 비결정질을 유지할 수 있다. 물질의 중합은 가열 속도를 조절함으로써, 공-용매(co-solvent)를 사용함으로써, 다른 적절한 방법들에 의하여 및 이러한 방법들의 모든 조합들 및 어떤 조합들에 의하여 제어될 수 있다. 본 개시의 비결정질 막들은 조직(grain) 경계에서의 결함 형성을 감소시킬 수 있고, 비정질-결정질(amorphous-to-crystalline) 전이에서 크랙이 형성되는 것을 감소시킬 수 있다. 게다가, 본 개시의 유전막들은 상당히 높은 유전 상수, 즉, 유기 화합물들의 유전 상수보다 더 높은 유전 상수를 가질 수 있다. 잉크젯 프린팅 응용과 같은 용액-기반 처리에 의하여 고품질의 유전체를 형성할 수 있는 능력은 저렴한 가격의, 전계 효과 트랜지스터들 또는 캐패시터들과 같은 전자 부품의 형성을 가능하게 한다.

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<37> 도 2는 유전 물질을 형성하기 위하여 전구체 용액(16)을 적용하기 위한 공정의 일 구현예를 개념적으로 나타낸다. 하프늄 옥시 설페이트와 같은 전구체 용액(16)이 적용자(applicator)(20)에 의하여 웨이퍼와 같은 기판(18)에 적용될 수 있다. 일 구현예에서, 적용자(20)는 노즐들(22)을 갖는 잉크젯 프린터를 포함할수 있다. 전구체 수용액(16)은 상기 잉크젯 프린터의 노즐들(22)을 통하여 분출된다. 다른 구현예들에서, 적용자(20)는 상기 전구체 용액의 적용 방법이 스핀-코팅, 딥(dip)-코팅, 또는 스프레이-코팅을 포함할 수 있도록 각각 스핀-코터, 딥-코터, 또는 스프레이-코터를 포함할 수 있다. 전구체 용액(16)의 비결정질의 용액-기반 성질들로 인하여 전구체 용액(16)은 적용되었을 때 우수한 콘포말(conformal) 도포성을 가능하게 할 수 있다. 일단 기판 표면에 또는 상기 기판 위에 증착된 막 또는 막들에 적용되면 상기 전구체 용액 내의 수분 함량을 제거하거나 감소시키기 위하여 상기 전구체 용액은 히터(24)로 가열함으로써 또는 다른 탈수(dehydration) 장치에 의하는 것과 같이 탈수될 수 있다. 상기 탈수 단계는 웨이퍼(18) 위에 하프늄 옥시 설페이트 박막과 같은 비결정질 유전 물질(26)의 침전을 가져올 수 있다.

<38> 도 3은 유전 물질 전구체 용액(16)(도 1 참조)의 일 구현에에 있어서, 특히, 황산(H_2SO_4)과 하프늄 옥시 클로라이드($HfOCl_2$)의 반응에 있어서, 상이한 전구체 농도들에 따른 가능한 용액 농도들을 나타내는 그래프이다. 더욱 구체적으로, 도 3은 전체 하프늄 농도(몰 농도(M))에 대한 전체 설페이트 농도(M)의 그래프를 나타낸다. 영역(28)은 투명한 용액, 즉, 시각적으로 감지할 수 있는 침전물이 그 안에 없는 용액을 나타내고, 영역(28)은 과량 황산(H_2SO_4)의 영역이다. 영역(30)은 투명한 용액, 즉, 시각적으로 감지할 수 있는 침전물이 그 안에 없는 용액을 나타낸다. 영역(30)은 과량 하프늄 옥시 클로라이드($HfOCl_2$)의 영역이다. 선분(32)은 황산과 하프늄 옥시 클로라이드가 일 대 일의 비율(1:1의 양론비)로 각각 존재하는 양론(stoichiometric) 선을 나타낸다. 영역(34)은 침전 영역, 즉, 시각적으로 감지할 수 있는 침전물이 그 안에 있는 용액을 나타낸다. 따라서, 영역(34) 또는 그의 일부는 잉크젯 프린팅 응용에 의하여 매끈하고도 실질적인 결함이 없는 막들을 형성하기에 가장 적합한 것은 아닌 용액들을 나타낼 수 있지만, 그의 사용이 배제되는 것은 아니다. 따라서, 전구체 용액(16)(도 2 참조)이 잉크젯 프린터 응용 장치(20)(도 2 참조)를 통해 적용될 때, 제 1 반응물 및 제 2 반응물의 농도가 영역(28) 또는 영역(30)의 어느 하나 안에 있고, 고체 영역(34) 안에 있지 않는 것이 바람직하다. 영역(34)의 용액에 존재하는 고체들은 노즐들(22)을 막거나, 매끈하지 않은 막을 형성할 수 있거나, 또는 바람직하지 않은 전구체 용액 적용을 가져올 수 있다. 다시 말하면, 상기 영역들(28 및 30)의 용액은 잉크젯 프린트헤드를 통해 또는 드롭퍼(dropper) 방법에 의하여 적용될 수 있는 가능한 "잉크" 전구체 용액을 나타낼 수 있다.

<39> **II. 일반 논의**

<40> 새로운 박막 유전체들 및 나노적층체들(nanolaminates)은 매끈하고 조밀한 막의 용액 증착을 이용하여, 통상 수용액 증착을 이용하여 개발되어 왔다. 용액 증착 기술들은 스핀 코팅 및 잉크젯 프린팅을 포함한다. 용액 증착에 이어서 적당한 열처리가 후속될 수 있다($T < 325℃$).

<41> 본 발명의 개시에 따라 분말 및 막으로서 제조된 물질 모두의 화학을 정의하기 위해 다양한 분석 기술들이 사용되어 왔다. 상기 막의 품질과 기능성은 X-선 반사도(reflectivity), 전자 현미경, 및 전자 소자들에서의 성능에 의하여 평가되었다. 유전 특성들이 작동 구현예들에 대하여 결정되었으며, 약 9 내지 약 12의 범위를 커버하는 유전율(permittivity); 적어도 6 $MVcm^{-1}$까지의 항복 전계(breakdown field); 및 1 $MV\ cm^{-1}$의 전계 강도에서 1 $nA\ cm^{-2}$ 에 가까운 누설 전류를 포함한다. 상기 막질의 표면의 매끈함 및 기공이 없는 특성은 적어도 약 2 나노미터의 얇은 개별층들을 갖는 독특한 나노적층된(nanolaminated) 구조물의 제조를 용이하게 한다. 비교적 높은 유전율 막들은 박막 금속-절연체-금속(MIM: metal-insulator-metal) 캐패시터들 및 박막 트랜지스터들(TFTs)에서 높은 항복 강도와 낮은 누설 전류를 제공하면서 본 발명의 개시된 구현예들을 이용하여 실현될 수 있다. 절연막들의 예외적인 특성들도 독특한 나노적층 구조물의 제조를 가능하게 한다.

<42> 박막 유전체로서 사용되기 위하여는 비결정질 물질들이 바람직한데, 그들은 조직(grain) 경계를 갖지 않고, 따라서 결정질과 관련된 거침(roughness)과 전하 전도의 여지가 적다. 지르코늄과 하프늄의 수많은 산화물들, 예를 들면, 단순한 이성분계(binary), 실리케이트류, 및 알루미네이트류가 고유전율(high-permittivity) 유전체 응용의 후보들로 검증되어 왔다. 다성분 물질들에서, 순수한 이성분 산화물들에 비하여 더욱 강건한 항복(breakdown) 특성을 만들기 위하여, 유전율을 희생할 수 있음에도 불구하고 결정화가 저해될 수 있다. 이들 유전막들은 종종 다양한 유기-금속 또는 금속-염 전구체들과, 원자층 증착(ALD: atomic layer deposition), 화학기상증착(CVD: chemica vapor deposition), 졸-겔 처리, 또는 이들의 조합과 같은 기술들을 이용하여 형성된다. 그러나, 용액 증착 방법에 의하여 조밀하면서도 비결정질인 유용한 유전막을 제조하는 것은 증착 및 후속 공정

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모두가 수행되는 동안 결정화와 크래킹(cracking)을 저해할 것이 요구될 수 있다.

<43> 본 발명의 개시된 어떤 구현예들은 금속 산화막의 개발에 관한 것이다. 금속 산화물들은 각각 $HfO_{2-x}(SO_4)_x$ 및 $ZrO_{2-x}(SO_4)_x$ (여기서, $0.1 \leq x \leq 1.5$)로 나타내어지는 화학식을 갖는 하프늄 및 지르코늄 설페이트계를 참조하여 여기에 일반적으로 예시된다. 이들 화합물들은 여기에 HafSOx 및 ZircSOx의 약어로 각각 지칭될 것이다. 이들 계의 화학과 물리적 성질을 정의하기 위하여, HafSOx 및 그의 도핑된 유사체(analog)를, 즉, La-치환된 유도체 HafSOx:La와 같은 유사체를 분말 및 박막으로 제조하였다. 캐패시터들과 TFT들을 제조함으로써 HafSOx, ZircSOx 및 선택된 유도체들의 박막 유전 특성들을 평가하였다. 이들 분석들은 매우 높은 품질의 조밀한 막이 제조될 수 있음을 나타내었다. 혼합 HafSOx/ZircSOx 나노적층체의 막 두께 및 제조가 스핀-코팅 공정에 의하여 이제 조절될 수 있다.

<44> 수많은 상(相)들 및 결정 구조들이 HfO_2-SO_3-H_2O 및 ZrO_2-SO_3-H_2O 계의 검증으로부터 보고되어왔다. 여러 구조들이 금속 원자, 설페이트 기 및 물의 응축과 관련된 구조적 차원(dimensionality)과 수화도의 변화를 보이는 화학식 $Hf(SO_4)_2 \cdot nH_2O$ 또는 $Zr(SO_4)_2 \cdot nH_2O$의 단순한 수화물들로 특성화된다. 설페이트에 비하여 금속이 풍부한 물질들이 알려져 있으며, $Zr_2(OH)_2(SO_4)_3 \cdot 4H_2O$; $Hf(OH)_2SO_4$, $Zr(OH)_2SO_4$와 이들의 수화물들; $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13} \cdot 33H_2O$ 및 $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$; 및 $Zr_3O_5SO_4$와 그의 수화물을 포함한다. 이러한 구조들 모두는 수소 결합의 변화 또는 탈수화로 인하여 실온과 약간의 가열조건에서 공기와 접촉할 때 모두 불안정할 것으로 보인다 ($Zr_3O_5SO_4$는 예외일 수 있다). 이것은 비결정질 막을 개발하기 위해 사용될 수 있는 탈수화 및 응축 공정을 가능하게 한다.

<45> (변수 x로 나타낸) 하프늄에 대한 설페이트의 선택된 분율을 갖는 수용액으로부터 시작하여 HafSOx 침전은 가열에 의하여 유발되었다. 도 1은 공기로 건조된 HafSOx 침전물의 TGA(thermogravimetric analysis) 결과이다. TGA는 샘플의 무게(질량) 변화를 온도의 함수로 측정하기 위해 사용되는 열분석 기술이다. 공기로 건조된 HafSOx 침전물의 가열은 세 영역에서의 질량 손실을 가져온다. 다른 HafSOx 유도체들에 대하여도 유사한 특성들이 관찰되었다. 약 200 ℃의 온도 아래에서의 큰 질량 손실은 포함되었던 물의 손실에 기인한다. 약 200 ℃ 내지 약 700 ℃의 온도 범위에서의 질량 손실은 주로 물보다 더욱 강하게 결합된 히드록시 종의 제거에 기인한다. 약 700 ℃를 넘어서 시작되는 급격한 질량 손실은 $SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$에 따른 설페이트 분해에 기인한다. 탈수된 HafSOx 분말이 700 ℃와 950 ℃ 사이에서 HfO_2로 완전히 전환된다고 가정할 때, 상기 설페이트 분율은 질량 손실로부터 계산될 수 있다. 샘플의 질량 손실의 결정은 모액(mother solution)에서 설페이트의 레벨을 증가시키는 것이 침전물에서의 설페이트의 레벨의 증가를 가져옴을 밝혔다. 특히, 탈수된 화학식 $HfO_{1.54}(SO_4)_{0.45}$ 및 $HfO_{1.29}(SO_4)_{0.71}$ 각각에 대하여 하프늄에 대한 설페이트의 비율은 약 46%에서 약 71%까지 변화하였다. 설페이트 공급원으로서 $H_2SO_4(aq)$가 사용되든 $(NH_4)_2SO_4(aq)$가 사용되든, 동일한 최대 설페이트 조성이 침전되었고, 설페이트 레벨 < 46%인 생성물은 검출되지 않았다. 모든 샘플들에 대하여, 열중량 측정 프로파일에서 일부 변화가 관찰되었지만 720 ℃ 이상에서 설페이트 손실의 시작이 발생하였다. 이러한 가열 곡선들의 도함수(derivative)들에 대한 정의 가능한 값으로서의 피크 위치들은 테스트된 샘플들에 대하여 793 ℃와 817 ℃ 사이에서 분해됨을 나타낸다. 설페이트 공급원으로서 $H_2SO_4(aq)$을 사용하고 최대 설페이트 함량을 갖는 샘플들에 대하여 가장 높은 분해 온도가 관찰되었다.

<46> 다시 도 1을 참조하면, 최대 설페이트 함량을 갖는 샘플들이 TGA 측정에 앞서 가열되었다. 수분과 관련된 질량 손실들이 감소되었고, 계산된 설페이트 함량들은 예열된 샘플들과 보통의 샘플들 모두가 비슷하였다. 이 70 내지 70%의 설페이트 함량은 보고된 결정들 $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$ 및 $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13} \cdot 33H_2O$의 조성들과 유사하다. TGA 연구로부터 Ahmed, Fjelvag, 및 Kjekhus는 그들의 연구에서의 Hf 및 Zr 디설페이트들에 대한 온도보다 더 높은 온도 및 다른 데서 보고된 염기성 설페이트들 $Hf(OH)_2SO_4 \cdot H_2O$ 및 $Zr_3O_5SO_4$에 대한 온도보다 더 높은 온도에서 $Hf_{18}O_{23}(SO_4)_{13}$ 및 $Zr_{18}O_{23}(SO_4)13$에 대하여 설페이트 분해가 일어남을 발견하였다. 향상된 열적 안정성 외에, 약 13:18의 설페이트-금속 비율은 이 계에 특별한 안정성을 보여준다. 따라서, 이 조성물은 용액처리 및 가열이 필요한 목적에 대하여 적합할 수 있다.

<47> 설페이트 $La_2O_2SO_4$는 1,300 ℃보다 큰 분해 온도를 갖는다. 란탄(La)은 변성된 탈수 성질 및 열적 성질들, 한 예로서 열적 안정성과 같은 변성된 물성을 갖는 추가적인 화합물을 만들기 위해 HafSOx 모액에 첨가되었다. 혼

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합-금속계인 $Hf_{1-z}La_zO_{2-x-z/2}(SO_4)_x$ (HafSOx:La)는 이러한 화합물을 예시한다. 이러한 화합물을 제조하기 위하여, 전구체 물질과 23% La (총 금속)을 포함하는 용액을 가열하여 침전물을 형성하였다. 화학 분석 결과 생성물에 3%의 La 만이 발견되는 것으로 나타났다. TGA로부터 금속에 대한 설페이트의 비율이 71%임이 입증되었고, 820 ℃에서의 (도함수 피크로서) 분해되는 것이 최대 설페이트 함량과 일치하는 것으로 발견되었다. 그런 후 32% La을 포함하는 구성 종의 염 용액에 NH_3(aq)를 첨가함으로써 공침전(co-precipitation)을 유발하였다. 생성물의 화학 조성을 분석한 결과, 모액에 존재하는 것과 동일한 La 분율인 것으로 밝혀졌다. 본 화학식에 대한 열분해는 도핑되지 않은 HafSOx와 현저하게 상이하였다. 비록 가열 특성들이 덜 급격하였지만 설페이트에 기인한 질량 손실은 700 ℃ 위에서 현저하였고, 2 ℃(분)$^{-1}$의 더 느린 승온 속도로 가열하였을 때에도 1,000 ℃까지 가열하면서 질량이 일정하게 달성되지 않았다. 이 가열 속도에 대하여, (도함수 피크로서) 분해는, 비록 가열 조건에 달려있기는 하지만, 약 870 ℃에서 일어난다. 산화물의 완전한 분해는 1,500 ℃까지 가열함으로써 달성되었는데, 건조된 침전물에 대하여 화학식 $Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$이 수득되었다.

<48> 침전된 HafSOx 분말에 대하여 XRD 데이터를 수집하여 결정상에 대한 온도 범위를 입증하였다. 공기 건조 후, 최대 설페이트 함량과 설페이트 공급원으로서 H_2SO_4(aq)를 갖는 샘플들에 대하여 복잡한 회절 패턴이 기록되었고, 다른 샘플들은 회절이 없거나 확산되는 것을 보였다. HafSOx(x=0.7)에 대한 XRD 데이터를 도 2에 나타내었다. 공기 건조된 샘플들을 약 100 ℃ 내지 약 700 ℃ 사이의 온도에서 1시간 동안 건조시킨 후, 상기 물질은 비결정질이 되었다. 모노리딕 HfO_2의 결정성 피크 특성이 750 ℃ 이상에서 1시간 동안 가열한 후 관찰되었다. TGA에 의하여 설페이트 손실의 개시가 720 ℃에서 일어나므로, 결정화는 설페이트 손실과 일치하는 것으로 밝혀졌다. 3% La을 포함하면, 1,000 ℃의 온도까지도 유사한 회절 프로파일이 생성된다.

<49> 도 3은 HafSOx:32% La에 대한 XRD 데이터를 나타낸다. 침전된 물질과 700 ℃에서 가열된 것 모두 X-선 비결정질이다. 비치환된 HafSOx에서와 같이, 감지할만한 결정상은 설페이트가 분해되기 시작하는 온도 구간인 700 ℃와 750 ℃ (1시간 가열) 사이에서 형성된다. 그러나 32% La의 치환으로는 모노리딕 HfO_2는 감지되는 상이 아니다. 오히려, 회절 프로파일은 입방계 (또는 정방정계) HfO_2와 일치한다. HfO_2의 상은 종종 란탄계 원자를 포함함으로써 안정화된다. 적절한 상 다이어그램으로 고려하면 예측할 수 있는 바와 같이, 고온으로 가열하면 $Hf_2La_2O_7$과 모노리딕 HfO_2가 생성될 수 있다. 중간 온도 산화물 상들은, 900 ℃에서 10 내지 37%의 란탄이 입방계 지르코니아를 안정화시키고 1,050 ℃에서 상분리가 일어남을 발견한 Zhang, Kershaw, 및 Dwight의 ZrO_2-La_2O_3 시스템에 관한 업적과 일관된다.

<50> 재료들을 특성화하기 위하여 약 200 나노미터 내지 약 300 나노미터의 두께를 갖는 HafSOx 및 HafSOx:La 박막들이 제조되었다. 상기 막들에 대한 조성들은 Hf, La, Cl 및 S의 상대적인 농도에 기초하여 EMPA로 결정되었다. 이 방법에 따르면 산소 레벨이 덜 정확하므로, 탈수된 화학식으로 표현하였다. 325 ℃에서 (5분간) 가열된 대표적인 두 HafSOx 닥들은 하프늄에 대한 설페이트의 비율이 각각 67%와 85%로 나타난 $HfO_{0.985}(SO_4)_{0.67}Cl_{0.69}$ 및 $HfO_{0.915}(SO_4)_{0.85}Cl_{0.47}$로 결정되었다. 상기 85% 설페이트막은 650 ℃로 (5분간) 더 가열되어 $HfO_{1.275}(SO4)_{0.71}Cl_{0.03}$으로 결정되었다. 또한, 330 ℃에서 (5분간) 가열된 상기 HafSOx:La 막은 $Hf_{0.76}La_{0.24}O_{0.73}(SO_4)_{0.96}Cl_{0.38}$인 것으로 결정되었다. 650 ℃로 가열된 HafSOx에 대하여, 설페이트 비율은 71%로 감소하였으며, 이는 최대 설페이트로 가열 침전된 HafSOxjc 대한 조성과 일치한다. HafSOx:La에 대하여, La의 측정된 분율(24%)은 전구체 용액에서의 La 농도 23%와 잘 맞는다.

<51> 선택된 온도에서 5분 동안 가열한 후 HafSOx(x~0.67 및 0.85)와 HafSOx:La 막들에 대한 투과 푸리에 변환 적외선 (FTIR: transmission Fourier transform infrared) 분석 결과들이 수집되었다. 주요한 두 개의 작용기를 감지하기 위하여 FTIR 스펙트럼들이 사용되었다. 3000 내지 3600 cm^{-1} 범위에서의 흡수는 히드록시기에 기인하고, 1000 내지 1200^{-1} 범위에서의 흡수는 설페이트 기에 기인한다. 가열과 함께, 히드록시기 흡수는 약 325 ℃ 내지 약 600 ℃의 범위에 걸쳐서 감소하는 반면, 설페이트 스트레치(stretch)는 HafSOx 막에 대하여는 약 650 ℃ 내지 700 ℃ 사이에서, HafSOx:La 막에 대하여는 약 700 ℃ 내지 750 ℃ 사이에서 거의 제거된다. (설페이트 흡수에 대한 프로파일은 기판으로부터의 SiO_2가 유사한 에너지를 흡수하기 때문에 약간 왜곡되지만, 스펙트럼들은 정성적으로 정확하다)

<52> 도 4 및 도 5에 각각 보인 바와 같이, HafSOx(x~0.67 및 0.85) 및 HafSOx:24% La 막들에 대하여 각각 표시된

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온도에서 5분간 가열한 후 박막 XRD 데이터가 수집되었다. 두 HafSOx 조성물 모두에 대하여, 막들은 약 325 ℃ 내지 약 650 ℃까지 X-선 비결정질이다. 모노클리닉 HfO_2는 약 700 ℃ 또는 그 이상에서 감지된다. HafSOx:La 막들은 약 330 ℃ 내지 약 700 ℃에서 비결정질인 반면, 입방계 상은 약 750 ℃ 내지 약 1000 ℃에서 감지된다. 상기 입방계 상은 1,100 ℃에서 모노클리닉 HfO_2와 $HfLa_2O_3$으로의 분리가 시작되기 때문에 외관상 불안정하다. HafSOx 및 HafSOx:La 막들에 대하여, 설페이트의 손실은 산화물 결정화와 시점 상관될 수 있으며, 이는 분말 거동과 일관된다.

<53> HafSOx, ZircSOx 및 이들의 유도체들의 막들을 유전체로서 사용하기 위한 스핀-코팅에 의하여 증착되었다. 전체 항복 강도뿐만 아니라 1 kHz에서의 손실 탄젠트와 유전율의 파라미터들을 결정하기 위하여 MIM 캐패시터들을 테스트하였다. "항복"은 전계 밀도가 10 μA cm^{-2}를 넘는 전계로서 정의된다. HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, 및 ZircSOx:Ca에 대하여 유사한 테스트들이 수행되었다. 도 6은 알루미늄 접 콘택들이 0.011 cm^2의 면적을 나타내는 HafSOx 유전막에 대한 유전 항복 분포를 나타낸다. HafSOx 및 ZircSOx 막들은 4 내지 6 MV cm^{-1}의 항복 전계를 가졌다. ZircSOx:Ca에 대한 항복 전계는 3.6 MV cm^{-1}이었다. 가해진 1 MV cm^{-1}의 전계에서, 여섯 번형 물질 모두가 50 nA cm^{-2} 미만의 누설 전류를 보였으며, 많은 조성물들에 대하여 10 nA cm^{-2} 미만의 누설 전류가 관찰되었다. 모든 번형 물질들에 대하여 약 9 내지 약 12의 유전율 값들과 손실 탄젠트 < 1%가 측정되었다.

<54> HafSOx:La 또는 ZircSOx:La를 게이트 유전체로서 이용하고, 아연 인듐 산화물 또는 아연 주석 산화물을 채널로서 이용하여 전계효과 트랜지스터(FET: field-effect transistor)를 제조하였다. 전류 변조(modulation)가 달성되었는데, 드레인-소오스 전압을 증가시킴에 따라 드레인-소오스 전류가 포화되었으며, 10^5보다 큰 온-투-오프 비율(on-to-off ratio)을 제공하고, pA cm^{-2}의 범위의 값을 갖는 게이트 누설 전류를 제공한다. 이러한 결과들은 HafSOx:La과 ZircSOx:La 막들이 소자 집적에 대하여 충분히 강건하고, 유전체/채널 계면의 품질의 용이도 만족됨을 나타낸다.

<55> 새로운 종류의 비결정질 다성분 산화물 유전막으로서, HafSOx, ZircSOx 및 이들의 유도체들은 다른 혼합 시스템, 특히 $(MO_2)_x(Al_2O_3)_y$ 및 $(MO_2)_x(SiO_2)_y$ (여기서, M = Hf 또는 Zr)로 나타내어지는 알루미네이트들 및 실리케이트들과 비교될 수 있다. 이들 시스템들 각각에 대한 다양한 넓 조성물들이 통상의 기상 기술들에 의하여 증착되었다. (유전체 응용에서 통상적인 조성으로서) 20 내지 50 몰%의 Al_2O_3 또는 SiO_2를 갖는 Hf 또는 Zr 알루미네이트와 실리케이트들의 경우에 있어서, 결정화는 통상 약 800 ℃ 내지 1,000 ℃에서 상 분정(phase segregation)과 함께 일어난다. 테스트된 HafSOx 분말 및 박막에 대하여, 결정화는 실페이트가 분해됨에 따라 약 700 ℃에서 일어났다. 유전체로서, 이들 알루미네이트들과 실리케이트들은 HafSOx 및 ZircSOx에 대한 9 내지 12의 값들과 비교해 볼 때 10 내지 15의 유전율 값을 보인다. 이들 새로운 종류의 산화물 실페이트 물질들은 비결정질, 중간 온도, 중간 유전율 유전체로 고려될 수 있다.

<56> 주사 전자 현미경(SEM: scanning electron microscopy) 및 반사 X-선(XRR: X-ray reflectivity)을 이용하여 막의 성질을 더 검사하였다. HafSOx 및 HafSOx:La 막들에 대한 SEM 이미지들을 도 7 및 도 8이 나타내었다. 이들 이미지들은 유전체 테스트로 의해 전형적으로 사용된 것과 같은 약 150 나노미터 내지 약 300 나노미터의 범위의 두께들을 갖는 막들의 대표적 표면과 조밀하고 균일한 구조를 나타낸다. 도 7은 그 위에 Ta 금속의 506-nm 층(712) 및 160 nm의 HafSOx 막(714)이 증착된 SiO_2 기판(710)을 나타낸다. 도 8은 그 위에 Ta 금속의 512-nm 층(812) 및 192 nm의 HafSOx/La 막(814)이 증착된 SiO_2 기판(810)을 나타낸다.

<57> 더 얇은 막 형성을 위한 제안성의 일관된 측정으로서 HafSOx/ZircSOx의 박막 기초를 갖는 다층 구조물들이 적층되었고 XRR로 분석되었다. 도 9는 XRR 스캔의 한 전형 패턴을 나타낸다. 반복되는 이중층의 두께를 찾기 위해 정상파 하모닉스를 나타내는 피크 정점의 위치가 사용되었다. HafSOx와 ZircSOx의 두께를 독립적으로 규칙적으로 변화시키면서, 세별 층들의 두께가 결정되었다. 나노적층체 스택 내에서, 약 3 나노미터 정도로 얇은 단일층이 측정되었다. 회절 패턴에서 그와 반사가 관찰됨에 따라, 각 이중층은 조도(roughness)를 포함하여 0.5 미만의 변동성(variability)으로 증착되었다.

<58> Si CMOS 기술에서 소자 크기의 축소는 유전체로서 얇고, 누설 전류가 높은 SiO_2의 교체의 필요성을 가져왔다. 교체되는 유전체들은 높은 유전율을 보여야 하고, 더 적은 누설 전류로 동일한 소자 캐패시턴스를 보이기 위해

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더 두꺼운 층을 가능하게 하여야 한다. HfO_2 및 ZrO_2는 이들의 바람직한 유전 특성 및 열적 특성으로 인하여 대체 게이트 유전체로서 상당한 주목을 끌어왔다. HfO_2 및 ZrO_2 유전체에 대한 도전의 하나는 매끈하고, 조밀하며, 핀-홀이 없고, 13 nm 이하의 두께를 갖는 초박막(ultra-thin films)을 만드는 것이다. 이전의 초박막들은 원자층 증착(ALD: atomic layer deposition)을 이용하여 형성되었다. ALD의 원부 유망한 결과들에도 불구하고, 이 방법은 긴 증착 시간(1 Å/분)과 함께 진공을 이용할 것이 요구되기 때문에 비용이 높고 생산성이 낮았다. 이로 인하여 HfO_2와 ZrO_2의 용액 기반 증착의 일부 연구가 촉발되었다. 현재까지 이들 막들은 ALD 막들과 동일한 균일성과 조밀성에 도달하지 못하였다.

<59> 교환 반응을 이용하여, ALD 품질에 필적하고 DRAM (dynamic random access memory) 및 Si CMOS (complementary metal-oxide semiconductor) 기술에 사용하기에 적합한 $M(OH)_x$ 및 MO_x 초박막을 제조할 수 있다. 개시된 구현예들에 대하여, 상기 박막은 스핀-코팅을 이용하여 무기 용액을 통해 실레이트 형태로 증착된다. 예를 들면, 반-고체 막이 $MO_x \cdot HCl \cdot H_2SO_4$ 조성으로 형성될 수 있다. 상기 실레이트는 수산화나트륨 용액을 이용하여 이온 교환으로 제거된다.

<60> $$MO_x \cdot HCl \cdot H_2SO_4 + OH^-(aq) \rightarrow M(OH)_x + Cl^-(aq) + SO_4^{2-}(aq)$$

<61> 결과적으로 얻어지는 히드록소(hydroxo) 및/또는 산화물 막들은 매끈하고, 조밀하며 핀홀이 없다. 예를 들면, 약 2 나노미터의 두께를 갖는 HfO_2 박막이 HafSOx 박막로부터 제조될 수 있다. 교환된 막들은 약 800 °C의 온도까지 약 10 초 내지 10 분 동안 열처리될 수 있고, 그 결과, 막의 표면 조도가 약 0.1 나노미터가 된다. 이러한 막의 특성들은 값비싼 원자층 증착 방법을 저비용 스핀-온 또는 분무(misting) 기술로 대체하면서 CMOS 및 관련 기술 분야에서 금속-유전체 게이트에 대한 요건들을 만족한다.

<62> 증착된 반-고체 수화 히드록소 막들은 막의 모폴로지(morphology)를 붕괴시키지 않으면서 유이온 교환을 가능하게 한다. 예를 들면, SO_4^{2-}, WO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-}, VO^{3-}, AlO^{3-}, GaO^{3-}과 같은 옥소 음이온들과 이들의 프로톤화된 형태들. 이를 들면, HPO_4^{2-}, $H_2PO_4^-$ 및 할로겐들 F, Cl, Br, 및 I 는, 예를 들면, $Na_2SO_4(aq)$와 같은 금속염 조(槽)에 상기 막들을 침윤으로써 선택적으로 교환될 수 있다. 이것은 전자 분야 응용 및 이온 교환 크로마토그래피 및 이와 같은 다른 분야 응용에 대하여 막 성능을 최적화하기 위한 기회들을 제공한다.

<63> 산화물 막들의 일부 구현예들에 대하여, 착체(complex) 조성물, 예를 들면, 물 또는 그 이상의 금속 원자들을 제공하기 위해 기판에 직접 적용될 수 있는 단일-공급원 전구체 현탁액(liquid suspensions)을 제조하기는 어렵다. 다음의 방법들은 소자 응용을 위해 적합한 품질을 갖는 막 증착을 위한 단일-공급원 전구체로서의 그러한 현탁액들의 제조와 그들의 사용을 가능하게 한다.

<64> 다음은 전구체 수용액의 합성과 상기 전구체를 이용하여 금속 산화물 막을 증착하기 위한 일반적인 방법을 설명한다. 상기 전구체 수용액은 비-수계 극성 용매 내에서 가수분해에 의하여 응축되고 이어서 증착을 위한 수성(aqueous) 환경으로 전환되는 졸로서 또는 올리고머 금속-히드록소 화합물들을 포함한다는 점에서 구분된다. 바람직한 박막 전기 및 광학 특성들 및 처리 온도들은 해로운 유기 오염물 없이 금속 수산화물들을 조밀한 고체 산화물들로 응축시킴으로써 달성된다. 합성 방법의 개시된 구현예들은 1) 극성 용매 내에 금속 염을 용해; 2) 가수분해 및 응축; 3) 용매 증발; 4) H_2O 내에 용해; 및 5) 용액 증착 및 경화의 일반 절차들을 따른다.

<65> 금속 양이온(M^{n+})과 하나 또는 그 이상의 음이온들(X^{b-})을 포함하는 하나 또는 그 이상의 가용 염들은, 지방족 알코올류 또는 니트릴류, 특히 (탄소수 10 또는 그 이하의) 저알킬(lower alkyl) 알코올류 및 니트릴류와 같은, 예를 들면, 메탄올, 에탄올, 아세토니트릴 또는 이들의 혼합물과 같이 비-수계 극성 용매에 용해된다. 많은 용매 시스템들이 가능하다. 특정 응용을 위해 적합한 용매들이 의도된 용액-상 반응과 양립할 수 있는 끓는점(통상 150 °C 미만), 저 유독성, 및 산-염기 및 산화환원 특성들을 고려하여 선택될 수 있다. 금속 공급원들은 단순 이온 또는 군자염($Zn(NO_3)_2$, $SnCl_4$ 등); 옥시 또는 히드록시염($ZrO(NO_3)_2$, $ZnOHCl$ 등); 또는 착체적인 유기염들($Fe(CH_3CO_2)_2$, $Cu(CHO)_2$ 등)을 포함할 수 있다. 금속 양이온들의 적어도 하나는 3보다 큰 형식 전하를 가져야 하고, 그러한 이온들(M^{a+}, 여기서 a>3)의 총 농도는 목적 산화물 내의 금속 양이온들의 50 몰%보다 커야 한다. 동시에, 소정량의 H_2O가 위에서 설명한 금속염들의 수화물로서, 순수한 액체로서, 또는 아래에 상술하는 염기성 용액으로서 상기 용매 내에 도입된다. 상기 물의 양은 선택된 양이온들에 의

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하여 결정되며, 물의 통상적인 양은 비-수계 극성 용매의 20 몰%를 넘지 않을 것이다.

<66> 그런 후, 상기 용액의 pH는 적절한 염기성 화합물으로써 또는 산화-환원 메커니즘을 통해 자유 프로톤들의 반응에 의하여 초기 pH에 비하여 증가될 수 있다. 증가된 pH는 적정(a>3) 양이온들에 의하여 결합된 H_2O 리간드들의 가수분해와 그 결과로서 생성되는 히드록소-양이온들의 응축을 촉진한다. 최종 용액 pH는 사용된 금속 양이온들에 달려있지만 약 2 내지 약 9의 범위에 통상 있게 될 것이다. 이는 다음 기술들 중의 하나 또는 그들의 어떠한 또는 모든 조합물을 이용하여 달성될 수 있다.

<67> a) NH4OH, $(NH_4)_3PO_4$, CsOH 또는 유사한 화합물들을 함유하는 염기성 수용액의 첨가. 후속 공정에서 분해 또는 증발시키기 위하여 복잡 화합물들(NH_4OH)이 선택될 수 있다. 달수에 이어서 고유한 모폴로지, 방향적 또는 전기적 특성들을 달성하기 위해 최종 산화물 막의 일부로 이루어지도록 의도된다면 다른 양이온들(예를 들면, Cs) 또는 다원자 음이온들(예를 들면, PO_4^{-3})이 사용될 수 있다.

<68> b) 최종 산화막에 유사한 목적으로 포함시키기 위해 CaO 또는 SrO와 같은 염기성 산화물을 소량 첨가 또는 용해.

<69> c) H_2O 내에 염기성 용액을 형성하는 NH_3 또는 다른 기체 화합물의 첨가.

<70> d) H_2에 대한 직접 환원을 통해 또는 NO_3의 환원과 같이 다른 양성자 소비성 산화-환원 과정의 일부로서 양성자들을 소비할 수 있는, Zn, Al 또는 Fe와 같은 양전성(electropositive) 금속 환원제의 첨가. 결과로서 일어지는 양성자 종들은 그 이후 최종 산화막 내에 포함된다.

<71> e) 최종 산화막 내에 포함되지 않으면서 양성자들을 소비하거나 상대 이온들을 분해하기 위한 유사한 목적으로 사용 염으로서 또는 액상의 H_2O_2, N_2H_4, 또는 H_2CO와 같은 수용액 또는 기상의 산화제 또는 환원제를 첨가.

<72> 상기 용액들은 원하는 최종 조성에 따라 일 가수분해 및 응축을 촉진하기 위해 실온, 가열, 또는 용매열(solvothermal) 조건에서 교반될 수 있다. 적절한 반응 시간이 경과한 후에 상기 용액은 하나 또는 그 이상의 사용 유리고비 또는 폴리머 금속-히드록소 양이온 종을 포함할 것이다. 이들 종들은 사실상 초분자 또는 헤테로-금속 종이다. H_2O에 비하여 비-수계 용매의 감소된 극성 및 보다 큰 입체 장애(steric) 효과 또는 변형된 전하-차폐(charge-screening) 성질들을 통하여 추가적인 응축 및 침전 과정을 방해할 수 있는 반면, 응축의 정도는 사용될 수 있는 H_2O(수성(aquo)- 또는 히드록소- 리간드들)의 제한된 몰비에 의하여 제한된다.

<73> 가용한 금속 종들은 상기 비-수계 용매를 증발시킴으로써 분리된다. 분리된 금속-히드록소 화합물들은 솔베트, 상대 이온, 및 가수 분해 비율(hydrolysis ratio) 등과 같은 특정 프로세싱 파라미터들에 따라 결정질 또는 비결정질 고체 또는 겔을 형성할 수 있다.

<74> 산화물 막을 위한 전구체 용액들은 상기 분리된 고체를 H_2O에 녹이거나 분산시킴으로써 제조된다. 결과로서 얻어지는 졸 또는 용액은 균일하고, 열역학적으로 안정할 수도 있고, 그렇지 않을 수도 있다.

<75> 전구체 용액들은 패터닝된 또는 블랭킷 액상 막을 형성하기 위해 포토톤, 스핀, 스프레이, 또는 딥-코팅을 포함하는 적합한 어떠한 기술이든 이용하여 기판에 적용된다. 액상 막은 약 100 ℃ 내지 600 ℃의 온도에서 약 5 내지 240 분 동안 대기 조건 하에서 연속으로 경화된다. 원하는 화학 또는 광전자 특성에 적합하도록 산소 양론 또는 양이온 산화 상태를 변화시키기 위해 진공 또는 형성 기체(forming gas) (예를 들면, H_2 및 흐르는 N_2 또는 Ar) 어닐링이 사용될 수 있다.

<76> 여기에 설명한 프로세싱 매개변수 및 높은 원자 밀도는 용액 공정을 통해 순수한 무기 나노적층체들의 제조를 가능하게 한다. 이들 막들은 이하에서 더욱 상세하게 논의하는 바와 같이, 넓은 응용범위들의 개발을 위한 새로운 플랫폼을 나타낸다.

<77> **III. 응용들**

<78> 당 기술분야에서 통상의 지식을 가진 자는 HafSOx 및 ZirconOx 화합물들과 이러한 화합물들을 포함하는 막들이 수많은 상이한 소자들을 만들기 위해 사용될 수 있고, 그러한 화합물들을 이용하는 수많은 공정들의 실행에 사용될 수 있음을 이해할 것이다. 금속-유기 전구체들이 무기 산화물들의 용액-기반 증착에 광범위하게 채용되어 왔다. 유기 모이어티의 존재는 코은 소각(burnout) 단계를 필요로 하고, 이는 상당한 부피 변화와 일반적으로

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결정화를 가져오고 또한 "머드 크래킹(mud cracking)" 현상을 가져온다. 비결정질 HafSOx 및 ZircSOx 막들을 형성하기 위해 적절한 유기 조성물들과 본 발명에 개시된 구현예들을 사용함으로써 이들 문제점들이 제거되며, 균일한 결함 및 공학은 막질 보존으로 이어진다. 상의 안정성을 이해하기 위하여, 대표적인 HafSOx 및 HafSOx:La 분말과 박막이 다양한 온도에서 특성화되었다. HafSOx 및 ZircSOx에 기초한 박막들은 상기 박막들의 품질과 유용성을 심층하기 위하여 다양한 구성으로 증착되었다. 케패시터 유전체를 제조하기 위해 여러 유도체들이 사용되었다. HafSOx:La 및 ZircSOx:La를 사용하여 FET 소자들의 게이트 유전체를 형성하였다. HafSOx 및 ZircSOx의 나노적층체의 증착은 주목할만한 미끈함을 2개의 원자층 이내로 재현성있게 시현하였다. 무엇보다도, HafSOx, ZircSOx 및 이들의 유도체들을 포함하는 막들의 종류는 전기 절연체, 고효 상비, 광학 코팅, 및/또는 포토리소그래피를 위한 유기 폴리머로서 유용하다.

<79> **A. 레지스트, 임프린트 리소그래피 및 프린팅을 위한 패턴된 막들**

<80> 포토리소그래피는 마스크 위의 기하학적인 형태를 실리콘웨이퍼 또는 다른 반도체의 표면에 전사하기 위하여 널리 사용된다. 지난 40년간, 포토리소그래피 공정은 마이크로 전자산업에서 소자 구조물의 치수 제어 및 분해능 개선의 구동력이었다. 이러한 발전들은 고성능 개인용 컴퓨터, 휴대 전화, CD 플레이어, 및 이제 우리 삶의 필수적인 부분으로 자리잡은 다른 수많은 신뢰할 전자 제품들을 가능하게 했다. 이들 제품들을 가능하게 하였던 포토리소그래피에서의 발전은 주로 짧은-파장으로 노광하는 도구의 개발과 폭넓게 레지스트들의 해상도 및 피치(feature)-크기 능력을 비상하게 확장하는 데 중심을 두어왔다. 그러나, 더욱 작은 피치들 및 소자-수율 개선을 위한 탐색이 계속됨에 따라 폭넓게 레지스트 기술의 한계와 비효율성이 점차 더욱 명백해지고 있다.

<81> 리소그래피를 통해 구현된 가장 작은 피치 크기는 광기 물질들의 선자빔 기록에 의하여 제조되었다. 그러나, 제조 환경에서 사용되기 위한 입과성 이상의 관심을 받기에는 이러한 피치들을 제조하기 위한 빔-노스 에너지는 과도하게 너무 높았다.

<82> 여기에 설명된 막들의 증착 및 처리가 이루어지는 동안, 막들의 수화 레벨을 조절하는 것이 가능한데, 이는 적층된 막들의 상호확산(interdiffusion)과 그 결과 얻어지는 분리력 및 화학적 특성의 조절을 위한 방법을 제공한다. 이러한 조절된 상호확산은 그 결과로서 얻어진 물질 용해도이 있어서의 유도된 변성과 함께 다들의 높은 품질과 결합되어 새로운 리소그래피 패터닝 방법을 개발하기 위하여 사용되었다. 이러한 방법론은 두 개의 구별되는 다들을 적층하는 단계와 반응시키는 단계를 수반하며, 이중층 확산(bilayer diffusion)으로 지칭된다. 또한, 피옥사이드(O_2^-)와 같은 작은 메위종들은 추가적인, 새로운 리소그래피 패터닝 방법을 제공하기 위해 수계 무기 현탁액들과 막들에 통합될 수 있다. 이 기술에서, 막들에 에너지(예를 들면, 빛, 전자빔, 열)가 적용될 수 있으며, 상기 막의 용해도를 변화시키는 응축 반응을 유도하고, 그에 의하여 리소그래피 패터닝을 가능하게 한다.

<83> 포지티브 또는 네거티브 포토레지스트를 이용하여 패턴들이 형성될 수 있다. 이 공정은 실리콘 기판(1012), 실리카층(1014) 및 레지스트층(1016)을 갖는 적층체 구조물(1010)을 참조하여 도 10에 개념적으로 도시된다. 포지티브 레지스트에 있어서, 상기 레지스트층(1016)은 UV광과 같은 에너지 공급원에 노출되고, 그 아래에 있는 물질들은 제거되게 된다. 이들 레지스트들에 있어서, UV 광에의 노출은 현상액(developer)이 더욱 잘 용해되게 되도록 상기 레지스트층(1016)의 화학 구조를 변화시킨다. 그런 후, 노출된 상기 레지스트층(1016)은 아래에 있는 원래의 물질 영역을 남긴 채 현상액에 의하여 제거된다. 다시 말해, "보이는 것은 무엇이든, 간다." 따라서, 상기 마스크(1018)은 웨이퍼 상에 남게 될 패턴의 복사본을 정확히 포함한다.

<84> 네거티브 레지스트들은 정반대의 방식으로 거동한다. UV 광에 대한 노출은 상기 네거티브 레지스트의 중합을 가져오고, 따라서, 더욱 용해되기 어렵게 된다. 그 결과 상기 네거티브 레지스트(1020)는 노출된 곳이면 어디나 표면 위에 남게 되고, 현상액은 노출되지 않은 부분 만을 제거한다. 따라서, 네거티브 포토레지스트를 위해 사용된 마스크들은 전사될 패턴의 역상(사진의 "네거티브")을 담는다.

<85> 전자 제품 제조를 위해 현재 사용되는 레지스트 물질들은 유기 폴리머들이다. 이들 폴리머들은 패턴 해상도를 제한하는 코일링(coiling)과 노출프로필을 보인다. 본 발명의 무기 박막들은 새로운 레지스트 기술을 위한 기초를 형성한다. 여기서, 네거티브 레지스트들은 반도체 형태의 상기 무기박막들을 및 또는 전사빔들에 노출시키고, 그에 의하여 용매로 잘 녹도록 함으로써, 막의 탈수 과정 동안 물을 잃게 함으로써 구현될 수 있다. 이는 나을 경화시키고, 이들이 산에 녹지 않도록 한다.

<86> 포지티브 레지스트의 일 구현예는 이중층 시스템을 이용하여 제조될 수 있다. 상기 이중층의 제1층은 하프늄 옥사이드 실페이트(HafSOx) 막 위에 증착된 포름산 구리 막을 포함한다. 상기 포름산 구리 막은 산에 용해될

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수 있고, 도핑되지 않은 HafSOx 막은 산에 불용성이다. 상기 이중층을 마스크를 통해 빛에 노출시키거나 포커스를 맞춘 전자빔에 노출시키는 것은 노출된 영역에서 상기 두 막의 상호확산을 가져오고, 그에 의하여 이전의 도핑되지 않았던 HafSOx 막을 용해될 수 있게 만든다.

<87> 본 공정의 일 구현예가 도 11에 개념적으로 도시되어 있다. 도 11을 참조하면, 적절한 물질을 스핀 코팅 또는 잉크젯 코팅함으로써, 작업 소자를 정의하기 위해 요구되는 바와 같이 원하는 순서 및 두께로 적층체 구조물(1110)이 먼저 형성된다. 더욱 구체적으로, 기판 물질(1112)이 먼저 선택된다. 당 기술 분야에서 통상의 지식을 가진 자는 수많은 기판 물질의 무엇이든 본 발명의 이 구현예를 실행하기 위해 잠재적으로 사용될 수 있음을 이해할 것이다. 오직 예로서, 한정함이 없이, 적합한 기판은 반도체 물질들, 금속, 유리, 고분자 물질 및 이들의 조합을 포함한다. 그로써 레지스트 기술은 반도체 제조에서 수많은 응용에 유용할 수 있다. 일단 적합한 기판(1112)이 선택되면, HafSOx의 제1층(1114)이 상기 기판(1112) 위에 용액 증착된다. 그런 후, Cu:ZircSOx의 층(1116)과 같은 제2층이 층(1114) 위에 용액 증착된다. 상기 적층체 구조물(1110)은 그 후 마스크를 통해 전자빔 또는 빛과 같은 에너지 공급원에 조사된다. 마스크를 통해 빛 또는 전자빔에 조사되면, 상기 두 막들은 노출된 영역에서 상호확산되어, 이전에는 도핑되지 않았던 HafSOx 막을 가용하게 하여 적층체 구조물(1120)이 만들어진다. 그런 후, 노출되었던 상기 구조물(1120)은 현상된다. 이전에는 도핑되지 않았던 HafSOx 막은 가용하며, 따라서, 적층체 구조물(1130)에 표시된 바와 같이 제거된다.

<88> 가요성 또는 유리 기판 위에, 구조물(1130)로 도시된 패턴은 임프린트 리소그래피를 위한 또는 그라비어 프린팅과 같은 일반화된 프린팅 공정을 위한 마스터 플레이트로 간주될 수 있다. 이러한 방식으로 HafSOx의 경화되고 패턴된 물질을 형성하는 것은 유체 제어 및 수송을 위한 소자의 제조에서 마이크로- 및 나노-채널 어레이를 개발하기 위한 수단들을 제공할 수도 있다. 그러한 소자들은 의료 진단, 잉크 수송 및 화학 합성에 응용될 수 있다.

<89> 이중층 공정의 다른 구현예가 도 12에 도시된다. 상기 공정은 선택된 기판(1210) 위에 패턴된 산화물을 제조한다. 상기 기판은, 예를 들면, 유리, 반도체 웨이퍼, 금속, 금속 합금, 플라스틱, 또는 이들의 조합일 수 있다. 상기 공정의 첫 번째 단계는 고체 산 또는 염기, 예를 들면, 금속 Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, 또는 Lu의 하나 또는 그 이상을 포함하는 수화된 설페이트, 포스페이트, 나이트레이트, 실리케이트, 알루미네이트, 보레이트 또는 이들의 혼합물들의 박막(약 1 nm 내지 약 100 nm)을 증착하는 단계를 수반한다. 또한, 상기 고체 산/염기는 NH_3, OH, F, Cl, Br, I의 하나 또는 그 이상을 포함할 수 있다. 상기 고체 산/염기는 스핀 코팅 또는 프린팅을 통해 증착되는 것이 바람직하고, 물리 및 기상 증착은 추가적인 옵션이다. 하나의 예로서, 상기 고체 산은 $HfOCl_2$ 및 H_2SO_4(aq)의 수용액으로부터 스핀 코팅을 통해 증착될 수 있다. 상기 고체 산은 약 50 ℃에서 약 2분 동안 가열함으로써와 같이, 충분히 가열되어 구조적으로 강직한 막(1212)을 만든다. 프린팅 방식의 작업에서, 상기 기판(1210)은 가열된(약 25 내지 300 ℃) 평판(platen) 위에 위치되어질 수 있고, 예를 들면, 포름산 구리와 같은 산화물 전구체(1214)를 포함하는 잉크가 잉크젯 헤드를 통해 수송함으로써 또는 상기 전구체(1214)를 포함하는 템플릿과 상기 기판(1210)을 접속시킴으로써 원하는 패턴으로 적용될 수 있다. 상기 템플릿은 그라비어 프린터, 활판(letterpress), 또는 마이크로콘택(microcontact)의 일부를 포함한다. 가열 조건에서(약 250 ℃보다 높은) 상기 전구체(1214)는 산화물로 분해되고, 이어서 상기 고체 산과 반응 및 상호확산하여 쉽게 세정 또는 식각되어 패턴(1218)을 드러낼 수 있는 생성물(1219)을 형성한다. 상기 산화물 전구체는 미세한 산화물 마이크로- 또는 나노-입자를 포함하는 페이스트 또는 현탁액 잉크에 의하여 대체될 수 있다. 가열과 함께 또는 가열 없이 미세한 입자들을 적용하는 것은 식각되어 패턴을 드러낼 수 있는 생성물을 형성하는 직접 반응을 가져오게 된다.

<90> 도 13에, 선택된 기판(1310) 위에 패터닝된 산화물을 제조하기 위한 선택적인 구현예를 나타내었다. 초기 단계는 상기 기판 위에 고체 산(1312) 또는 염기를 증착하는 단계를 수반한다. 그런 후, 상기 산화물 전구체(1314)는 스핀 코팅, 프린팅, 화학 기상 증착 또는 물리 기상 증착을 통해 블랭킷 코팅으로서 적용된다. 그런 후, 광 마스크를 통해 빛과 같은 에너지 공급원에 노출시킴으로써 활성화된 전구체(1316)의 패턴이 형성된다. 적절한 광원은 무엇보다도, 필터링되지 않은 중수소 램프 또는 193 nm에서 빛을 만드는 광원을 포함한다. 선택적으로, 포커스를 맞춘 레이저 또는 전자빔으로 직접 기록함에 의하여 활성 전구체(1316)의 패턴이 형성된다. 그런 후, 만일 필요하다면, 상기 활성화되고 패터닝된 구조물(1316)은 두 층들의 상호확산을 촉진하기 위해 약 125 ℃ 내지 약 350 ℃의 온도로 가열될 수 있다. 그런 후, 상기 노출된 영역들은 원하는 패턴(1318)을 생성하기 위해 식각될 수 있다. 노출 감도를 개선하기 위한 절차로서 상기 고체 산 위에 산화물 전구체의 매우 얇은(약 2 nm) 막을 사용하는 것이 수반된다. 그런 후, 상기 전구체층은 산화물 나노입자들의 용액 캐스팅에 의하여,

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또는 화학 기상 증착 또는 물리 기상 증착과 같은 적절한 어떠한 방법에 의해서든 증착된 산화물의 층으로 덮여진다. 상기 층들은 전구체 박막의 노출에 이어 상호확산된다.

<91> 위에서 설명한 공정들은 포지티브 레지스트 기술에 관련된다. 고체 산/염기 및 전구체들은 불용성 생성물을 생성하게 선택하는 것도 가능하다. 이들 생성물들은 적어도 두 가지 방법으로 포지티브 이미지들을 생성하기 위해 사용될 수 있다. 하나의 구현예에서, 상기 두 층들은 하나의 불용성 층을 형성하기 위해 완전히 상호확산된다. 프린팅 또는 노출 및 현상에 이어서, 상기 막의 가용한(soluble) 부분들은 세정 또는 식각되어 포지티브 패턴을 드러낸다. 다른 접근에서는, 상호확산이 전구체와 고체 산/염기 사이에서만 일어나, 얇은 불용성의 장벽층을 생성한다. 그 후, 이 장벽층은 포지티브 이미지를 생성하기 위한 막의 스택의 식각을 조절하기 위해 사용된다. 상기 장벽층은 감광성이다. 그것은, 빛에 노출시키기 전에, 그렇지 않았다면 접촉과 함께 즉시 상호확산하였을 상기 전구체와 상기 고체 산/염기 층 사이의 반응을 방해한다. 일단 상기 장벽층이 감광되면, 그것은 반응성 산화물이 된다. 상기 장벽이 "깨어지고", 그런 후 상기 상부 층은 하부 층과 상호확산할 수 있다.

<92> 광에 기반을 두든 임프린팅에 기반을 두든, 차세대 패터닝은 전자빔 리소그래피에 의하여 통상 제조되는 마스크 또는 템플릿들을 사용한다. 이들 템플릿들 또는 마스크들의 많은 것들은 하드마스크 HSQ (hydrogen silsesquioxane)으로 제조되고 있다. HSQ 마스크들은 다양한 전자, 데이터 저장, 및 미세전자기계 소자들의 제조에 널리 사용된다. HSQ는 또한 임프린트 리소그래피를 위한 하드 마스터/템플릿으로서 개발되고 있다.

<93> 마스크들 및 템플릿들은 도 14에 나타낸 단일층 공정에서 여기서 설명된 막들을 이용하여 제조될 수 있다. 상기 공정의 제 1 단계는 기판(1412) 위에 무기 전구체(1410)의 박막(약 1 nm 내지 약 100 nm)을 증착하는 단계를 수반한다. 상기 무기 전구체(1410)는 퍼옥사이드 또는 유사한 배위 음이온과 함께 있는 고체 산 또는 염기, 예를 들면, 금속 Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, 또는 Lu의 하나 또는 그 이상을 포함하는 수화된 설페이트, 포스페이트, 나이트레이트, 실리케이트, 알루미네이트, 보레이트 또는 이들의 혼합물일 수 있다. 또한, 상기 고체 산/염기와 퍼옥사이드 혼합물은 NH_3, OH, F, Cl, Br, I의 하나 또는 그 이상을 포함할 수 있다. 상기 고체 산/염기는 스핀 코팅, 액체 미스팅(misting) 또는 프린팅을 통해 증착되는 것이 바람직하고, 물리 및 기상 증착은 추가적인 옵션이다. 하나의 예로서, 상기 고체 산은 $HfOCl_2$, H_2SO_4(aq), 및 H_2O_2(aq)의 수용액으로부터 스핀 코팅을 통해 증착될 수 있다. 상기 고체 산은 약 50 ℃ 내지 약 125 ℃의 온도에서 약 10초 내지 약 10분 동안의 시간 동안 가열함으로써와 같이, 충분히 가열되어 구조적으로 강직한 막을 만든다. 그런 후, 상기 막은 광 마스크를 통해 또는 정의된 레이저 또는 전자빔을 통해 노출되고, 노출된 영역에서 응축을 유발한다. 노출된 영역(1414)들의 용해도는 노출되지 않은 영역들에 비하여 감소되고, 따라서 상기 노출되지 않은 영역들은 산 또는 염기에 선택적으로 식각될 수 있다. 사용될 수 있는 산 또는 염기들의 예는, 무엇보다도, 염산, 황산, 과산화수소, 수산화나트륨, 및 터셔리메틸 암모늄 히드록사이드를 포함한다. 통상, 사용되는 산 또는 염기들의 농도는 약 0.1 M 내지 약 1 M의 범위 내이다. 그런 후, 약 100 ℃보다 높은 온도에서의 선택적인 열경화에 이어서 상기 막은 수성 산 또는 염기 내에서 노출되지 않은 영역들을 식각하기 위해 현상된다. 이 공정은 막 내에 네거티브-톤의 이미지를 생성한다. 적용된 막을 필드(field) 노출 시키기 전에 더 높은 온도로 예열함으로써, 포지티브-톤 이미지를 구현하도록 차별적인(differential) 식각 속도가 유발될 수 있다. 도 15는 열적으로 예열된 단일층 막에 대한 차별적인 식각 속도를 설명한다. 상기 그래프는 노출된 영역이 노출되지 않은 영역에 비하여 초기시간 이후에 더 빨리 식각되도록 열처리가 식각 속도에 영향을 미치는 것을 설명한다.

<94> 또 다른 구현예에서, HafSOx 막은 수산화나트륨과 과산화수소의 혼합물로 처리되어, 음이온 교환 및 $M(OH)_x/H_2O_2$ 막의 형성을 가져온다. 선택적으로, $M(OH)_x/H_2O_2$ 막을 형성하기 위하여, 이전에 제조한 $M(OH)_x$ 막을 과산화수소에 적실 수 있다. 결과로서 얻어지는 $M(OH)_x/H_2O_2$ 막은, 그런 후, 빛 또는 전자빔에 노출됨으로써 패터닝된다. 이들 기술들은 폴리머 레지스트 없이 복합 MO_x 막의 단순한 직접 패터닝하기 위한 수단들을 제공한다. 예를 들면, HfO_2 막들은 Si CMOS 회로 및 프린트된 전자공학 응용에서 하이 k 유전체로서 사용되기 위해 직접 패터닝될 수 있다. 또 다른 예에서, 패터닝된 TiO_2 막은 H_2O_2 내에서 $Ti(OH)_4$를 용액 증착함으로써 형성된 $Ti(OH)_x/H_2O_2$ 막으로부터 제조될 수 있다.

<95> 이들 방법들은 실질적으로 2-층 구현예들에서 사용된 확산을 제거하고, 노출 도스를 낮추며, 라인-에지 조도와 임계 치수(critical dimension)를 개선한다. 도 16은 전자빔이 0 $\mu C/cm^2$ 보다 크고 적어도 400 $\mu C/cm^2$까지의 범위의 도스 레벨을 갖는 단일층, 네거티브 톤 공정을 통해 패터닝된 HafSOx 막의 AFM(atomic force

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microscope) 이미지이다. 상기 이미지의 오른쪽의 나노미터 스케일은 상기 막 내부로 식각된 피처들의 높이를 나타낸다. 도 16에 나타낸 바와 같이, 피처들은 2 $\mu C/cm^2$라는 낮은 도스 레벨로 전자빔 노출을 통해 기록되었다. 이 도스 레벨은 알려진 최고의 화학 증폭형 폴리머 레지스트들에 필적한만하며, 무기 레지스트에 대하여 이전에 입증된 것보다 1000 배나 낮다. 피처들은 약 20 nm 미만의 해상도로 제조될 수 있다. 또한, 상기 막들은 HSQ에 대하여 증명된 것보다 거의 하나의 차수(an order of magnitude)만큼 작은 3 nm 미만으로 구조적 집적도(integrity)(예를 들면, 매끈하고, 조밀하고, 핀홀이 없는)를 증명한다.

<96> 무기 물질의 전공 및 그은 처리 단계들뿐만 아니라 폴리머 레지스트로 전사된 막의 적용, 가열, 및 식각 단계들이 패터닝 과정에서 제거되었다.

<97> 결과로서 얻어지는 막은 전자 소자의 기능적인 부품, 아래에 있는 기판의 후속 패터닝을 위한 하드 마스크, 또는 인프린팅을 위한 템플릿일 수 있다. 진공 노출을 제외하고, 모든 처리는 상기 층의 보풍의 환경에서 수행된다. 여러 처리 단계들의 제거를 고려할 때, 개시된 기술은 소자 제조 수율을 개선하고 제조 비용을 낮추기 위한 새로운 방법을 제공한다. 주성 화학의 특별한 사용에 따르면, 상기 공정은 또한 환경 친화적이며, 세정된 생성물들은 완전히 회수되어 재생될 수 있다. 상기 기술은 많은 고급 기술들에 응용성을 갖는다. 그의 사용은 여기에 설명한 시스템에만 한정되지 않는다.

<98> **B. 핫 엠보싱(hot embossing) 리소그래피**

<99> 핫 엠보싱 리소그래피는 HafSOx, ZircSOx 및 관련 물질에 패턴을 생성하기 위한 다른 방법이다. 도 17에 기본적으로 도시한 본 방법은 유기 폴리머로 패턴을 생성하기 위해 매우 널리 적용되어 왔다. HafSOx 및 관련 조성물의 반고체 형태는 유기 폴리머들에 비하여 훨씬 더 높은 기계적 강도, 화학적 안정성 및 고유한 전기적 및 광학적 특성을 갖는 무기 물질의 패터닝할 기회를 제공한다.

<100> 도 17을 참조하면, HafSOx 또는 관련된 무기 물질은, 유기 폴리머 대신, HafSOx 층(1714)을 형성하기 위해 적합한 기판(1712) 위에 스핀 코팅 또는 잉크젯 프린팅에 의하는 것과 같이 용액 증착된다. 기판(1712)과 HafSOx 층(1711)은 적층체 구조물(1710)을 정의한다. 나노미터, 마이크로 미터 또는 밀리미터 크기 스케일과 같은, 원하는 크기의 스케일의 단위 피처들을 갖는 스탬프(1716)가 상기 반고체 HafSOx 또는 관련된 막의 층(1714)에 프레스되어 스탬프된 층(1718)을 형성한다. 스탬프된 층(1718) 및 기판(1712)은, 그런 후, 가열되어 HafSOx를 경화시킨다. 그런 다음, 상기 스탬프가 제거되어 패터닝된 적층체 구조물(1720)에 패터닝된 HafSOx 물질을 정의한다.

<101> **C. 측정 장치**

<102> 위에서 설명한 이중층 포지티브 레지스트 기술을 위해 개발된 화학은 전자 현미경과 같이 적합한 분야에서 측정을 표준화하는 데 사용하기 위한 도 18에 도시한 바와 같은 물리적 자의 제조하기 위해 사용될 수도 있다. 특정 응용에서, 예를 들면 산-가용성 층들(1812)과 산-불용성 층들(1814)의 다수 적층체(1820)가 증착된다. 상기 산-가용성 층들은 하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{2-x-z/2}(OH)_z(SiO_4)_x$) 화합물의 용액 증착에 의하여 형성된다. 통상 이 층은 교대로 도포된다. 상기 산-불용성 층들은 하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{2-x-z/2}(OH)_z(SiO_4)_x$) 화합물의 용액 증착에 의하여 형성된다(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 종하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음).

<103> 상기 층들(1812 및 1814)의 특들은 반사 X-선에 의하는 것과 같이, 정확하게 설정된다. 그런 후, 상기 산-가용성 층들(1812)은 식각되어 전자 현미경에서 목적물을 정확하게 측정하는 데 2차적인 척도로서 사용될 수 있는 펑거-타입 패턴(1820)을 도출한다.

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<104> **D. 부식 장벽**

<105> 금속 또는 합금 또는 세라믹과 같은 적절한 기판 위에 전구체 액체가 코팅되어 부식 장벽을 형성할 수 있다. 또한, 상기 액체는 몰드 내에 위치하거나 또는 흡로 사용되는 섬유 내부로 위입될 수도 있다. 상기 액체는 공기 중에서 가수분해, 어닐링 또는 열분해를 포함하는 적합한 어떠한 공정에 의하여든 고체, 안정한 형태로 전환된다. 통상, 이것은 적어도 수 초동안, 더욱 전형적으로는 적어도 수 분동안 보통 100 ℃ 이상의 온도와 같이 원하는 결과를 얻기 위해 유효한 온도로, 시간 동안 가열하는 것이 요구된다.

<106> 상기 막들의 기계적으로 조밀한 성질로 인하여, 잠재적인 응용은 다른 많은 것들뿐만 아니라, 금속 및 금속/세라믹-계 열 보호(thermal protection) 시스템, 우기계 디스플레이 및 전자 제품, 태양 전지, 고 방사율(emissivity) 코팅, 산화물계 세라믹 매트릭스 시스템에 대한 계면 코팅, 인광체(phosphor) 위의 보호 코팅, 금속- 및 세라믹계 시스템에 대한 주변적 장벽 코팅, 복합체 및 섬유 리이저용 섬유, 용해 금속 치료에서의 부식 방지, 던연용 보호러더 물질 및 축매 담체에 대한 연, 부식 및 산화 방지를 포함하지만 여기에 한정되는 것은 아니다. 상기 막들을 적층할 수 있는 능력은 다른 층의 완화하여 한 층에서 결함의 위치를 무작위화(randomize)한 기회를 제공하여 개선된 부식 보호를 제공한다.

<107> **E. 광학 코팅**

<108> 상기 전구체 액체들은 반사 방지 코팅, 유전체 거울(dielectric mirror), X-선 거울, 간섭 필터, 회절 격자, 도파로(waveguide), 평면 코팅 및 내-스크래치 표면을 만들기 위해 적절한 광학 기판 위에 개별 층들로서 및 다층 형식으로 코팅될 수 있다. 적어도 두 개의 물질 조성물을 교호 적층하으로써 다층 주기성이 달성된다. 단층 주기성은 보토리소그래피 공정에 대하여 설명한 바와 같이 식각에 의하여 달성될 수 있다. 디젠성질적인 성질, 층들 사이의 명확한 계면, 및 유전 상수를 조절하는 능력은 이론적 한계에 가까운 성능을 구현하기 위한 공정을 제공한다.

<109> 전형적으로 증착되거나 식각된 다층 또는 단일층 구성에서, 주기적인 구조물은 회절 응용에 적합하다. 보이드 및/또는 단일 또는 다중 물질들의 조합은 구조물을 정의할 수 있다. 보이드 공간의 사용은 주어진 구조물 내에서 물리적 성질의 큰 대비를 가능하게 한다. 기능적인 특성들은 보이드 공간의 사용에 의하여 개선되거나 구현될 수 있다. 광학 격자도 유사하게 정의될 수 있다.

<110> 실질적으로 매끈한 표면 막들은 여기에 개시된 방법의 구현예들에 따라 증착될 수 있기 때문에, 더 큰 정도의 조도(roughness)를 보이는 금속, 세라믹, 및 플라스틱과 같은 기판 층들을 평탄화하기 위해 다층이 사용될 수 있다.

<111> **F. 발광막**

<112> 몰질은 수많은 발광 과정들에서 에너지를 흡수하고 광자를 방출할 수 있다. 발광 현상은 지배적인 상(또는 호스트) 만을 수반할 수도 있고, 또는 첨가된 원소들을 포함할 수도 있다. 단일 물질은 수많은 발광 첨가제에 대하여 호스트로서 작용할 수 있다. 개시된 막 조성물들의 많은 수는 시각적으로 투명하고, 투명성이 스펙트럼의 자외선 부분으로 잠재적으로 연장되고 있다. 이러한 물질들은 발광 호스트 물질로서 잠재적으로 기능한다. 이들 물질들은 조명 및 디스플레이 응용을 위해 관심이 있는 발광파을 가져오기 위하여, 예를 들면, Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Ce^{3+}, Tb^{3+}, Eu^{3+}, Gd^{3+}, Tm^{3+} 및 이들의 조합을 포함하는 통상의 발광성 이온들로 선택적으로 도핑될 수 있으나 이기에 한정되지 않는다.

<113> **G. 프린트된 전자 제품**

<114> 제조업자들은 종래의 기상 증착 및 리소그래피 공정의 한계를 제거하 새롭고, 효율적인 제조 방법들을 찾고 있다. 프린팅 및 관련 마스크리스(maskless) 기술들은 백-플레인(back-plane) 전자공학의 있어서, 제조 효율의 개선을 구현하기 위한 길로서 널리 간주되고 있다.

<115> 개시된 용액-처리된 박막들은 대두유의 발견된 기상 처리 방법에 의하여 달성되는 것들과 유사한 모폴로지 및 소자-기능적 특성들을 보인다. 개시된 조성물의 용액들은 마이크로콘택, 그라비어, 잉크젯 프린터 또는 다른 적합한 수단들에 의해서와 같이 임프린트될 수 있다. 결과적서 얻어지는 임프린트된 용액들은 약 20 nA/cm^2 미만의 유전체 누설 전류 밀도를 갖고, 약 10 cm^2/Vs의 소자 이동도를 보이는 안정한 부기 트랜지스터 어레이들을 제조하기 위해 사용될 수 있다. 유전체 및 전도체 잉크들은 또한 약 100 nA/cm^2 미만의 유전체 누설 전류 밀도

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와 약 1 cm^2/Vs의 이동도를 갖는 트랜지스터 어레이를 제조하기 위해 유리 기판 위에 프린트될 수 있다. MIM 캐패시터 어레이들은 약 5보다 큰 상대 유전 상수 및 약 50 nA/cm^2 미만의 누설 전류 밀도로 제조될 수 있다.

실 시 예

<153> **실시예들**

<154> 본 발명의 작동 및/또는 가상의 구현예들의 특정한 특성들을 예시하기 위하여 다음 실시예들이 제공된다. 당 기술분야에서 통상의 지식을 가진 자는 본 발명의 범위가 이들 실시예에서 언급된 특정한 특성들에 한정되지 않음을 이해할 것이다.

<155> **실시예 1**

<156> 본 실시예는 박막 전구체들을 위한 또는 박막 전구체들로서 사용하기 위한 공급원으로서 용액들을 제조하기 위해 사용된 일반적인 방법을 설명한다. 다음 시약들이 사용되었다. $HfOCl_2 \cdot 8H_2O$ (Alfa Aesar, 99+% (1.5%Zr 제외)); $ZrOCl_2 \cdot 8H_2O$ (Wah Chang 분광 등급(spectrographic grade)); $La_2(SO_4)_3$ (Alfa Aesar, 99.9%); $La(NO_3)_3 \cdot 6H_2O$ (Johnson Matthey, 99.9%); $Ce_2(SO_4)_3 \cdot 8H_2O$ (Strem, 99%); CaC (Alfa Aesar, 99.95%); $(NH_4)_2SO_4$ (Mallinkrodt AR); $H_2SO_4(aq)$ (EM Science, GR ACS, 95-98%); 및 $NH_3(aq)$ (EM Science, GR ACS, 28-30%). 모든 용액들은 $HfOCl_2$ 또는 $ZrOCl_2$를 약 0.8 M의 총 금속 농도를 위하여 필요한 만큼의 $La_2(SO_4)_3$, $Ce_2(SO_4)_3$, 또는 CaO와 결합하고, 이어서 약 0.5 M의 총 금속 농도를 위하여 신페이트 용액을 첨가함으로써 제조되었다. 이들 용액들은 열-유발된 침전 및 스핀-코팅 유전막들에 대하여 직접 사용되었다. 하드록사이드 침전 반응 또는 나노적층체 증착을 위해 전구체로서 작용하는 데 필요한 바에 따른 추가적인 부경이 이루어졌다.

<157> **실시예 2**

<158> 본 실시예는 실시예 1에 따라 제조된 용액들로부터의 벌크 침전을 위해 사용된 일반적인 방법을 설명한다. 침전은 끓는 수조에 용액의 튜브를 40분간 침지시킴으로써 유발되었다. 하드록사이드-유발된 침전에 대하여, $HfOCl_2$ 및 $La_2(SO_4)_3$는 23% La(금속 백분율)이 되도록 혼합되고, 이어서 $La(NO_3)_3$ 및 $(NH_4)_2SO_4$의 용액들을 첨가함으로써 약 0.39 M의 하프늄 농도([Hf]), 약 0.18 M의 란탄 농도([La]), 및 약 0.42 M의 신페이트 농도([SO_4])를 제공하였다. 그런 후, (총 금속과 관련하여) 1.9 몰 당량의 $NH_3(aq)$가 신속히 첨가되고, 그 결과로서 얻어지는 혼합물을 1분 동안 교반하였다. 모든 침전물들은 석션이 달린 종이 여과 및 여러 차례 탈이온수로 세척함에 의하여 상청액(supernatant)으로부터 분리되었다. 여과물은 1일 동안 실온에서 건조되었다. 이어서 건조된 분말을 주위 공기에서 알루미나 도가니에 넣고 약 100 ℃에서 약 1,500 ℃의 온도로 약 1 시간 내지 약 4 시간 동안 가열하였다. Siemens D5000 회절계로 Cu K α 방사선을 이용하여 XRD 데이터를 수집하였다. 열중량분석 데이터는 Shimadzu TGA-50을 이용하여 $N_2(g)$를 흘리면서 Pt 도가니에서 건조분말(10-20 mg)을 통상 10 ℃ 분$^{-1}$의 속도로 가열하고 최고 온도에서 1분 동안 유지함으로써 수집하였다. 유도 결합 플라스마 원자 발광 분석(ICPAES: inductively coupled plasma atomic emission spectroscopy)이 Jobin Yvon JY2000 분석 설정으로 수행되었다. 건조분말은 침지 밤(digestion bomb)에 넣고 수 시간 동안 200 ℃에서 용해시키고 측정 가능한 수준으로 희석하였다.

<159> **실시예 3**

<160> 본 실시예는 실시예 1에 따라 제조된 용액들을 이용하여 박막을 증착하기 위해 사용되는 일반적인 방법을 설명한다. HafSOx, ZircSOx 및 La, Ce 또는 Ca 첨가된 유도체들의 박막이 3,000 rpm으로 30초 동안 스핀코팅에 의하여 Si 기판 위에 증착되고, 즉시 이어서 135 ℃에서 1.5 내지 2 분 동안 열판 증발을 하였다(15초 내지 약 2 분 동안 325 ℃ 오븐 표면 위에서 추가적인 가열이 특정 도함수에 대하여 필요할 수 있다). 이 공정은 원하는 증착 박 두께가 얻어질 때까지 반복되었다. 325 ℃에서의 최종 오븐 어닐링은 5 내지 10분 동안 사용되었다.

<161> 나노 적층체 막들을 위한 전구체들이 $HfOCl_2$ 또는 $ZrOCl_2$에 H_2SO_4를 금속에 대하여 40% 설페이트가 되도록 첨가함으로써 제조되었다. 용액은 금속 농도가 0.03 내지 0.13 M로 희석되었다. HafSOx와 ZircSOx의 교호하는 층들이 유전막에 대하여 설명한 바와 동일한 방식으로 증착되었다.

<162> 상기 실리콘 기판은 SiO_2 또는 Ta 금속의 표면을 가졌다. 유전 테스트를 위하여 500-나노미터 Ta 표면이 이용

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되었다. 모든 다른 목적으로는 200-나노미터 SiO_2 조면이 사용되었다. 상기 조면물은 45℃의 (Decon Labs, Contrad 70) 용액 내에서 15분간 초음파 처리를 한 후 증착하기 전에 Millipore 물로서 완전히 표면을 세정함으로써 증착을 위한 준비를 하였다.

<163> XRD 데이터는 50 kV 및 270 mA에서 회전 음극으로부터 생성된 Cu Kα 방사선을 채용한 Rigaku RAPID 회절기로 수집되었다. 회절된 빔이 이미지 판에 수집되는 동안 입사빔의 각도는 7.6° 이였다. Cu Kα 방사선으로 XRR 데이터가 수집되었다. 낮은 각도 반사가 10° (2θ)까지 0.005° 단위로 수집되었다. 투과 FTIR 데이터가 코팅되지 않은 기판을 레퍼런스로 하여 Nicolet 5PC 스펙트로미터를 이용하여 수집되었다. EMPA가 수집되었다.

<164> 증착된 유전체 위의 Al의 원형 콘택(1.2 mm 직경)들을 열적으로 증발시킴으로써 MIM 캐패시터 구조물들이 완성되었다. 유전 상수 및 손실 탄젠트의 파라미터들을 얻었다. 하부-게이트 트랜지스터 구조물도 홀성 영역의 가열 없이 부기 채널 물질들을 스퍼터링함으로써 제조되었다. 이어서 ZTO-채널 소자들이 325 ℃로 1 시간 동안 가열되었다. 알루미늄 소오스 및 드레인 콘택들이 열적으로 증발되었다. 트랜지스터 특성화가 수행되었다.

<165> **실시예 4**

<166> 본 실시예는 매끈하고, 조밀하며 핀홀이 없는 약 2 nm만큼 얇은 초박(ultra-thin) 나노적층체 막을 제조하기 위한 일반적인 방법을 설명한다. 비합중국 특허청기 제2005/0242330A1호에 설명된 바와 같이 $HfOCl_2 \cdot 8H_2O$ 또는 $ZrOCl_2 \cdot 8H_2O$, H_2O_2 (30%) 및 H_2SO_4(aq)를 포함하는 전구체 용액이 준비되었다. 상기 전구체 용액은 약 0.05 M 내지 0.4 M의 금속 이온 농도 및 금속에 대하여 70% H_2O_2 및 50% 설페이트를 포함하였다. 금속 이온 농도에서의 상기 차이는 주형당 두께의 변화를 3 nm에서 25 nm로 변화시키는 것을 가능하게 하였다. 실리카 기판 위에 열성장 SiO_2의 박막이 증착되었다. 기판은 25 ℃에서 60 분간 Contrad-70 용액으로 초음파 조를 이용함으로써 세정되고, 이어서 탈이온수로 헹구어졌다. 스핀 코터를 이용하여 3000 rpm의 스핀 속도로 30초 동안 막이 증착되고, 이어서 125 ℃에서 1 내지 2 분 동안 열판(hotplate) 상에 건조되었다. 스핀-코팅과 건조 절차는 원하는 두께에 도달할 때까지 반복되었다. 원하는 두께에 도달한 후, 일부 막들은 결정화 온도까지 가열되었다. 다른 막들은 0.1 M 내지 0.5 M NaOH 조에서 1 내지 2분 동안 1차 처리되고, 그런 후, 연처리하기 전에 탈이온수 조에서 1 내지 2 분 동안 세정되었다.

<167> X-선 회절(XRD) 분석을 이용한 막 특성화가 Cu Kα 방사선을 채용한 Rigaku R-axis RAPID로 수행되었다. Veeco NP-20 SiN 탐침 및 1.15 Hz의 스캔 주파수를 갖고 접촉 모드로 동작하는 Digital Instruments Nanoscope IIIa Multimode AFM으로 원자력 현미경(AFM: atomic force microscopy) 측정을 수행하였다. Bruker Discover D8을 이용하여 만사 X-선 측정이 수행되었고, 상기 막의 표면과 계면 조도를 결정하기 위해 사용되었다. 시판의 튜닝가능한 파장 분산 분광기를 장착한 Cameca SX-50 전자 마이크로탐침 상에서 조성 분석이 일어났다. O, Cl, Ka, S, 및 Si의 Kα 세기와 Zr 및 Hf의 Lα 세기를 모니터하기 위해 12, 15 및 22 kV의 가속 전압들이 사용되었고 5 점에 걸쳐 평균을 내었다. 분석을 위해 사용된 스탠다드는 MgO, Hf, Zr, FeS_2 (pyrite), $Ca_5(PO_4)_3Cl$ (apatite), Si, and Si_3AlNaO_8 (albite)이었다. Probe for Windows 자동화 및 분석 패키지를 이용하여 원본 세기(raw intensity)에 대한 수정이 이루어졌다. StrataGEM 조성 분석 소프트웨어 패키지를 사용하여 실험으로 구한 K-비율들과 모사된 값들을 비교함으로써 마막 기하구조를 수정하였다.

<168> 비결정질이고, 원자 수준에서 평탄하고, 조밀하고, 핀홀이 없는 박막들이 증착된대로의(as-deposited) 박막들과 교환된 박막들에 대하여 스핀 코팅을 통해 증착되었다. 도 18는 약 0.1 nm의 조도를 갖는, 교환되지 않은 HafSOx 막의 AFM 이미지이다. 도 20은 HafSOx의 이온 교환과 850 ℃에서의 열처리 다음의 HfO_2 막의 TEM 이미지이다. 교환되지 않은 막들은 Zr에 대하여는 600 ℃까지, Hf에 대하여는 650 ℃까지 비교적 비결정질로 남았다. 그러나, 이들 온도보다 높게 가열한 후에는, 막들이 결정화되고 표면에 화산과 같은 피처들을 형성하면서 거칠게 되었다. 도 21은 실리콘 위에 증착된 HfO_2 막의 AFM 이미지이다. 상기 HfO_2 막은 HafSOx의 열분해에 의하여 형성되었다. 결과로서 얻어지는 막은 약 5 nm의 조도를 가졌고, 화산과 같은 피크들을 가지었다. 이들 피처들은 SO_3의 손실에 의하여 야기되었을 것으로 추측하게 측정되었다. 이것은 700 ℃를 넘는 온도에서 설페이트 분해(SO_3 (g) → SO_2 (g) + ½O_2 (g))가 일어나는 Hf 설페이트 분말의 열중량 분석에 의하여 뒷받침된다. 화산 형상을 없애기 위하여, 막들은 0.1 내지 0.5 M NaOH(aq) 조 내에서 1분 내지 2분 동안 처리되고, 가열하기 전에 막으로부터 SO_4^{2-} 및 Cl^- 음이온들이 제거된다. 이전부터 NaOH는 히드록시 음이온을 지르코늄 염과 다른 음이온과 효과적으로 교환하는 것으로 알려지었다. 상기 NaOH 처리는 40 내지 40%의 두께 감소를 가지었지만(2 내지

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15 nm의 두께의 층을 가져옴), 상기 처리는 지르코니아와 하프니아 대하여 각각 500 ℃와 550 ℃ 이하로 가열한 후 막의 매끄럼(smoothness)(~1Å) 또는 비결정질 성질에는 영향이 거의 없다.

<169> 도 22는 실리카 위에 증착되고, 이어서 0.1 M NaOH로 처리되고 450 ℃에서 10분간 가열된 HafSOx 막의 AFM 이미지이다. 결과로서 얻어지는 막은 약 0.1 nm의 조도를 가졌다. 이들 온도 위로 가열된 막들은 결정화되었지만 850 ℃까지의 온도에서는 매끄럼을 유지하였다.

<170> 도 23은 실리카 위에 증착되고, 이어서 0.1 M NaOH로 처리되고 850 ℃에서 10분간 가열된 HfO_2 막을 나타낸다. 결과로서 얻어지는 결정화된 막은 약 0.2 nm의 조도로 매끈하게 유지되었다.

<171> X-선 회절 그래프에서(도 24 내지 도 27) 결정화 온도의 감소가 관찰되었다. 도 24 내지 도 27에서, 기판의 피크들은 소프트웨어에 의하여 제거되었다. "*"는 주요 정방정계(tetragonal) 상의 피크들을 나타낸다. 도 24는 700 ℃에서 정방정계와 단사정계(monoclinic) 상의 혼합물로 결정화된 처리되지 않은 HfO_2 막의 XRD 그래프이다. HfO_2 그래프는 단사정계 상에 대한 기준 그래프이다. 대조적으로, 도 25는 550 ℃에서 단사정계 상에서만 결정화된 0.1 M NaOH로 처리된 하프니아 막의 XRD 그래프이다. HfO_2 그래프는 단사정계 상에 대한 기준 그래프이다. 도 26은 650 ℃에서 단사정계와 정방정계 상이 혼합되어 결정화된, 처리되지 않은 지르코니아 막의 XRD 그래프이다. ZrO_2 그래프는 단사정계 상에 대한 기준 그래프이다. 도 27에서 보는 바와 같이, 0.13 M NaOH 처리된 지르코니아 막들은 500 ℃에서 정방정계에서만 결정화되었다. 계속 가열하면, 막은 단사정계와 정방정계 상 모두로 변천되었다. HfO_2와 ZrO_2의 정방정계 상들은 이전의 박막 연구에서 관찰되었다. 너 낮은 결정화 온도, 결정화 및 두께 손실은 NaOH 처리가 막으로부터 음이온(SO_4^{2-} 및 Cl)을 제거함을 가리켰다.

<172> 0.1 M HF 용액으로부터 증착되고 350 ℃까지 5분 동안 가열된 막의 전자 탐침 미세 분석(EPMA: electron probe microanalysis)은 $HfO_{1.88}(SO_4)_{0.03}Cl_{0.13}$의 조성을 가져왔다. 상기 막 내의 원소는 균일한 열 분포의 결과로 동적 트립핑된 결과였다. NaOH(aq) 조 내에서의 처리된 막들은 측정 가능한 황의 레벨을 갖지 않았고(0.01 원자 퍼센트 미만), 0.3 원자 퍼센트 미만의 Cl이 관찰되었다. 이것은 황과 염소가 모두 NaOH(aq) 조 내에서 상기 막으로부터 제거되었음을 확인하였다. EMPA는 또한 상기 처리 후에 상기 막에 남은 초류 나트륨은 0.3 원자 퍼센트 미만임을 확인하였다.

<173> **실시예 5**

<174> 위에서 설명한 접근방법들의 구체적인 구현예들에서, 수화된 인듐 및 갈륨 나이트레이트 염들($In(NO_3)_3 \cdot 0.5H_2O$ 및 $Ga(NO_3)_3 \cdot 0.5H_2O$)을 메탄올(CH_3OH) 내에 용해시켰다. 최종 농도는 [In] = 0.288 M, [Ga] = 0.170 M이었다. 그런 후, 아연 분말을 상기 용액에 첨가하고, 플라스크를 밀봉하였다. 아연의 최종 농도는 0.2 M이었다. 1일 내지 7일의 기간에 걸쳐 반응시키고, 상기 분말은 서서히 산화되고 용해되어 선택 금속 이온 농도를 0.658 M까지 변화시켰다. 상기 메탄올 용액을 상기 병에 노출시키고, 실온에서 증발할 수 있도록 하였다. 그런 후, 상기 용액 내에 산포하는 고체 산화물을 H_2O에 용해시켜 총 금속 농도를 0.395 M로 하였다. 이 전구체 용액은 도전성 백 콘택(back contact)을 갖는 SiO_2 기판 위에 스핀-코팅되고, 450 ℃에서 1 시간 내지 4 시간 동안 어닐링되었다. 어닐링에 이어서, 투명하고 비결정질인 $InGa_{0.5}Zn_{0.5}O_{3.15}$ 반도체 다음 도 28의 SEM 이미지에 나타낸 바와 같이 수득하였다. 알루미늄 소오스 및 드레인 콘택들은 박막 트랜지스터(TFT)를 제조하기 위해 섀도우 마스크를 통해 산화물 반도체 막 위로 열 증발되었다. 이들 TFT들의 전계 효과 이동도는 8 $cm^2 V^{-1} s^{-1}$을 넘는 것으로 나타났다.

<175> **실시예 6**

<176> 본 실시예는 이중층 무기 리소그래피 공정의 두 개의 일반적인 방법들을 설명한다. 하나의 작동 구현예에서, 약 30 nm 내지 약 60 nm의 두께를 갖는 HafSOx 막이 SiO_2/Si 기판 위에 용액 증착되었다. 상기 기판은 약 50 ℃로 설정된 열판(hot-plate)의 직접 위에 위치되고, 상기 막에 구조적 집적도를 부여하기 위해 가열되었다. 결과로서 얻어지는 막은 산에 분용성이었다. 그런 후, 상기 기판을 잉크젯 프린터의 가열된 평판(platen)(약 50 ℃ 내지 260 ℃) 위에 위치되고, 열 잉크젯 헤드를 통하여 기판 위에 포름산 구리의 선들이 프린트되었다. 포름산 구리는 가열됨에 따라 분해되고 HafSOx 막 내부로 확산되어 상기 막을 가용성으로 만들었다. 분로 세정한 후에, 약 300 ℃로 추가 가열하고, 묽은 산 내에서 현상한 결과, 도 29에 나타낸 바와 같이, 구리의 선들은

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명백히 드러났다.

<177> 다른 작동 구현에서, 패턴이 역시 포토리소그래피를 통해 생성되었다. 도 30에 나타낸 패턴의 후속적인 상호확산 및 현상을 위해, 여과되지 않은 중수소 램프를 이용하여 $HfO_{4-x}(SO_4)_x$ 이중층을 심자외선 광에 노출하여 포름산 구리의 분해를 촉진하였다. 먼저 크기는 전자빔 기록(writing)에 따라 약 22 nm로 감소되었다. 상기 상호확산 과정은 패턴과 목적물을 나노스케일로 리소그래픽 전자빔 에너지를 통해 공간적으로 제어될 수 있다. 고해상도의 패턴들이 150 $\mu C/cm^2$ 근처의 전하 도스 레벨에서 생성되었는데, 많은 폴리머 레지스트들의 그것과 유사한 민감도를 나타낸다. 도 31 및 32는 약 200 $\mu C/cm2$의 도스 레벨에서의 전자빔 기록에 의해 생성된 두 패턴들이다. 도 31에서, 전자 현미경으로 측정한 바와 같이 상기 선의 간격은 500 nm이다.

<178>

실시예 7

<179> 본 실시예는 나일층 부기막을 패터닝하기 위한 일반적인 방법들을 설명한다. 레지스이트 또는 관련된 배위종들을 포함하는 단일 부기막을 적절한 기판 위에 스핀-캐스트(spin-cast), 에어 본부(misted), 또는 잉크젯 프린트된다. 상기 막은 200 ℃ 미만의 중간 정도의 온도에서 가열되어 막의 구조적 집적도를 제공한다. 그런 후, 상기 막을 패턴 또는 다른 미분적한 막 덕처들을 정의하기 위해, 포토마스크를 통해 고에너지 광에 노출되거나, 공간 광 모듈레이션을 통한 마스크리스 패턴, 성의된 레이저 빔, 또는 전자빔에 노출된다. 도 33 및 도 34는 사진 공정으로 패터닝된 막들의 두 예들을 나타낸다. 도 33은 패터닝된 $ZrO_{4-x}(SO_4)_x$ 막이다. 도 34는 패터닝된 TiO_2 막이다. 상기 TiO_2 막은 약 15 내지 50 nm 두께이었다. 여과되지 않은 중수소 램프를 이용하여 패터닝하였고, 이어서 0.1 내지 0.2 M HCl로 60초 미만 동안 스각하였다. 도 35 내지 도 37은 전자빔의 의하여 패터닝된 $HfO_{4-x}(SO_4)_x$ 막들이다. 상기 막들은 약 30 내지 60 nm 두께이었다. 이들은 200 $\mu C/cm^2$의 도스 레벨로 전자빔을 이용하여 패터닝되었고, 이어서 5 내지 12 M HCl로 1 내지 4분 동안 식각되었다.

<180> 개시된 본 발명의 원리가 적용될 수 있는 가능한 많은 구현예들의 관점에서, 예시된 구현예들은 오직 본 발명의 바람직한 실시예일 뿐이고, 본 발명의 범위를 한정하는 것으로 받아들여서는 안된다. 오히려, 본 발명의 범위는 첨부된 청구항들에 의하여 정의된다. 따라서, 우리는 이들 청구항들의 범위와 정신의 범위 내에 들어오는 모든 것을 우리의 발명으로 청구한다.

도면의 간단한 설명

<116> 도 1은 다양한 전처리들과 함께 샘플들을 $N_2(g)$을 흘리면서 10℃ $분^{-1}$의 속도로 가열하면서 HafSOx (x = 0.70)에 대한 열질량 분석(TGA: thermogravimetric analysis)(온도에 따른 상대 손실) 결과를 제공한다.

<117> 도 2는 표시된 것을 제외하고는 인용된 온도로 상기 중에서 1 시간 동안 가열한 후의 HafSOx 분말에 대한 XRD 패턴이다.

<118> 도 3은 표시된 것을 제외하고는 인용된 온도로 1 시간 동안 가열한 후의 HafSOx:32% La 분말에 대한 XRC 패턴이다.

<119> 도 4는 공기 중에서 주어진 온도로 5 분 동안 가열한 후의 HafSOx 막에 대한 XRD 패턴으로, 31.8° 와 45.6° 에서의 매우 작은 피처(feature)들은 기판에 기인한 것이다.

<120> 도 5는 언급된 온도로 상기 중에서 5 분 동안 가열한 후의 HafSOx:24% La 박막에 대한 XRD 패턴이다.

<121> 도 6은 HafSOx 막에 대한 유전 항복 특성을 도시한다.

<122> 도 7은 이산화실리콘 기판 위의 탄탈룸(Ta) 금속 위에 증착된 HafSOx의 일 구현예를 나타낸 SEM이다.

<123> 도 8은 Ta위에 증착된 HafSOx:24% La에 대한 SEM이다.

<124> 도 9는 이중층이 17.6 nm의 두께를 갖는 14 개의 교호층들(7개의 이중층들)을 포함하는 HafSOx/ZircSOx 다층 박막에 대한 XRR 패턴이다.

<125> 도 10은 포지티브 또는 네거티브 포토레지스트 절차들을 나타낸 개념도이다.

<126> 도 11은 이중층 시스템을 이용하는 포지티브 레지스트를 도시한 개념도로서 도시된 구현예가 하프늄 산화물 설페이트 (HafSOx) 막 위에 증착된 Cu-포함된 지르코늄 산화물 설페이트 (Cu:ZircSOx) 막을 포함한다

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<127> 도 12는 기판 위에 패터닝된 산화물을 생성하기 위한 이중층 공정을 나타낸 개념도이다.

<128> 도 13은 기판 위에 패터닝된 산화물을 생성하기 위한 이중층 공정을 나타낸 개념도이다.

<129> 도 14는 기판 위에 패터닝된 막을 생성하기 위한 단일층 공정을 나타낸 개념도이다.

<130> 도 15는 열적으로 전처리된, 단일층 막에 대한 식각 시간에 따른 두께의 그래프이다.

<131> 도 16은 전자빔에 의하여 패터닝된 막이다.

<132> 도 17은 유기 고분자에 비하여 훨씬 더 높은 기계적 강도, 화학적 안정성 및 고유의 전기 및 광학적 특성을 갖는 여기에 거시된 화합물들의 반-고체 형태로 사용되기 위한 핫 엠보싱 리소그래피를 도시한 개념도이다.

<133> 도 18은 전자 워크성과 같은 응용 분야에서 표준화 측정으로 사용되기 위한 물리적 자의 한 제조 방법을 도시한 개념도이다.

<134> 도 19는 실리카 위에 증착된, 어닐링되지 않은 HafSOx 막의 AFM 이미지이다.

<135> 도 20은 HafSOx의 이온 어닐과 850 ℃에서의 열처리 후의 HfO_2의 TEM 이미지이다.

<136> 도 21은 700 ℃ 이상으로 가열된 후 HafSOx 열분해로부터 형성되고 실리카 위에 증착된 HfO_2 막의 AFM 이미지이다.

<137> 도 22는 0.1 M NaOH로 처리되고, 450 ℃로 10 분 동안 가열된, 실리카 위에 증착된 HafSOx 막의 AFM 이미지이다.

<138> 도 23은 0.1 M NaOH로 처리되고, 850 ℃로 10 분 동안 가열된, 실리카 위에 증착된 HfO_2 막의 AFM 이미지이다.

<139> 도 24는 처리되지 않은 하프니아 막의 XRD 그래프를 제공한다.

<140> 도 25는 처리된 하프니아 막의 XRD 그래프를 제공한다.

<141> 도 26은 처리되지 않은 지르코니아 막의 XRD 그래프를 제공한다.

<142> 도 27은 처리된 지르코니아 막의 XRD 그래프를 제공한다.

<143> 도 28은 실리카 위에 증착된 인듐 주석 산화물 반도체 막의 SEM 이미지이다.

<144> 도 29는 복수 확산-반응과 잉크젯 프린팅을 통해 생성된 선형 패턴이다.

<145> 도 30은 이중층 막을 UV 광에 노출시킴으로써 생성된 패턴이다.

<146> 도 31은 전자빔 기록에 의하여 패터닝된 막이다.

<147> 도 32는 전자빔 기록에 의하여 패터닝된 막이다.

<148> 도 33은 사진적으로 패터닝된 막이다.

<149> 도 34는 사진적으로 패터닝된 막이다.

<150> 도 35는 전자빔에 의하여 패터닝된 $HfO_{2-x}(SO_4)_x$ 막이다.

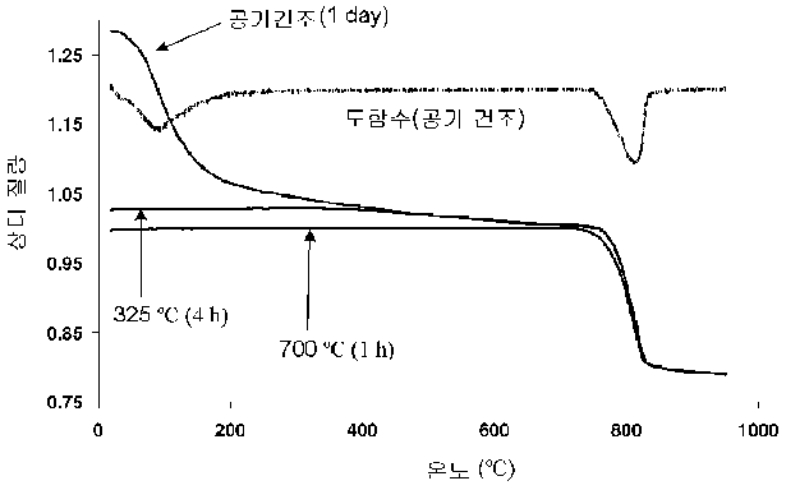
<151> 도 36은 전자빔에 의하여 패터닝된 $HfO_{2-x}(SO_4)_x$ 막이다.

<152> 도 37은 전자빔에 의하여 패터닝된 $HfO_{2-x}(SO_4)_x$ 막이다.

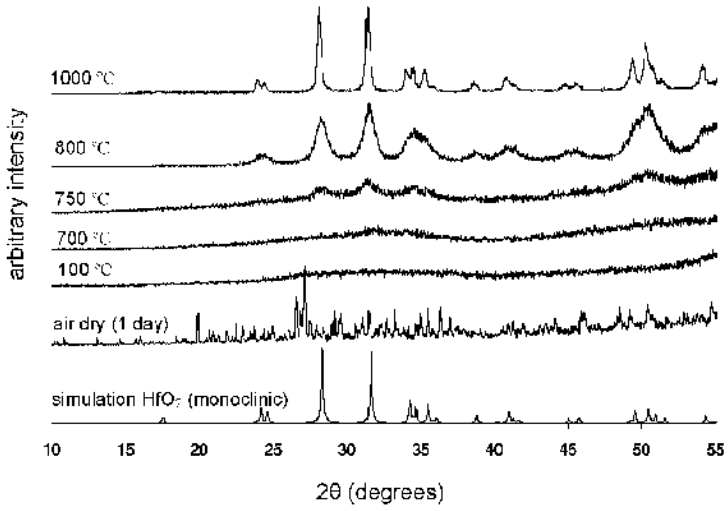
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도면

도면1

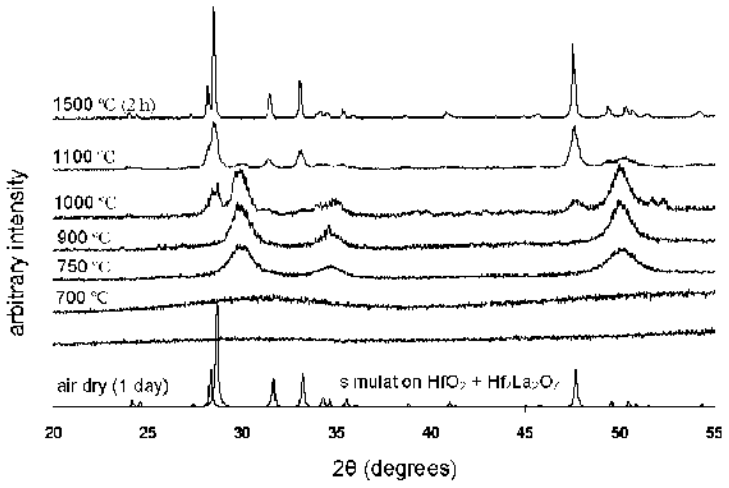


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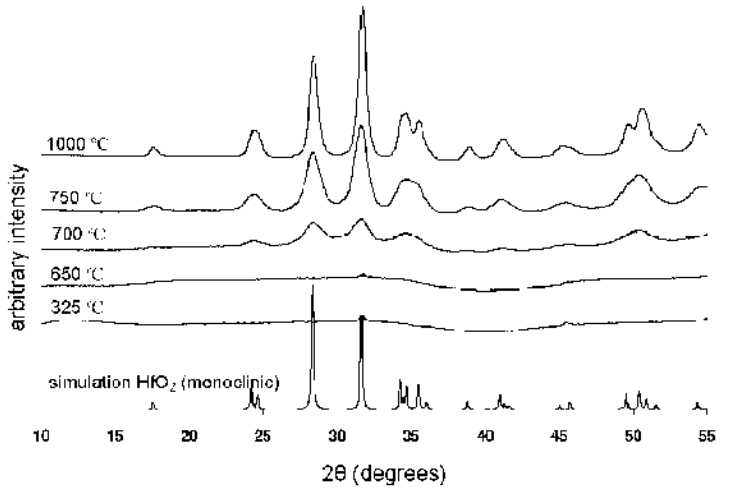


Lam Research Ex. 1004 - Page 470 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

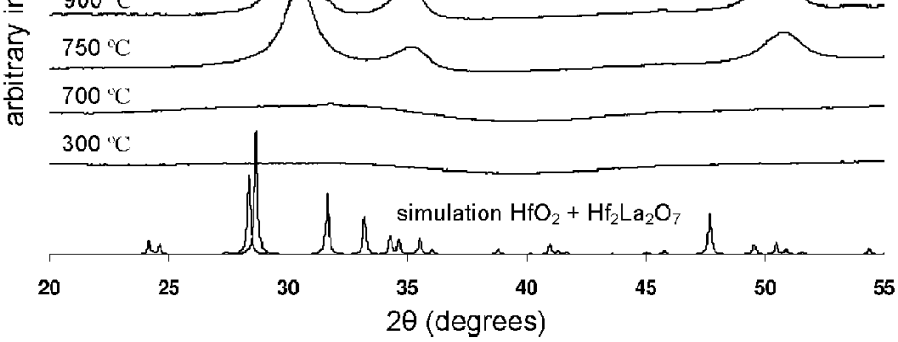
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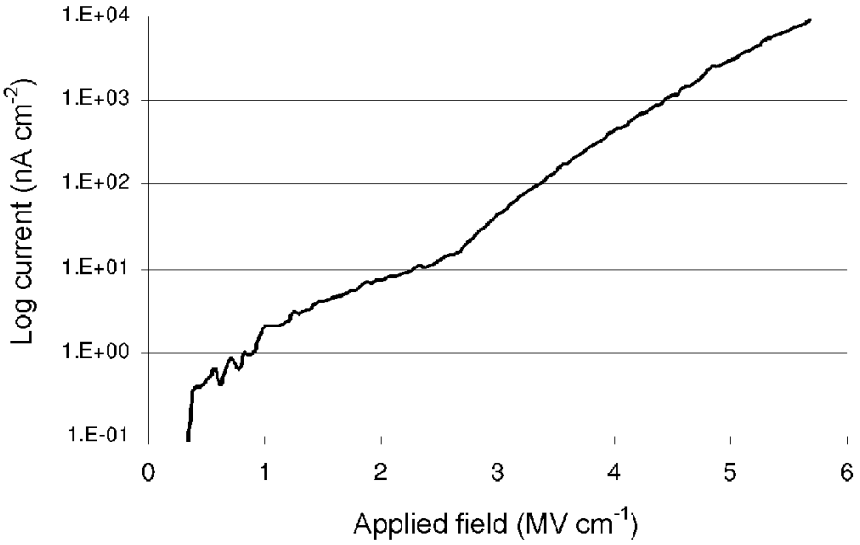


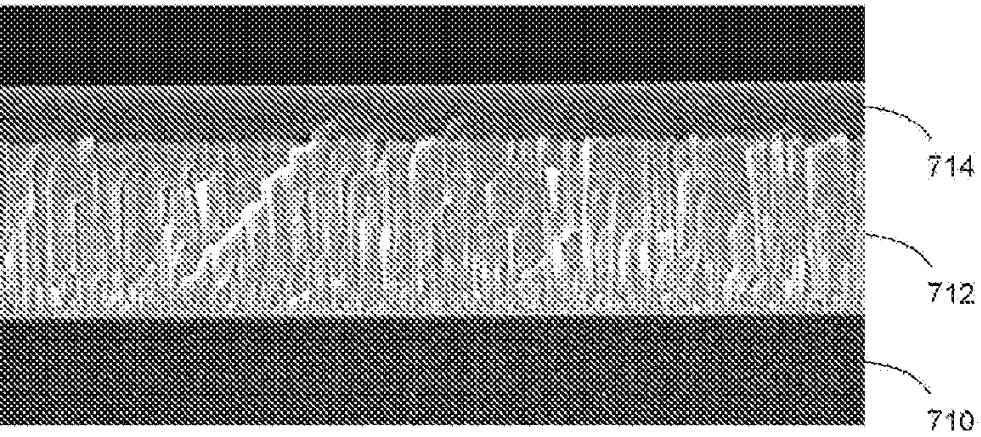
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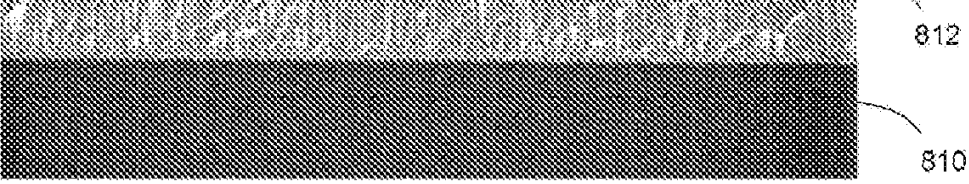


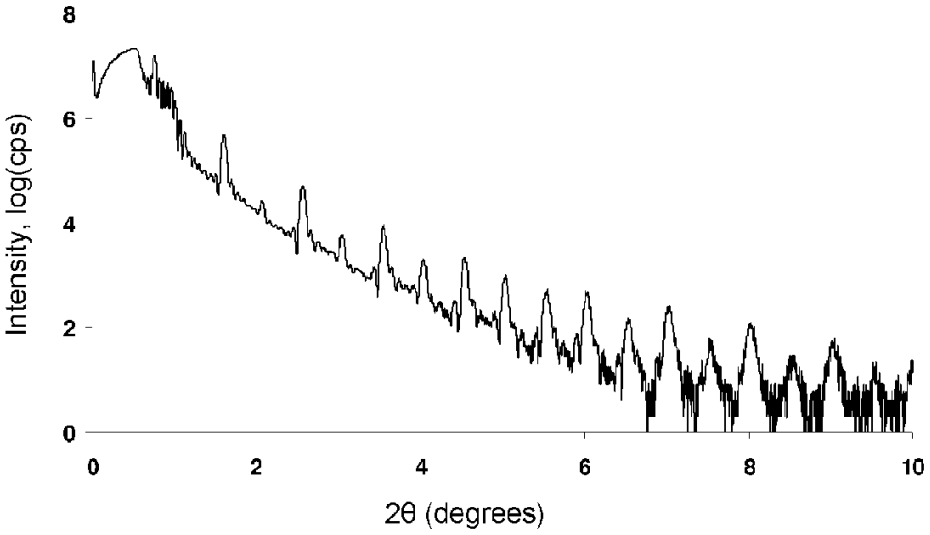
Lam Research Ex. 1004 - Page 471 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564


arbitrary
750 ℃
700 ℃
300 ℃
simulation $HfO_2 + Hf_2La_2O_7$
20
25
30
35
40
45
50
55
2θ (degrees)

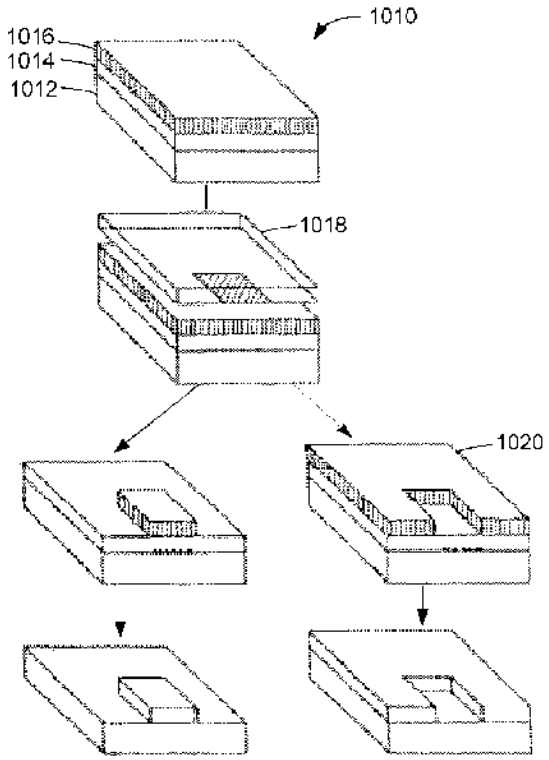

1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
Log current (nA cm^{-2})
0
1
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3
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5
6
Applied field (MV cm^{-1})


714
712
710

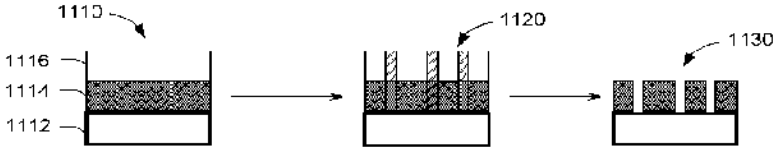

812
810


8
6
4
2
0
Intensity, log(cps)
0
2
4
6
8
10
2θ (degrees)

도면10

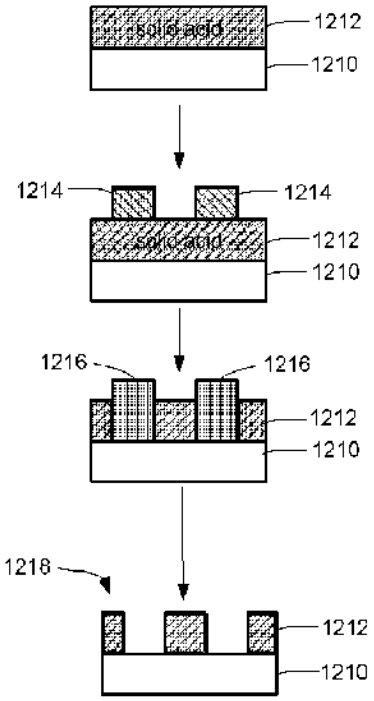


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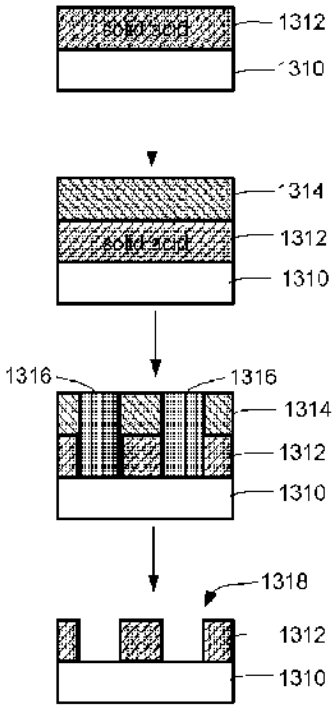


Lam Research Ex. 1004 - Page 474 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

도면12

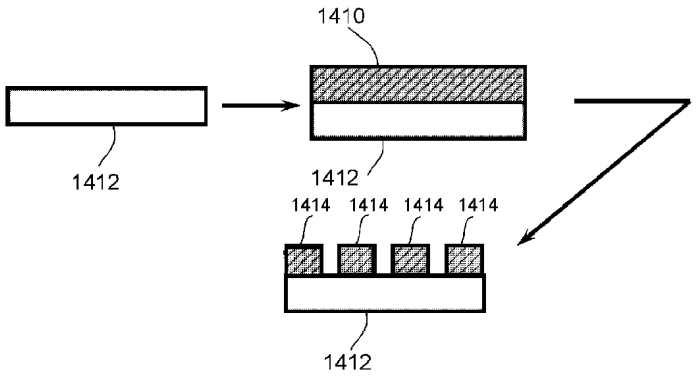


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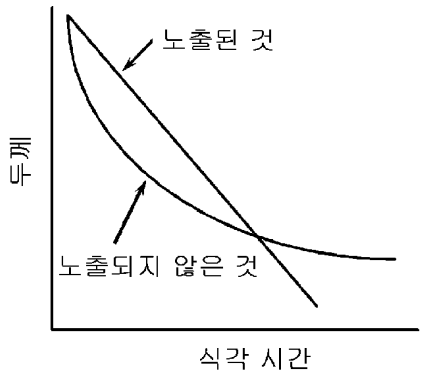


Lam Research Ex. 1004 - Page 475 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

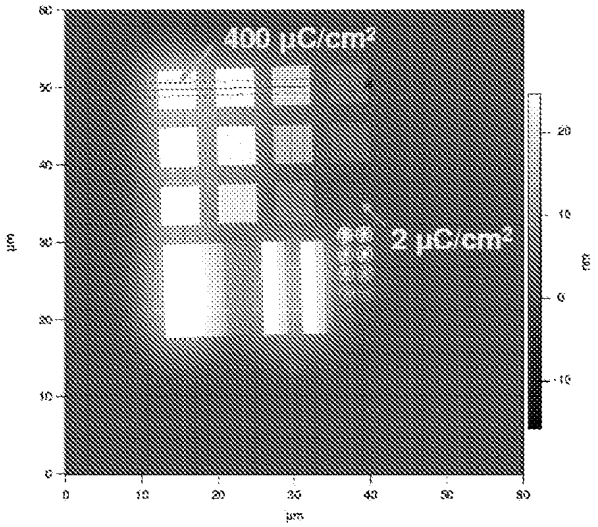
도면14



도면15

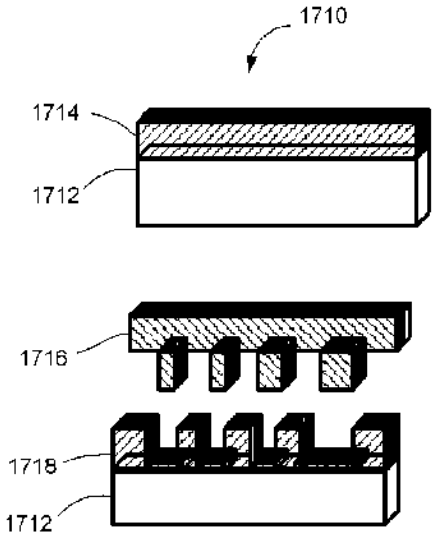


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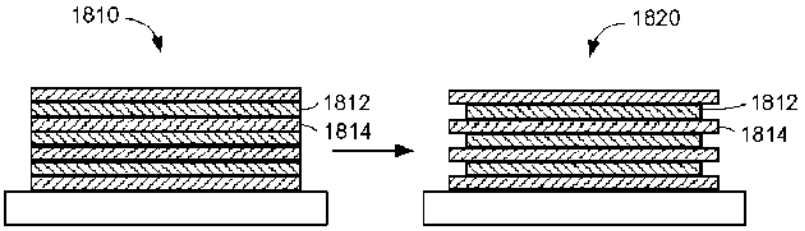


Lam Research Ex. 1004 - Page 476 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

도면17

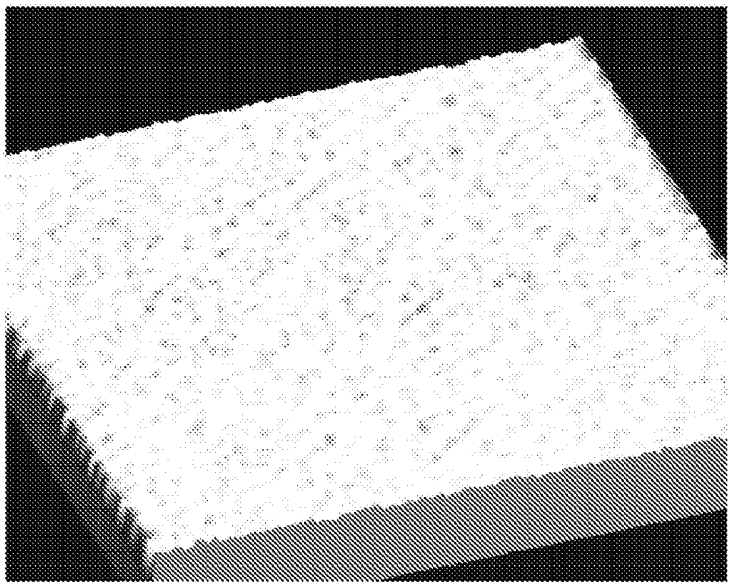


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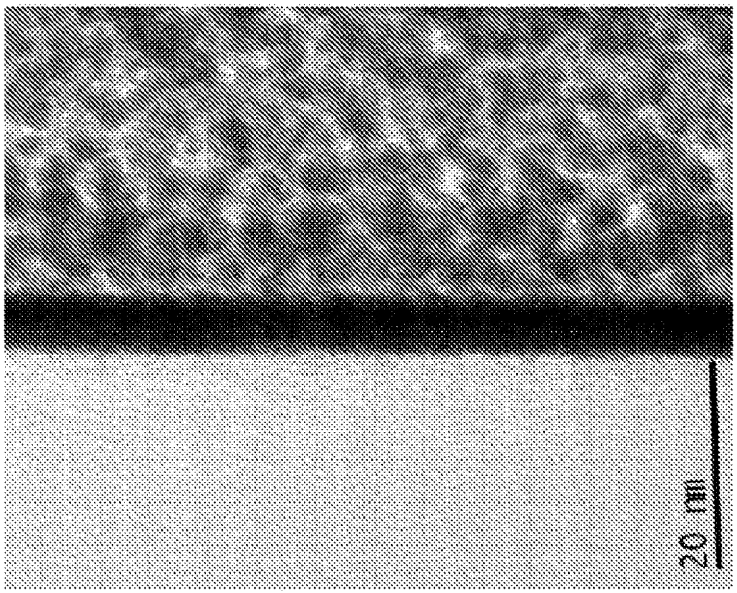


Lam Research Ex. 1004 - Page 477 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

도면19

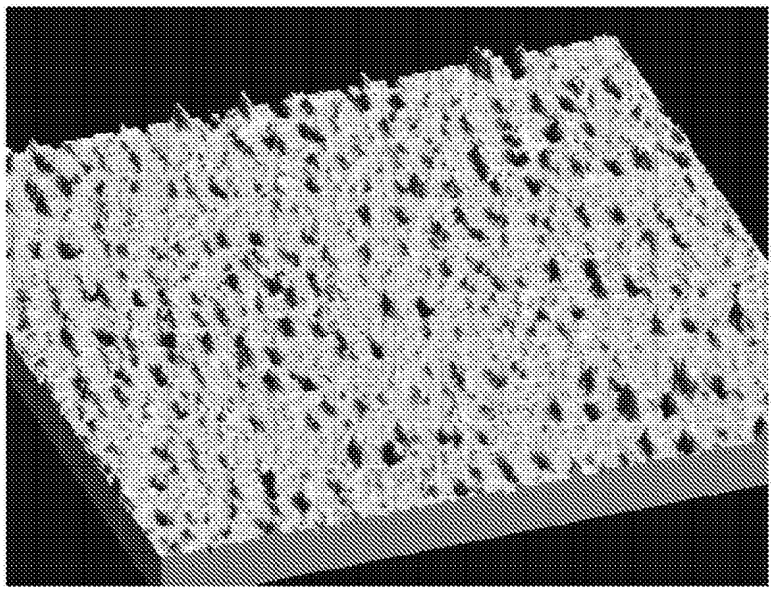


도면20

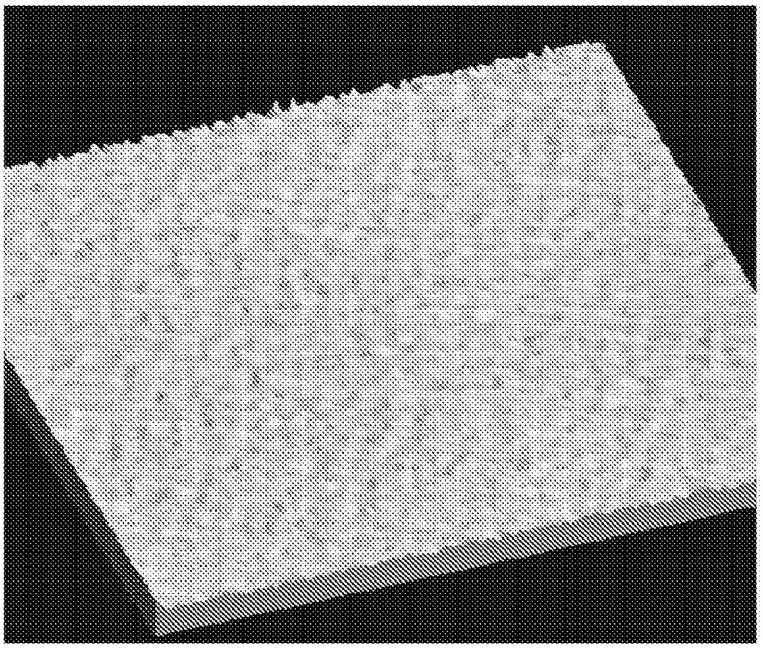


Lam Research Ex. 1004 - Page 478 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

도면21

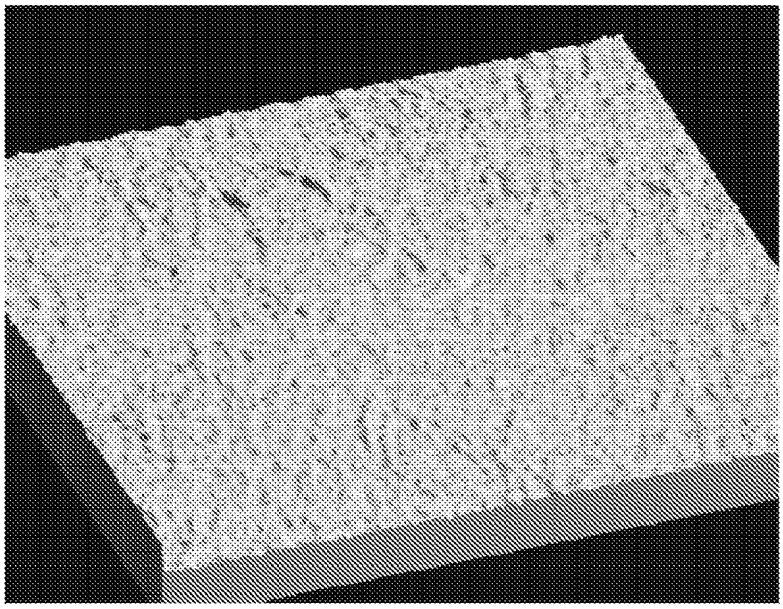


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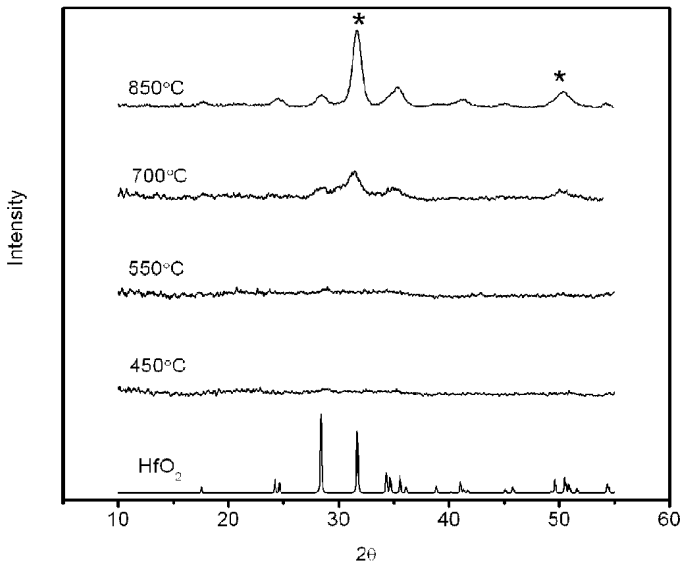


Lam Research Ex. 1004 - Page 479 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

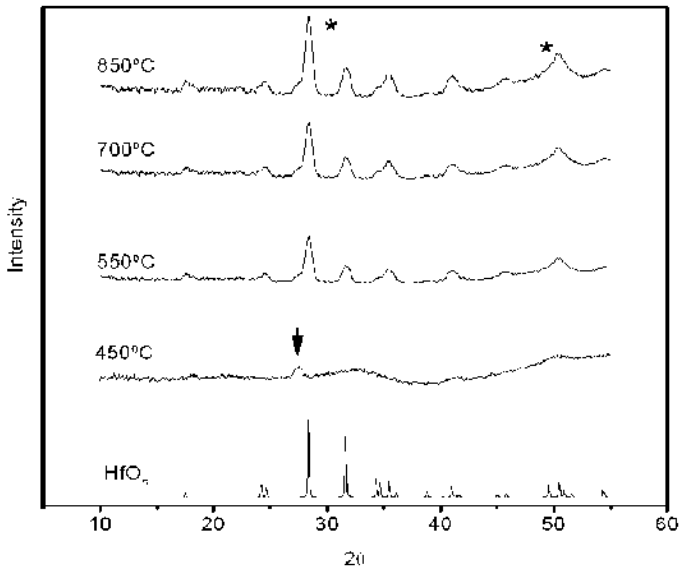
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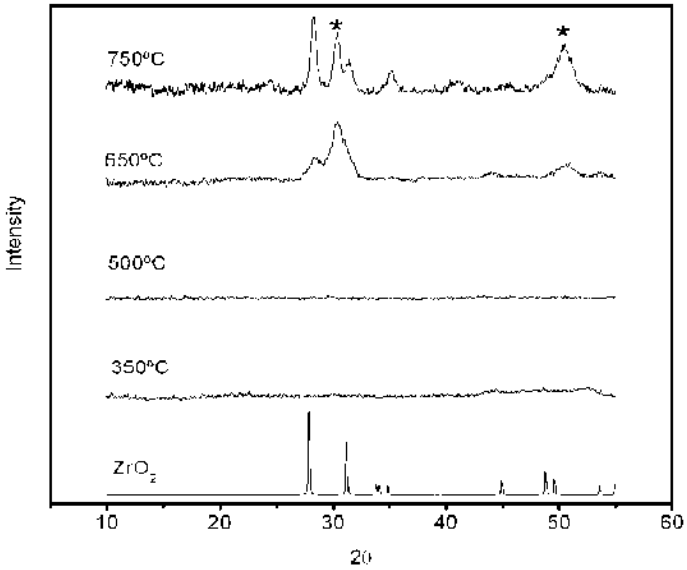
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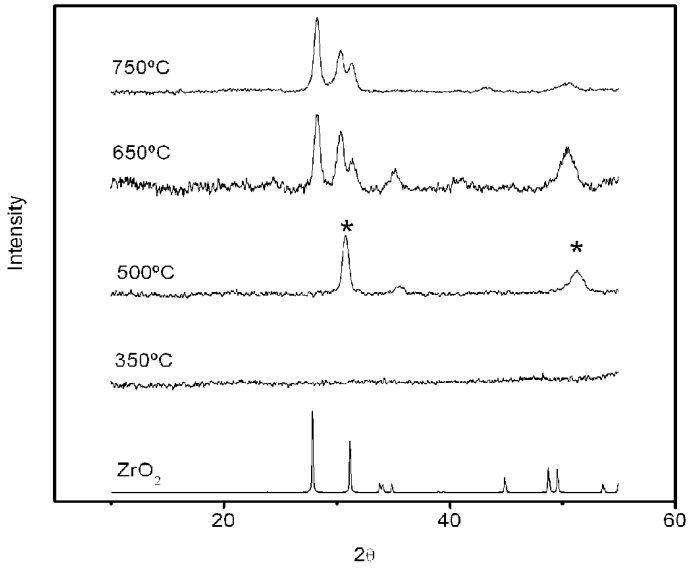
도면25


850°C
700°C
550°C
450°C
HfO2
Intensity
10
20
30
40
50
60
2θ

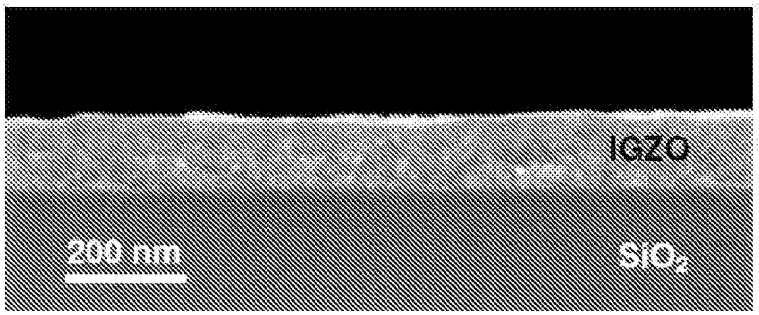
도면26


750°C
650°C
500°C
350°C
ZrO2
Intensity
10
20
30
40
50
60
2θ

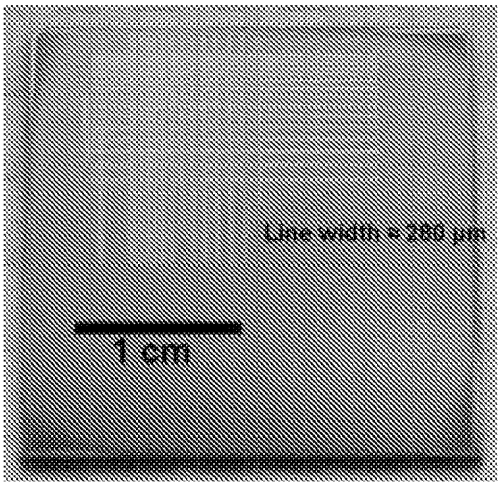
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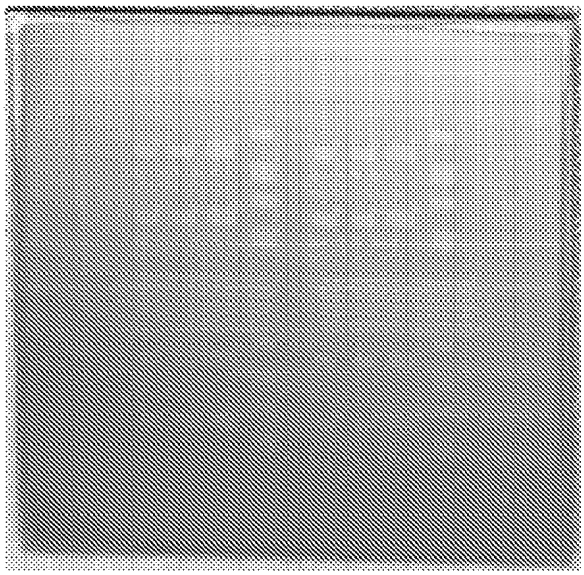
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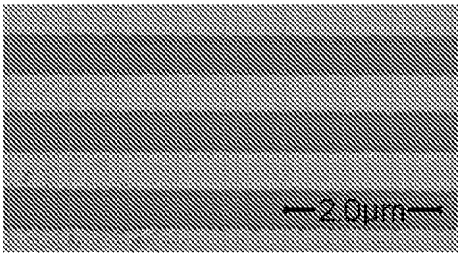
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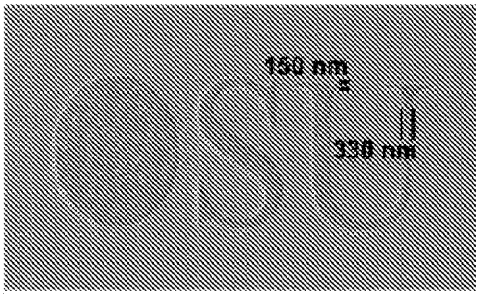
도면30



도면31

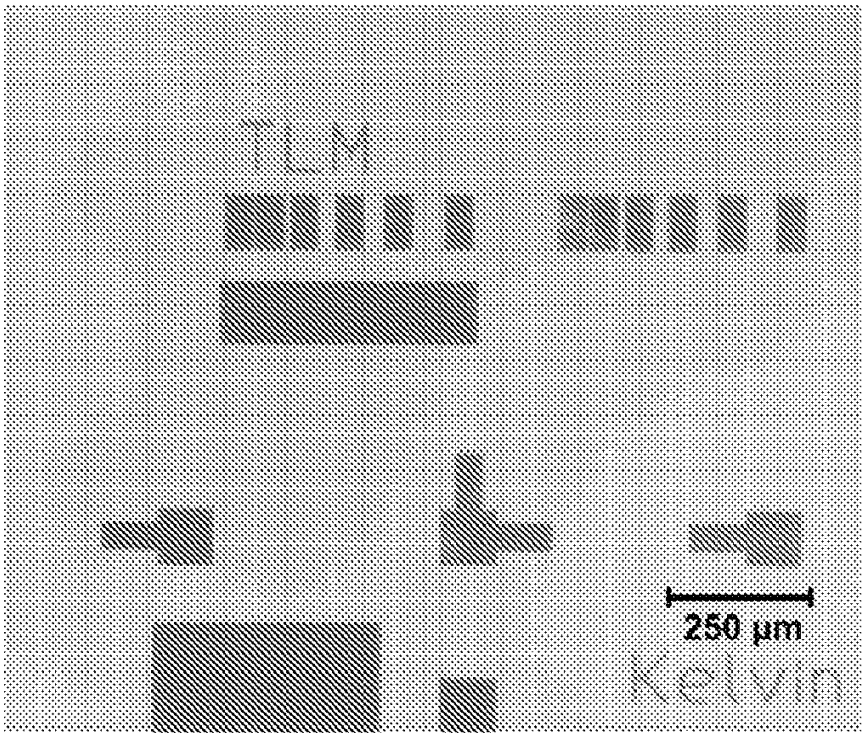


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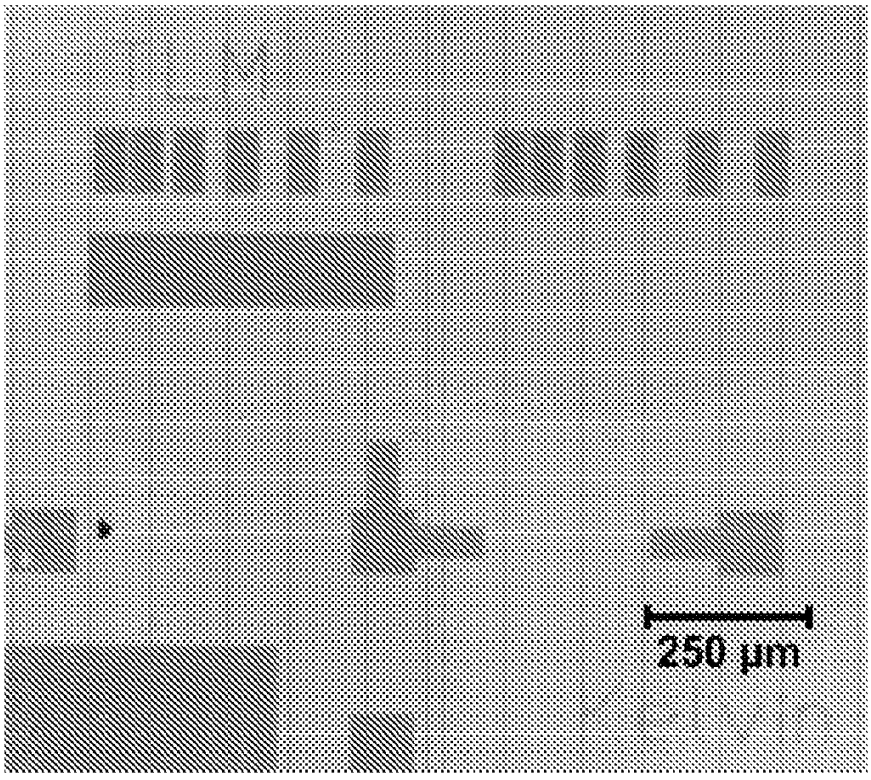


Lam Research Ex. 1004 - Page 483 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

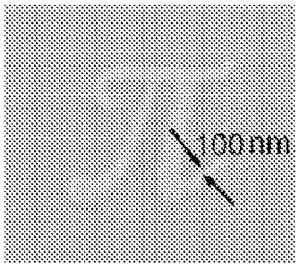
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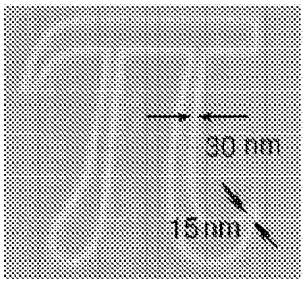
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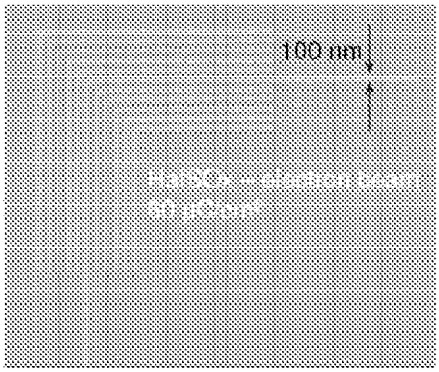
도면35



도면36



도면37



Lam Research Ex. 1004 - Page 485 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1781
Examiner Name	Nicole T. Gugliotta
Attorney Docket Number	5063.02-US-02

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	2	2006-284947	JP	A	2006-10-19	Nakamura	Abstract only	☐

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Application Number	12850867 12850867 - GAU: 1722
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1781
Examiner Name	Nicole T. Gugliotta
Attorney Docket Number	5063.02-US-02

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	Office Action from copending Japanese Application No. 2011-120402 dated June 11, 2013 ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./	☐

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Examiner Signature	/Chanceity Robinson/	Date Considered	09/08/2013

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	1	("20050242330").PN.	US-PGPUB; USPAT	OR	OFF	2013/09/09 11:09
L2	0	("102008009009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:14
L3	0	("2008009009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:15
L4	6	("2008009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:15
L5	2	("20110045406").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:18
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L8	1	5 and 7	US-PGPUB; USPAT	OR	ON	2013/09/09 11:51
L9	1	5 and (suboxide)	US-PGPUB; USPAT	OR	ON	2013/09/09 11:52
L10	17460	(430/270.1,302,322,325,325,946).CCLS.	US-PGPUB; USPAT	OR	OFF	2013/09/09 12:18
L11	10	10 and (ligand with peroxide)	US-PGPUB; USPAT	OR	ON	2013/09/09 12:19
S1	4	(water and suboxide and polyatomic) with ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2013/09/08 19:11

Lam Research Ex. 1002, Page 488 of 1488 TEL Research Corp. v. Lam Research Corp. IPR2024-00036 U.S. Patent No. 9,823,564

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Lam Research Ex. 1001 - Page 1481 - TEL Research Corp. v. Lam Research Corp., IPR2024-00036 - U.S. Patent No. 9,823,564

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CONFIRMATION NO. 1662

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
12/850,867	08/05/2010	430	1722	5063.02US02

APPLICANTS

Jason K. Stowers, Corvallis, OR;
Alan J. Telecky, Corvallis, OR;
Douglas A. Keszler, Corvallis, OR;
Andrew Grenville, Eugene, OR;

**** CONTINUING DATA ***************************

This appln claims benefit of 61/350,103 06/01/2010

**** FOREIGN APPLICATIONS ***************************

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED **** ** SMALL ENTITY **
09/07/2010

Foreign Priority claimed ☐ Yes ☑ No 35 USC 119(a-d) conditions met ☐ Yes ☐ No Verified and Acknowledged /CHANCEITY N ROBINSON/ Examiner's Signature	☐ Met after Allowance CR Initials	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
		OR	8	38	5

ADDRESS

DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432
UNITED STATES

TITLE

PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

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Approved for use through 07/31/2012. OMB 0651-0031
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Art Unit	1781
Examiner Name	Gugliotta, Nicole T
Attorney Docket Number	5063.02US02

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Receipt date: 10/23/2012	Application Number	12850867	12850867 - GAU: 1722
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	Attorney Docket Number	5063.02US02	

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CLAIMS

[Claim(s)]
[Claim 1]
A photosensitive resin composition for light-shielding films containing binder resin, a photo-oxide generating agent which absorbs light and generates acid, a cross linking agent cross-bridged by operation of the aforementioned photo-oxide generating agent, and metal particles and/or metallic-compounds particles.
[Claim 2]
The photosensitive resin composition for light-shielding films according to claim 1 which includes paints further.
[Claim 3]
The photosensitive resin composition for light-shielding films according to claim 2 whose aforementioned paints are carbon black or black lead.
[Claim 4]
A photosensitive resin composition for light-shielding films of a description in any 1 item of Claims 1-3 whose optical density at the time of forming a light-shielding film of 1.0 micrometer of thickness is 4.0 or more.
[Claim 5]
A photosensitive resin composition for light-shielding films of a description in any 1 item of Claims 1-4 used for formation of a light-shielding film which constitutes a display device.
[Claim 6]
A transfer material comprising:
On temporary support, it is binder resin of at least one layer.
A photo-oxide generating agent which absorbs light and generates acid.
A cross linking agent cross-bridged by operation of the aforementioned photo-oxide generating agent.
A photosensitive resin layer containing metal particles and/or metallic-compounds particles.

[Claim 7]
The transfer material according to claim 6 used for formation of a light-shielding film.
[Claim 8]

The transfer material according to claim 6 or 7 used for formation of a light-shielding film which constitutes a display device.
[Claim 9]
A process of making any 1 item of Claims 1-5 applying and drying a photosensitive resin composition for light-shielding films of a description, and forming a photosensitive resin layer on a substrate,
A process of exposing the formed aforementioned photosensitive resin layer to pattern form,
A process of heating the formed aforementioned photosensitive resin layer,
A process of developing the aforementioned photosensitive resin layer after the aforementioned exposure at least, and removing an unexposed part,
****** -- a manufacturing method of a light-shielding film characterized by things.
[Claim 10]
A manufacturing method of the light-shielding film according to claim 9 which performs the aforementioned application using a coater which has a slit shaped nozzle.
[Claim 11]
A process of transferring a photosensitive resin layer of at least one layer on temporary support to a substrate using a transfer material of a description in any 1 item of Claims 6-8,
A process of exposing the transferred aforementioned photosensitive resin layer to pattern form,
A process of heating the transferred aforementioned photosensitive resin layer,
A process of developing the aforementioned photosensitive resin layer after the aforementioned exposure at least, and removing an unexposed part,
****** -- a manufacturing method of a light-shielding film characterized by things.
[Claim 12]
It is a manufacturing method of a transfer material of a description in any 1 item of Claims 6-8,
A manufacturing method of a transfer material painting a photosensitive resin layer on temporary support by application using a coater which has a slit shaped nozzle.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[Field of the Invention]

[0001]
The present invention relates to a manufacturing method of the photosensitive resin composition for light-shielding films preferable for the film formation of a light sheilding, and the light-shielding film using this, a transfer material, and a manufacturing method for the same.
[Background of the Invention]
[0002]
It combines as recent years, for example, a liquid crystal display element, and a solid state image pickup device, and the color filter aiming at obtaining a color picture is capturing the spotlight. This color filter is 2 or more type of pixels (it comprises a color picture layer with which it comes to combine R (red), G (green), B (blue), light-shielding films (black matrix etc.), a transparent area, a transparent pixel, etc.).
[0003]
As a manufacturing method of a color filter, conventionally, The photopolymer solution containing colorant is applied to the object face in which a color filter is installed, The method of performing by exposing that application membrane to pattern form, forming a picture element layer, applying the photopolymer solution containing colorant of other colors subsequently to that picture element layer top, exposing this application membrane to pattern form, and repeating the process of forming a first picture element layer and the picture element layer from which coloring differs is generally used.
[0004]
On the other hand, applied the photopolymer solution containing colorant on the substrate sheet (temporary support) prepared independently, and formed the coloring photosensitive resin layer and it was constituted, Prepare the photosensitive transfer sheet (transfer material) of two or more sheets in which colors differ, put the photosensitive transfer sheet of one sheet on a color filter installation object surface first, and a coloring photosensitive resin layer is transferred, As this is exposed to pattern form, a picture element layer is formed and the picture element layer is subsequently covered, further, A coloring photosensitive resin layer is transferred for the photosensitive transfer sheet of other colors in piles, the method of performing by exposing this to pattern form and repeating the process of forming a first picture element layer and the picture element layer from which coloring differs is proposed, and use of this method is increasing in recent years. When based on this method, the picture element layer which comprised a coloring photosensitive resin layer which has high homogeneity and highly precise thickness uniformity can be formed.
[0005]
By any above-mentioned method, for production of the colored pixel which constitutes a color filter. Using the photo mask clipped by the pattern form for pixel formation, the opening part is passed, a photosensitive resin layer is exposed, the exposed part is stiffened, and the way carry out the development of the unexposed part (non-hard spot), and a developing solution subsequently removes it is used.
[0006]
However, in the case of the conventional transfer material, a photosensitive resin layer is constituted by radical polymerization system including a photopolymerization initiator, a photopolymerization nature monomer, an acrylic polymerization binder, photopolymerization inhibitor, paints, etc.
When the surface which has such a photosensitive resin layer is exposed, conversion changes with attenuation of the light accompanying the depth in the depth direction (thickness direction)

of a photosensitive resin layer, The substrate side of specifically near the interface of a substrate and a photosensitive resin layer, such as glass which is distant from a layer surface, in order for conversion to be deteriorated remarkably and to hardly carry out polymerization curing, when a development was carried out, or side etch went into a thin line image easily and a small-gage wire was not made, there was a problem that a development latitude was narrow.

Although the use of light-shielding films (black matrix etc.) requires high shielding performance especially, attenuation of the light accompanying thickness becomes largely, so that black density becomes high, and generating of side etch and deterioration of a development latitude become more remarkable.

[0007]

The photosensitive resin composition containing a binder, a photo-oxide generating agent, the cross linking agents (melamine system resin etc.) cross-bridged by operation of a photo-oxide generating agent, etc. is proposed to this problem (for example, see Patent Document 1). This generates and carries out polymerization curing of the bridging body from an acid reactivity molecule (cross linking agent) by the catalysis of the acid ($I->I^- +H^+$) generated from a photo-oxide generating agent in response to light (PAG;Photo Acid Generator).

[0008]

In this case, when the black density of a photosensitive resin layer is high. Since the yield of the acid by which it is generated after all at the time of exposure decreases near an interface with the substrate which there were and is distant from a layer surface near a layer surface, [many] Polymerization curing of a photosensitive resin layer can be performed good until it promotes diffusion of acid, and is urged to crosslinking reaction toward a thickness direction from a layer surface and it results near the interface with a substrate by furthermore heat-treating.

[Patent document 1] JP,2002-351075,A

[Description of the Invention]

[Problem to be solved by the invention]

[0009]

However, in PAG using the catalysis of acid, In order to diffuse not only in the thickness direction of a layer but in all the directions (transverse direction to the longitudinal direction which is a thickness direction, etc.), even if the film of higher hardness is obtained at high concentration, it is difficult for the acid (H^+) diffused by heat-treatment (heating diffusion) to form a small-gage wire. It is insufficient also in respect of a development latitude. As a result, only the image which faded is acquired. When it is going to constitute on the film of high black density especially, a certain amount of thickness is required for a photosensitive resin layer, if heating after exposure not only taking a long time for obtaining sufficient polymerization curing nature but cooking time becomes long, in a layer, acid will diffuse widely and the degree of a Japanese quince will also get worse.

[0010]

The present invention is made in view of the above, and high black density is obtained with a thin film, and excel in a light sheilding, and. The photosensitive resin composition for light-shielding films which is excellent in the heat cure nature in a short time, and can form the image of high resolution, A transfer material which enables formation of the film whose black density was high at the thin film, and which was excellent in a light sheilding and the heat cure nature in a short time, and a manufacturing method for the same, And let it be problem to attain this purpose with a thin film for the purpose of providing the manufacturing method of the light-

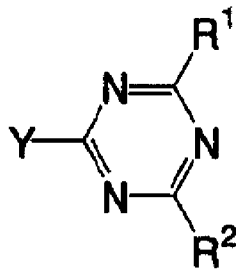
shielding film which black density can form in high resolution the light-shielding film which was highly excellent in shielding performance, and can perform hardening by heating diffusion in shorter time.
[Means for solving problem]
[0011]
When forming a high-concentration black pattern with high resolution using the aforementioned PAG, the present invention acquires the knowledge that metal system particles are effective, for inhibition of the diffusion to the direction of [other than the thickness direction of the acid generated from high-concentration-izing and a photo-oxide generating agent], and is attained based on this knowledge.
The concrete means for attaining the aforementioned problem is as follows.
[0012]
It is a photosensitive resin composition for light-shielding films containing <1> binder resin, the photo-oxide generating agent which absorbs light and generates acid, the cross linking agent cross-bridged by operation of the aforementioned photo-oxide generating agent, and metal particles and/or metallic-compounds particles.
It is a photosensitive resin composition for light-shielding films of the description to the above <1> which includes <2> paints further.
[0013]
The <3> aforementioned paints are the photosensitive resin compositions for light-shielding films of the description to the above <2> which is carbon black or black lead.
The optical density at the time of forming the light-shielding film of 1.0 micrometer of <4> thickness is a photosensitive resin composition for light-shielding films of any one description of aforementioned <1>- <3> which is 4.0 or more.
It is a photosensitive resin composition for light-shielding films of any one description of aforementioned <1>- <4> used for formation of the light-shielding film which constitutes <5> display devices.
[0014]
It is a transfer material having a photosensitive resin layer which contains binder resin of at least one layer, the photo-oxide generating agent which absorbs light and generates acid, the cross linking agent cross-bridged by operation of the aforementioned photo-oxide generating agent, and metal particles and/or metallic-compounds particles on <6> temporary support.
It is a transfer material of the description to the above <6> used for formation of <7> light-shielding films.
It is a transfer material of the description to the above <6> or <7> used for formation of the light-shielding film which constitutes <8> display devices.
[0015]
The process of applying the photosensitive resin composition for light-shielding films of any one description of aforementioned <1>- <5>, and making it drying and forming a photosensitive resin layer on <9> boards, It is a manufacturing method of a light-shielding film including the process of exposing the formed aforementioned photosensitive resin layer to pattern form, the process of heating the formed aforementioned photosensitive resin layer, and the process of developing the aforementioned photosensitive resin layer after the aforementioned exposure at least, and removing an unexposed part.
The <10> aforementioned application is a manufacturing method of the light-shielding film of the description to the above <9> performed using the coater which has a slit shaped nozzle.

[0016]
The process of transferring the photosensitive resin layer of at least one layer on temporary support to a substrate using the transfer material of any one description of <11> aforementioned <6>- <8>, It is a manufacturing method of a light-shielding film including the process of exposing the transferred aforementioned photosensitive resin layer to pattern form, the process of heating the transferred aforementioned photosensitive resin layer, and the process of developing the aforementioned photosensitive resin layer after the aforementioned exposure at least, and removing an unexposed part.
It is a manufacturing method of the transfer material of any one description of <12> aforementioned <6>- <8>, and is a manufacturing method of the transfer material painting a photosensitive resin layer by application using the coater which has a slit shaped nozzle on temporary support.
[Effect of the Invention]
[0017]
According to the present invention, high black density is obtained with a thin film, and excel in a light sheilding, and. The photosensitive resin composition for light-shielding films which is excellent in the heat cure nature in a short time, and can form the image of high resolution, A transfer material which enables formation of the film whose black density was high at the thin film, and which was excellent in a light sheilding and the heat cure nature in a short time, and a manufacturing method for the same, And black density can form in high resolution the light-shielding film which was highly excellent in shielding performance with a thin film, and the manufacturing method of the light-shielding film which can perform hardening by heating diffusion in shorter time can be provided.
[Best Mode of Carrying Out the Invention]
[0018]
Hereafter, it describes in detail about a manufacturing method of the photosensitive resin composition for light-shielding films of the present invention, and a light-shielding film, a transfer material, and a manufacturing method for the same.
[0019]
<The photosensitive resin composition for light-shielding films>
The photosensitive resin composition for light-shielding films of the present invention can be constituted using the component of others, such as colorant and a surfactant, if needed, including binder resin, a photo-oxide generating agent, a cross linking agent, and metal particles and/or metallic-compounds particles at least.
[0020]
In the photosensitive resin composition for light-shielding films of the present invention, Make crosslinking reaction cause between the below-mentioned binder resin and a cross linking agent (for example, methylol-ized melamine resin of acid cross-linking) by the catalysis of the acid (H^+) generated from a photo-oxide generating agent in response to light, and. By furthermore adding heat-treatment, by promoting diffusion of acid, it is urged to crosslinking reaction toward the layer depth part near a substrate interface from the surface of a layer, and the photosensitive resin layer from the surface to the layer depth part of a thickness direction carries out polymerization curing sufficiently (PAG). Therefore, even if black density is high concentration, crosslinking reaction can be sufficiently carried out to a substrate interface, and the tolerance of development is wide, and by one side, mixing of a component, application, and the crosslinking reaction in a drying stage are suppressed, and can take sufficient largely the soluble contrast over

the developing solution of an exposure part and an unexposed part. Therefore, high-concentration and high definition light-shielding films (black matrix etc.) can be obtained with a thin film.
The photosensitive resin composition for light-shielding films of the present invention, Since high concentration is obtained with a thin film, including metal particles and metallic-compounds particles as a black agent so that it may mention later, when based on the aforementioned PAG, since diffusion of acid takes place in a film, it can perform hardening by heating diffusion in a short time, and ****** of a pattern does not produce it easily, either. Therefore, it has high concentration with a thin film, and the light-shielding films (black matrix etc.) of high resolution are obtained.
[0021]
- Binder resin -
The photosensitive resin composition for light-shielding films of the present invention contains at least 1 type of binder resin. This binder resin builds and stiffens a below-mentioned cross linking agent and bridging body (polymer) by pattern exposure by the catalysis of the acid generated from the below-mentioned photo-oxide generating agent.
[0022]
As binder resin, it can choose suitably from publicly known binder resin, such as acrylic (meta) resin, polyester resin, vinyl system resin, novolak resin (phenol novolak resin, cresol novolak resin, etc.), and polyhydroxy styrene, for example.
[0023]
The vinyl system copolymer especially obtained by copolymerization of an acrylic (meta) monomer in the present invention is preferable, and methacrylic acid alkyl ester, acrylic acid alkyl ester, or the copolymer that contains a carboxyl group containing monomer as a constitutional unit is more preferable. acrylic (meta-) is preferable at the point which gives adaptability -- weak alkali development -- it is preferable to contain a carboxyl group in respect of proper grant.
An acrylic (meta) shows that an acrylic or methacrylic both can be taken. It is the same as that of the following.
[0024]
Also in the above, the copolymer containing especially at least one of methyl methacrylate and the benzyl methacrylate is preferable. The copolymer containing the copolymer containing methyl methacrylate, the copolymer containing benzyl methacrylate, methyl methacrylate, and benzyl methacrylate are mentioned to the copolymer containing at least one of methyl methacrylate and the benzyl methacrylate.
[0025]
In the copolymer containing the aforementioned methyl methacrylate, methacrylic acid / methyl methacrylate copolymer (copolymerization ratio: -- 14-17.6mol %/-- 82.4-86 mol %) The weight average molecular weight 20,000-140,000, methacrylic acid / methyl methacrylate / ethyl acrylate copolymer (copolymerization ratio: 5-10 mol % / 70-60 mol % / 25-30 mol %, weight average molecular weight 20,000-140,000), etc. are mentioned.
[0026]
In the copolymer containing the aforementioned benzyl methacrylate, methacrylic acid / benzyl methacrylate copolymer (copolymerization ratio: -- 25-37mol %/-- 75-63 mol %) The weight average molecular weight 20,000-150,000, methacrylic acid / benzyl methacrylate / styrene copolymer (copolymerization ratio: 20 mol %/17.8 mol % [62.2 mol %] /, weight average

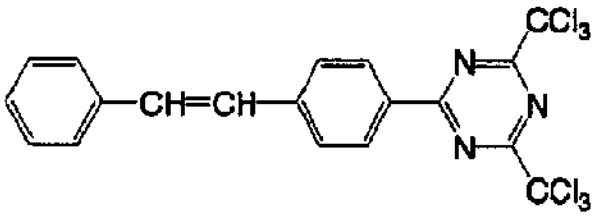
molecular weight 20,000-140,000), etc. are mentioned.
[0027]
In the copolymer containing the aforementioned methyl methacrylate and benzyl methacrylate, methacrylic acid / methyl methacrylate / benzyl methacrylate copolymer (copolymerization ratio: -- 14.6-27.2mol %/79.1-32.7mol %/-- 16.3-40 mol %) the weight average molecular weight 20,000-150,000, and methacrylic acid / methyl methacrylate / benzyl methacrylate / 2-ethylhexyl acrylate copolymer (copolymerization ratio: -- 10-15 mol % / 70-65 mol %/-- 10 mol %/10 mol %) The weight average molecular weight 20,000-150,000 etc. are mentioned.
[0028]
Although the cresol novolak resin more often [a commercial negative resist composition] than before used, polyhydroxy styrene, and its derivative will be colored after exposure and bake, There is little coloring in the time of baking treatment after such exposure, and especially methacrylic acid / benzyl methacrylate copolymer, methacrylic acid / methyl methacrylate / benzyl methacrylate copolymer, etc. above-mentioned in that light transmittance is not deteriorated is preferable.
[0029]
As content in the photosensitive resin composition for light-shielding films of the aforementioned binder resin, the 10 - 90 mass % is preferable to the total solids of this constituent, and the 20 - 70 mass % is more preferable.
[0030]
- Photo-oxide generating agent -
The photosensitive resin composition for light-shielding films of the present invention contains at least 1 type of a photo-oxide generating agent. When this photo-oxide generating agent is exposed to pattern form, it generates acid (H^+), and it promotes the polymerization curing by crosslinking reaction.
[0031]
An organic halogenated compound, onium salt, sulfonic ester, etc. are mentioned to the photo-oxide generating agent which generates acid by the exposure of light. In these, an organic halogenated compound is preferable and a halomethyl-ized triazine compound and a halomethyl-ized oxadiazole compound are especially preferable.
[0032]
As the aforementioned halomethyl-ized triazine compound, the compound denoted by a following general formula (1) is mentioned. However, in the present invention, it is not limited to these.
[0033]
[Chemical formula 1]

(1)

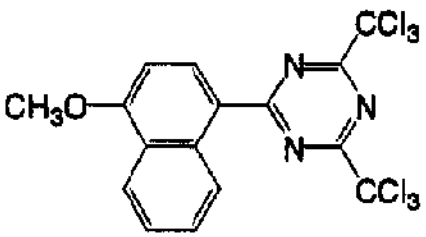


[0034]
R^1 and R^2 express a halomethyl group independently respectively among the aforementioned general formula (1), and Y expresses a with a carbon numbers of five or more organic group.
[0035]
As the aforementioned halomethyl group, they are mentioned by a trichloromethyl group, a tribromomethyl group, a dichloromethyl group, dibromomethyl group, etc., and, for example as a with an aforementioned carbon numbers of five or more organic group, For example, the phenyl group, the naphthyl group, the styryl group, styryl phenyl group and furil vinyl group which may have a substituent, the fourth class-ized aminoethyl amino group, etc. are mentioned.
[0036]
Hereafter, the examples [illustration compound (2) - (23)] of a halomethyl-ized triazine compound are enumerated.
[0037]
[Chemical formula 2]

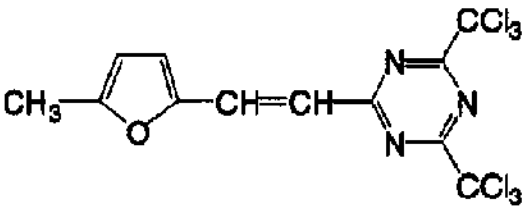
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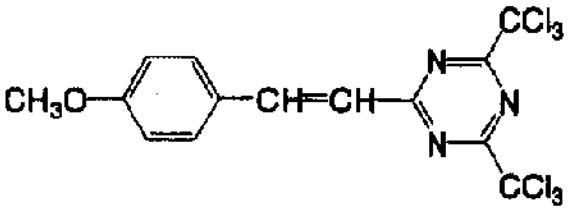
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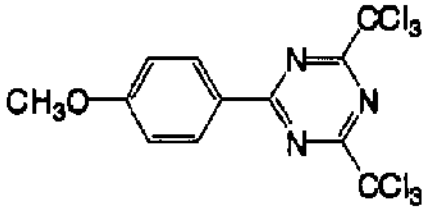
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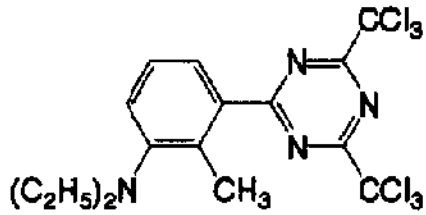
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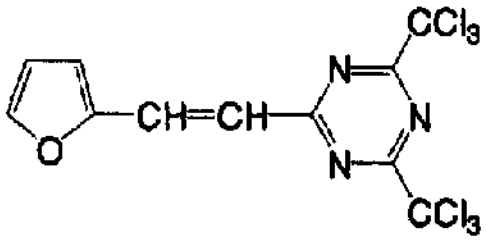


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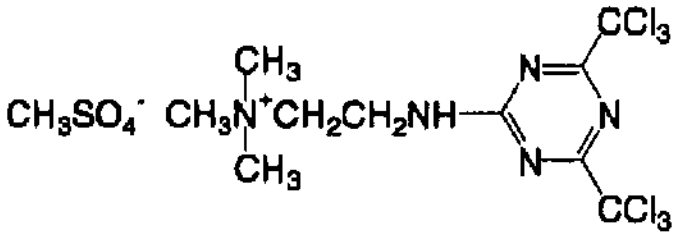


[0038]
[Chemical formula 3]

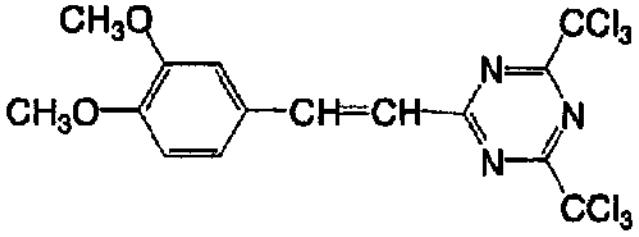
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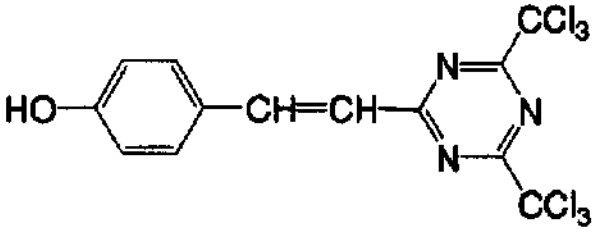
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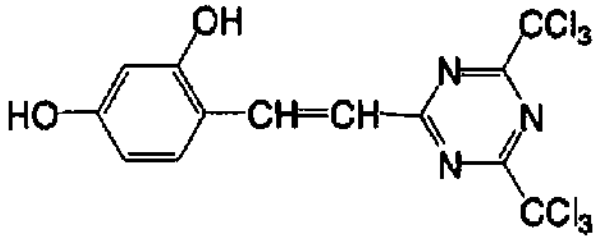
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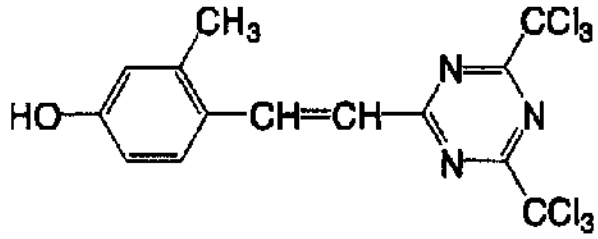
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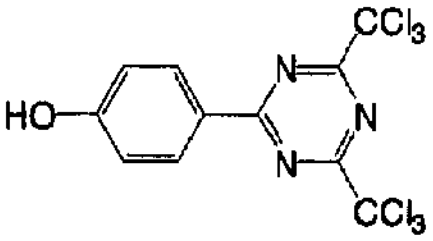


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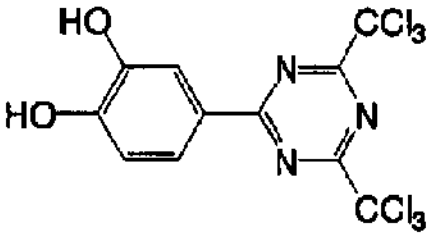


[0039]
[Chemical formula 4]

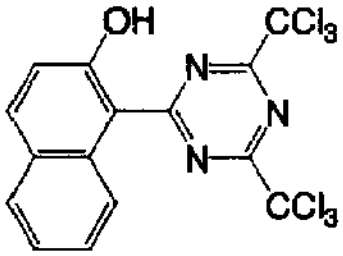
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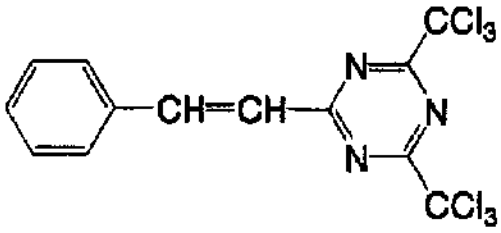
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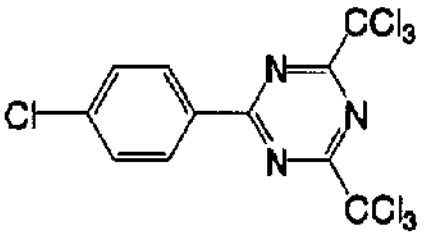
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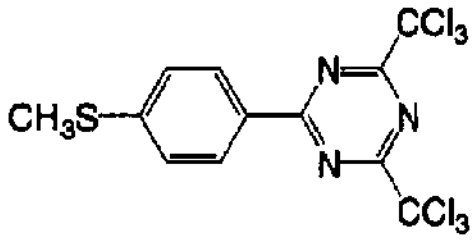
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(18)

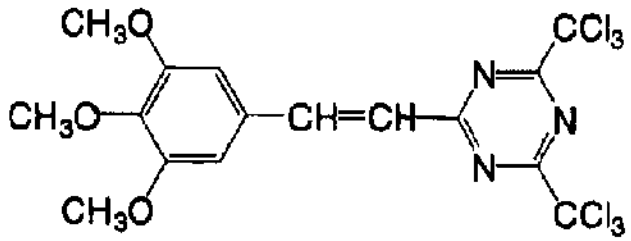


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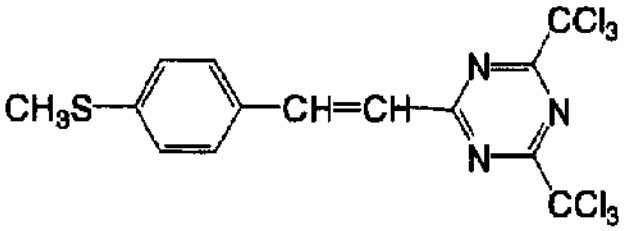


[0040]
[Chemical formula 5]

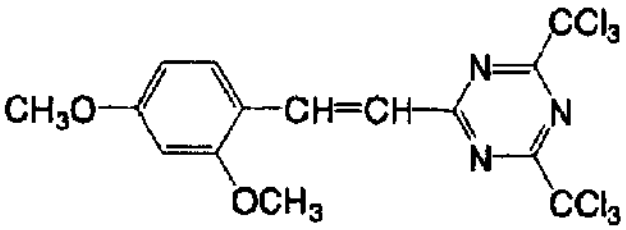
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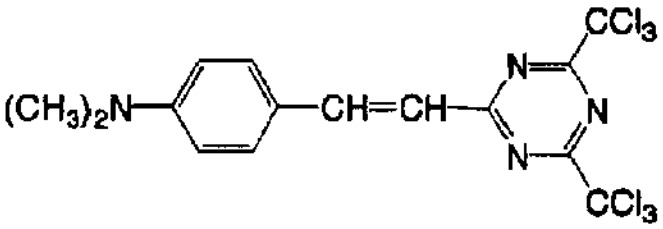
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(22)

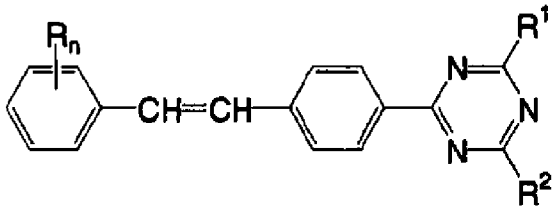


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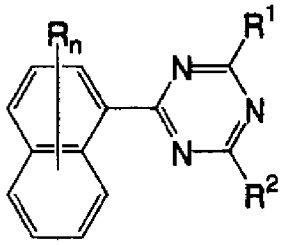
[0041]
A thing preferable also in the halomethyl-ized triazine compound denoted by the aforementioned general formula (1) is a compound denoted by (24), (25), or the following general formula (26).
[0042]
[Chemical formula 6]

(24)



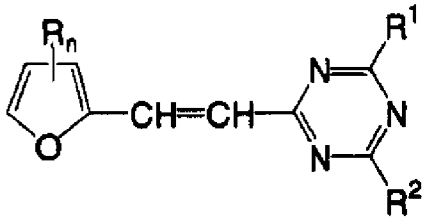
[0043]
R^1 in the aforementioned general formula (24) and R^2 express a halomethyl group independently respectively, and R expresses the alkyl group of the carbon numbers 1-4, or the alkoxy group of the carbon numbers 1-4. n expresses the number of R and is an integer of 0-3.
[0044]
[Chemical formula 7]

(25)



[0045]
R^1 in the aforementioned general formula (25) and R^2 express a halomethyl group independently respectively, and R expresses the alkyl group of the carbon numbers 1-4, or the alkoxy group of the carbon numbers 1-4. n expresses the number of R and is an integer of 0-3.
[0046]
[Chemical formula 8]

(26)



[0047]
R^1 in the aforementioned general formula (26) and R^2 express a halomethyl group independently respectively, and R expresses the alkyl group of the carbon numbers 1-4. n expresses the number of R and is an integer of 0-1.
[0048]

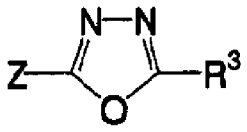
In each general formula a thing preferable also in the compound denoted by the above-mentioned general formula (24) (26) -, It is a compound which R^1 and R^2 are trichloromethyl groups, and R is an alkyl group of the carbon numbers 1-2, and also is [n are is an integer of 0-2 in the general formula (24) and (25)] an integer of 0-1 in a general formula (26).

[0049]

As the aforementioned halomethyl-ized oxadiazole compound, the compound denoted by a following general formula (27) is mentioned.

[0050]

[Chemical formula 9]

(27) 

[0051]

R^3 expresses a halomethyl group among the aforementioned general formula (27), and Z expresses the benzo furil group or benzo furil vinyl group which may have a substituent.

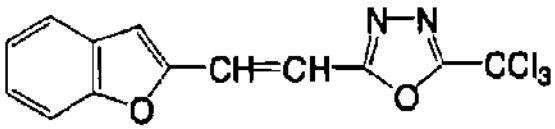
[0052]

Hereafter, the examples [illustration compound (28) - (45)] of a halomethyl-ized oxadiazole compound are enumerated.

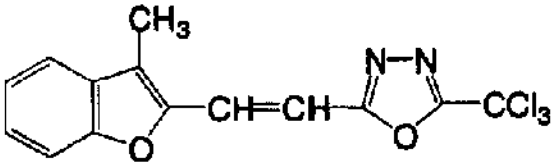
[0053]

[Chemical formula 10]

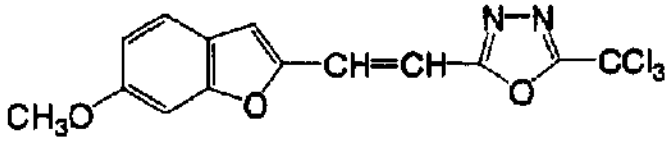
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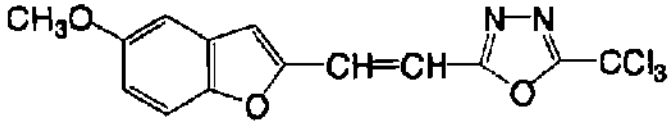
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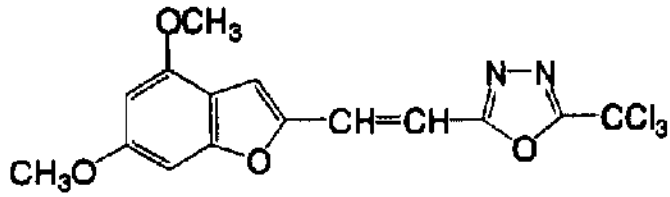
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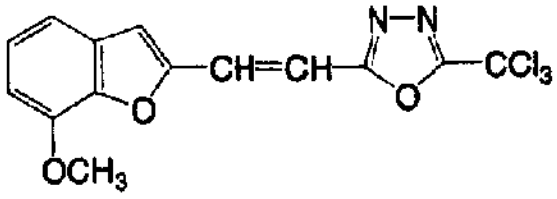
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(32)

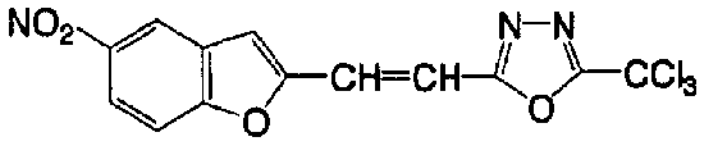


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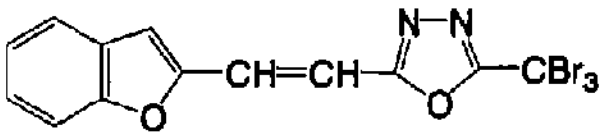


[0054]
[Chemical formula 11]

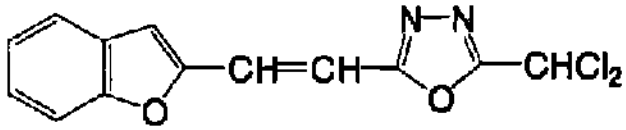
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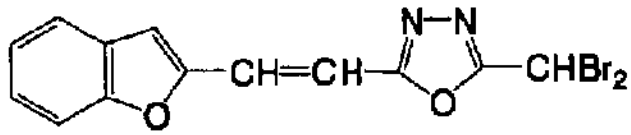
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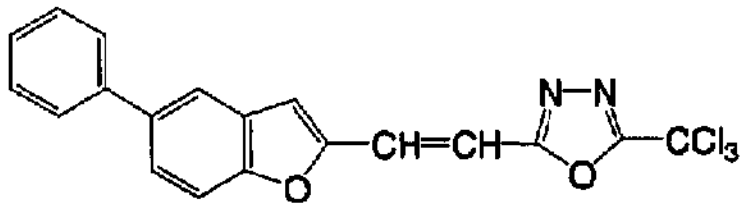
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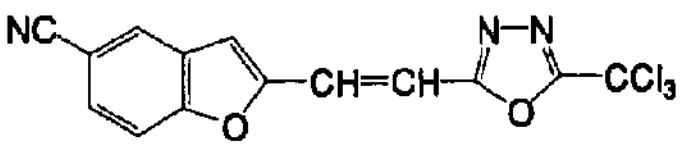
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(38)

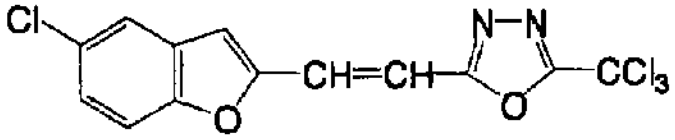


(39)

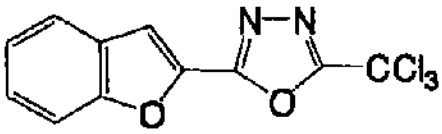


[0055]
[Chemical formula 12]

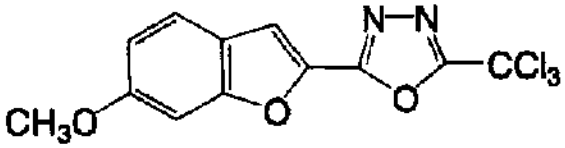
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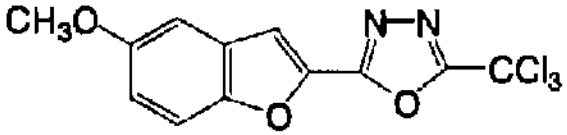
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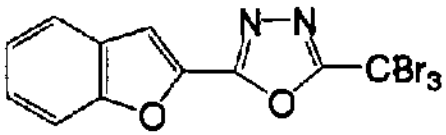
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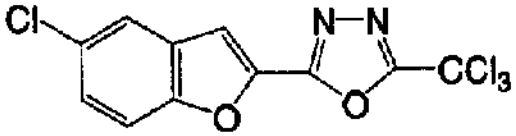
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(44)

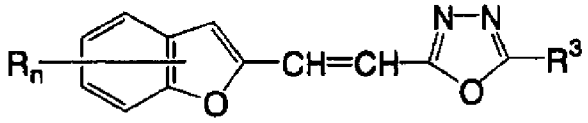


(45)



[0056]
A preferable halomethyl-ized oxadiazole compound denoted by the aforementioned general formula (27) is a compound denoted by a following general formula (46).
[0057]
[Chemical formula 13]

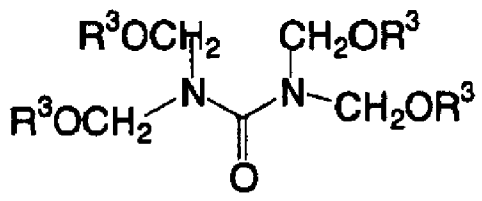
(46)



[0058]
R^3 in the aforementioned general formula (46) expresses a halomethyl group, and R expresses the alkyl group of the carbon numbers 1-4, or the alkoxy group of the carbon numbers 1-4. n expresses the number of R and is an integer of 0-2. The compound whose R^3 is a trichloromethyl group, whose R is the alkyl group or alkoxy group of the carbon numbers 1-2 and whose n is an integer of 0-1 is preferable.
[0059]
receiving the solid content of this constituent as content in the photosensitive resin composition for light-shielding films of a photo-oxide generating agent -- the 0.05 to 15 mass % -- it is the five to 15 mass % preferably. Sufficient acid is generated by exposure as the quantity of a photo-oxide generating agent is the aforementioned range, crosslinking reaction of binder resin and the below-mentioned cross linking agent can be performed good, the remaining rate of membrane after development is high, and the image provided with heat resistance, chemical resistance, etc. can be formed.
[0060]
- Cross linking agent -
The photosensitive resin composition for light-shielding films of the present invention contains at least 1 type of a cross linking agent. This cross linking agent has the operation which causes crosslinking reaction by the catalysis of the acid generated from the aforementioned photo-oxide generating agent at the time of exposure, and is hardened. That is, crosslinking reaction can be carried out between binder resin as stated above, a bridging body can be formed, and an exposure part can be hardened and imaged.
[0061]
The compound which has a substituent (a "cross-linking substituent" is called hereafter.) containing at least 1 type of cross-linking groups as a cross linking agent is mentioned.
[0062]
The following (i) - (vi) are mentioned as an example of the aforementioned cross-linking substituent.
(i) A hydroxyalkyl group or its derivatives, such as a hydroxyalkyl group, an alkoxyalkyl group, and an acetoxy alkyl group;
(ii) A carbonyl group or its derivatives, such as a formyl group and a carboxy alkyl group;

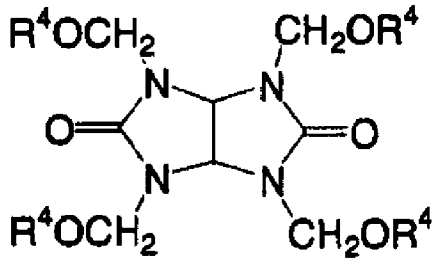
(iii) Nitrogen-containing basis content substituents, such as a dimethyl aminomethyl group, a diethyl aminomethyl group, a dimethylol aminomethyl group, a JIECHI roll aminomethyl group, and a morpholino methyl group;
(iv) Glycidyl group content substituents, such as a glycidyl ether group, a glycidyl ester group, and a glycidyl amino group;
(v) Aromatic derivatives, such as allyloxy alkyl groups, aralkyloxy alkyl groups, etc., such as a benzyloxymethyl group and a benzo yloxy methyl group;
(vi) Polymerizable multiple bond content substituents, such as a vinyl group and an isopropenyl group;
** can be mentioned.
Among the above, as a cross-linking substituent of the cross linking agent in the present invention, a hydroxyalkyl group, an alkoxyalkyl group, etc. are preferable and especially an alkoxy methyl group is preferable.
[0063]
as the cross linking agent which has the aforementioned cross-linking substituent -- for example
(i) Methylol group content compounds, such as a methylol group content melamine compound, a methylol group content benzoguanamine compound, a methylol group content urea compound, a methylol group content glycoluryl compound, and a methylol group content phenolic compound;
(ii) An alkoxyalkyl group content melamine compound, an alkoxyalkyl group content benzoguanamine compound, Alkoxyalkyl group content compounds, such as an alkoxyalkyl group content urea compound, an alkoxyalkyl group content glycoluryl compound, and an alkoxyalkyl group content phenolic compound;
(iii) Carboxymethyl group content compounds, such as a carboxymethyl group content melamine compound, a carboxymethyl group content benzoguanamine compound, a carboxymethyl group content urea compound, a carboxymethyl group content glycoluryl compound, and a carboxymethyl group content phenolic compound;
(iv) a bisphenol A system epoxy compound and bisphenol F system -- an epoxy compound -- a bisphenol S system -- epoxy compound [, such as an epoxy compound, a novolak resin system epoxy compound, a resole resin system epoxy compound, and a poly (hydroxystyrene) system epoxy compound,]; etc. can be mentioned.
[0064]
Also in the above-mentioned cross linking agent, an alkoxy methylation urea compound or its resin, an alkoxy methylation glycoluryl compound, or its resin is preferable.
As a preferable cross linking agent, the alkoxy methylation urea compound denoted by a following general formula (47) or the alkoxy methylation glycoluryl compound denoted by a following general formula (48) can be mentioned especially.
[0065]
[Chemical formula 14]

(47)



[0066]
R^3 in the aforementioned general formula (47) expresses the alkyl group of the carbon numbers 1-4.
[0067]
[Chemical formula 15]

(48)



[0068]
R^4 in the aforementioned general formula (47) expresses the alkyl group of the carbon numbers 1-4.
[0069]
In the aforementioned general formula (47) and (48), a methyl group, an ethyl group, a propyl group, a butyl group, etc. can be mentioned as an alkyl group denoted by R^3 or R^4.
[0070]
The above-mentioned alkoxy methylation urea compound and an alkoxy methylation glycoluryl compound, For example, after carrying out the condensation reaction of a urea compound, a glycoluryl compound, and the formalin and introducing a methylol group, It etherifies with lower alcohol, such as methyl alcohol, ethyl alcohol, propyl alcohol, and butyl alcohol, and is obtained by collecting the compound which subsequently cools reaction mixture and deposits, or its resin. It can also obtain as commercial items, such as CYMEL (trade name; made by Mitsui Cyanamid), and NIKARADDO (made in Sanwa Chemical).
[0071]
As a cross linking agent, the compounds on which formaldehyde was made to act or those alkyl modified compounds, an epoxy compound, a resol compound, etc. are effective in melamine, benzoguanamine, glycoluryl, or urea, and the following are mentioned as the example.
[0072]
As a specific example, Mitsui Cyanamid Cymel. (Registered trademark) 300 -- said -- 301 -- said -- 303 -- said -- 350 -- said -- 736 -- said -- 738 -- said -- 370 -- said -- 771 -- said -- 325 -- said -- 327 -- said -- 703 -- said -- 701 -- said -- 266 -- said -- 267 -- said -- 285 -- said -- 232 -- said -- 235 -- said -- 238 -- said -- 1141 -- said -- 272 -- said -- 254 -- said -- 202. said -- 1156 -- said -- 1158 is an example of the compound which made formaldehyde act on melamine, or its alkyl modified thing. Cymel (registered trademark) 1123 -- said -- 1125 -- said -- 1128 is an example of the compound on which formaldehyde was made to act at benzoguanamine, or its alkyl modified thing. Cymel (registered trademark) 1170 -- said -- 1171 -- said -- 1174 -- said -- 1172 is an example of the compound which made formaldehyde act on glycoluryl, or its alkyl

modified thing. furthermore -- as the example of the compound which made formaldehyde act on urea, or its alkyl modified thing -- Mitsui Cyanamid65 [UFR(registered trademark)] -- said -- 300 can be mentioned.
[0073]
moreover -- as the example of the aforementioned epoxy compound -- novolak epoxy resin, such as 704, VDPN-638 by Tohto Kasei Co., Ltd. -- said -- 701 -- said -- 702 -- said -- 703 -- said -- -- Amine epoxy resins (YH-434 by Tohto Kasei Co., Ltd., etc.), a bisphenol A epoxy resin, Sorbitol (poly) glycidyl ether, glycerol (poly) (poly) glycidyl ether, Pentaerythritol (poly) glycidyl ether, triglycidyl tris hydroxyethyl isocyanurate, Allyl glycidyl ether, ethylhexyl glycidyl ether, phenyl glycidyl ether, Phenol glycidyl ether, lauryl alcohol glycidyl ether, Adipic acid glycidyl ether, phthalic acid glycidyl ether, dibromo phenyl glycidyl ether, Dibromoneopentylglycol diglycidyl ether, a glycidyl phthalimide, (Poly) Ethylene glycol glycidyl ether, polypropylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, glycerin poly glycidyl ether, trimethylolpropane polyglycidyl ether, butyl glycidyl ether, ** can be mentioned.
[0074]
As a preferable compound, the compound (R expresses a hydrogen atom or an alkyl group.) which has a $-N(CH_2OR)_2$ group is especially mentioned into a molecule. In detail, the compound which made formaldehyde act on urea or melamine, or especially its alkyl modified thing is preferable.
[0075]
As an example of the aforementioned resol compound, PP-3000s by Gunei Chemical Industry Co., Ltd., PP-3000A, RP-2978, SP-1974, SP-1975, SP-1976, SP-1977, RP-3973, etc. are mentioned.
[0076]
As content in the photosensitive resin composition for light-shielding films of a cross linking agent, the 5 - 70 mass % is preferable to the quantity of the aforementioned binder resin, and the 10 - 40 mass % is more preferable.
[0077]
- Metal particles and/or metallic-compounds particles -
The photosensitive resin composition for light-shielding films of the present invention contains at least 1 type (henceforth "the metal particles concerning the present invention") chosen from the group which consists of metal particles and metallic-compounds particles. Since the metal particles concerning the present invention are selectively used as a black material for protection from light, Since high black density is obtained, and an advanced light sheilding is acquired with a thin form and it is constituted by the thin form, ****** of the pattern accompanying diffusion of acid at the time of heating in the case of being based on PAG can be prevented, and shortening of the cure time by heating diffusion can also be aimed at.
The below-mentioned composite particle and a core shell composite particle are contained in the metal particles concerning the present invention.
[0078]
<Metal particles>
as metal particles -- the long period periodic table (IUPAC 1991) -- for example, It is preferable that carry out the main component of the metal chosen from the group which consists of the 3rd cycle of the periodic table of the elements, the 4th cycle, the 5th cycle, and the 6th cycle, and it is included, It is preferable that carry out the main component of the metal chosen from the group which consists of the 2nd fellows, the 8th fellows, the 9th fellows, the 10th fellows, the 11th

fellows, the 12th fellows, the 13th fellows, and the 14th fellows, and it is included. As metal particles which start the present invention among these metal, it is metal of the 4th cycle, the 5th cycle, or the 6th cycle, and the metal of the 2nd fellows, the 10th fellows, the 11th fellows, the 12th fellows, or the 14th fellows is still more preferable.
[0079]
The others whose metal particles in the present invention have a globular shape, the shape of a right side face body containing a cube, etc., Length, width, the form of the shape anisotropy from which at least one of the ratios of height differs. They may be any, such as (for example, the globular shape which has shape anisotropy, the shape of a bean-jam bun, the shape of a potato, plate-like [rod-like] (square pillar forms, such as a needle, a cylindrical shape, and a rectangular parallelepiped, a Rugby ball type, etc.) (the shape of a scale, the shape of an elliptic plate, tabular), fibrous, the shape of konpeito, a coiled form, etc.).
The same may be said of the case of the metallic-compounds particles mentioned later, a composite particle, and a core shell composite particle.
[0080]
A preferable example as the aforementioned metal particles Copper, silver, gold, platinum, palladium, Nickel, tin, cobalt, rhodium, iridium, iron, a ruthenium, calcium, osmium, manganese, molybdenum, tungsten, niobium, Tan Tell, titanium, bismuth, antimony, lead or these alloys, and at least 1 type of ********** can be mentioned. Still more preferable metal is at least 1 type as which copper, silver, gold, platinum, palladium, nickel, tin, cobalt, rhodium, iridium or these alloys, and more preferable metal are chosen from copper, silver, gold, platinum, tin, or these alloys. Gold, silver, copper, and tin are preferable and silver is [among these] especially preferable. As silver, silver and colloidal silver which carried out rod form are also preferable. It is also possible to combine 2 or more type of aforementioned metal, and to use it for manufacture of metal particles as an alloy.

It can also use as complex particulates of metallic compounds and metal.
[0081]
<Metallic-compounds particles>
Metallic-compounds particles are particles of a compound with other elements other than the aforementioned metal and metal, and there are a metaled oxide, a sulfide, sulfate, carbonate, etc. as "a compound of metal and other elements." Among these, a sulfide is preferable especially from the ease of carrying out of a color tone or microparticle formation. As an example of these metallic compounds, although copper(II) oxide, an iron sulfide, a silver sulfide, copper sulfide (II), titanium black, etc. are mentioned, especially a silver sulfide is preferable in view of the ease of carrying out and stability of a color tone and microparticle formation.
[0082]
<Composite particle>
In the present invention, the composite particle which these joined together and turned into one particle can also be used using the aforementioned metal particles and the aforementioned metallic-compounds particles. There is no restriction in particular in the form of a composite particle. For example, that from which composition differs on the inside and the surface of particles, the thing with which two kinds of particles were united, etc. can be mentioned. Metallic compounds and at least 1 type of metal may be 2 or more type, respectively. As an example of the composite particle of metallic compounds and metal, there are a composite particle of silver and a silver sulfide, a composite particle of silver and copper(II) oxide, etc.

[0083]
<Core shell composite particle>
In the present invention, a core shell type composite particle (core shell composite particle) can also be used. The coat of the surface of core materials is carried out to a core shell type composite particle with shell material.
[0084]
As a shell material which carries out the coat of the aforementioned core materials, For example, Si, germanium, AlSb, InP, Ga, As, GaP, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, PbS, PbSe, PbTe, Se, Te, CuCl, CuBr, CuI, TlCl, TlBr, TlI(s) and these solid solutions, or these -- more than 90mol% -- at least 1 type of semiconductors chosen from the included solid solution -- Or copper, silver, gold, platinum, palladium, nickel, tin, cobalt, At least 1 type of metal chosen from rhodium, iridium, iron, a ruthenium, osmium, manganese, molybdenum, tungsten, niobium, Tan Tell, titanium, bismuth, antimony, lead, or these alloys can be used.
[0085]
As a preferable shell material, at least 1 type chosen from copper, silver, gold, palladium, nickel, tin, bismuth, AMMOCHIN, lead, or these alloys can be mentioned.
The aforementioned shell material is preferably used also as a regulator of a refractive index the making reflectance be deteriorated purpose.
[0086]
As core materials which constitute a core shell composite particle, at least 1 type of metal chosen from copper, silver, gold, palladium, or these alloys can be used, for example.
[0087]
There is no restriction in particular in the manufacturing method of the core shell composite particle which has core shell structure, and the following methods are mentioned to it as a typical method.
(1) Are the method of forming the shell of metallic compounds, for example, dispersion media, such as water, are made to distribute metal particles on the surface of the metal particles produced by the publicly known method by oxidation, sulfuration, etc., and the method of adding sulfides, such as a sodium sulfide and ammonium sulfide, is shown in it. Are sulfuration [the surface of particles] with this method and a core shell composite particle is formed.
In this case, the metal particles to be used are producible by publicly known methods, such as a gaseous phase method and a liquid phase process. About the manufacturing method of metal particles, it describes, for example in "the newest trend II in the technology of an ultrafine particle, and application" (** BETEKUNORISACHI, Inc., 2002 issue).
(2) The circumference of the metal particles which are the methods of forming the shell of metallic compounds in the surface continuously in the process in which metal particles are produced, for example, added the reducing agent to the metal salt solution, returned some metal ion, produced metal particles, and subsequently added and produced the sulfide has the method of forming metallic sulfide.
[0088]
-Production of metal particles-
Metal particles can use a commercial thing, and also can be prepared with the chemical reduction method of metal ion, an electroless deposition method, a metaled evaporation method, etc.
In the case of the particles constituted by the form of shape anisotropy, especially in the case of a cylindrical silver granule child (silver rod), By making a globular form silver granule child into a seed particle child, after that, a silver salt is added further and a silver rod and a wire are obtained

under surfactant existence, such as CTAB (Sept Iles trimethylammonium star's picture), by using reducing agents with comparatively weak reducing power, such as ascorbic acid. This has a description in Adv.Mater.2002, 14, and 80-82. The same description is made by Mater.Chem.Phys.2004, 84,197-204, Adv.Funct.Mater.2004, and 14,183-189. J.Mater.Res.2004 and 19,469-473 have the method of a description as a method using electrolysis as the method of the description to Mater.Lett.2001,49,91-95, and a method of generating a silver rod by irradiating with microwave. As an example which reversed micelle and an ultrasonic wave used together, J.Phys.Chem.B-2003, 107, and 3679-3683 are mentioned.
It describes in J.Phys.Chem.B 1999, 103, 3073-3077 and Langmuir1999, 15, 701-709, J.Am.Chem.Soc.2002, 124, and 14316-14317 similarly about gold.
Even if the formation method of rod-like particles improves the above-mentioned method (addition amount adjustment, PH control), it can be prepared.
[0089]
-Particle diameter-
When the metal particles (a composite particle and a core shell composite particle are included.) concerning the present invention are a real ball or a globular form, as the particle diameter, 2-600 nm is preferable and 10-300 nm is more preferable.
[0090]
When you are the particles of shape anisotropy, let the particle diameter be a diameter of the three dimensions. That is, it is a method which one metal particles consider the box (rectangular parallelepiped) settled exactly (just), and define as the dimension of these metal particles with length L [of this box], width b, height, or thickness t. When storing metal particles in a box, there are some methods, but the following methods are adopted in the present invention.
First, on a plane, metal particles are placed so that it may be stood still stably [the center of gravity is the lowest and]. Next, metal particles are inserted with the parallel plate of two sheets stood right-angled to the plane, and the plate interval makes the plate interval of the position which becomes the shortest "the width b." Next, to the plate of two sheets which settles the aforementioned width b, are right-angled, and metal particles are inserted with the parallel plate of two right-angled sheets also to the aforementioned plane, and let this plate interval of two sheets be "length L." A top plate is carried in parallel with the aforementioned plane so that the highest position of metal particles may finally be contacted, and the interval of a top plate and a plane is set to height or thickness t (the rectangular parallelepiped to draw is formed by the plane, the plate of two sheets each, and a top plate of this gentleman method.). The axis applicable to the longest thing of the diameter of the three dimensions b, L, and t of metal particles is defined as a "major axis", and the diameter at the time of carrying out perfect circle conversion of the project area produced in the length in a major axis direction by irradiating metal particles with a light parallel to a major axis with "long axis length" again is defined as "minor-axis length."
[0091]
-Aspect ratio-
The aspect ratio of the metal particles (a composite particle and a core shell composite particle are included.) concerning the present invention means the value which broke the long axis length whom metal particles or metallic-compounds particles defined as mentioned above by minor-axis length, and it is defined as the average value of the value measured about 100 metal particles. The project area of particles measures the area on an electron microscope photograph, and is obtained by correcting photographing magnification.
[0092]

As for the aspect ratio (ratio of the minor-axis length of the long axis length/particles of particles) of particles, it is preferable that it is two or more, and it is more preferable that it is four or more. The maximum of an aspect ratio is about 100. It is effective for high-resolution-izing, without black particles' being easy to be obtained, and being too large and absorption of a light region becoming small in this range. Still more preferably, it is 4-80 and is 10-60 most preferably. As for the minor-axis length of particles, 4-50 nm is preferable, it is more preferable, and is the most preferable. [of 15-30 nm] [of 15-50 nm] As for the long axis length (maximum length) of particles, 10-1000 nm is preferable, his 100-1000 nm is more preferable, his 400-800 nm is still more preferable, and it is most preferable that it is shorter than a visible light wavelength.

[0093]

By mixing the particles from which particle diameter and form differ, absorption-spectrum control can be carried out and hue can also be brought close colorless.

[0094]

-Particle size distribution-

As for particle size distribution, it is preferable that the particle-size-distribution width D90/D10 of long axis length's mean particle diameter is less than [2 or more] 20. D90 is a maximum diameter by which 90% of particles are found out here, and D10 is a maximum diameter by which 10% of particles are found out. Particle size distribution is 15 or less [2 or more] more preferably in view of a color tone, and is ten or less [4 or more] still more preferably. Muddiness by dispersion according that particle size distribution is the aforementioned range to a coarse particle can be prevented from arising.

[0095]

Although it changes with the kinds and descriptions of particles to be used as content in the photosensitive resin composition for light-shielding films of "metal particles and/or metallic-compounds particles", the 2 - 40 volume % is preferable, and the 5 - 30 volume % is more preferable.

[0096]

- Colorant -

With the aforementioned metal particles and/or metallic-compounds particles, the photosensitive resin composition for light-shielding films of the present invention can use paints and/or a color together further, and can constitute them preferably.

[0097]

As the aforementioned paints, for example Barium sulfate, lead sulfate, titanium oxide, yellow lead, Inorganic pigments, such as red ocher, chrome oxide, and carbon black, anthraquinone system paints, Organic colors, such as perylene system paints, a disazo pigment, a phthalocyanine pigment, isoindoline paints, dioxazine paints, a quinacridone pigment, peri non system paints, triphenylmethane series paints, and thioindigo paints, etc. are mentioned. A 1 type independent or 2 type or more can be mixed and used for these.

Also in the aforementioned paints, anthraquinone system paints, a phthalocyanine pigment, dioxazine paints, and especially carbon black are preferable.

[0098]

Hereafter, a Color Index (C. I.) number shows specifically.

C. I. red : 9,97,122, 123,149,168, 177,180,192, 215,216,217, 220,223,224, 226,227,228,240;

C. I. blue : 15, 15:6, 22, 60, 64;

C. I. green : 7, 36;

C. I. black : seven;
C. I. yellow : 12,20,24, 86,93,109, 110,117,125, 137,138,147, 148, 153,154,166,168;
C. I. orange : 36, 43, 51, 55, 59, 61;
C. I. violet : 19, 23, 29, 30, 37, 40, 50;
C. I. tea : 23, 25, 26;
[0099]
As for the mean particle diameter of paints, it is preferable that it is in the range of 0.005-3 micrometers. It is 0.01-1 micrometer more preferably. In order to use the particle diameter of this range, distributed processing, such as a ball mill, a sand mill, a bead mill, 3 rolls, a paint shaker, and an ultrasonic wave, is effective.
[0100]
As the aforementioned color, Crystal Violet, Methyl Violet, ethyl violet, and oil blue #603, Victoria pure blue BOH, malachite green, DAIMONDO green, etc. are mentioned, for example. In addition to the above, black lead can also be used preferably.
[0101]
According to a use etc., the aforementioned paints and a color may be used together, and it is not necessary to necessarily contain paints and/or the color.
In the present invention, the mode used together with the metal particles concerning the present invention of previous statement of carbon black and/or black lead is the most preferable.
[0102]
In the above, the black pigment of carbon systems, such as carbon black, has [the following / 50 m^2/g] the preferable specific surface area measured with the nitrogen gas adsorption process. Especially, within the limits of 50-10 m^2/g is within the limits of 30-15 m^2/g preferable still more preferably. Good shielding performance is obtained as specific surface area is [aforementioned] within the limits, and the dispersion stability at the time of distribution is good.
[0103]
When using together colorant (especially carbon black, black lead), as a quantity of colorant, the 10 - 90 volume % is preferable to the total amount of the metal particles concerning the present invention, and it is the 20 to 50 volume % more preferably. It is effective in controlling the reflectance etc. of the formed light-shielding film by using colorant together with the metal particles concerning the present invention, and when quantity of colorant is carried out especially aforementioned within the limits, while it has a high light sheilding with a thin film, it is effective for forming the light-shielding film which does not have optical leak and was excellent in surface surface smoothness. Also when a substrate independent is pinched with a polarizing plate from both sides and intersects perpendicularly the polarization axis of these two polarizing plates, there is no light leakage, a high light sheilding is acquired, a highly efficient color filter can be obtained, and it contributes to manufacture of the liquid crystal display element which can display a high-definition image. industrially, sufficient in manufacture of the color filter by an advantageous electrodeposition process, also when forming a light-shielding film by the back face exposing method -- increase -- membranous -- a light sheilding can be acquired.
[0104]
- Other components -
In the photosensitive resin composition for light-shielding films of the present invention, various additive agents can be contained according to the various purposes and uses. As an additive agent, a surfactant, an adhesion accelerating agent, a plasticizer, etc. are mentioned, for example.
[0105]

Can use the aforementioned surfactant in order to improve the application nature in the case of using the photosensitive resin composition for light-shielding films as coating liquid, and the smooth nature of the coating film obtained, and as an example, BM-1000 (made by BM Chemie), the megger fax F142D, Said F172, said F173, said F183, the F176PF, the F177PF (all are the Dainippon Ink & Chemicals, Inc. make), Fluorad FC-135, FC-170C, and Fluorad FC-430, the FC-431 (all are the Sumitomo 3M make), The Sir chlorofluocarbon S-112, said S-113, said S-131, said S-141, said S-145 (all are the Asahi Glass Co., Ltd. make), The fluorine system or silicon system surfactant marketed with the trade name of SH-28PA, SH-190, SH-193, SZ-6032, SF-8428, DC-57, and DC-190 (all are the products made from Toray Industries Silicone) is mentioned.

[0106]

As content in the case of containing a surfactant, the 0.05 - 10 mass % is preferable to the total solids of the photosensitive resin composition for light-shielding films. If contained in this range, it is especially effective in respect of the pattern adhesion to a substrate. The range of the 0.08 - 5 mass % is preferable, and especially the range of the 0.1 - 3 mass % is preferable.

[0107]

The photosensitive resin composition for light-shielding films of the present invention can be prepared as coating liquid, for example using organic solvents, such as ketone, such as acetone, methyl ethyl ketone, and methyl butyl ketone, various ether, and ester. This coating liquid can be preferably used, in order to form a photosensitive resin layer in the surfaces which serve as a coated object by application, such as temporary support (sheet etc.) and a liquid crystal display element (this coating liquid may be hereafter called "coating liquid for photosensitive resin layers".). Although there is no restriction in particular in the thickness of this photosensitive resin layer and it can choose suitably, 0.2-1.3 micrometers is preferable and 0.3-0.8 micrometer is more nearly preferable. Even if constituted in the thin film of this range, high black density is obtained.

[0108]

That is, the mode constituted so that the optical density of this light-shielding film might become 4.0 or more, when the photosensitive resin composition for light-shielding films of the present invention formed light-shielding films of 1.0 micrometer of thickness, such as a coating film by the above application, is preferable. A color filter including the light-shielding films (black matrix etc.) to constitute Printing materials, such as a proof, In the use as which advanced shielding performance and thin-film-forming nature, such as a partitioning material for PDP (Plasma Display Panel), ink jet ink, and resist ink, are required, It is important that high black density is obtained, using a thin film, and, in this case, the photosensitive resin composition for light-shielding films of the present invention can be used preferably. The photosensitive resin composition for light-shielding films of the present invention is preferable for especially formation of the light-shielding films (black matrix etc.) of the color filter which constitutes a liquid crystal display etc., and ideal for formation of a black matrix.

[0109]

The photosensitive resin composition for light-shielding films of the present invention can form a light-shielding film with the application of the following method in addition to the method by application of the above-mentioned coating liquid.

-The ink jet method-

Using the ink jet method, the photosensitive resin composition for light-shielding films of the present invention can be discharged, and a light-shielding film can be formed. This is preferable

in respect of a cost cut. As this ink jet method, the bubble jet (registered trademark) type which used the electrothermal conversion object as an energy generation element, or the piezo jet type using a piezoelectric device is usable, and coloring area and a coloring pattern can be set up arbitrarily. Although there is a tendency for ink to be unable to diffuse sufficiently easily in the ink jet method and it is easy to become a cause which produces a blind spot and invites color unevenness and a contrast drop, In this case, it is preferable to prepare to the thing which made the organic solvent distribute paints by the concentration more than the at least 10 mass % to the mass of the whole constituent (ink). For details, the description of JP,2004-325736,A can be referred to.

[0110]

In order to produce the light-shielding film which it got wet at the time of discharging the photosensitive resin composition for light-shielding films, controlled breadth, and was excellent in concentration homogeneity, as a solvent kind to be used, the surface tension of the fitness in ink jet printing is 35 or less mN/m, and a not less than 130 degrees C thing has the preferable boiling point. The drying property near the nozzle is suppressed as the stability of the dot shape at the time of discharge is good in surface tension being 35 or less mN/m and the boiling point is not less than 130 degrees C, and discharge failures, such as nozzle plugging, can be avoided. By getting wet and controlling breadth, a light-shielding film with clear film form and edge sharp at uniform high concentration without defects, such as mixed colors at the time of forming a colored pixel and a blind spot in a light-shielding film, is obtained.

[0111]

It is also possible to improve the productivity at the time of producing a light-shielding film by applying a means which is described in JP,2002-372615,A and which ink hardens in an instant, also combines reservation of the dispersion stability of paints, and reservation of adhesion with a base material, and they improve.

[0112]

-Print processes-

A light-shielding film can be produced in a short time using print processes. As print processes, it hits carrying out print formation of the shielding pattern to this transparent base material through a transparent base material between a printing cylinder and an impression cylinder, In the letterpress part which the aforementioned printing cylinder is provided with the printing plate of the letterpress corresponding to the aforementioned shielding pattern, and constitutes the aforementioned printing plate, Transfer ink is transferred with a shielding pattern with the letterpress object provided with the letterpress which faced the aforementioned letterpress part and was used as the shielding pattern from the transfer sheet provided with the photosensitive resin composition for optical thin-film (transfer ink), There is the method of transferring the aforementioned transfer ink which provided transfer ink to the printing plate of the aforementioned printing cylinder at the shielding pattern, and was provided by the shielding pattern from the printing plate of a printing cylinder to the aforementioned transparent base. As for the printing plate of a printing cylinder, it is good to have ink repellent property. It is good to apply a binder to the transfer starting position and transfer end position in a printing plate. In order that transfer ink may be provided by the shielding pattern by the printing plate of a printing cylinder and may transfer this transfer ink to a transparent base material at once, the time which production of the light-shielding film by printing takes is shortened, and. There is no aim gap of the transfer ink which forms the light-shielding film formed in a transparent base material, and a proper light-shielding film is obtained by the printing method using a transfer sheet. And if the

letterpress of the letterpress part in the printing plate of a printing cylinder is provided with ink repellent property, transfer of the transfer ink from a printing plate to a transparent base material will become good, and washing of a printing plate also becomes easy.
[0113]
It hits carrying out print formation of the shielding pattern to this transparent base material through a transparent base material between a printing cylinder and an impression cylinder besides the aforementioned printing method, The aforementioned printing cylinder is provided with the printing plate of the letterpress corresponding to the aforementioned shielding pattern, and the photosensitive resin composition for light-shielding films (black ink) is filled up with an ink jet feeding means into the cell which constitutes the aforementioned printing plate, After providing black ink with a shielding pattern to the printing plate of the aforementioned printing cylinder and drying this, there is a printing method transferred from the printing plate of a printing cylinder to the aforementioned transparent base. In this case, a printing cylinder is provided with the printing plate of an intaglio, and the photosensitive resin composition for light-shielding films (black ink) is filled up with an ink jet feeding means into the cell which constitutes a printing plate, Since it has composition transferred from the printing plate of a printing cylinder to the aforementioned transparent base after providing black ink with a shielding pattern to the aforementioned printing plate and drying this, Since process time is shortened still more nearly substantially, and there is no aim gap, ink form is stabilized in a cell and it can transfer to cell shape at the transparent base material side, a light-shielding film can be formed precisely.
[0114]
<A transfer material and a manufacturing method for the same>
-Transfer material-
The transfer material of the present invention can provide and constitute the photosensitive resin layer of at least one layer on temporary support, and also can also provide and constitute other layers, such as an intermediate layer, a thermoplastic resin layer, and a protective film, if needed.
[0115]
The photo-oxide generating agent which the aforementioned photosensitive resin layer absorbs binder resin and light, and generates acid, It is a layer containing the cross linking agent cross-bridged by operation of the aforementioned photo-oxide generating agent, and metal particles and/or metallic-compounds particles, It can form by a publicly known method in the mode containing these each component, and can form most preferably using the photosensitive resin composition for light-shielding films of the present invention as stated above (it paints on the surface of temporary support (sheet etc.) by application of coating liquid preferably). It is as the previous statement about the details of each component, such as binder resin.
[0116]
Although the thickness of the photosensitive resin layer which constitutes the transfer material of the present invention can be chosen according to a use or the purpose, For the use as which thin films, such as light-shielding films, such as a black matrix, are required, it is so good that it is thin, and it is preferable to consider it as the range of 0.2-1.3 micrometers, and it is more preferable to consider it as the range which is 0.3-0.8 micrometer. Even if this photosensitive resin layer is transferred by the transferred object, constitutes a black image (for example, black matrix) and constitutes it in the film of the aforementioned range, it can satisfy high black density and a light sheilding.
[0117]

Next, the temporary support and other layers which constitute the transfer material of the present invention are described.
- Temporary support -
To temporary support, a plastics film is preferable. For example, films, such as polyethylene terephthalate, polyethylenenaphthalate, cellulose triacetate, cellulose acetate butylate, cellulose acetate propionate, polycarbonate, polystyrene, and polyethylene, can be mentioned. Especially, a polyethylene terephthalate film is preferable and biaxial extension and the polyethylene terephthalate film by which heat setting was carried out are preferable especially especially from points, such as stability and toughness.
[0118]
Although there is no restriction in particular in the thickness of temporary support, the range of 5-200 micrometers is common, and the range which are 10-especially 150micro is preferable in respect of the ease of dealing with it, flexibility, etc.
[0119]
- Thermoplastic resin layer -
A thermoplastic resin layer is a thermoplastic resin layer of alkali solubility, and, as for the resin which constitutes this layer, it is preferable that substantial softening temperature is 80 degrees C or less.
Softening temperature as thermoplastics of alkali solubility of 80 degrees C or less, The saponification thing of ethylene and an acrylic ester copolymer, the saponification thing of styrene and a (meth)acrylic ester copolymer, The saponification thing of vinyltoluene and a (meth)acrylic ester copolymer, It is preferable that it is at least one chosen from the copolymer of poly(meta) acrylic ester and (meta) butyl acrylate, a saponification thing with (meth)acrylic ester copolymers, such as vinyl acetate, etc. and acrylic acid (meta), and an ethylene unsaturation group containing monomer. The softening temperature by a "plastic performance manual" (Japan Plastics Industry Federation, all Japan plastic-molding industrial joint association written and edited, Kogyo Chosakai Publishing, October 25, 1968 issue) can use a meltable thing for an alkaline aqueous solution among organic high polymers of about 80 degrees C or less.
[0120]
It is also possible to lower substantial softening temperature to 80 degrees C or less, and to use it because softening temperature adds the various plasticizers which have this organic high polymer substance and compatibility in the organic high polymer substance in a not less than 80 degrees C organic high polymer substance. In order to adjust adhesive strength with temporary support, it is also possible to add various kinds of polymer, a supercooling substance, an adhesion improving agent or a surfactant, mold lubricant, etc. into an organic high polymer substance in the range in which substantial softening temperature does not exceed 80 degrees C.
[0121]
especially -- the (A) weight average molecular weight 50,000-500,000 and the glass-transition-temperature Tg=0-140 degree C alkali of the description to JP,H7-28232,A -- with meltable thermoplastics, (B) the weight average molecular weight 3000-30,000 and Tg=30-170 degree C alkali -- meltable thermoplastics -- (A)/(B) -- the thing mixed in ratio =5 / 95 - 95/5 [a mass ratio] is preferable. Especially the preferable examples of the above (A) are methacrylic acid / 2-ethylhexyl methacrylate / benzyl methacrylate / methyl methacrylate copolymer (copolymerization mole ratio: 5/10/30/55, average-molecular-weight:100,000, Tg: about 70 degrees C). Especially the preferable examples of the above (B) are styrene/acrylic acid copolymer (copolymerization-composition mole ratio: 65/35, average-molecular-weight:10,000,

Tg: about 100 degrees C). Especially the preferable ranges of the aforementioned (A) / (B) ratio are 30 / 70 - 60/40.
[0122]
As a preferable example of the aforementioned plasticizer, a polypropylene glycol, A polyethylene glycol, dioctyl phthalate, diheptylphthalate, Dibutyl phthalate, tricresyl phosphate, cresyl diphenyl phosphate, Biphenyl diphenyl phosphate, polyethylene-glycol mono- (meta) acrylate, Polyethylene glycol di(meta)acrylate, polypropylene-glycol mono- (meta) acrylate, The addition reaction product of polypropylene glycol di(meta)acrylate, and an epoxy resin and polyethylene-glycol mono- (meta) acrylate, The addition reaction product of organic diisocyanate and polyethylene-glycol mono- (meta) acrylate, Di(meth)acrylate of the addition reaction product of organic diisocyanate and polypropylene-glycol mono- (meta) acrylate and a bisphenol A-polyethylene oxide addition can be mentioned.
[0123]
The quantity of a plasticizer is 0 to 200% [mass ratio] preferably to the quantity (preferably the aforementioned thermoplastics (A) and the total quantity of (B)) of the thermoplastics which constitutes a thermoplastic resin layer, and is 20 to 100% [mass ratio] more preferably. Especially the preferable example of a plasticizer is the compound which added 10 mol of ethylene oxide to bisphenol A and 1 mol in total, and carried out methacrylic esterification of the both-ends alcohol. Especially the preferable addition amount of a plasticizer is the 30 to 60 mass % of the quantity (preferably the aforementioned thermoplastics (A) and the total quantity of (B)) of thermoplastics.
[0124]
A thermoplastic resin layer can be painted by application of the coating liquid which dissolves each of above-mentioned components in a solvent uniformly, and drying. The preferable example of the aforementioned solvent Methoxy propylene glycol acetate, 2-hydroxypropyneacid ethyl, 3-methoxy methyl propionate, It is a mixture of the mixture of retarder thinner, such as 3-ethoxyethyl propionate, methyl lactate, ethyl lactate, cyclohexanone, and methyl isobutyl ketone, and these retarder thinner, low boilers, such as methyl ethyl ketone and acetone, and these low boilers. An application drying rate is good, is a point of dry unevenness prevention, and can choose preferably the mass composition ratio of retarder thinner and a low boiler from 1 / 99 - 99/1. The ranges of the mass ratio of retarder thinner/low boiler are 90 / 10 - 10/90 preferably, and the range of 80 / 20 - 20/80 is the most preferable.
[0125]
The coating method with which the thermoplastic resin layer was generally known on temporary support, for example, a dip coating method, By the air-knife-coat method, the curtain coat method, the wire bar coat method, the gravure coating method, extrusion die coating method, the slit coat method, etc., The coating liquid (it may be hereafter called "the coating liquid for thermoplastic resin layers".) containing the aforementioned thermoplastics etc. can be applied, and it can form by making it dry.
[0126]
When the thickness of a thermoplastic resin layer transfers a photosensitive resin layer, the viewpoint of absorbing completely the unevenness of 0.5 micrometers or more which exists in a transferred surface to its 1 micrometers or more are preferable. About a maximum, about 100 micrometers or less are common from restriction of application production aptitude, about 50 micrometers or less are preferable, and especially about 20 micrometers or less are preferable.
[0127]

- Intermediate layer -
It provides in order to prevent a component from being mutually mixed between a thermoplastic resin layer and a photosensitive resin layer as an intermediate layer (it is also called a detached core.).
It distributes or dissolves in water or an alkaline aqueous solution, and if the intermediate layer is insoluble or refractory to the organic solvent in the coating liquid for thermoplastic resin layers provided in contact with an intermediate layer, he is good for it, he is publicly known, and can constitute.
For example, the polyvinyl ether / maleic anhydride polymer of the description to JP,S46-2121,A or JP,S56-40824,B, The water soluble salt of carboxy alkylcellulose, water-soluble cellulose ether, The salt of carboxy alkyl starch, a monohydrate, polyvinyl alcohol, a polyvinyl pyrrolidone, Various kinds of polyacrylamides, various kinds of water soluble polyamide, the water soluble salt of polyacrylic acid, The water soluble salt of the group which consists of gelatin, an ethyleneoxide polymer, various kinds of starch, and its prototype, the copolymer of styrene/maleic acid, MAREINETO resin, and the thing that combined these 2 or more type can be mentioned.
[0128]
In particular, the combination of 1 water-solubility polyvinyl-butyral independent, and 2 polyvinyl alcohol and a polyvinyl pyrrolidone is preferable.
That [polyvinyl alcohol's] whose saponification value is 80 mol % or more is preferable, the content of a polyvinyl pyrrolidone has the common 1 - 75 mass % of intermediate-layer solid content, and the 1 - 60 mass % is the ten to 50 mass % preferable especially preferably. If it is this range, an adhesive property with a photosensitive resin layer will be acquired sufficiently, and will not impair the solvent resistance over the coating liquid for photosensitive resin layers.
[0129]
About 0.1-5 micrometers is preferable, and, as for an intermediate layer's thickness, 0.5-2 micrometers is especially preferable. If it is this range, it has the solvent resistance over the coating liquid for photosensitive resin layers, and option of application speed and drying can be performed without restriction.
[0130]
The solvent of intermediate layer coating liquid is chosen from the mixture of a water independent, water, the organic solvent of miscibility, and water. In order to improve an adhesive property with the thermoplastic resin layer used as a lower layer, it is preferable to choose so that a thermoplastic resin layer may be swollen slightly. As an example of a preferable solvent, water/methanol, water/ethanol, water/propanol, water / methoxy ethanol, water / methoxy propanol, water/acetone, etc. can be mentioned. The composition ratio of water and these organic solvents can be chosen from the range of 99 / 1 - 50/50 with a mass ratio. By considering it as this range, the addition effect of a solvent is acquired and sufficient solubility of water soluble resin can be acquired.
[0131]
The coating method with which the intermediate layer was generally known on the thermoplastic resin layer, for example, a dip coating method, It can form by applying intermediate layer coating liquid by the air-knife-coat method, the curtain coat method, the wire bar coat method, the gravure coating method, extrusion die coating method, the slit coat method, etc.
[0132]
- Protective film

As for a protective film, it is preferable to provide in order to avoid the adhesion and damage to the impurity to the photosensitive resin layer at the time of saving a transfer material, and its thin protective film is preferable.
Although a protective film is the same as that of temporary support or consists of a similar material, at the time of use, it is easily disengageable and needs to consist of photosensitive resin layers.
[0133]
The smooth nature of a surface in contact with a photosensitive resin layer is important for a protective film, and since it will serve as damage to a photosensitive resin layer if it has the projection it is [projection] about 0.01 micrometer, it becomes a problem easily. Therefore, as a material used as a protective film, silicon paper, polyolefin, or a poly tetrafluoroethylene sheet is preferable, for example. They are a polypropylene film or a polyethylene film especially preferably.
[0134]
1-100 micrometers is preferable, 3-50 micrometers is preferable especially preferable, and the thickness of a protective film is 5-20 micrometers. Strength can be maintained as it is this range, and the adhesive property between photosensitive resin layers can also be maintained.
[0135]
-A manufacturing method of a transfer material-
The transfer material of the present invention by applying and drying the coating liquid for thermoplastic resin layers on the aforementioned adhesive surface of the temporary support which has an antistatic layer and the adhesive surface preferably, for example, The intermediate layer coating liquid which uses the solvent swollen to some extent although the thermoplastic resin layer of alkali solubility is painted and this layer is not dissolved on this thermoplastic resin layer after that is applied, After making it dry and laminating an intermediate layer, the coating liquid for photosensitive resin layers prepared using the solvent which does not dissolve this intermediate layer further is applied, it is made to dry and a photosensitive resin layer is laminated. Then, a protective film can be laminated and produced on a photosensitive resin layer. The coating liquid for forming the above-mentioned each layer can be applied with the coating method generally learned like previous statement.
[0136]
The manufacturing method of the transfer material of the present invention carries out the characteristics of producing the transfer material of the present invention as stated above, and performing painting of the photosensitive resin layer to a temporary support top by application using the coater which has a slit shaped nozzle among the above. That is, a photosensitive resin layer is formed by the slit coat method performed into the portion which discharges liquid using the slit shaped nozzle which has a slit shape hole. By using a slit shaped nozzle, the stratification of uniform thickness is more possible.
[0137]
Specifically JP,2004-89851,A, JP,2004-17043,A, The slit shaped nozzle and slit coating machine of a description are preferably used for JP,2003-170098,A, JP,2003-164787,A, JP,2003-10767,A, JP,2002-79163,A, JP,2001-310147,A, etc.
[0138]
The 1st sheet that provided the thermoplastic resin layer and the intermediate layer sequentially from this temporary support side on temporary support besides depending above, It is also producible by preparing the 2nd sheet that provided the photosensitive resin layer on a protective

film, and sticking so that the intermediate-layer surface of the 1st sheet and the surface of a photosensitive resin layer may touch. The 1st sheet that provided the thermoplastic resin layer on temporary support, and the 2nd sheet that provided the photosensitive resin layer and the intermediate layer sequentially from this protective film side on the protective film are prepared, It is also producible by sticking so that the intermediate-layer surface of the 1st sheet and the surface of the thermoplastic resin layer of the 2nd sheet may touch.

[0139]

Since the transfer material of the present invention is what provides the photosensitive resin layer which contains metal particles and/or metallic-compounds particles, has high black density with a thin film, and was excellent in the light sheilding as mentioned already, It is preferable for the use as which an advanced light sheilding is required, and preferable for formation of the light-shielding film represented by especially the black matrix etc.

[0140]

<A manufacturing method of a light-shielding film>

A way the manufacturing method of the light-shielding film of the present invention applies soon the photosensitive resin composition for light-shielding films of the present invention as stated above on a substrate (the applying method), Or a light-shielding film is produced by the method (replica method) of transferring on a substrate the photosensitive resin layer of the transfer material once constituted using the photosensitive resin composition for light-shielding films of the present invention as stated above.

[0141]

The photosensitive resin composition for light-shielding films of the present invention is used for the light-shielding film produced by the manufacturing method of the light-shielding film of the present invention, and since, black density is highly excellent in a light sheilding with a thin film. Therefore, it is preferable for the use asked for thin films, such as a black matrix, and in that case, the range of 0.2-1.3 micrometers is preferable, and the range which is 0.3-0.8 micrometer is more nearly preferable.

[0142]

The manufacturing method of the first light-shielding film of the present invention is based on the applying method. Namely, the process (application process) of applying the photosensitive resin composition for light-shielding films of the present invention as stated above, and making it drying and forming a photosensitive resin layer on a substrate, It constitutes from a process (pattern exposure process) of exposing the photosensitive resin layer formed by the application process to pattern form, a process (heating step) of heating the photosensitive resin layer formed by the application process, and a process (developing process) of developing the photosensitive resin layer after exposure at least, and removing an unexposed part.

[0143]

The manufacturing method of the second light-shielding film of the present invention is based on a replica method. Namely, the process (transfer process) of transferring the photosensitive resin layer of at least one layer on temporary support to a substrate using the transfer material of the present invention as stated above, It constitutes from a process (pattern exposure process) of exposing the photosensitive resin layer transferred by the transfer process to pattern form, a process (heating step) of heating the photosensitive resin layer transferred by the transfer process, and a process (developing process) of developing the photosensitive resin layer after exposure at least, and removing an unexposed part.

The pattern exposure process in a replica method, a heating step, and a developing process can

be performed like the case of the aforementioned applying method.
After an application process or a transfer process, any may be previous processes, a pattern exposure process and a heating step may be simultaneous processes, and any may be previous processes and a heating step and a developing process may be simultaneous processes.
[0144]
Hereafter, it describes about each process.
- Application process -
In the application process in the applying method, on the substrate which is a coated object, the photosensitive resin composition for light-shielding films of the present invention as stated above is applied, it is made to dry and a photosensitive resin layer is formed. The coating method generally learned, for example, a dip coating method, the air-knife-coat method, the curtain coat method, the wire bar coat method, the gravure coating method, an extrusion die coating method, the slit coat method, etc. are applicable to application.
[0145]
Especially, the slit coat method performed into the portion which discharges liquid using the slit shaped nozzle which has a slit shape hole is preferable, and can apply preferably using the coater (slit coating machine) which has a slit shaped nozzle.
The thickness of the light-shielding film obtained eventually should just choose the coating thickness suitably in the aforementioned range and the becoming range.
[0146]
A glass plate with a preferable for example, transparent base, publicly known soda glass board, low thermal expansion glass, non alkaline glass, quartz glass plate which have a silicon-oxide coat on the surface, etc., or a plastics film can be mentioned to the aforementioned substrate. The substrate can make good adhesion between the photosensitive resin layers of the constituent of the present invention, or the transfer material of the present invention by performing coupling processing previously. As coupling processing, the method of a JP,2000-39033,A description is used preferably.
[0147]
- Transfer process -
In the transfer process in a replica method, the photosensitive resin layer of at least one layer currently provided on temporary support is transferred to a substrate using the transfer material of the present invention as stated above.
[0148]
Transfer of the photosensitive resin layer to a substrate After washing the transferred surface (it is the forming face when the precedent pattern and the thin film are already formed) of a substrate, The strip of the protective film is carried out from a transfer material, the cleaning surface of a substrate and the surface of the photosensitive resin layer which the transfer material exposed are stuck under heat pressing by the heating roller of a laminating machine, and are made into a laminated body, temporary support is exfoliated from this laminated body, and it transfers on a substrate. The laminating machine can choose a commercial laminating machine suitably.
[0149]
As for the temperature of the heating roller at the time of transfer, 50 degrees C - 150 degrees C are preferable, and the linear pressure at the time of sticking by pressure has 5 kg/cm - preferable 25 kg/cm. As for lamination speed, the amount of 0.2-4-m/is preferable at a conveying speed.
It is a part for heat crimping roll temperature [of 130-140 degrees C], linear pressure [at the

time of sticking by pressure] 10 - 15 kg/cm, and conveying speed/of 1-3 m using the heat crimping roll which can be especially heated with application of pressure as preferable conditions.

[0150]

- Pattern exposure process -

In a pattern exposure process, the photosensitive resin layer formed by the application process or the transfer process is exposed to pattern form. This process may be performed as a previous process of the below-mentioned heating step, and may be performed as a post process of a heating step, and can be performed simultaneously with a heating step.

[0151]

Exposure can be performed by irradiating the formed photosensitive resin layer via the mask of a predetermined pattern, and it forms a latent image so that a desired pattern may be obtained, when it passes through the below-mentioned developing process. That is, in an exposure region, acid (H^+) is generated from a photo-oxide generating agent, crosslinking reaction is carried out between binder resin and a cross linking agent by the catalysis of acid, a bridging body is formed, and polymerization curing is carried out to pattern form.

[0152]

As a light source, for example g line (wavelength of 436 nm), i line (wavelength of 365 nm), Charged particle beams, such as X-rays, such as far ultraviolet rays, such as ultraviolet rays of the continuous state from publicly known light sources, such as an ultrahigh pressure mercury lamp, xenon light, a carbon arc lamp, and an argon laser, and/or the shape of a luminescent line and a KrF excimer laser, and a synchrotron radiation line, and an electron beam, etc. are mentioned. Especially, g line, i line, and the ultraviolet rays of the 300-440-nm wavelength zone containing these are preferable. Like the description to JP,H6-59119,A, light transmittance with a wavelength of not less than 400 nm may use together the light filter etc. which are 2% or less.

[0153]

- Heating step -

In a heating step, heating (bake) processing is performed at the time of pattern exposure after pattern exposing by the aforementioned pattern exposure process. By heating the exposure region by which pattern exposure was carried out after crosslinking reaction's beginning under existence of the acid by which it was generated at the time of pattern exposure, diffusion of acid is promoted, it is urged to crosslinking reaction toward a thickness direction near the surface of a photosensitive resin layer, and polymerization curing of a photosensitive resin layer is performed good to the film depths. In the present invention, since the formed photosensitive resin layer is constituted by the thin film, unnecessary diffusion (for example, diffusion to the transverse direction to the longitudinal direction which is a thickness direction, etc.) of acid can be suppressed, and it can prevent ****** of a pattern, and can obtain the small-gage wire of high resolution.

[0154]

This process can be performed as a previous process of the above-mentioned pattern exposure process, can also be performed as a post process of a pattern exposure process, and can be performed to a pattern exposure process and coincidence (it includes heating from before pattern exposure.). This process may be performed as a previous process of the below-mentioned developing process, and may be performed as a post process of a developing process, and can be performed simultaneously with a developing process. Although the photosensitive resin layer has disappeared photosensitivity after development, it may describe as a photosensitive resin layer in

view of simplification of a description in this Description.
[0155]
Although the conditions of baking treatment change with a photo-oxide generating agent, cross linking agents, etc., 15 seconds - their 1 minute are preferably public at 100-120 degrees C preferably 80-140 degrees C for 15 seconds - 3 minutes.
[0156]
- Developing process -
In a developing process, when a heating step is provided after exposure and to a previous process, the development of the photosensitive resin layer after heating is carried out, development removal of the unexposed part is carried out, and a pattern is actualized. It is preferable to perform development using a weak alkali developing solution under the temperature of 26-40 degrees C and the conditions of pH 9-11.
[0157]
This developing process is provided in order to mainly give patternizing by the development of a photosensitive resin layer, but. When a photosensitive resin layer is formed according to the transfer process in a replica method, Since it is in the state where the thermoplastic resin layer and the intermediate layer were laminated with the photosensitive resin layer, it is desirable to comprise first alkaline development for removing a thermoplastic resin layer and an intermediate layer and second alkaline development for removing the unexposed part of a photosensitive resin layer.
[0158]
In this case, first alkaline development is performed using a weak alkali developing solution under the temperature of 26-40 degrees C, and the conditions of pH 9-11, and, as for second alkaline development, it is preferable to carry out using a weak alkali developing solution under the temperature of 26-40 degrees C and the conditions of pH 9-11 like the above.
[0159]
As a developing solution for photosensitive resin layer development, the thin aqueous solution of an alkaline substance can be used and what added a little water and organic solvents of miscibility further to this may be used.
as a suitable alkaline substance -- alkali metal hydroxide (an example and sodium hydroxide --) A potassium hydrate, alkali metal carbonate (an example, sodium carbonate, potassium carbonate), Alkali metal bicarbonate (an example, sodium bicarbonate, potassium bicarbonate), Alkali metal silicates (an example, a sodium silicate, a potassium silicate), Alkaline metal metasilicates (an example, metasilicic acid sodium, metasilicic acid potassium), Ammonia, ethylamine, n-propylamine, diethylamine, Triethylamine, methyldi ethylamine, dimethylethanolamine, Triethanolamine, diethanolamine, monoethanolamine, morpholine and tetra alkyl AMMONNIUMU hydroxide (for example, tetramethylammonium hydroxide --) Tetraethylammoniumhydroxide, pyrrole, piperidine, 1,8-diazabicyclo [5,4,0]-7-undecene, 1,5-diazabicyclo [4, 3, 0]-5-nonane, or trisodium phosphate can be mentioned.
[0160]
As water and an organic solvent of miscibility, for example Methanol, ethanol, 2-propanol, 1-propanol, butanol, diacetone alcohol, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, Ethylene glycol mono-n-butyl ether, benzyl alcohol, Acetone, methyl ethyl ketone, cyclohexanone, epsilon-caprolactone, Gamma-butyrolactone, dimethylformamide, dimethylacetamide, hexamethylphosphoramide, ethyl lactate, methyl lactate, epsilon caprolactam, N-methyl pyrrolidone, etc. can be mentioned preferably. The concentration of

water and the organic solvent of miscibility has the common 0.1 - 30 mass %.
[0161]
To a developing solution, a still more publicly known anionic form or an Nonion type surfactant can be added. The concentration of a surfactant has the preferable 0.01 - 10 mass %. A developing solution can be used as bath liquid or spray liquid, and can use a liquid peak method, a dipping method, swing dip coating, a spray method, etc. about a developing method.
[0162]
This process may be performed as a previous process of the aforementioned heating step, and may be performed as a post process of a heating step, and may be performed simultaneously with a heating step.
[0163]
Like previous statement, by using the photosensitive resin composition for light-shielding films of the present invention, it has high concentration with a thin film, and the light-shielding film of high resolution can be obtained. It is useful although the black matrix (a black matrix here is a black part arranged between pixels, and there are a thing etc. stripe shape and in the shape of a lattice.) of the liquid crystal display element (especially color filter) which constitutes a display device especially is obtained. It is also the same as when based on the transfer material of the present invention, and the manufacturing method of a light-shielding film.
[0164]
The black matrix needs to have not only a light sheilding but electric insulation from the necessity colored to the liquid crystal cell which performs liquid crystal display of performing voltage impressing for every pixel. Specifically, as for the volume resistance value of a black matrix, it is preferable to hold more than $1x10^8$ omega-cm. Although electric field are built over liquid crystal layer surface inboard by an IPS system, if the electrical resistance of the black matrix of a counter substrate is in the aforementioned range, electric field can be applied normally, and the display which has neither disorder nor display unevenness in liquid crystal orientation is attained. Therefore, the black matrix used for the liquid crystal display of an IPS system not only needs to have a high light sheilding, but needs to show high resistance. In order to make a volume resistance value into the aforementioned range, it is preferable that a black matrix shall be consisted of the particles and polymer of 1 or more ohm-cm of volume resistance values, and the surface roughness of this black matrix shall be 100 A or less.
[0165]
A volume resistance value shows an unit area and the resistance per unit length here, It asks from a current value when predetermined voltage is applied to the electrode surface provided like measurement of polymer volume resistivity by the upper and lower sides of the application membrane of the photosensitive resin composition for light-shielding films which make a black matrix by a 3 terminal method with a guard ring. The counterelectrode which was formed on the substrate and which opposes mutually may be covered with the photosensitive resin composition for light-shielding films, predetermined voltage may be applied between this counterelectrode, and it may ask based on a current value and electrode shape.
[0166]
Not less than 80% of the voltage retention of a black matrix is preferable, and is not less than 90% more preferably. Impurities, such as ionic matter, elute in a liquid crystal that aforementioned voltage retention is within the limits, there is no generating of the white unevenness in accordance with the ionic matter to a liquid crystal layer mixing etc., etc., and a good display image is obtained. In order to make voltage retention into not less than 80%, it is

preferable to adjust the quantity of the photo-oxide generating agent used at the time of formation of a black matrix, heating conditions, etc., and to raise a degree of cross linking. making voltage retention into not less than 80% -- especially, even if it is the prolonged display under a display condition with severe high-humidity/temperature etc., generating of display failures, such as printing and white unevenness, is prevented, and the liquid crystal display excellent in display quality becomes possible.
[Working example]
[0167]
Hereafter, although the present invention is described according to an working example, the present invention is not limited to these working examples. The "part" in an working example is a mass basis.
[0168]
(Working example 1)
(1) Production of a photosensitive transfer sheet
The 100-micrometer-thick polyethylene terephthalate film (PET temporary support) was prepared, on this PET temporary support, the coating liquid which consists of the following composition was applied and dried, and dry layer thickness formed the thermoplastic resin layer which is 20 micrometers.
[0169]
<Composition of thermoplastic resin layer ********>
- Methyl methacrylate / 2-ethylhexyl acrylate / benzyl methacrylate / methacrylic acid (=55/11.7/4.5/28.8 [mole ratio]) copolymer -- 15 copies
(Weight average molecular weight 90000)
- Polypropylene-glycol diacrylate
(Average molecular weight 822) -- 6.5 copies
- Tetraethylene glycol dimethacrylate -- 1.5 copies
- P-toluenesulfonamide -- 0.5 copy
- Benzophenone -- 1.0 copy
- Methyl ethyl ketone -- 30 copies
[0170]
Subsequently, on the thermoplastic resin layer formed from the above, the coating liquid which consists of the following composition was applied and dried, and dry layer thickness formed the intermediate layer who is 1.6 micrometers.
[0171]
<Composition of intermediate layer coating liquid>
- Polyvinyl alcohol
(PVA-205, 80% of a saponification value, Kuraray Make) -- 130 copies
- Polyvinyl pyrrolidone -- 60 copies
(Product made from GAF condominium RESHON PVP K-90)
- Fluorochemical surfactant
(The Sir chlorofluocarbon S-131, Asahi Glass Co., Ltd. make) -- Ten copies
- Distilled water -- 3350 copies
[0172]
Subsequently, the coating liquid for black-photosensitive-resin layers which consists of the following composition was prepared, this coating liquid for black-photosensitive-resin layers is further applied on an intermediate layer, was dried, and dry layer thickness formed the black-

photosensitive-resin layer of the Ag particle content which is 0.60 micrometer. Then, the polypropylene film was stuck on the surface of a black-photosensitive-resin layer as a protective film. The transmitted light study concentration of the obtained black-photosensitive-resin layer was 4.0, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 6.7. The photosensitive transfer sheet of the present invention constituted by the laminated structure of PET temporary support / thermoplastic resin layer / intermediate layer / black-photosensitive-resin layer / protective film as mentioned above was produced.
[0173]
In this example, it asked for transmitted light study concentration as follows.
Measure the transmitted light study concentration (OD) of a photosensitive transfer sheet (with no protective film) on the wavelength of 555 nm using spectrophotometer UV-2100 (made by Shimadzu Corp.), and. The value (penetration OD;=OD-OD^0) which deducted OD^0 from OD obtained by measuring the transmitted light study concentration (OD^0) of the PET temporary support in which the thermoplastic resin layer and intermediate layer in front of the black-photosensitive-resin stratification were furthermore formed in a similar way was made into transmitted light study concentration.
[0174]
<Composition of the coating liquid for black-photosensitive-resin layers>
- Methacrylic acid / benzyl methacrylate copolymer -- 19.98 copies
(Mole ratio: 28/72, weight-average-molecular-weight:30000)
- Cross linking agent (MW-30M, made in Sanwa Chemical) -- 4.76 copies
- Ag particle (mean particle diameter of 80 nm) -- 51.3 copies
- Surfactant -- 0.17 copy
(The Dainippon Ink & Chemicals, Inc. make, F177P)
- Photo-oxide generating agent -- 2.38 copies
(2,4-bis(trichloro)-6,4-[4-N,N-diethoxycarbomethyl)-3-bromophenyl-s-triazine
- Methyl ethyl ketone -- 106.80 copies
- Propylene-glycol-monomethyl-ether acetate
-- 44.70 copies
[0175]
(2) Image formation by a replica method
A protective film from the photosensitive transfer sheet obtained from the above the surface of peel-off and the exposed black-photosensitive-resin layer, the surface of a 1.1-mm-thick glass substrate is touched -- as -- a laminator (a LamicII type --) Lamination and PET temporary support were exfoliated on condition of 130 degrees C, 0.2 m/min, and 10 kg/cm using Made in Hitachi Industries, the black-photosensitive-resin layer was transferred with the thermoplastic resin layer and the intermediate layer, and the black-photosensitive-resin layer of optical density 4.0 obtained the glass substrate by which transfer formation was carried out.
[0176]
Then, it exposes to pattern form in 400 mj/cm^2 via a photo mask on the surface of this black-photosensitive-resin layer, After it finished exposure and 1 minute passed, on the hot plate heated by 140 degrees C, as it touched, it placed in the glass substrate surface, and heat-treatment (after-exposure bake) was performed for 12 seconds.
[0177]
10 time dilution liquid of alkali developing solution T-PD2 for removal of after after-exposure

bake, a thermoplastic resin layer, and an intermediate layer (made by Fuji Photo Film Co., Ltd.) (33 degrees C) Development removal of a thermoplastic resin layer and the intermediate layer is carried out using pH=10.7, After carrying out rinsing treatment furthermore, continuously, the unexposed part of the black-photosensitive-resin layer was developed using the 5 time dilution liquid (33 degrees C, pH=9.9) of alkali developing solution T-CD (made by Fuji Photo Film Co., Ltd.), rinsing treatment was performed, and the black image of the light sheilding was formed on the glass substrate.

[0178]

(3) Evaluation

It evaluates by measuring as follows and the result of measurement and evaluation is shown in the following table 1.

-1. resolution -

Pattern exposure was carried out using the mask which has a pattern of the form line which becomes narrow for every 2-micrometer interval to 50 micrometers - 4 micrometers about the above-mentioned black-photosensitive-resin layer similarly formed by carrying out transfer formation of the black-photosensitive-resin layer on the glass substrate using the photosensitive transfer sheet obtained from the above. Then, the linewidth (micrometer) of the above-mentioned portion in which the development was similarly performed and the line remains was measured using the optical microscope, and this was made into resolution. It is shown that the one where a value is smaller is excellent in resolution.

[0179]

-2. display Mullah

To the glass substrate in which the black image was formed, the colored pixel was formed as follows, it was considered as the color filter, and the thickness measurement using a laser beam microscope etc. estimated the existence of the projection. When image display of the projection here is carried out, it serves as a cause which starts display unevenness.

A lapped part of a colored pixel when a colored pixel is provided, and a black image serves as a corniform projection, and it occurs.

[0180]

<Production of a color filter>

- Production of a photosensitive resin transfer material -

On 75-micrometer-thick polyethylene terephthalate film temporary support (PET temporary support), the slit shaped nozzle was used, the coating liquid for cushion layers which consists of the following formula H1 was applied and dried, and the cushion layer was formed. Next, the intermediate layer coating liquid which consists of the following formula P1 was applied and dried on this cushion layer, and the intermediate layer (oxygen interception film) was laminated. The following table 1 was made to apply and dry further the coloring photosensitive resin composition R2 which consists of composition of a description on this intermediate layer, and the photosensitive resin layer was laminated. Thus, on PET temporary support, the thermoplastic resin layer whose dry membrane thickness is 14.6 micrometers, the intermediate layer whose dry membrane thickness is 1.6 micrometers, and dry membrane thickness provided the photosensitive resin layer which is 2.4 micrometers, and stuck the protective film (12-micrometer polypropylene film in thickness) by pressure on the photosensitive resin layer.

[0181]

[Table 1]

着色感光性樹脂組成物	R1	G1	B1	R2	G2	B2
R顔料分散物1 (C. I. P. R. 254)	44	-	-	44	-	-
R顔料分散物2 (C. I. P. R. 177)	5.0	-	-	5.0	-	-
G顔料分散物1 (C. I. P. G. 36)	-	24	-	-	24	-
Y顔料分散物1 (C. I. P. Y. 150)	-	13	-	-	13	-
B顔料分散物1 (C. I. P. B. 15:6 + C. I. P. V. 23)	-	-	8.0	-	-	7.2
B顔料分散物2 (C. I. P. B. 15:6)	-	-	14.4	-	-	13
プロピレングリコールモノメチルエーテルアセテート	7.6	29	28	7.6	29	23
メチルエチルケトン	37	26	41	37	26	35
シクロヘキサノン	-	1.3	-	-	1.3	-
バインダー1	-	2.5	-	-	3	-
バインダー2	0.7	-	-	0.8	-	-
バインダー3	-	-	19	-	-	17
DPHA液	3.8	3.5	4.2	4.4	4.3	3.8
2-トリクロロメチル-5-(p-スチリルメチル)1, 3, 4-オキサジアゾール	0.12	0.1	0.17	0.14	0.15	0.15
2, 4-ビス(トリクロロメチル)-6-[4-(N, N-ジエトキシカルボニルメチル)-3-ブロモフェニル]-s-トリアジン	0.050	0.050	-	0.058	0.060	-
フェノチアジン	0.010	0.005	0.020	0.010	0.005	0.020
添加剤1	-	-	-	0.52	-	-
界面活性剤1	0.060	0.070	0.060	0.060	0.070	0.050

質量部

[0182]
The photosensitive resin transfer material which temporary support, the thermoplastic resin layer, the intermediate layer (oxygen interception film), and the red photosensitive resin layer were laminated as mentioned above, and was constituted by the laminated body was produced (the photosensitive resin transfer material R2 is called hereafter).
[0183]
[The formula H1 of the coating liquid for cushion layers]
- Methanol -- 11.1 copies
- Propylene-glycol-monomethyl-ether acetate -- 6.4 copies
- Methyl ethyl ketone -- 52.4 copies
- Methyl methacrylate / 2-ethylhexyl acrylate / benzyl methacrylate / methacrylic acid copolymer -- 5.83 copies
[Copolymerization ratio (mole ratio) =55/11.7/4.5/28.8, weight-average-molecular-weight =100,000, Tgnearly equal to70 degree C]
- Styrene/acrylic acid copolymer -- 13.6 copies
[Copolymerization ratio (mole ratio) =63/37, weight-average-molecular-weight =10,000,

Tgnearly equal to100 degree C]
- Compound (the Shin-Nakamura Chemical Co., Ltd. make, 2,2-bis[4-(methacryloxy-polyethoxy) phenyl] propane) which carried out dehydration condensation of 2 Eq of the pentaethylene glycol monometer cleats to bisphenol A -- 9.1 copies
- Surfactant 1 -- 0.54 copy
[0184]
* Surfactant 1 :
Megger fuck F-780-F (made by Dainippon Ink & Chemicals, Inc.)
[Composition]
- $C_6F_{13}CH_2CH_2OCOCH=CH_2$ (40 copies), $H(O(CH_3)\ CHCH_2)_7OCOCH=CH_2$ (55 copies), and $H(OCH_2CH_2)_7OCOCH=CH_2$. Copolymer with (five copies) (weight average molecular weight 30,000) -- 30 copies
- Methyl isobutyl ketone -- 70 copies
[0185]
[The formula P1 of intermediate layer coating liquid]
- Polyvinyl alcohol -- 2.1 copies
(PVA-205 (saponification value = 88%), Kuraray Make)
- Polyvinyl pyrrolidone -- 0.95 copy
(PVP, K-30;GAF corporation company make)
- Methanol -- 44 copies
- Distilled water -- 53 copies
[0186]
Next, the photosensitive resin transfer material G2 and B-2 were produced by the same method as the above except having replaced the aforementioned coloring photosensitive resin composition R2 used in production of the obtained photosensitive resin transfer material R2 with the coloring photosensitive resin composition G2 and B-2 which consist of composition of the description to the aforementioned table 1.
[0187]
The preparing method of the coloring photosensitive resin composition R2, G2, and B-2 carries out the postscript of the preparing method of the coloring photosensitive resin composition R1, G1, and B1 according to the preparing method of the coloring photosensitive resin composition R1 in the aforementioned table 1, G1, and B1, respectively. In the preparing method of the coloring photosensitive resin composition R1 preparation of the coloring photosensitive resin composition R2, The additive agent 1 of the quantity of the description to the aforementioned table 1 is measured, and it mixes at the temperature of 24 degrees C (**2 degrees C), and was made to stir for 20 minutes in 150r.p.m. before addition of the surfactant 1 after addition of phenothiazin etc.
* Additive agent 1 : phosphoric ester system special active agent (HIPLAAD ED152, made in Kusumoto Chemicals)
[0188]
- Formation of a red (R) pixel -
The exposed photosensitive resin layer the protective film of the aforementioned photosensitive resin transfer material R2 after exfoliating, It piled up so that the surface of a glass substrate in which the light-shielding film (black image of a light sheilding) was formed from the above might be touched, and it laminated on condition of for rubber roller temperature [of 130 degrees C], linear pressure 100 N/cm, and conveying speed/of 2.2 m using the laminator LamicII type

[Made in Hitachi Industries]. Subsequently, it exfoliated and PET temporary support was transferred on the glass substrate.
[0189]
An ultrahigh pressure mercury lamp using the proximity type exposure machine (made by Hitachi Electronics Engineering) which it has Next, a mask (quartz exposure mask which has an image pattern), Where the glass substrate arranged so that this mask and a thermoplastic resin layer may face each other is stood vertically substantially parallel, The distance between the surfaces of the side which touches the intermediate layer of a mask surface and a photosensitive resin layer was set as 200 micrometers, and pattern exposure was carried out by light exposure 40 mJ/cm^2 from the thermoplastic resin layer side via the mask.
[0190]
next, a triethanolamine system developing solution (2.5% of triethanolamine --) A nonionic surface active agent and polypropylene system defoaming agent content; shower development was carried out by flat nozzle pressure 0.04MPa for 50 seconds at 30 degrees C at trade name:T-PD1 and the Fuji Photo Film Co., Ltd. make, and the thermoplastic resin layer and the oxygen interception film were removed.
[0191]
next, a carbonic acid Na system developing solution (0.06 mol/liter of sodium bicarbonate --) Sodium carbonate of the concentration, 1% of dibutyl sodium naphthalenesulfonate, Shower development of an anionic surface active agent, a defoaming agent, and the stabilizer was carried out by corn type nozzle pressure 0.15MPa for 35 seconds at 35 degrees C using content; trade name:T-CD1 and the Fuji Photo Film Co., Ltd. make, and the pattern pixel was obtained.
[0192]
Next, a detergent (phosphate, silicate, a nonionic surface active agent, a defoaming agent, and stabilizer content; trade name:T-SD1, Fuji Photo Film Co., Ltd. make) is used, The red (R) pixel was formed by performing residue removal for 20 seconds using a shower and a rotary brush with nylon hair by corn type nozzle pressure 0.02MPa at 33 degrees C. After carrying out postexposure with the light of 500 mJ/cm^2 with an ultrahigh pressure mercury lamp to this substrate from the side in which K image is formed further after that, it heat-treated for 15 minutes at 220 degrees C.
[0193]
The thickness of R pixel was 2.0 micrometers and the coverage of C.I. pigment red (C. I.P.R.) 254 and C.I.P.R.177 was 0.88g/m^2 and 0.22g/m^2, respectively.
Then, after carrying out brush washing of the glass substrate in which R pixel was formed again using the detergent as mentioned above and carrying out shower washing with pure water, silane coupling liquid was heated for 2 minutes at 100 degrees C with the substrate preheating device, without using it.
[0194]
- Formation of a green (G) pixel -
Next, using the photosensitive resin transfer material G2 obtained from the above, the same process as formation of the aforementioned R pixel was performed, and the green pixel (G pixel) was formed in the side in which the light-shielding film and R pixel of the glass substrate are formed. However, the light exposure in the exposure process carried out shower development by 40mJ/cm^2 and a carbonic acid Na system developing solution for 45 seconds at 34 degrees C, and heat treatment was carried out for 15 minutes at 220 degrees C.
The thickness of G pixel was 2.0 micrometers and the coverage of the C.I. pigment green (C.

I.P.G.) 36 and the C.I. pigment yellow (C. I.P.Y.) 150 was 1.12g/m^2 and 0.48g/m^2, respectively.
[0195]
Then, after carrying out brush washing of the glass substrate in which R pixel and G pixel were formed again using the detergent as mentioned above and carrying out shower washing with pure water, silane coupling liquid was heated for 2 minutes at 100 degrees C with the substrate preheating device, without using it.
[0196]
- Formation of a blue (B) pixel -
Next, using photosensitive resin transfer material B-2 obtained from the above, the same process as formation of the aforementioned R pixel was performed, and the blue pixel (B pixel) was formed in the side in which the light-shielding film, R pixel, and G pixel of the glass substrate are formed. However, the light exposure in the exposure process carried out shower development by 30mJ/cm^2 and a carbonic acid Na system developing solution for 40 seconds at 36 degrees C. The thickness of B pixel was 2.0 micrometers and the coverage of the C.I. pigment blue (C. I.P.B.) 15:6 and the C.I. pigment violet (C. I.P.V.) 23 was 0.63g/m^2 and 0.07g/m^2, respectively.
[0197]
Then, bake of the glass substrate in which each pixel of R, G, and B was formed was carried out for 50 minutes at 240 degrees C, and the color filter was obtained.
[0198]
(Working example 2)
The coating liquid for black-photosensitive-resin layers was prepared like the working example 1. Next, the 1.1-mm-thick glass substrate was prepared, and on this glass substrate, using the slit & spin coater, it applies and the obtained coating liquid for black-photosensitive-resin layers was dried so that dry membrane thickness might be set to 0.60 micrometer, and the black-photosensitive-resin layer was painted.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer here was 4.0, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 6.7.
[0199]
Then, it exposes to pattern form in 400 mj/cm^2 via a photo mask on the surface of the painted black-photosensitive-resin layer, After it finished exposure and 1 minute passed, on the hot plate heated by 140 degrees C, as it touched, it placed in the glass substrate surface, and heat-treatment (after-exposure bake) was performed for 12 seconds.
[0200]
10 time dilution liquid of alkali developing solution T-PD2 for removal of after after-exposure bake, a thermoplastic resin layer, and an intermediate layer (made by Fuji Photo Film Co., Ltd.) (33 degrees C) Development removal of a thermoplastic resin layer and the intermediate layer is carried out using pH=10.7, Furthermore rinsing treatment was carried out, continuously, the unexposed part of the black-photosensitive-resin layer was developed using the 5 time dilution liquid (33 degrees C, pH=9.9) of alkali developing solution T-CD (made by Fuji Photo Film Co., Ltd.), rinsing treatment was performed, and the black image of the light sheilding was formed on the glass substrate. Then, the same evaluation as the working example 1 was performed. However, formation of the color filter was performed as follows.
[0201]
<Production of a color filter (application by a slit & spin coater)>

- Formation of a red (R) pixel -
The coloring photosensitive resin composition R1 which is on the light-shielding film forming face side of the glass substrate in which the light-shielding film (black image of a light sheilding) was formed as mentioned above from composition of the description to the aforementioned table 1 in a slit & spin coater was applied. Then, after drying some solvents for 30 seconds using the vacuum dryer VCD (Tokyo adaptation shrine make) and losing the mobility of application membrane, The unnecessary coating liquid of the circumference of a substrate was removed in EBR (edge bead remover), it prebaked for 3 minutes at 120 degrees C, and the photosensitive resin layer R1 of 2.4 micrometers of thickness was formed.
[0202]
Next, where a mask (quartz exposure mask which has an image pattern), and the glass substrate in which the photosensitive resin layer R1 was provided are vertically stood using the proximity type exposure machine (made by Hitachi Electronics Engineering) provided with the ultrahigh pressure mercury lamp, The distance of Hazama of a mask surface and the surface of the photosensitive resin layer R1 was 200 micrometers, and pattern exposure was carried out by light exposure 150 mJ/cm^2.
Next, after spraying purity from the shower nozzle and making the surface of the photosensitive resin layer R1 become wet uniformly, KOH system developing solution CDK-1 (the product made from Fuji Photo Film Electronics Materials; KOH and nonionic surface active agent content alkali developing solution) was injected for 60 seconds in 23 degrees C and nozzle pressure 0.04MPa from the flat nozzle, shower development was carried out, and the red pattern was obtained. Then, ultrapure water was injected by the pressure of 9.8MPa by the ultra-high pressure washing nozzle to the side in which the red pattern of the glass substrate was formed, residue was removed, and the red (R) pixel was formed on the glass substrate. Then, it heat-treated for 30 minutes at 220 degrees C (bake).
[0203]
The thickness of R pixel was 1.6 micrometers and the coverage of C.I. pigment red (C. I.P.R.) 254 and C.I.P.R.177 was $0.88g/m^2$ and $0.22g/m^2$, respectively.
[0204]
- Formation of a green (G) image -
Next, the coloring photosensitive resin composition G1 which becomes the glass substrate in which the aforementioned light-shielding film and R pixel were formed from the composition shown in the aforementioned table 1 is used, Application, exposure, development, and bake as well as formation of the aforementioned R pixel were performed, and the green pixel (G pixel) was formed in the side in which the light-shielding film and R pixel of the glass substrate are formed. However, the light exposure in the exposure process was made into 150 mJ/cm^2, the shower development in the developing process considered it as 60-second Hazama at 23 degrees C, and heat treatment was set as 30-minute Hazama at 220 degrees C.
[0205]
The thickness of G pixel was 1.6 micrometers and the coverage of the C.I. pigment green (C. I.P.G.) 36 and the C.I. pigment yellow (C. I.P.Y.) 150 was $1.12g/m^2$ and $0.48g/m^2$, respectively.
[0206]
- Formation of a blue (B) image -
To next, the glass substrate in which the aforementioned light-shielding film, R pixel, and G pixel were formed, Using the coloring photosensitive resin composition B1 which consists of composition shown in the aforementioned table 1, application, exposure, development, and bake

as well as formation of the aforementioned R pixel were performed, and the blue pixel (B pixel) was formed in the side in which the light-shielding film, R pixel, and G pixel of the glass substrate are formed. However, the light exposure in the exposure process was made into 150 mJ/cm^2, the shower development in the developing process considered it as 60-second Hazama at 23 degrees C, and heat treatment was set as 30-minute Hazama at 220 degrees C.
[0207]
The thickness of B pixel was 1.6 micrometers and the coverage of the C.I. pigment blue (C. I.P.B.) 15:6 and the C.I. pigment violet (C. I.P.V.) 23 was $0.63g/m^2$ and $0.07g/m^2$, respectively.
[0208]
Then, bake of the glass substrate in which each pixel of R, G, and B was formed was carried out for 50 minutes at 240 degrees C, and the color filter was obtained.
[0209]
Here, it describes about preparation of the coloring photosensitive resin composition R1 of the description to the aforementioned table 1, G1, and B1.
<Preparation of the coloring photosensitive resin composition R1>
The coloring photosensitive resin composition R1 measures R pigment dispersion thing 1, R pigment dispersion thing 2, and propylene-glycol-monomethyl-ether acetate of quantity of the description to the aforementioned table 1, Mix at the temperature of 24 degrees C (**2 degrees C), and in 150r.p.m., stir for 10 minutes and it ranks second, Methyl ethyl ketone of the quantity of the description to the aforementioned table 1, the binder 2, DPHA liquid, 2-trichloromethyl 5-(p-styryl methyl)-1, 3, 4-oxadiazole, 2,4-bis(trichloromethyl)-6-[4-(N,N-diethoxy carbonylmethyl)-3-bromophenyl]-s-triazine, And measure phenothiazin, add in this order at the temperature of 24 degrees C (**2 degrees C), and it stirs for 30 minutes in 150r.p.m., The surfactant 1 of the quantity of the description to the aforementioned table 1 was measured, and it added at the temperature of 24 degrees C (**2 degrees C), stirred for 30 minutes in 30r.p.m., and obtained by filtering by nylon mesh #200.
[0210]
The details of each composition in the constituent R1 of the description to the aforementioned table 1 are as follows. Composition of the surfactant 1 is as stated above.
* Composition of R pigment dispersion thing 1
**C. 254--8.0 copies of I. pigment red
- 5-[3-oxo 2-[4-[3,5-bis(3-diethylamino propylamino carbonyl)phenyl] aminocarbonyl] phenylazo]-BUCHIRO ylamino benz imidazolone -- 0.8 copy
- Polymer [random copolymer (weight average molecular weight 37,000) of benzyl methacrylate/methacrylic acid (= 72/28 [a mole ratio])] -- 8.0 copies
- Propylene-glycol-monomethyl-ether acetate -- 83.2 copies
[0211]
* Composition of R pigment dispersion thing 2
**C. 177--18 copies of I. pigment red
- Polymer [random copolymer (weight average molecular weight 37,000) of benzyl methacrylate/methacrylic acid (= 72/28 [a mole ratio])] -- 12 copies
- Propylene-glycol-monomethyl-ether acetate -- 70 copies
* Composition of the binder 2
- Random copolymer of benzyl methacrylate / methacrylic acid / methyl methacrylate (=38/25/37 [a mole ratio]) (weight average molecular weight 30,000) -- 27 copies
- Propylene-glycol-monomethyl-ether acetate -- 73 copies

* Additive agent 1 : phosphoric ester system special active agent (HIPLAAD ED152, made in Kusumoto Chemicals)
* Composition of DPHA liquid
- Dipentaerythritol hexaacrylate (trade name: KAYARAD DPHA, Nippon Kayaku Co., Ltd. make) -- 76 copies
- Propylene glycol monomethyl ether -- 24 copies
[0212]
<Preparation of the coloring photosensitive resin composition G1>
The coloring photosensitive resin composition G1 measures G pigment dispersion thing 1, Y pigment dispersion thing 1, and propylene-glycol-monomethyl-ether acetate of quantity of the description to the aforementioned table 1, Mix at the temperature of 24 degrees C (**2 degrees C), and in 150r.p.m., stir for 10 minutes and it ranks second, Methyl ethyl ketone of the quantity of the description to the aforementioned table 1, cyclohexanone, the binder 1, DPHA liquid, 2-trichloromethyl 5-(p-styryl methyl)-1, 3, 4-oxadiazole, 2,4-bis(trichloromethyl)-6-[4-(N,N-diethoxy carbonylmethyl)-3-bromophenyl]-s-triazine, And measure phenothiazin, add in this order at the temperature of 24 degrees C (**2 degrees C), and it stirs for 30 minutes in 150r.p.m., The surfactant 1 of the quantity of the description to the aforementioned table 1 was measured, and it added at the temperature of 24 degrees C (**2 degrees C), stirred for 5 minutes in 30r.p.m., and obtained by filtering by nylon mesh #200.
[0213]
The details of each composition in the constituent G1 of the description to the aforementioned table 1 are as follows. It is as the previous statement about composition of DPHA liquid and the surfactant 1.
* Composition of G pigment dispersion thing 1
**C. 36--18 copies of I. pigment green
- Polymer [random copolymer (weight average molecular weight 37,000) of benzyl methacrylate/methacrylic acid (= 72/28 [a mole ratio])] -- 12 copies
- Cyclohexanone -- 35 copies
- Propylene-glycol-monomethyl-ether acetate -- 35 copies
* Y pigment dispersion thing 1
Trade name: CF yellow EX3393 (made by a country pigment company)
* Binder 1
- Polymer [random copolymer (molecular weight 40,000) of benzyl methacrylate/methacrylic acid (= 78/22 [a mole ratio])] -- 27 copies
- Propylene-glycol-monomethyl-ether acetate -- 73 copies
[0214]
<Preparation of the coloring photosensitive resin composition B1>
The coloring photosensitive resin composition B1 measures B pigment dispersion thing 1, B pigment dispersion thing 2, and propylene-glycol-monomethyl-ether acetate of quantity of the description to the aforementioned table 1, Mix at the temperature of 24 degrees C (**2 degrees C), and in 150r.p.m., stir for 10 minutes and it ranks second, Methyl ethyl ketone of the quantity of the description to the aforementioned table 1, the binder 3, DPHA liquid, Measure 2-trichloromethyl 5-(p-styryl methyl)-1,3,4-oxadiazole and phenothiazin, and it adds in this order at the temperature of 25 degrees C (**2 degrees C), Further, the surfactant 1 of the quantity of the description to the aforementioned table 1 was measured, and it added at the temperature of 24 degrees C (**2 degrees C), stirred [it stirred for 30 minutes in 150r.p.m. with the temperature of

40 degrees C (**2 degrees C), and] for 5 minutes in 30r.p.m., and obtained by filtering by nylon mesh #200.
[0215]
The details of each composition in the constituent B1 of the description to the aforementioned table 1 are as follows. It is as the previous statement about composition of DPHA liquid and the surfactant 1.
* B pigment dispersion thing 1
Trade name: CF blue EX3357 (made by a country pigment company)
* B pigment dispersion thing 2
Trade name: CF blue EX3383 (made by a country pigment company)
* Composition of the binder 3
- Random copolymer of benzyl methacrylate / methacrylic acid / methyl methacrylate (=36/22/42 [a mole ratio]) (weight average molecular weight 30,000) -- 27 copies
- Propylene-glycol-monomethyl-ether acetate -- 73 copies
[0216]
(Working example 3)
In the working example 2, the black image of the light sheilding was formed on the glass substrate like the working example 2 except having replaced the slit & spin coater with coating-machine MH-1600 [provided with the slit shaped nozzle] (made in F Ey S Japan) for glass substrates.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration per unit thickness (thickness of transmitted light study concentration / black-photosensitive-resin layer) was 6.7. The same evaluation as the working example 1 was performed. However, formation of the color filter was performed as follows.
[0217]
<Production of a light filter (production by the application using a slit shaped nozzle)>
It is made to be the same as that of the working example 2 except having replaced the slit & spin coater with coating-machine MH-1600 [provided with the slit shaped nozzle] (made in F Ey S Japan) for glass substrates in production of the color filter of the working example 2, The color filter was formed in the glass substrate in which the light-shielding film (black image of a light sheilding) obtained from the above was formed.
[0218]
(Working example 4)
In the working example 1, 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers>, 41 copies of Ag particles (mean particle diameter of 80 nm), and carbon black (CB) Replace with 1.76 copies (addition volume ratio (Ag/CB) = 80/20), and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 0.70 micrometer.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration per unit thickness (thickness of transmitted light study concentration / black-photosensitive-resin layer) was 5.7. The same evaluation as the working example 1 was performed.
[0219]
(Working example 5)

In the working example 1, 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers>, 25.7 copies of Ag particles (mean particle diameter of 80 nm), and carbon black (CB) Replace with 4.4 copies (addition volume ratio (Ag/CB) = 50/50), and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 0.90 micrometer.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration per unit thickness (thickness of transmitted light study concentration / black-photosensitive-resin layer) was 4.4. The same evaluation as the working example 1 was performed.
[0220]
(Working example 6)
In the working example 1, 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers>, 10.3 copies of Ag particles (mean particle diameter of 80 nm), and carbon black (CB) Replace with 7.04 copies (addition volume ratio (Ag/CB) = 20/80), and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 1.00 micrometers.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration per unit thickness (thickness of transmitted light study concentration / black-photosensitive-resin layer) was 4.0. The same evaluation as the working example 1 was performed.
[0221]
(Working example 7)
In the working example 1, replace 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers> with 51.3 copies of the silver / silver sulfide core shell particles (mean particle diameter of 90 nm) which were obtained from the following, and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 0.80 micrometer.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 3.9, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 4.9. The same evaluation as the working example 1 was performed.
[0222]
<Production of silver / silver sulfide core shell particles>
0.95g added to 200 g of the silver granule child's acetone dispersed matters (mean particle diameter of 30 nm, concentration 2.5 mass %), and vinyl pyrrolidone/vinyl acetate copolymer (= 60/40 [a mass ratio], weight average molecular weight 5000) was stirred for 30 minutes to them. Subsequently, stirring, the sodium sulfide aqueous solution (23 degrees C) of the concentration 7.2 mass % was added to this so that the metaled rate of sulfuration might be 30%, stirring was performed to it for 30 minutes as it was after the end of addition, and silver / silver sulfide core shell particles with the shell of a silver sulfide were obtained.
Here, the rate of sulfuration is the ratio, sulfuration [metal particles], and 0% of the rate of sulfuration expresses the state where the whole particle is a sulfide completely 100% about the state, sulfuration at all.

[0223]
(Working example 8)
In the working example 1, replace 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers> with 51.3 copies of Sn particles (the mean particle diameter of 36 nm, 20 nm of minor axes, 50 nm of major axes), and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 0.90 micrometer.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 4.4. The same evaluation as the working example 1 was performed.
[0224]
(Working example 9)
In the working example 1, replace 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers> with 51.3 copies of Ag particles (the mean particle diameter of 117 nm, 60 nm of minor axes, 180 nm of major axes), and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 0.80 micrometer.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 5.0. The same evaluation as the working example 1 was performed.
[0225]
(Comparative example 1)
In the working example 1, replace the Ag particle (51.3 copies) under <composition of the coating liquid for black-photosensitive-resin layers> with carbon black (21.17 copies), and replace methacrylic acid / benzyl methacrylate copolymer with an acrylic resin, and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 1.50 micrometers.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 3.5, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 2.3. The same evaluation as the working example 1 was performed.
[0226]
[Table 2]

実施例1	(転写法)	Ag粒子	100%	0%	80			0.60	12	4.0	6.7
実施例2	(塗布法) ｽﾘｯﾄ& ｽﾋﾟﾝｺｰﾄ	Ag粒子	100%	0%	80			0.60	12	4.0	6.7
実施例3	(塗布法) ｽﾘｯﾄｺｰﾄ	Ag粒子	100%	0%	80			0.60	12	4.0	6.7
実施例4	(転写法)	Ag粒子	80%	20%	80			0.70	12	4.0	5.7
実施例5	(転写法)	Ag粒子	50%	50%	80			0.90	12	4.0	4.4
実施例6	(転写法)	Ag粒子	20%	80%	80			1.00	12	4.0	4.0
実施例7	(転写法)	銀-硫化銀 ｺｱｼｪﾙ	100%	0%	90			0.80	12	3.9	4.9
実施例8	(転写法)	Sn粒子	100%	0%	36	20	50	0.90	12	4.0	4.4
実施例9	(転写法)	Ag粒子	100%	0%	117	60	180	0.80	12	4.0	5.0
比較例1	(転写法)	—	0%	100%	—			1.50	30	3.5	2.3

※　添加体積比(%)の計算は、銀の比重を10．5とし、カーボンブラックの比重を1．8とし、その他を1．0として行

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[0227]
As shown in the aforementioned table 2, in the working example, performing after-exposure bake for a short time, the black image of high resolution could be formed, and the formed black image has the high concentration of 4.0, and was also able to raise the concentration per unit volume. There is also no display unevenness and the good display image was obtained.
On the other hand, in the comparative example 1 which constituted only carbon black not using metal particles, it became obtaining it being not only low but this concentration with the thick film, and after-exposure bake took the long time to the concentration of the black image, and it was inferior also to the resolution of the formed black image, and display unevenness.
[0228]
In addition to the above-mentioned working example, it is also the same as when it is made to heat before exposure (bake), and it is also the same as when it is made to heat after developing negatives after exposure (bake).

[Translation done.]

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	1	2007-514182	JP	A	2008-05-31	Punsalan et al.	corresponds to WO 2005/043246	☐
	2	10-2008-7010346	KR		2008-10-08	Keszler et al.	corresponds to US 2011/0045406	☐
	3	2005/043246	WO		2005-05-12	Punsalan et al.		☐

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Receipt date: 07/10/2013	Application Number	12850867	12850867 - GAU: 1722
INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99**)	Filing Date	2010-08-05	
	First Named Inventor	Jason K. Stowers	
	Art Unit	1781	
	Examiner Name	Nicole T. Gugliotta	
	Attorney Docket Number	5063.02US02	

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	1	Office Action from copending Korean Application No. 10-2011-0052919 dated March 14, 2013 ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./	☐

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Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	09/09/2013								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
	8	✓								
	9	✓								
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CLAIM		DATE								
Final	Original	09/09/2013								
	37	-								
	38	-								

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

CPC- SEARCHED		
Symbol	Date	Examiner

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner
430	270.1, 302, 322, 325, 326, 942	09/09/2013	CR

SEARCH NOTES		
Search Notes	Date	Examiner
East, Assignee, IDS asnd Inventorship Search	09/09/2013	CR

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1783
Examiner Name	Gugliotta, Nicole T.
Attorney Docket Number	5063.02US02

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	3385915		1968-05-28	Hamling	
	2	5025094		1991-06-18	King	
	3	6183716	B1	2001-02-06	Sleight et al.	
	4	6197896	B1	2001-03-06	Aviram et al.	
	5	6583071	B1	2003-06-24	Weidman et al.	
	6	6844604	B2	2005-01-18	Lee et al.	
	7	6927108	B2	2005-08-09	Weng et al.	
	8	6946677	B2	2005-09-20	Ostergard	

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Receipt date: 08/15/2011	Application Number	12850867 12850867 - GAU: 1722
INFORMATION DISCLOSURE STATEMENT BY APPLICANT	Filing Date	2010-08-05
(Not for submission under 37 CFR 1.99)	First Named Inventor	Jason K. Stowers
	Art Unit	1783
	Examiner Name	Gugliotta, Nicole T.
	Attorney Docket Number	5063.02US02

	9	7208341	B2	2007-04-24	Lee et al.	
	10	7773365	B2	2010-08-10	Herman et al.	

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	1	20050242330	A1	2005-11-03	Herman et al.	
	2	20060088962	A1	2006-04-27	Herman et al.	
	3	20080286683	A1	2008-11-20	Brodsky et al.	
	4	20100044698	A1	2010-02-25	Herman et al.	
	5	20110045406	A1	2011-02-24	Keszler et al.	

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	First Named Inventor	Jason K. Stowers	
	Art Unit	1783	
	Examiner Name	Gugliotta, Nicole T.	
	Attorney Docket Number	5063.02US02	

	1	2008/082448	WO	A1	2008-07-10	Keszler et al.		☐
	2	2009/120169	WO	A1	2009-10-01	Keszler et al.		☐

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	1	AHMED ET AL., "Synthesis and Characterization of Zirconium and Hafnium Sulfates, Hydroxide Sulfates and Oxide Sulfates", Acta Chemica Scandinavica, 53:24-33 (1999).	☐
	2	International Standard ISO 21348 "Space Environment (natural and artificial) - Process for determining solar irradiances", First Edition 2007, Reference number: ISO 21348:2007(E) (20 pages).	☐
	3	STOWERS, "Direct Patterning of Solution Deposited Metal Oxides", A Dissertation to Oregon State University, August 14, 2008 (149 pages).	☐
	4	STOWERS ET AL., "High resolution, high sensitivity inorganic resists", Microelectronic Engineering, 86:730-733 (2009).	☐
	5	ZHANG ET AL., "Stabilization of Cubic ZrO2 with Rh(III) and/or La(III), Journal of Solid State Chemistry, 72:131-136 (1988).	☐
	6	ZIMMERMAN, "Extension Options for 193nm Immersion Lithography", Journal of Photopolymer Science and Technology, 22(5):625-634 (2009) (Abstract), for full article please see http://www.jstage.jst.go.jp/article/photopolymer/22/5/625/_pdf.	☐

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Examiner Signature	/Chanceity Robinson/	Date Considered	09/08/2013

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4102683		1978-07-25	DiPiazza	
	2	4370405		1983-01-25	O'Toole et al.	
	3	4732841		1988-03-22	Radigan	
	4	4891303		1990-01-02	Garza et al.	
	5	4910122		1990-03-20	Arnold et al.	
	6	5672243		1997-09-30	Hsia et al.	
	7	6020269		2000-02-01	Wang et al.	
	8	6060380		2000-05-09	Subramanian et al.	

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Receipt date: 08/28/2012

INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	12850867 12850867 - GAU: 1722
Filing Date	2010-08-05
First Named Inventor	Stower et al.
Art Unit	1783
Examiner Name	Gugliotta, Nicole T
Attorney Docket Number	5063.02US02

	9	6194323		2001-02-27	Downey et al.	
	10	6268457		2001-07-21	Kennedy et al.	
	11	6287951		2001-09-11	Lucas et al.	
	12	6420088		2002-07-16	Angelopoulos et al.	
	13	6730454		2004-05-04	Pfeiffer et al.	
	14	7001821		2006-02-21	Aggarwal et al.	
	15	7256129		2007-08-14	Nam et al.	
	16	8053370		2011-08-11	Yang et al.	
	17	8092703		2012-01-10	Ishibashi et al.	

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	First Named Inventor	Stower et al.	
	Art Unit	1783	
	Examiner Name	Gugliotta, Nicole T	
	Attorney Docket Number	5063.02US02	

	1	20060234138		2006-10-19	Fehlhaber et al.	
	2	20080055597		2008-03-06	Sun et al.	
	3	20090174036		2009-07-09	Fuller et al.	
	4	20100184259		2010-07-22	Radigan et al.	
	5	20110293888		2011-12-01	Stowers et al.	

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	1	MEYERS ET AL., "Solution-Processed Aluminum Oxide Phosphate Thin-Flim Dielectrics" Chem Mater., 2007, 19, 4023-4029 Abstract Only	☐

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	Art Unit	1783	
	Examiner Name	Gugliotta, Nicole T	
	Attorney Docket Number	5063.02US02	

	2	NAKATTA ET AL., "Improvement of InGaZnO4 Thin Film Transistors Characteristics Utilizing Excimer Laser Annealing" The Japan Society of Applied Physics, 2009 Abstract Only	☐
	3	NEEF ET AL., "Effects of carbon/hardmask interactions on hardmask performance", Proceedings of SPIE, 7273, 2009, 72731-1 - 727311-7	☐
	4	OWEN ET AL., "1/8 μm optical lithography" J. Vac. Sci. Technol. B 10, 3032 1992 Abstract Only	☐
	5	STOWERS ET AL., "Directly patterned inorganic hardmask for EUV lothography," Proc. SPIE 7969, 796915 (2011); Http://dx.doi.org/10.1117/12.879542	☐
	6	WANG ET AL.,"TiO2 micro-devices fabricated by laser direct writing" Optics Express, August 29, 2011, 19, 17390-17935 ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./	☐

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Examiner Signature	/Chanceity Robinson/	Date Considered	09/08/2013

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	Examiner Name	Nicole T. Gugliotta
	Attorney Docket Number	5063.02-US-02

	1	Office Action from copending Taiwan Application No. 100116897 dated July 29, 2013, 15 pages with translation.	☒

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First Named Inventor	Jason K. Stowers
Art Unit	1781
Examiner Name	Nicole T. Gugliotta
Attorney Docket Number	5063.02-US-02

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☒ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

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☐ See attached certification statement.

☐ Fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☐ None

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Peter S. Dardi/	Date (YYYY-MM-DD)	2013-10-04
Name/Print	Peter S. Dardi, Ph.D.	Registration Number	39650

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EFS ID:	17040299
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	04-OCT-2013
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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	US_IDS_Form__SB_08a.pdf	611937 66fe6ee5970623b48e5f8e99b2532ed94490dc5d	no	4

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2	Non Patent Literature	TW_OA_7-29-13.pdf	857024 2764edc8e993511be737a9f6552b51cde0653ea7	no	15

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

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New International Application Filed with the USPTO as a Receiving Office

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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US02
Jason K. Stowers et al.	Confirmation No.: 1662
Application No.: 12/850,867	Examiner: Chanceity N. Robinson
Filed: August 5, 2010	Group Art Unit: 1722

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

AMENDMENT

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

In response to the Office Action dated September 16, 2013, please enter the following amendments and consider the following remarks. This Amendment includes the following Sections:

A. Amendments to the Claims

B. Remarks

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

January 13, 2014
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. # 69,343

AMENDMENTS TO THE CLAIMS

A detailed listing of all claims that are, or were, in the present application, irrespective of whether the claim(s) remains under examination in the application are presented below. The claims are presented in ascending order and each includes one status identifier. Those claims not cancelled or withdrawn but amended by the current amendment utilize the following notations for amendment: 1. deleted matter is shown by strikethrough for six or more characters and double brackets for five or less characters; and 2. added matter is shown by underlining.

1. (Currently Amended) An aqueous inorganic patterning precursor solution comprising a mixture of water, metal suboxide cations, polyatomic inorganic anions and radiation sensitive ligands comprising peroxide groups, wherein the ~~composition~~ solution has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours without additional mixing.

2. (Currently Amended) The aqueous inorganic patterning precursor solution ~~composition~~ of claim 1 having a metal suboxide cation concentration from about 0.01 M to about 1.4 M.

3. (Currently Amended) The aqueous inorganic patterning precursor solution ~~composition~~ of claim 2 having a polyatomic anion concentration from about 0.75 to about 1.5 times the metal suboxide cation concentration.

4. (Currently Amended) The aqueous inorganic patterning precursor solution ~~composition~~ of claim 1 wherein tbe metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof.

5. (Currently Amended) The aqueous inorganic patterning precursor solution ~~composition~~ of claim 1 wherein the polyatomic anions comprise sulfate.

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6. (Currently Amended) The aqueous inorganic patterning precursor solution ~~composition~~ of claim 1 wherein the polyatomic anions comprise borate, phosphate, tungstate, silicate or combinations thereof.

7. (Currently Amended) The aqueous inorganic patterning precursor solution ~~composition~~ of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

8. (Currently Amended) The aqueous inorganic patterning precursor solution ~~composition~~ of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 7.

9. (Currently Amended) The aqueous inorganic patterning precursor solution ~~composition~~ of claim 1 having a stability of at least 24 hours without additional mixing.

10. (Currently Amended) The aqueous inorganic patterning precursor solution ~~composition~~ of claim 1 wherein the metal suboxide cations ~~comprising~~ comprise Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or a combination thereof ~~within an appropriate oxygenated ion~~.

11. (Original) A method for formation of a radiation sensitive inorganic coating precursor solution, the method comprising:

combining a first aqueous solution comprising metal suboxide cations, a complexing solution comprising a ligand having a peroxide group and a composition comprising a polyatomic inorganic anion to form the coating precursor solution, wherein the molar concentration ratio of ligands to metal suboxide cations is at least about 2.

12. (Original) The method of claim 11 wherein the first aqueous solution is mixed with the complexing solution to form a ligand-cation mixture solution prior to introduction of the inorganic anions.

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13. (Original) The method of claim 12 wherein the ligand-cation mixture solution is aged at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion.

14. (Withdrawn, Currently Amended) [[A]] The method of claim 11 ~~for patterning an inorganic material on a substrate, the method~~ further comprising:

forming a layer of a radiation patternable coating material comprising the coating precursor solution ~~a solvent, metal suboxide cations, ligands comprising a peroxide group and inorganic polyatomic anions~~ to form a coated substrate;

heating the coated substrate to remove at least a portion of the solvent;

irradiating the coated substrate [[to]] with a pattern of radiation to condense [[the]] a coating at the irradiated locations; and

heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the coating with a developer.

15. (Withdrawn) The method of claim 14 wherein the radiation is ultraviolet light.

16. (Withdrawn) The method of claim 14 wherein the radiation is light having a wavelength of about 193 nm.

17. (Withdrawn) The method of claim 14 wherein the radiation is extreme ultraviolet light.

18. (Withdrawn) The method of claim 14 wherein the radiation comprises an electron beam.

19. (Withdrawn) The method of claim 14 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof and wherein the polyatomic anions comprise sulfate anions.

20. (Withdrawn) The method of claim 14 wherein the coating material comprises a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

21. (Withdrawn, Currently Amended) The method of claim 14 wherein the formation of the ~~coating~~ coated substrate is performed using spin coating, spray coating, dip coating or knife edge coating.

22. (Withdrawn) The method of claim 14 wherein the layer of coating material has an average thickness from about 1 nm to about 40 nm.

23. (Withdrawn) The method of claim 14 wherein the radiation is directed through a mask to expose selected portions of the coated substrate.

24. (Withdrawn) The method of claim 14 wherein a laser beam or an electron beam is scanned over the coated substrate to expose selected portions of the coated substrate.

25. (Withdrawn) The method of claim 14 further comprising exposing the coated substrate with a developing composition to at least partially remove the coating composition at unexposed locations.

26. (Withdrawn) The method of claim 25 wherein the developing composition is contacted with the coated suhstrate for no more than about 75 seconds.

27. (Withdrawn) The method of claim 25 wherein the developing composition comprises tetramethyl ammonium hydroxide.

28. (Withdrawn) The method of claim 27 wherein the developing composition has a concentration of tetramethyl ammonium hydroxide of about 2.38 weight percent.

29. (Withdrawn) The method of claim 14 wherein the substrate is treated along a surface with a hydrophilic surface treatment prior to the forming of the radiation patternable coating material.

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30. (Withdrawn) The method of claim 14 wherein the forming of the radiation patternable coating material comprises a plurality of coating steps to form a coating material of a selected thickness.

31.-38. (Cancelled)

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REMARKS

Claims 1-30 are pending. By this Amendment claims 1-10, 14 and 21 are amended. Claims 14-30 are withdrawn pending the allowance of a linking claim. For the record, Applicant notes that an unintentional typographical error has been found in Example 1 in the Specification. Specifically, for Zr based patterning composition the amount of peroxide solution added should have been 18 mL not 1.8 mL. Based on the corrected amount of peroxide added, the ratio of peroxide to metal ions was 7.5 not 0.75.

Restriction Requirement

The Examiner stated that a provisional election was made with traverse in January 2012 to prosecute the invention of Group I, claims 1-13. Applicant affirms the election of Group I, claim 1-13 without traverse. Claims 14-30 have been made dependent on independent claim 11. Thus, claim 10 is a linking claim with respect to claims 14-30.

Claim Rejections under 35 U.S.C. § 112

Claims 1-10 are rejected under 35 U.S.C. §112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the applicant regards as the invention.

With respect to claims 1-10, the Examiner noted that there was no antecedent basis for the term "the composition" or "the aqueous inorganic patterning composition". The Applicant thanks the Examiner for a careful reading of the claims. Claim 1-10 have been amended to correct the antecedent basis.

With respect to claim 10, the Examiner indicated that the expression "within an appropriate oxygenated ion" was not clear. Claim 10 has been amended to clarify the scope of the present invention.

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In view of the above comments and amendments, Applicant believes that the claims are presently clear. Applicant respectfully requests withdrawal of the rejection of claims 1-10 under 35 U.S.C. § 112, second paragraph as being indefinite.

Claim Rejections under 35 U.S.C. § 103

Rejection over Stowers as evidenced by Nakamura

The Examiner rejected claims 1-5 and 7-10 under 35 U.S.C. 103(a) as obvious over Jason Stowers, Douglas A. Keszler, "High Resolution, High sensitivity inorganic resists", (2009) (Stowers) as evidenced by JP 2006/284947 A to Nakamura (Nakamura). Claims 2-5 and 7-10 directly or indirectly depend on claim 1. Since Stowers does not disclose all the features of claim 1, Stowers does not *prima facie* render obvious Applicant's presently claimed invention. Applicant respectfully requests reconsideration of the rejection based on the following comments.

"In rejecting claims under 35 U.S.C. §103, the examiner bears the initial burden of presenting a prima facie case of obviousness." In re Rijckaert, 28 USPQ2d 1955, 1956 (Fed. Cir. 1993). Prima facie obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. In re Ochiai, 37 USPQ 1127, 1131 (Fed. Cir. 1995). "The test for obviousness *vel non* is statutory. It requires that one compare the claim's 'subject matter as a whole' with the prior art 'to which said subject matter pertains.'".

With regard to Stowers, respectfully, Stowers does not teach or suggest each and every aspect of the claimed invention. The Examiner has argued that optimization of concentrations based on known properties to achieve predicted results is obvious. With all due respect, Stowers simply does not indicate that the peroxide concentration is a result effective variable. The Examiner has further presented Nakamura as evidence that stability of the precursor improves the contrast as described in the Specification. In particular, the Examiner has argued that

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because Stowers states that the presence of peroxide containing ligands inhibits condensation reactions it would be known to a person of skill in the art to adjust the peroxide concentration to stabilize the precursor. Nakamura though is directed to crosslinked organic polymers, so respectfully the relevance of the teachings of Nakamura to the present inorganic materials is tenuous at best. Respectfully, it does not appear that the instability of the precursor, as it regards the phase separation, was known prior to the present invention, nor known to be dependent on the concentration of the peroxide. Stowers mentions the significance of the peroxide, but does not suggest that the peroxide concentration is significant. Stowers, page 732. Stowers teaches a peroxide to metal mole ratio of 0.5, which is significantly less than the claimed values and less than the peroxide ratios exemplified in the present application. Stowers does not discuss the stability of the precursor with respect to the peroxide concentration. Nakamura does not teach the relationship between stability and peroxide ligand concentrations. The present application, on the other hand, acknowledges the stability problem of the precursor and increases the peroxide concentration to solve a problem that does not appear to be appreciated by Stowers. The increase in the peroxide concentration surprisingly and significantly increased both the stability of the precursor and the contrast. Neither Stowers nor common knowledge in the art provides a motivation or expectation for skilled artisans to prepare the claimed precursor solutions with the above-mentioned surprising effects. Therefore, Stowers as evidenced by Nakamura does not *prima facie* anticipate the present invention.

Applicant respectfully requests withdrawal of the rejection of claims 1-5 and 7-10 under 35 U.S.C. § 103(a) as obvious over Stowers as evidenced by Nakamura. While Applicant does not acquiesce in the assertions regarding the dependent claims, these issues are not discussed further in view of the discussion of claim 1 that makes the issue of dependent claims presently moot.

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Rejection over Stowers as evidenced by Nakamura, in view of Keszler

The Examiner rejected claim 6 under 35 U.S.C. 103(a) as obvious over Stowers as evidenced by Nakamura, in further view of WO 2009/120169 to Keszler et al. (Keszler 2009). Claim 6 directly depends on claim 1. Since the combination of Stowers and Keszler 2009 does not disclose all the features of claim 1, the combination does not *prima facie* render obvious Applicant's presently claimed invention. Applicant respectfully requests reconsideration of the rejection based on the following comments.

As discussed in the above section, Stowers as evidenced by Nakamura does not teach or suggest a precursor with a ligand to metal ratio of at least 2. Keszler 2009 does not make up for the deficiencies of Stowers. The combination of Stowers and Keszler 2009 does not teach or suggest each and every element of claim 1. The combination therefore does not render claim 6 *prima facie* obvious. Thus, Keszler 2009 and Stowers does not render the presently claimed invention *prima facie* obvious.

Applicant respectfully requests withdrawal of the rejection of claim 6 under 35 U.S.C. § 103(a) as obvious over Stowers as evidenced by Nakamura, in further view of Keszler 2009. While Applicant does not acquiesce in the assertions regarding the dependent claims, these issues are not discussed further in view of the discussion of claim 1 that makes the issue of dependent claims presently moot.

Rejection over Herman and Keszler 2008

The Examiner rejected claims 1-13 under 35 U.S.C. 103(a) as obvious over US Pub. No. 2005/0242330 to Herman et al. (Herman) in view of KR2008/0090383 to Keszler et al. (Keszler 2008). Claims 2-10 directly or indirectly depend on claim 1. Claims 12 and 13 directly or indirectly depend on claim 11. Since the combination of Herman and Keszler 2008 does not

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disclose all the features of claims 1 and/or 11, the combination does not *prima facie* render obvious Applicant's presently claimed invention. Applicant respectfully requests reconsideration of the rejection based on the following comments.

With regard to claim 1, respectfully, the combination of Herman and Keszler 2008 does not teach or suggest each and every aspect of the claimed invention. As stated by the examiner, Herman does not teach peroxide comprising ligands or a particular radio sensitive ligand to metal ratio. Similarly, Keszler 2008 does not teach a ratio of radio sensitive ligands to metal of at least 2. As discussed above, this high ratio resulted in surprising properties not suggested in the prior art or common knowledge. Keszler 2008 does not make up for the deficiencies of Herman. The combination of Herman and Keszler 2008 does not teach or suggest each and every element of claim 1. The combination therefore does not render claims 1-13 *prima facie* obvious. Thus, Herman in view of Keszler 2008 does not render the presently claimed invention *prima facie* obvious.

Applicant respectfully requests withdrawal of the rejection of claims 1-13 under 35 U.S.C. § 103(a) as obvious over Herman and Keszler 2008. While Applicant does not acquiesce in the assertions regarding the dependent claims, these issues are not discussed further in view of the discussion of claims 1 and 11 that makes the issue of dependent claims presently moot.

Double Patenting Rejection

Claims 1-13 are rejected on the ground of non-statutory double patenting as being unpatentable over claims 1-23 of U.S. Pat. No. 8,206,892 to Keszler et al. (US '892). Claims 2-13 are directly or indirectly dependent on claim 1. As the US '892 patent does not claim the high particular radio sensitive ligand to metal ratio, Applicant maintains that there is no double patenting.

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A double patenting rejection of the obviousness-type, is "analogous to [a failure to meet] the nonobviousness requirement of 35 U.S.C. § 103". *In re Braithwaite*, 379 F.2d 594, 600 (CCPA 1967). Therefore, the analysis employed in an obviousness-type double patenting rejection parallels the guidelines for analysis of a 35 U.S.C. § 103 obviousness determination. *In re Braat*, 937 F.2d 589, 592-93 (Fed. Cir. 1991); *In re Longi*, 759 F.2d 887, 892 (Fed. Cir. 1985).

The claims of US '892 does not teach or suggest the high particular radio sensitive ligand to metal ratio. Since the claims of US '892, or even the text, does not teach or suggest each and every element of claim 1, the reference does not render claim 1 *prima facie* obvious. As discussed in detail above, the high radio sensitive ligand to metal ratio would not have been obvious at the time the application was filed. Thus, US '892 does not render the presently claimed invention *prima facie* obvious.

Applicant respectfully requests withdrawal of the rejection of claims 1-13 under an obviousness type double patenting rejection as obvious over US '892. While Applicant does not acquiesce in the assertions regarding the dependent claims, these issues are not discussed further in view of the discussion of claim 1 that makes the issue of dependent claims presently moot.

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CONCLUSION

In view of the foregoing, it is submitted that this application is in condition for allowance. Favorable consideration and prompt allowance of the application are respectfully requested.

The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,

/Kayla J. Fossen/

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Electronic Acknowledgement Receipt

EFS ID:	17897362
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Kayla Jo Fossen
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	13-JAN-2014
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Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Amendment/Req. Reconsideration-After Non-Final Reject	Amdt.pdf	34696 ea22a9ad168bc42eee5867f7f888217c1ff0fd67	no	1

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2	Claims	Claims.pdf	190416 4a03c615a793d1832c3294f26a7582c07adab02f	no	5
Warnings:					
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3	Applicant Arguments/Remarks Made in an Amendment	Remarks.pdf	302840 445238ca99400c28047ed074f4115ea8b00ccf5b	no	7
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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US02
Jason K. Stowers et al.	Confirmation No.: 1662
Application No.: 12/850,867	Examiner: Chanceity N. Robinson
Filed: August 5, 2010	Group Art Unit: 1722

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

PETITION FOR EXTENSION OF PERIOD FOR RESPONSE
UNDER 37 C.F.R. § 1.136(a)

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Pursuant to 37 C.F.R. § 1.136(a), an extension of time of one (1) month (from December 16, 2013 to January 16, 2014) within which to respond to the Office Action dated September 16, 2013 is requested. The Commissioner is authorized to charge to Deposit Account No. 50-3863 the $100.00 small entity extension fee and any underpayments, overpayments or additionally required fees. The Commissioner is authorized to charge Deposit Account No. 50-3863 for any underpayments, overpayments or additionally required fees.

Respectfully submitted,

/Kayla J. Fossen/

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Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

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January 13, 2014
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. # 69,343

Electronic Patent Application Fee Transmittal

Application Number:	12850867
Filing Date:	05-Aug-2010
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Kayla Jo Fossen/Jill Friederichs
Attorney Docket Number:	5063.02US02

Filed as Small Entity

Utility under 35 USC 111(a) Filing Fees

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Petition:				
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Extension - 1 month with $0 paid	2251	1	100	100

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
		Total in USD ($)		**100**

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EFS ID:	17900153
Application Number:	12850867
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First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Kayla Jo Fossen
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	13-JAN-2014
Filing Date:	05-AUG-2010
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Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	$100
RAM confirmation Number	5356
Deposit Account	503863
Authorized User	
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1	Extension of Time	Ext.pdf	43966 4cf3ba825e79590393704527c3b994efacb47f79	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30526 6ab59af315242c55b7aef12e8d700448902391b0	no	2
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 12/850,867	Filing Date 08/05/2010	☐ To be Mailed

ENTITY: ☐ LARGE ☒ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT 01/13/2014	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	* 30	Minus	** 38	= 0	X $40 =	0
Independent (37 CFR 1.16(h))	* 2	Minus	***5	= 0	X $210 =	0
☐ Application Size Fee (37 CFR 1.16(s))						
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
					TOTAL ADD'L FEE	0

AMENDMENT	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
☐ Application Size Fee (37 CFR 1.16(s))						
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
					TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

LIE
/KIMBERLY PANNELL/

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02	1662

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EXAMINER	
ROBINSON, CHANCEITY N	
ART UNIT	**PAPER NUMBER**
1722	

MAIL DATE	DELIVERY MODE
05/06/2014	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No. 12/850,867	Applicant(s) STOWERS ET AL.	
	Examiner CHANCEITY ROBINSON	Art Unit 1722	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *3* MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *01/13/2014*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☒ This action is **FINAL**. 2b)☐ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5)☒ Claim(s) *1-30* is/are pending in the application.

5a) Of the above claim(s) *14-30* is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-13* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☒ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date *10/04/2013*.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

1. The present application is being examined under the pre-AIA first to invent provisions.

DETAILED ACTION

2. The Applicant's request for reconsideration filed on January 13, 2014 was received. Claims 1-10 have been amended. Claims 31-38 have been canceled. Claims 15-20 and 22-30 are withdrawn. Claims 14 and 21 are withdrawn, currently amended.

3. The text of those sections of Title 35, U.S.C. code not included in this action can be found in the prior Office Action issued on September 16, 2013.

Election/Restrictions

4. Applicant's election without traverse of Group I, claims 1-13 in the reply filed on 01/13/2014, page 7 is acknowledged. Therefore, claims 1-13 are currently pending. Claims 14-30 are withdrawn, based on the non-traversal of Group I.

Double Patenting

5. Claims 1-13 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-23 of U.S. Patent No. 8,206,892. Although the claims at issue are not identical, they are not patentably distinct from each other because both the US Patent '892 and the instant claims have claims drawn to an aqueous inorganic patterning precursor solution. Both the US Patent '892 and the instant claims recite open claim language, "comprising"; therefore, other elements and steps may be added to their respective inventions. Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide cations to yield desired molar concentration ratio. Discovery of

optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Claim Rejections - 35 USC § 103

6. Claims 1-5 and 7-10 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Jason Stowers, Douglas A. Keszler, "High resolution, high sensitivity inorganic resists", (2009) as evidenced by Nakamura (JP 2006/284947 A).

Regarding claims 1-5 and 7-10, Stowers et al. disclose an aqueous precursor solutions (aqueous inorganic patterning precursor solution) comprising $ZrOCl_2 \cdot 8H_20$, $HfOCl_2 \cdot H_20$, H_2SO_4, $H_20_2$and purified water (especially, please see 2. Experimental). Stowers et al. disclose that a final metal concentration is 0.5M and metal-to-sulfate ratios 1:05-0.7.

Stowers et al. do not explicitly disclose the molar concentration ratio of ligands to metal suboxide cations is at least about 2 or least about 5 or at least about 7 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours or 24 hours without additional mixing as instantly recited. It is noted that the term “about" is relative terminology. The molar concentration ratio is optimizable. In general, it is the exertion of creative capability for those skilled in the art to optimize or adapt number-range of compositional ration. If the difference is only the number-range of the compositional ratio, it is obvious for those skilled in the art to optimize or adapt number-range of compositional ratio unless there are grounds which can suppose existence of non-obviousness except advantageous effects compared with the invention of Reference. Thus, in the invention of Stowers et al., the content of H202 is within

optimal range which can be properly adjusted by those skilled in the art unless there are grounds which can suppose existence of non-obviousness except advantageous effects compared with the invention of Reference.

Therefore, it is discussed below whether or not the invention of this application has advantageous effects compared with the invention of Stowers et al. Since Stowers et al. disclose that peroxide inhibits condensation of metal oxides (please see page 732, lines 4-7 of left column.), it is obvious for those skilled in the art to predict function effects of stability with respect to phase separation in the invention of this application by increasing concentration ratio of peroxide.

With respect to the above, it is described in the specification that the increase in the radiation sensitive ligand concentration reduces agglomeration of the metal cations to stabilize, the precursor solution and thus the precursor solution can be stable relative to settling of solids without further stirring for at least two hours (please see from page 7, lines 30-31 to page 8, lines 1-2). However, the above matter does not specifically support in practical examples and quantitative function in the differences of the ratio of mole concentration cannot be understood. If the increase of stability in precursor solution is qualitative function, it is obvious for those skilled from indication of Stowers et al. It is described in the specification that significantly increasing the radiation sensitive ligand concentration in the precursor solutions results in a coating material that has greater contrast following radiation exposure so that there are surprising added benefits where precursor solution stabilization further accomplishes improved patterning and shorter development times (please see page 8, lines 18-22 and page 13, lines 16-21).

However, it is technical common sense in filing time that the contrast to developer increases if stabilization in the precursor solution increases and thus unnecessary reaction of an unexposed area does not arise as evidenced by Nakamura (see entire reference). Thus, those skilled in the art can qualitatively predict the above advantages. Specific composition of the precursor solution is described in Example 1 and patterning by using the precursor solution is described in Example 3 and 4. However, it is not described in the specification that there are quantitative differences as to contrast and developing time in between a molar concentration ratio of ligands to metal suboxide cations of more than 2 (Hf based coating material) and less than 2 (Zr based coating material). Thus, special technical sense is not found as to a molar concentration ratio of ligands to metal suboxide cations of more than 2.

Therefore, it is not considered that the invention of this application has advantageous effects compared with the invention of Stowers et al. and thus the content of H_2O_2 in the invention of Stowers et al. is within optimal range which can be properly adjusted by those skilled in the art from indication of Stowers et al.

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide cations to yield desired molar concentration ratio. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

7. Claim 6 is rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Jason Stowers, Douglas A. Keszler, "High resolution, high sensitivity inorganic resists",

(2009) as evidenced by Nakamura (JP 2006/284947 A) as applied to claims 1-5 and 7-10 above, and further in view of Keszler et al. (WO 2009/120169 A1).

Regarding claim 6, Stowers et al. do not explicitly disclose the polyatomic anions comprise borate, phosphate, tungstate, silicate or combinations thereof as instantly recited. However, Keszler et al. teach a precursor solution (abstract and title and page 30, lines 10-17) comprising borate, phosphate and silicate and combinations thereof in view of aiding in coating, liquid misting, physical and vapor deposition and solubility. Keszler et al. and Stowers et al. are analogous art in the inorganic precursor solution. Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify the polyatomic anions of Stowers et al. to include borate, phosphate and silicate and combinations thereof in view of aiding in coating, liquid misting, physical and vapor deposition and solubility.

8. Claims 1-13 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Herman et al. (US 2005/0242330 A1) in view of Keszler et al. (KR2008/0090383; citations from corresponding US PGPUB 2011/0045406 A1).

Regarding claims 1 and 7-9, Herman et al. disclose an aqueous inorganic patterning precursor solution (dielectric material) comprising a meta containing cation a polyatomic anion, wherein the metal containing cation includes one or more HfO^{2+}, ZrO^{2+}, etc and the polyatomic anion includes one or more of sulfate, borate and tungstate, and etc (figures, claims and [0009-0010 and 0014-0016]).

Herman et al. do not explicitly disclose the precursor solution comprises radiation sensitive ligands comprising peroxide groups as instantly recited. Also, Herman et al. do

not explicitly disclose the molar concentration ratio of ligands to metal suboxide cations is at least about 2 or least about 5 or at least about 7 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours or 24 hours without additional mixing as instantly recited. It is noted that the term “about" is relative terminology. The molar concentration ratio is optimizable. Nonetheless, Keszler et al. teach a laminate structure comprising a layer comprising solid inorganic acid or base and peroxide (abstract, claims and [0018-0019 and 0065-0068]). The molar concentration of ligands to metal suboxide cations could have been easily selected by one of ordinary skill in the art to adjust the properties of the precursor solution. It would have been obvious to one of ordinary skill in the art at the time of the invention to include a ligand comprising peroxide group to the precursor solution of Herman et al. in view of aiding in bonding and oxidation.

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide cations to yield desired molar concentration ratio. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Further regards to claims 2 and 3, Herman et al. do not explicitly disclose the metal suboxide cation concentration from about 0.01 M to about 1.4M as instantly recited or polyatomic anion concentration about 0.75 to about 1.5 times the metal suboxide cation concentration as instantly recited. It is noted that the term “about" is relative terminology. The concentration is optimizable.

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the polyatomic anion and metal suboxide cations to yield desired concentration. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Further regards to claims 4, 5 and 6, Herman et al. teach HfO^{2+} and ZrO^{2+} as metal containing cations and sulfate, borate and tungstate as polyatomic inorganic anions (figures, claims and [0009-0010 and 0014-0016]).

Further regards to claim 10, Herman et al. teach metal such as HF and Zr (claims).

Regarding claims 11-13, Herman et al. do not explicitly disclose a method of formation of a radiation sensitive inorganic coating precursor solution as instantly recited. However, Keszler et al. teach a method for formation of an inorganic precursor composition combining a first aqueous solution comprising metal suboxide cations and a complexing solution comprising a ligand having peroxide group ([0064 and 0097] and, claims and figures examples).The first aqueous solution is mixed with the complexing solution to form a ligand-cation mixture prior to introduction of the inorganic anions ([0064 and 0097] and, claims and figures examples). The ligand-cation mixture solution is aged at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion ([0064 and 0097] and, claims and figures examples).

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to easily conceive the teaching of Keszler et al. to the method of patterning a dielectric material in Herman et al.

9. Claims 1-13 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Keszler et al. (WO 2009/120169 A1).

Regarding claim 1, Keszler et al. teach an aqueous inorganic patterning precursor solution (line 20 on page 25 to line 12 on page 32) comprising water, HfOCl2 (metal suboxide cations), H2O2 and H2SO4 (polyatomic inorganic anions).

However, Keszler et al. do not teach the precursor solution has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours without additional mixing as instantly recited. Although Keszler et al. do not teach the molar concentration ratio and the solution stabilization time, it is well known to one of ordinary skill in the art at the time of the invention that an increase in the ratio of ligands can improve the stability of the metal suboxide cations. Therefore, the invention of claim 1 can be achieved by any person skilled in the art by simplying adjusting or optimizing the compounds. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Regarding claim 2, Keszler et al. teach in example 4 that the metal suboxide cations have a concentration of 0.05M -0.4 M.

Regarding claim 3, Keszler et al. teach in example 4 that the sulfate has a concentration of 50% of the total concentration of the metal cations. Although the concentration is lower than the range claimed in claim 3, Keszler et al. teach in lines 28-29 on page 16 disclosed that excellent stability is exhibited when the ratio of the sulfate radical to the metal ions is 13:18. Therefore, it would have been obvious to one of ordinary skill in the art by simply adjusting (optimizing) the ratio. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Regarding claim 4, Keszler et al. teach on lines 3-14 on page 15 discloses that the metal oxide is HfO2.x(SO4)×, ZrO2.x(SO4)x, wherein 0.1≤X≤ 1.5.

Regarding claims 5 and 6, Keszler et al. teach on line 31 on page 21 to line 5 on page 22 disclose that in the precursor solution, the polyatomic inorganic anions WO_4^{2-}, PO43-, AsO43-, SiO_4^{4-}, GaO_4^{5-} and SO_4^{2-}.

Regarding claims 7-9, it is known to persons having ordinary skill in the art that an increase in the ratio of ligands can improve the stability of the metal suboxide cations. Therefore, the stability of the solution can be formed by persons having ordinary skill in the art by simply adjusting or optimizing the concentration. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Regarding claim 10 , Keszler et al. teach on lines 12-17 on page 30 that the metal can be Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sin, Eu, Gd, Tb, Dy, Ho, Er, Tin, Yb and Lu.

Regarding claim 11, Keszler et al. teach a method for forming a radiation sensitive inorganic

coating precursor solution. Keszler et al. teach on line 20 on page 25 to line 12 on page 32 a method for formation of an inorganic pattern precursor solution comprising using an aqueous solution of HfOC12 (corresponding to the metal suboxide cations), H_2O_2 and H_2SO_4 (corresponding to the polyatomic inorganic anions) as a precursor solution. However, the mixing method of dissolving HfOCI2 in water followed by mixing it with H_2O_2 and H_2SO_4 can be easily derived by persons skilled in the art. Therefore, the invention of claim 1 can be achieved by any person skilled in the art by simplying adjusting or optimizing the compounds. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Regarding claims 12 and 13, Keszler et al. teach on line 5 on page 26 to line 9 on page 27 that O_2 of hydrogen peroxide can provide ligands (i.e. forming a ligand-cation mixture solution). Furthermore, aging the ligand-cation mixture solution at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion can be easily adjusted or optimized and changed by a person skilled in the art through routine experimentation.

Response to Arguments

10. Applicant's arguments filed 01/13/2014 have been fully considered but they are not persuasive. Applicants argue the following:

A) Applicants argue the US '892 patent does not claim the high particular radio sensitive ligand to metal ratio, Applicant maintains that there is no double patenting. US '892 does not render the presently claimed invention prima facie obvious.

A) Examiner respectfully disagrees. The US '892 recites that the patterning composition comprises metal suboxide cations, which are the same as the metal suboxide cations recited by the instant claims. The US '892 recites that the patterning composition comprises coordinating species comprising a peroxide group, which corresponds to the ligands comprising peroxide group recited by the instant claims. It is well-understood in the art that both components must be presented in the patterning composition in a content amount. Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide cations to yield desired molar concentration ratio. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Therefore, the rejection is maintained.

B) Applicants argue since Stowers does not disclose all the feature of claim 1, Stowers does not prima facie render obvious Applicant's presently claimed invention. Stowers simply does not indicate that the peroxide concentration is a result effective variable. It does not appear that the instability of the precursor, as it regards the phase separation, was known prior to the present invention, nor known to be dependent on the concentration of the peroxide. Stowers mentions the significance of the peroxide, but does not suggest that the peroxide concentration is significant. Stowers does not

discuss the stability and peroxide ligand concentrations. Neither Stowers nor common knowledge in the art provides a motivation or expectation for skilled artisans to prepare the claimed precursor solutions with the above-mentioned surprising effects. Therefore, Stowers as evidenced by Nakamura does not prima facie anticipate the present invention.

B) Examiner respectfully disagrees that Stowers does not prima facie render obvious Applicant's presently claimed invention. However, the examiner agrees that Stowers et al. do not explicitly disclose the molar concentration ratio of ligands to metal suboxide cations is at least about 2 or least about 5 or at least about 7 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours or 24 hours without additional mixing as instantly recited. Stowers et al. recognize that the final metal concentration is 0.5 M and “metal to sulfate ration” is 1:0.5-0.7 (page 730-733).

The molar concentration ratio is optimizable. In general, it is the exertion of creative capability for those skilled in the art to optimize or adapt number-range of compositional ration. If the difference is only the number-range of the compositional ratio, it is obvious for those skilled in the art to optimize or adapt number-range of compositional ratio unless there are grounds which can suppose existence of non-obviousness except advantageous effects compared with the invention of Reference. Thus, in the invention of Stowers et al., the content of H202 is within optimal range which can be properly adjusted by those skilled in the art unless there are grounds

which can suppose existence of non-obviousness except advantageous effects compared with the invention of Reference.

Therefore, it is discussed below whether or not the invention of this application has advantageous effects compared with the invention of Stowers et al. Since Stowers et al. disclose that peroxide inhibits condensation of metal oxides (please see page 732, lines 4-7 of left column.), it is obvious for those skilled in the art to predict function effects of stability with respect to phase separation in the invention of this application by increasing concentration ratio of peroxide.

Stowers et al. describes in the specification that significantly increasing the radiation sensitive ligand concentration in the precursor solutions results in a coating material that has greater contrast following radiation exposure so that there are surprising added benefits where precursor solution stabilization further accomplishes improved patterning and shorter development times (please see page 8, lines 18-22 and page 13, lines 16-21).

However, it is technical common sense in filing time that the contrast to developer increases if stabilization in the precursor solution increases and thus unnecessary reaction of an unexposed area does not arise as evidenced by Nakamura (see entire reference). Thus, those skilled in the art can qualitatively predict the above advantages. Specific composition of the precursor solution is described in Example 1 and patterning by using the precursor solution is described in Example 3 and 4. However, it is not described in the specification that there are quantitative differences as to contrast and developing time in between a molar concentration ratio of ligands to

metal suboxide cations of more than 2 (Hf based coating material) and less than 2 (Zr based coating material). Thus, special technical sense is not found as to a molar concentration ratio of ligands to metal suboxide cations of more than 2.

Therefore, the rejection is maintained.

C) Applicants argue that the combination of Herman and Keszler 2008 does not teach or suggest each and every aspect of the claimed invention. Keszler does not make up for the deficiencies of Herman. The combination therefore does not render claims 1-13 prima facie obvious.

C) Examiner respectfully disagrees. Applicants have not provided any evidence why it will not be obvious to optimize the concentration amounts. Applicants only recite that combination of Herman and Keszler 2008 does not teach or suggest each and every aspect of the claimed invention.

The molar concentration of ligands to metal suboxide cations could have been easily selected by one of ordinary skill in the art to adjust the properties of the precursor solution. It would have been obvious to one of ordinary skill in the art at the time of the invention to include a ligand comprising peroxide group to the precursor solution of Herman et al. in view of aiding in bonding and oxidation.

It would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the polyatomic anion and metal suboxide cations to yield desired concentration. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Therefore, the rejection is maintained.

Conclusion

11. Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CHANCEITY ROBINSON whose telephone number is (571)270-3786. The examiner can normally be reached on Monday to Friday (with every other Friday off): 9:00 -6:00 pm eastern time.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Cynthia Kelly can be reached on (571)272-1526. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CHANCEITY ROBINSON/
Primary Examiner, Art Unit 1722

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	5	(water and suboxide and polyatomic) with ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2014/05/04 19:46
L2	5	1 AND ((G03F7/0042).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2014/05/04 19:46
S2	1	("20050242330").PN.	US-PGPUB; USPAT	OR	OFF	2013/09/09 11:09
S3	0	("102008009009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:14
S4	0	("2008009009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:15
S5	6	("2008009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:15
S6	2	("20110045406").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:18
S7	0	S6 and age	US-PGPUB; USPAT	OR	ON	2013/09/09 11:51
S8	63710	complexing	US-PGPUB; USPAT	OR	ON	2013/09/09 11:51
S9	1	S6 and S8	US-PGPUB; USPAT	OR	ON	2013/09/09 11:51

Lam Research Ex. 1002, Page 1691 TEL Research Corp. v. Lam Corp. IPR2024-00036 | U.S. Patent No. 9,823,564

S10	1	S6 and (suboxide)	US-PGPUB; USPAT	OR	ON	2013/09/09 11:52
S11	17460	(430/270.1,302,322,325,325,946).CCLS.	US-PGPUB; USPAT	OR	OFF	2013/09/09 12:18
S12	10	S11 and (ligand with peroxide)	US-PGPUB; USPAT	OR	ON	2013/09/09 12:19

EAST Search History (Interference)

< This search history is empty>

5/4/2014 7:47:15 PM
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Lam Research Ex. 1001 - Page 610 of 1471 - Lam Research Corp. v. Ironclad Corp. - IPR2024-00036 - U.S. Patent No. 9,823,564

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

CPC- SEARCHED		
Symbol	Date	Examiner
G03F7/0042	05/04/2014	CR

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner
430	270.1, 302, 322, 325, 326, 942	09/09/2013	CR

SEARCH NOTES		
Search Notes	Date	Examiner
East, Assignee, IDS asnd Inventorship Search	09/09/2013	CR
East and IDS Search	05/04/2014	CR

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner

/CHANCEITY ROBINSON/ Examiner.Art Unit 1722	/CHANCEITY ROBINSON/ Primary Examiner.Art Unit 1722

PTO/SB/08a (01-10)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1781
Examiner Name	Nicole T. Gugliotta
Attorney Docket Number	5063.02-US-02

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

Receipt date: 10/04/2013	Application Number	12850867 12850867 - GAU: 1722
INFORMATION DISCLOSURE STATEMENT BY APPLICANT	Filing Date	2010-08-05
(Not for submission under 37 CFR 1.99)	First Named Inventor	Jason K. Stowers
	Art Unit	1781
	Examiner Name	Nicole T. Gugliotta
	Attorney Docket Number	5063.02-US-02

	1	Office Action from copending Taiwan Application No. 100116897 dated July 29, 2013, 15 pages with translation. ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./	☒

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EXAMINER SIGNATURE

Examiner Signature	/Chanceity Robinson/	Date Considered	04/28/2014

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	**Art Unit**
	CHANCEITY ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	05/04/2014								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
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	36	-								

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
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	CHANCEITY ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	05/04/2014								
	37	-								
	38	-								

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US02
Jason K. Stowers et al.	Confirmation No.: 1662
Application No.: 12/850,867	Examiner: Chanceity N. Robinson
Filed: August 5, 2010	Group Art Unit: 1722

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

AMENDMENT

Mail Stop AF
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

In response to the Office Action dated May 6, 2014, please enter the following amendments and consider the following remarks. The present response comprises the following sections:

A. Listing of the Claims

B. Remarks

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

July 7, 2014
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. # 69,343

LISTING OF THE CLAIMS

A detailed listing of all claims that are, or were, in the present application, irrespective of whether the claim(s) remains under examination in the application are presented below. The claims are presented in ascending order and each includes one status identifier. Those claims not cancelled or withdrawn but amended by the current amendment utilize the following notations for amendment: 1. deleted matter is shown by striketbrougb for six or more characters and double brackets for five or less characters; and 2. added matter is shown by underlining.

1. (Previously Presented) An aqueous inorganic patterning precursor solution comprising a mixture of water, metal suboxide cations, polyatomic inorganic anions and radiation sensitive ligands comprising peroxide groups, wherein the solution has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours without additional mixing.

2. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 having a metal suboxide cation concentration from about 0.01 M to about 1.4 M.

3. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 2 having a polyatomic anion concentration from about 0.75 to about 1.5 times the metal suboxide cation concentration.

4. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof.

5. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the polyatomic anions comprise sulfate.

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6. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the polyatomic anions comprise borate, phosphate, tungstate, silicate or combinations thereof.

7. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

8. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 7.

9. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 having a stability of at least 24 hours without additional mixing.

10. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the metal suboxide cations comprise Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or a combination thereof.

11. (Original) A method for formation of a radiation sensitive inorganic coating precursor solution, the method comprising:

combining a first aqueous solution comprising metal suboxide cations, a complexing solution comprising a ligand having a peroxide group and a composition comprising a polyatomic inorganic anion to form the coating precursor solution, wherein the molar concentration ratio of ligands to metal suboxide cations is at least about 2.

12. (Original) The method of claim 11 wherein the first aqueous solution is mixed with the complexing solution to form a ligand-cation mixture solution prior to introduction of the inorganic anions.

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13. (Original) The method of claim 12 wherein the ligand-cation mixture solution is aged at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion.

14. (Withdrawn) The method of claim 11 further comprising:

forming a layer of a radiation patternable coating material comprising the coating precursor solution to form a coated substrate;

heating the coated substrate to remove at least a portion of the solvent;

irradiating the coated substrate with a pattern of radiation to condense a coating at the irradiated locations; and

heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the coating with a developer.

15. (Withdrawn) The method of claim 14 wherein the radiation is ultraviolet light.

16. (Withdrawn) The method of claim 14 wherein the radiation is light having a wavelength of about 193 nm.

17. (Withdrawn) The method of claim 14 wherein the radiation is extreme ultraviolet light.

18. (Withdrawn) The method of claim 14 wherein the radiation comprises an electron beam.

19. (Withdrawn) The method of claim 14 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof and wherein the polyatomic anions comprise sulfate anions.

20. (Withdrawn) The method of claim 14 wherein the coating material comprises a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

21. (Withdrawn) The method of claim 14 wherein the formation of the coated substrate is performed using spin coating, spray coating, dip coating or knife edge coating.

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22. (Withdrawn) The method of claim 14 wherein the layer of coating material has an average thickness from about 1 nm to about 40 nm.

23. (Withdrawn) The method of claim 14 wherein the radiation is directed through a mask to expose selected portions of the coated substrate.

24. (Withdrawn) The method of claim 14 wherein a laser beam or an electron beam is scanned over the coated substrate to expose selected portions of the coated substrate.

25. (Withdrawn) The method of claim 14 further comprising exposing the coated substrate with a developing composition to at least partially remove the coating composition at unexposed locations.

26. (Withdrawn) The method of claim 25 wherein the developing composition is contacted with the coated substrate for no more than about 75 seconds.

27. (Withdrawn) The method of claim 25 wherein the developing composition comprises tetramethyl ammonium hydroxide.

28. (Withdrawn) The method of claim 27 wherein the developing composition has a concentration of tetramethyl ammonium hydroxide of about 2.38 weight percent.

29. (Withdrawn) The method of claim 14 wherein the substrate is treated along a surface with a hydrophilic surface treatment prior to the forming of the radiation patternable coating material.

30. (Withdrawn) The method of claim 14 wherein the forming of the radiation patternable coating material comprises a plurality of coating steps to form a coating material of a selected thickness.

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31.-38. (Cancelled)

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REMARKS

Claims 1-30 are pending. Claims 14-30 were previously withdrawn pending rejoinder. By this Amendment, no claims are amended or cancelled.

Double Patenting

Claims 1-13 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-23 of US Pat. No. 8,206,892. The Examiner has stated that "it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide cations to yield the desired molar concentration ratio." Claims 1-23 of US Pat. No. 8,206,892 do not teach the high molar ratio of peroxide ligands to metal suboxide cations of the present invention. Office Action, page 2. Respectfully, as discussed in detail below, the high molar ratio of peroxide ligands to metal suboxide cations would not have been obvious to a person of skill in the art at the time of the invention. Withdrawal of the rejection of claims 1-13 for douhle patenting over claims 1-23 of US Pat. No. 8,206,892 is respectfully requested.

Claim Rejections under 35 U.S.C. § 103

Rejections over Stowers

The Examiner rejected claims 1-5 and 7-10 under 35 U.S.C. 103(a) as obvious over Jason Stowers, Douglas A. Keszler, "High resolution, high sensitivity inorganic resists", (2009) (Stowers) as evidenced by JP 2066/174947 to Nakamura. Claims 2-5 and 7-10 directly or indirectly depend on claim 1. Since Stowers does not disclose all the features of claim 1, Stowers does not *prima facie* render obvious Applicant's presently claimed invention. Applicant respectfully requests reconsideration of the rejection based on the following comments.

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"In rejecting claims under 35 U.S.C. §103, the examiner bears the initial burden of presenting a *prima facie* case of obviousness." *In re Rijckaert*, 28 USPQ2d 1955, 1956 (Fed. Cir. 1993). *Prima facie* obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. *In re Ochiai*, 37 USPQ 1127, 1131 (Fed. Cir. 1995). "The test for obviousness *vel non* is statutory. It requires that one compare the claim's 'subject matter as a whole' with the prior art 'to which said subject matter pertains.'".

The Examiner asserted that "[t]he molar concentration is optimizable." "Discovery of optimum value of result effective variable in known process is ordinarily within skill of the art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ 215." Office Action page 15. Respectfully, the Examiner has made significant errors of law and fact. "The Board affirmed the examiner's rejection 'because one of ordinary skill in the art would have recognized after reading the prior art that the dimension recited in the claims are result-effective variables, **and because the prior art further discloses values including those in the claims**.'" *In re Applied Materials, Inc.*, 692 F.3d 1289, 1295 (Fed. Cir. 2012)(emphasis added). "First, the Board's conclusion that the prior art discloses dimensional values **overlapping the ranges** claimed in Applied's Patent is supported by substantial evidence." *Id.* (emphasis added.).

"We are aware that precedent of our reviewing court holds that it is not inventive to discover the optimum or workable ranges of a result-effective variable by routine experimentation, where the general conditions of a claim are disclosed in the prior art. *In re Applied Materials, Inc.*, 692 F.3d 1289, 1297 (Fed. Cir. 2012). Yet the *Applied Materials* court held that the general conditions of the claim were met because the prior art disclosed values overlapping the claimed ranges. *Id.* Thus, the situation we consider here is more like that before the court in *Sebek*, rather than that in *Applied Materials*, because the prior art disclosed values are all substantially outside the claimed range." *Ex parte Shimamura*, 2013 WL 6907688 (Patent Tr. & App. Bd. 2013). "While it may ordinarily be the case that determination of optimum values for parameters of prior art process would be at least

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prima facie obvious, that conclusion depends upon what prior art discloses with respect to those parameters and, if prior art disclosure suggests the outer limits of the range of suitable variables, and that the optimum resides within that range, and if there are indicates elsewhere that in fact that optimum should be sought within that range, determination of optimum values outside that range may not be obvious." *In re Sebek*, 465 F.2d 904, 907 (CCPA 1972). With all due respect, the cited references do not cite overlapping values of the parameters of the claimed invention. Thus, under the law, *prima facie* obviousness has not been established, and respectfully the Examiner has not pointed to any additional teachings of the art that would suggest obviousness..

While Applicant respectfully maintains that *prima facie* obviousness has not been established, even if it were established, this has also been soundly rebutted on the current facts. "It is well settled that a prima facie case of obviousness may be rebutted 'where the results of optimizing a variable, which was known to be result effective, (are) unexpectedly good.'" *In re Boesch*, 617 F.2d 272, 276 (C.C.P.A. 1980) (citing *In re Antonie*, 559 F.2d 618, 620, (C.C.P.A. 1977)). "It is also well settled that proof of unexpected properties may be in the form of direct or indirect comparative testing of the claimed compounds ... and the closest prior art." *In re Boesch*, 617 F.2d at 276 (citing *In re Payne*, 606 F.2d 303, 316, (C.C.P.A. 1979)).

As stated by the Examiner, Stowers "does not explicitly disclose the molar concentration ratio of ligand to metal suboxide cations..." nor does it disclose that "the precursor solution is stable with respect to phase separation..." Office Action, page 3. The Examiner further states that the peroxide concentration could be "properly adjusted by those skilled in the art" to arrive at the present ratio. In particular, Stowers teaches a peroxide to metal suboxide cation ratio of 1:2. Stowers 730, Experimental. Respectfully, however, a person of skill in the art would not expect a ratio of ligands to metal suboxide cations of at least about two to result in the high performance found by Applicant. Most chemists involved in the field would predict that the maximum bound peroxide/metal suboxide cation ratio would be 1:1, as each metal atom should

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be capable of binding to one peroxide. The maximum observed ratio of bound peroxide to metal suboxide cation, however, is 0.5:1 (1:2). So the improved performance is based on the unexpected effect of peroxide that is not bound to the metal in solution. With this in mind, it is not surprising that the reference used what would have been understood at the time to have been the optimum value based on the understanding of the chemistry. Thus, the high peroxide to metal suboxide cation ratio described in claim 1, results in unexpected improvement in the properties over Stowers. Stowers, therefore, does not render claim 1 *prima facie* obvious. Thus, Stowers does not render the presently claimed invention *prima facie* obvious.

Applicant respectfully requests withdrawal of the rejection of claims 1-5 and 7-10 under 35 U.S.C. § 103(a) as obvious over Stowers. While Applicant does not acquiesce in the assertions regarding the dependent claims, these issues are not discussed further in view of the discussion of claim 1 that makes the issue of dependent claims presently moot.

Rejections over Stowers and Keszler 2009

The Examiner rejected claim 6 under 35 U.S.C. 103(a) as obvious over Stowers as evidenced by Nakamura in further view of WO 2009/120169 to Keszler et al. (Keszler 2009). Claim 6 directly depends on claim 1. Since the combination of Stowers and Keszler 2009 does not disclose all the features of claim 1, the combination does not *prima facie* render obvious Applicant's presently claimed invention. Applicant respectfully requests reconsideration of the rejection based on the following comments.

As discussed above, Stowers does not teach or suggest a ratio of ligands to metal suboxide cations of at least about two and the high ligand to metal suboxide cation ratio leads to unexpected improvement in the properties over Stowers. Keszler 2009 does not make up for the deficiencies of Stowers. See Office Action, page 9. Stowers in view of Keszler 2009 does not teach or suggest each and every element of claim 1. The combination of Stowers and Keszler

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2009 therefore does not render claim 6 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious.

Applicant respectfully requests withdrawal of the rejection of claim 6 under 35 U.S.C. § 103(a) as obvious over Stowers and Keszler 2009. While Applicant does not acquiesce in the assertions regarding the dependent claims, these issues are not discussed further in view of the discussion of claim 1 that makes the issue of dependent claims presently moot.

Rejections over Herman and Keszler 2008

The Examiner rejected claims 1-13 under 35 U.S.C. 103(a) as obvious over US Pub. No. 2005/0242330 to Herman et al. (Herman) in view of KR2008/0090383 to Keszler et al. (Keszler 2008) (citations from corresponding US Pub. No. 2011/0045406). Claims 2-10 directly or indirectly depend on claim 1. Claims 12 and 13 are directly or indirectly dependent on claim 11. Since the combination of Herman and Keszler 2008 does not disclose all the features of claim 1 or claim 11, the combination does not *prima facie* anticipate or render obvious Applicant's presently claimed invention. Applicant respectfully requests reconsideration of the rejection based on the following comments.

With regard to claim 1, as stated by the Examiner, Herman does not teach radiation sensitive ligands comprising peroxide groups. Office Action, page 6. Keszler 2008 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two. Office Action, page 8. Keszler 2008, therefore, does not make up for the deficiencies of Herman. Furthermore, as discussed in the above section, a person of skill in the art would not have expected unbound ligand in the precursor solution to result in improved stability and patterning properties. Herman in view of Keszler 2008 does not teach or suggest each and every element of claim 1. The combination of Herman and Keszler 2008 therefore does not render

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claims 1-10 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious.

With regard to claim 11, as stated by the Examiner, Herman does not teach radiation sensitive ligands comprising peroxide groups. Office Action, page 8. Keszler 2008 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two. Office Action, page 8. Keszler 2008, therefore, does not make up for the deficiencies of Herman. Furthermore, as discussed above, a person of skill in the art would not have expected unbound ligand in the precursor solution to result in improved stability and patterning properties. Herman in view of Keszler 2008 does not teach or suggest each and every element of claim 11. The combination of Herman and Keszler 2008 therefore does not render claims 11-13 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious.

Applicant respectfully requests withdrawal of the rejection of claims 1-13 under 35 U.S.C. § 103(a) as obvious over Herman and Keszler 2008. While Applicant does not acquiesce in the assertions regarding the dependent claims, these issues are not discussed further in view of the discussions of claims 1 and 11 that make the issue of dependent claims presently moot.

Rejections over Keszler 2009

The Examiner rejected claims 1-13 under 35 U.S.C. 103(a) as obvious over Keszler 2009. Claims 2-10 directly or indirectly depend on claim 1. Claims 12 and 13 directly or indirectly depend on claim 11. Since Keszler 2009 does not disclose all the features of claim 1 or claim 11, Keszler 2009 does not *prima facie* render obvious Applicant's presently claimed invention. Applicant respectfully requests reconsideration of the rejection based on the following comments.

Lam Research Ex. 1004 - Page 627 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

With regard to claim 1, as stated by the Examiner, Keszler 2009 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two. Office Action, page 9. Furthermore, as discussed above, a person of skill in the art would not have expected unbound ligand in the precursor solution to result in improved stability and patterning properties. Keszler 2009 does not teach or suggest each and every element of claim 1. Keszler 2009 therefore does not render claims 1-10 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious.

With regard to claim 11, as stated by the Examiner, Keszler 2009 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two. Office Action, page 9. Furthermore, as discussed above, a person of skill in the art would not have expected unbound ligand in the precursor solution to result in improved stability and patterning properties. Keszler 2009 does not teach or suggest each and every element of claim 11. Keszler 2009 therefore does not render claims 11-13 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious.

Applicant respectfully requests withdrawal of the rejection of claims 1-13 under 35 U.S.C. § 103(a) as obvious over Keszler 2009. While Applicant does not acquiesce in the assertions regarding the dependent claims, these issues are not discussed further in view of the discussions of claims 1 and 11 that make the issue of dependent claims presently moot.

Lam Research Ex. 1004 - Page 628 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

CONCLUSION

In view of the foregoing, it is submitted that this application is in condition for allowance. Favorable consideration and prompt allowance of the application are respectfully requested.

The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,

/Kayla J. Fossen/

Kayla J. Fossen
Registration No. 69,343

Customer No. 62274
Dardi & Herbert, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
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Telephone: (763) 412-3827

Lam Research Ex. 1004 - Page 629 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Acknowledgement Receipt

EFS ID:	19502138
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Kayla Jo Fossen
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	07-JUL-2014
Filing Date:	05-AUG-2010
Time Stamp:	14:09:14
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Response After Final Action	AmdtAF.pdf	33822 5e12e7f8928ff844177c7492ea7e4ee68202eecd	no	1

Warnings:	
Information:	

2	Claims	Claims.pdf	172946 1733023ee031ae0dcd0ed3198457361f2045b3b6	no	5
Warnings:					
Information:					
3	Applicant Arguments/Remarks Made in an Amendment	Remarks.pdf	372922 24c46ce75c1e0cef2ca08dc6890dbac7117b29a8	no	8
Warnings:					
Information:					
		Total Files Size (in bytes):	579690		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 12/850,867	Filing Date 08/05/2010	☐ To be Mailed

ENTITY: ☐ LARGE ☒ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT **07/07/2014**

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	* 30	Minus	** 38	= 0	X $40 =	0
Independent (37 CFR 1.16(h))	* 2	Minus	***5	= 0	X $210 =	0
☐ Application Size Fee (37 CFR 1.16(s))						
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
					TOTAL ADD'L FEE	0

AMENDMENT

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
☐ Application Size Fee (37 CFR 1.16(s))						
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
					TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

LIE
/CRYSTAL QUEEN/

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
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Address: COMMISSIONER FOR PATENTS
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www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02	1662

62274 7590 07/10/2014

DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

EXAMINER	
ROBINSON, CHANCEITY N	
ART UNIT	**PAPER NUMBER**
1722	

MAIL DATE	DELIVERY MODE
07/10/2014	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Advisory Action Before the Filing of an Appeal Brief	**Application No.** 12/850,867	**Applicant(s)** STOWERS ET AL.	
	Examiner CHANCEITY ROBINSON	**Art Unit** 1722	**AIA (First Inventor to File) Status** No

--The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

THE REPLY FILED 07 July 2014 FAILS TO PLACE THIS APPLICATION IN CONDITION FOR ALLOWANCE.

NO NOTICE OF APPEAL FILED

1. ☒ The reply was filed after a final rejection. No Notice of Appeal has been filed. To avoid abandonment of this application, applicant must timely file one of the following replies: (1) an amendment, affidavit, or other evidence, which places the application in condition for allowance; (2) a Notice of Appeal (with appeal fee) in compliance with 37 CFR 41.31; or (3) a Request for Continued Examination (RCE) in compliance with 37 CFR 1.114 if this is a utility or plant application. Note that RCEs are not permitted in design applications. The reply must be filed within one of the following time periods:
   a) ☐ The period for reply expires _____months from the mailing date of the final rejection.
   b) ☒ The period for reply expires on: (1) the mailing date of this Advisory Action; or (2) the date set forth in the final rejection, whichever is later. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of the final rejection.
   c) ☐ A prior Advisory Action was mailed more than 3 months after the mailing date of the final rejection in response to a first after-final reply filed within 2 months of the mailing date of the final rejection. The current period for reply expires months from the mailing date of *the prior Advisory Action* or SIX MONTHS from the mailing date of the final rejection, whichever is earlier.
   Examiner Note: If box 1 is checked, check either box (a), (b) or (c). ONLY CHECK BOX (b) WHEN THIS ADVISORY ACTION IS THE FIRST RESPONSE TO APPLICANT'S FIRST AFTER-FINAL REPLY WHICH WAS FILED WITHIN TWO MONTHS OF THE FINAL REJECTION. ONLY CHECK BOX (c) IN THE LIMITED SITUATION SET FORTH UNDER BOX (c). See MPEP 706.07(f).

Extensions of time may be obtained under 37 CFR 1.136(a). The date on which the petition under 37 CFR 1.136(a) and the appropriate extension fee have been filed is the date for purposes of determining the period of extension and the corresponding amount of the fee. The appropriate extension fee under 37 CFR 1.17(a) is calculated from: (1) the expiration date of the shortened statutory period for reply originally set in the final Office action; or (2) as set forth in (b) or (c) above, if checked. Any reply received by the Office later than three months after the mailing date of the final rejection, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

NOTICE OF APPEAL

2. ☐ The Notice of Appeal was filed on _____. A brief in compliance with 37 CFR 41.37 must be filed within two months of the date of filing the Notice of Appeal (37 CFR 41.37(a)), or any extension thereof (37 CFR 41.37(e)), to avoid dismissal of the appeal. Since a Notice of Appeal has been filed, any reply must be filed within the time period set forth in 37 CFR 41.37(a).

AMENDMENTS

3. ☐ The proposed amendments filed after a final rejection, but prior to the date of filing a brief, will not be entered because
   a) ☐ They raise new issues that would require further consideration and/or search (see NOTE below);
   b) ☐ They raise the issue of new matter (see NOTE below);
   c) ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal; and/or
   d) ☐ They present additional claims without canceling a corresponding number of finally rejected claims.
   NOTE: _____. (See 37 CFR 1.116 and 41.33(a)).
4. ☐ The amendments are not in compliance with 37 CFR 1.121. See attached Notice of Non-Compliant Amendment (PTOL-324).
5. ☐ Applicant's reply has overcome the following rejection(s): _____.
6. ☐ Newly proposed or amended claim(s) _____ would be allowable if submitted in a separate, timely filed amendment canceling the non-allowable claim(s).
7. ☒ For purposes of appeal, the proposed amendment(s): (a) ☒ will not be entered, or (b) ☐ will be entered, and an explanation of how the new or amended claims would be rejected is provided below or appended.

AFFIDAVIT OR OTHER EVIDENCE

8. ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.
9. ☐ The affidavit or other evidence filed after final action, but before or on the date of filing a Notice of Appeal will not be entered because applicant failed to provide a showing of good and sufficient reasons why the affidavit or other evidence is necessary and was not earlier presented. See 37 CFR 1.116(e).
10. ☐ The affidavit or other evidence filed after the date of filing the Notice of Appeal, but prior to the date of filing a brief, will not be entered because the affidavit or other evidence failed to overcome all rejections under appeal and/or appellant fails to provide a showing of good and sufficient reasons why it is necessary and was not earlier presented. See 37 CFR 41.33(d)(1).
11. ☐ The affidavit or other evidence is entered. An explanation of the status of the claims after entry is below or attached.

REQUEST FOR RECONSIDERATION/OTHER

12. ☒ The request for reconsideration has been considered but does NOT place the application in condition for allowance because: See Continuation Sheet.
13. ☐ Note the attached Information *Disclosure Statement*(s). (PTO/SB/08) Paper No(s). _____
14. ☐ Other: _____.

STATUS OF CLAIMS

15. The status of the claim(s) is (or will be) as follows:
    Claim(s) allowed: .
    Claim(s) objected to: .
    Claim(s) rejected: 1-13.
    Claim(s) withdrawn from consideration: 14-30.

/CHANCEITY ROBINSON/
Primary Examiner, Art Unit 1722

Continuation of 11. does NOT place the application in condition for allowance because: Arguments presented by the applicant was previously addressed in the final office action mailed on 05/06/2014. Therefore, the rejection is maintained for reasons of record in Final Rejection.
.

DO NOT ENTER: /C.R./
07/09/2014

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US02
Jason K. Stowers et al.	Confirmation No.: 1662
Application No.: 12/850,867	Examiner: Chanceity N. Robinson
Filed: August 5, 2010	Group Art Unit: 1722

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

AMENDMENT

Mail Stop AF
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

In response to the Office Action dated May 6, 2014, please enter the following amendments and consider the following remarks. The present response comprises the following sections:

A. Listing of the Claims

B. Remarks

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

July 7, 2014
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. # 69,343

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US02
Stowers et al.	Confirmation No.: 1662
Application No.: 12/850,867	Examiner: Chanceity N. Robinson
Filed: August 5, 2010	Group Art Unit: 1722

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

NOTICE OF APPEAL

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In accordance with 37 C.F.R. § 1.191, Applicant hereby appeals to the Patent Trial and Appeal Board from the Office Action mailed May 7, 2014, finally rejecting claims 1-13 in the above-identified patent application. A credit card payment in the amount of $400.00 to cover the fee for a small entity is submitted herewith.

Respectfully submitted,

/Kayla J. Fossen/

Kayla J. Fossen
Registration No. 69,343

Customer No. 62274
Dardi & Herbert, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432
Telephone: (763) 412-3827

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No.50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

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July 31, 2014
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. # 69,343

Electronic Patent Application Fee Transmittal

Application Number:	12850867
Filing Date:	05-Aug-2010
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Kayla Jo Fossen/Jill Friederichs
Attorney Docket Number:	5063.02US02

Filed as Small Entity

Utility under 35 USC 111(a) Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Notice of Appeal	2401	1	400	400
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
		Total in USD ($)		**400**

Electronic Acknowledgement Receipt

EFS ID:	19737576
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Kayla Jo Fossen
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	31-JUL-2014
Filing Date:	05-AUG-2010
Time Stamp:	11:44:31
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$400
RAM confirmation Number	9544
Deposit Account	503863
Authorized User	FOSSEN, KAYLA J.

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Notice of Appeal Filed	Notice_of_Appeal.pdf	37665 44d617798136a43e0331a605453edc61a4cd3ae7	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30519 10d9169112f2499b0b3aa4574a8ecd36b08639e4	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	68184		

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US02
Jason K. Stowers et al.	Confirmation No.: 1662
Application No.: 12/850,867	Examiner: Chanceity N. Robinson
Filed: August 5, 2010	Group Art Unit: 1722

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

BEFORE THE BOARD OF PATENT TRIAL AND APPEALS BOARD

BRIEF FOR APPELLANT

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US02
Jason K. Stowers et al.	Confirmation No.: 1662
Application No.: 12/850,867	Examiner: Chanceity N. Robinson
Filed: August 5, 2010	Group Art Unit: 1722

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

BEFORE THE BOARD OF PATENT TRIALS AND APPEALS BOARD
APPEAL BRIEF

Mail Stop Appeal Brief - Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

This is an appeal of the final rejection of claims 1-13. A Final Rejection was mailed May 6, 2014. A Notice of Appeal was filed on July 31, 2014. An extension of time request for one month has been filed. This Appeal Brief is thus timely filed.

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

October 31, 2014
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. # 69,343

REAL PARTY IN INTEREST

The real party in interest is the assignee, Inpria Corporation.

RELATED APPEALS AND INTERFERENCES

There are no related appeals or interferences.

STATUS OF CLAIMS

Claims 1-13 are pending, claims 14-30 are withdrawn, and claims 31-38 are cancelled.

STATUS OF AMENDMENTS

All amendments have been entered.

Lam Research Ex. 1004 - Page 644 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

SUMMARY OF CLAIMED SUBJECT MATTER

The presently claimed invention is directed to an aqueous inorganic patterning precursor solution. Claims 1 and 11 are independent claims on appeal. Citations in this section are directed to the application as filed

Claim 1 is directed to an "aqueous inorganic patterning precursor solution comprising a mixture of water, metal suboxide cations, polyatomic inorganic anions and radiation sensitive ligands comprising peroxide groups". See Specification page 2, lines 24-26. The precursor solution has "a molar concentration ratio of ligands to metal suboxide cations of at least about 2". See Specification page 2, lines 26-27. The precursor solution is also "stable with respect to phase separation for at least about 2 hours without additional mixing." See Specification page 2, lines 28-29.

Claim 11 is directed to a "method for formation of a radiation sensitive inorganic coating precursor solution". See Specification page 2, line 30 to page 3, line 4. In the method, a first aqueous solution comprising metal suboxide cations, a complexing solution comprising a ligand having a peroxide group and a composition comprising a polyatomic inorganic anion are combined to form the coating precursor solution. See Specification page 2, lines 24-26. Thus, two separately prepared solutions and a distinct composition, which may or may not be a solution, are explicitly combined. The molar concentration ratio of ligands to metal suboxide cations is at least about 2. See Specification page 2, lines 26-27.

Claim 12 is a dependent claim directed to the method of claim 11 where "the first aqueous solution is mixed with the complexing solution to form a ligand-cation mixture solution prior to introduction of the inorganic anions." See Specification page 18 lines 18-27.

Claim 13 depends from claim 12 and further specifies that "the ligand-cation mixture solution is aged at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion." See Specification page 18, lines 27-29. In the method of claim 13, three distinct solutions are formed in the overall process.

GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

1. The rejection of claims 1-13 on the ground of nonstatutory double patenting as being unpatentable over claims 1-23 of U.S. Patent No. 8,206,892 to Keszler et al.

Lam Research Ex. 1004 - Page 645 Lam Research Corp. v. Inpria Corp IPR2024-00033 - U.S. Patent No. 9,823,564

2. The rejection of claims 1-5 and 7-10 under pre-AIA 35 U.S.C. § 103(a) as being unpatentable over Stowers et al., "High Resolution, High Sensitivity Inorganic Resists", (2009) as evidenced by JP 2006/284947 to Nakamura.

3. The rejection of claim 6 under pre-AIA 35 U.S.C. § 103(a) as being unpatentable over Stowers et al., "High Resolution, High Sensitivity Inorganic Resists", (2009) as evidenced by JP 2006/284947 to Nakamura in further view of WO 2009/120169 to Keszler et al.

4. The rejection of claims 1-13 under pre-AIA 35 U.S.C. § 103(a) as being unpatentable over U.S. Publication No. 2005/0242330 to Herman et al. in view of KR 2008/0090383 to Keszler et al.

5. The rejection of claims 1-13 under pre-AIA 35 U.S.C. § 103(a) as being unpatentable over WO 2009/120169 to Keszler et al.

ARGUMENT

A. Grouping of Claims

Appellant argues claims 1, 4, 5, and 7-9 as a single group and acknowledges that the claims stand or fall together.

Appellant argues claims 11, 12, and 13 individually.

B. Legal Authority

The Court of Appeals for the Federal Circuit has exclusive appellate jurisdiction for cases arising under the patent law under 28 U.S.C. § 1295 (a)(1). Federal Circuit patent law is subject to review by the U.S. Supreme Court, and the Supreme Court occasionally rules on patent cases that provide ultimate authority for interpreting the patent statutes.

C. Principles of Law

1. Non-Statutory Double Patenting

"[A] rejection based upon double patenting of the obviousness type [...] is a judicially created doctrine grounded in public policy (a policy reflected in the patent statute) rather than based purely on the precise terms of the statute." In re Longi, 759 F.2d 887, 892 (Fed. Cir.1985) (emphasis in original). "The purpose of this rejection is to prevent the extension of the term of a

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patent, even where an express statutory basis for the rejection is missing, by prohibiting the issuance of the claims in a second patent not patentably distinct from the claims of the fist patent. Id. at 892. The doctrine of obviousness type double patenting reflects the policy that, "[t]he public should ... be able to act on the assumption that upon the expiration of the patent it will be free to use not only the invention claimed in the patent but also modifications or variants which would have been obvious to those of ordinary skill in the art at the time the invention was made." Id. at 892 citing In re Zickendraht, 50 C.C.P.A. 1529, 1537,319 F.2d 225, 232, (C.C.P.A. 1963) (emphasis in original).

In determining whether a rejection for double patenting is appropriate, "an obviousness determination similar to, but not necessarily the same as, that undertaken under 35 USC § 103" is used. In re Braat, 937 F.2d 589, 592 (Fed. Cir. 1991). In particular, the test for obviousness type double patenting involves two steps: (1) "as a matter of law, a court construes [a] claim in [an] earlier patent and [a] claim in [a] later patent and determines the differences" and (2) "the court determines whether the differences in subject matter between the two claims render the claims patentably distinct." Eli Lilly and Co. v. Barr Laboratories, Inc., 251 F.3d 955, 968 (Fed. Cir. 2001). Where a person of ordinary skill in the art finds the differences between the two claims obvious in light of the prior art, the claims are not patentably distinct. See In re Basell, 547 F.3d 1371, 1379 (Fed. Cir. 2009); See also In re Longi, 759 F.2d 887, 896 (Fed. Cir. 1985). However, where there is no reasonable expectation of success in the combination of the claims in the earlier filed patent and the teachings of the prior art, the differences between the claims in the later filed application and the earlier filed patent would not be obvious to the person of ordinary skill in the art. In re Longi, 579 F.2d at 897.

With respect to obviousness-type double patenting, in considering whether a claim in a later filed patent applications is an obvious variation of a claim in an earlier filed patent, the earlier filed patent may not be used as prior art. In re Vogel, 57 C.C.P.A. 920, 924, 422 F.2d 438, 441 (C.C.P.A 1970). In particular, an earlier patent's specification is not available to show obviousness type double patenting. In re Basell, 547 F.3d at 1379. However, "certain instances may exist where a patent's disclosure may be used." Id. at 1379. Specifically, an earlier patent's specification may be used "to determine whether an application claim is merely an obvious variation of an invention claimed in a patent", "to learn the meaning of [claim] terms," and "in

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interpreting the coverage of [a] claim." Id. at 1379 (internal quotes omitted) citing In re Vogel, 422 F.2d at 441. However, with respect to using an earlier patent's specification to determine whether an application claim is merely an obvious variation of an invention claimed in a patent, only the portion of the specification that provides support for the claim upon which an obviousness type double patenting rejection is based may be considered in a determination of obviousness type double patenting. See In re Vogel, 422 F.2d at 442.

2. Obviousness

"A patent may not be obtained ... if the differences between the [claimed invention] and the prior art are such that the subject matter as a whole would have been obvious **at the time the invention was made** to a person of ordinary skill in the art." *Ecolochem, Inc. v. Southern California Edison Company*, 227 F.3d 1361, 1371 (Fed. Cir. 2000), citing 35 U.S.C. § 103(a) (emphasis added).

a. Prima Facie Case

"In rejecting claims under 35 U.S.C. §103, the examiner bears the initial burden of presenting a prima facie case of obviousness." *In re Rijckaert*, 28 USPQ2d 1955, 1956 (Fed. Cir. 1993). "The test for obviousness vel non is statutory. It requires that one compare the claim's 'subject matter as a whole' with the prior art 'to which said subject matter pertains.'"). If the Examiner fails to establish a prima facie case of obviousness, the obviousness rejection must be withdrawn as a matter of law. *In re Ochiai*, 37 USPQ at 1131 ("When the references cited by the examiner fail to establish a prima facie case of obviousness, the rejection is improper and will be overturned.").

The objective analysis for applying 35 U.S.C. § 103 requires: (1) determination of the scope and content of the prior art are; (2) ascertaining the differences between the prior art and claims at issue; (3) resolving the level of ordinary skill in the art and (4) against the previous background, determining the obviousness or nonobviousness of the subject matter." *KSR Intern. Co. v. Teleflex Inc.*, 550 U.S. 398, 400 (2007) citing *Graham v. John Deere Co. of Kansas City*, 383 U.S. 1, 17–18, 86 S.Ct. 684, 15 L.Ed.2d 545.

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Significantly, ***prima facie* obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art**. *In re Ochiai*, 37 USPQ 1127, 1131 (Fed. Cir. 1995) (emphasis added). "It is impermissible, however, to simply engage in a hindsight reconstruction of the claimed invention, using applicant's structure as a template and selecting elements from references to fill the gaps." *In re Gorman*, 18 USPQ2d 1885, 1888 (Fed. Cir. 1991).

b. Discovery of Optimum Values and Obviousness

"Discovery of optimum value of result effective variable in known process is ordinarily within skill of the art." *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ 215." "The Board affirmed the examiner's rejection 'because one of ordinary skill in the art would have recognized after reading the prior art that the dimension recited in the claims are result-effective variables, **and because the prior art further discloses values including those in the claims**.'" *In re Applied Materials, Inc.*, 692 F.3d 1289, 1295 (Fed. Cir. 2012)(emphasis added). "First, the Board's conclusion that the prior art discloses dimensional values **overlapping the ranges** claimed in Applied's Patent is supported by substantial evidence." *Id.* (emphasis added.).

"While it may ordinarily be the case that determination of optimum values for parameters of prior art process would be at least prima facie obvious, that conclusion depends upon what prior art discloses with respect to those parameters and, if prior art disclosure suggests the outer limits of the range of suitable variables, and that the optimum resides within that range, and if there are indicates elsewhere that in fact that optimum should be sought within that range, determination of optimum values outside that range may not be obvious." *In re Sebek*, 465 F.2d 904, 907 (CCPA 1972).

"We are aware that precedent of our reviewing court holds that it is not inventive to discover the optimum or workable ranges of a result-effective variable by routine experimentation, where the general conditions of a claim are disclosed in the prior art. *In re Applied Materials, Inc.*, 692 F.3d 1289, 1297 (Fed. Cir. 2012). Yet the *Applied Materials* court held that the general conditions of the claim were met because the prior art disclosed values overlapping the claimed ranges. *Id.* Thus, the situation we consider here is more like that before the court in *Sebek*, rather than that in *Applied*

Materials, because the prior art disclosed values are all substantially outside the claimed range." *Ex parte Shimamura*, 2013 WL 6907688 (Patent Tr. & App. Bd. 2013).

The case law regarding close ranges in determining obviousness is consistent with these rulings. A *prima facie* case of obviousness exists if the claimed ranges "overlap or lie inside ranges disclosed by prior art." *In re Wertheim*, 541 F.2d 257, 191 USPQ 90 (CCPA 1976); *In re Woodruff*, 919 F.2d 1575, 16 USPQ2d 1934 (Fed. Cir. 1990); *In re Geisler*, 116 F.3d 1465, 1469-71, 43 USPQ2d 1362, 1365-66 (Fed. Cir. 1997). If the claimed ranges do not overlap with the prior art ranges, a *prima facie* case of obviousness exists if they are so close that one skilled in the art would have expected them to have the same properties. "[A] prior art reference that discloses a range encompassing a somewhat narrower claimed range is sufficient to establish a *prima facie* case of obviousness." *In re Peterson*, 315 F.3d 1325, 1330, 65 USPQ2d 1379, 1382-83 (Fed. Cir. 2003). See also *In re Harris*, 409 F.3d 1339, 74 USPQ2d 1951 (Fed. Cir. 2005). Based on a fact intensive inquiry, a range may be disclosed in multiple prior art references instead of a single prior art reference. *Iron Grip Barbell Co., Inc. v. USA Sports, Inc.*, 392 F.3d 1317, 1322, 73 USPQ2d 1225, 1228 (Fed. Cir. 2004).

c. Obvious to Try

The Supreme Court has recently clarified that the examination of the teachings of the prior art should not be performed rigidly. Specifically, "a court must ask whether the improvement is more than the predictable use of prior art elements according to their established functions." *KSR Int'l Co.*, 550 U.S. 398, 402 (2007). "Often, it will be necessary for a court to look to interrelated teachings of multiple patents; the effects of demands known to the design community or present in the marketplace; and the background knowledge possessed by a person of ordinary skill in the art, all in order to determine whether there was an apparent reason to combine the known elements in the fashion claimed by the patent at issue." *Id.* at 402.

"To differentiate between proper and improper applications of 'obvious to try,' this court outlined two classes of situations where 'obvious to try' is erroneously equated with obviousness under § 103. In the first class of cases, 'what would have been "obvious to try" would have been to vary all parameters or try each of numerous possible choices until one possibly arrived at a successful result, where the prior art gave no indication of which parameters were critical or no direction as to which of many possible choices is likely to be successful.'" *In re Kubin*, 561 F.2d 1351, 1359 (Fed. Cir. 2009), quoting *In re O'Farrell*, 853 F.2d 894, 903 (Fed. Cir. 1988). "The inverse of this proposition is succinctly encapsulated by the Supreme Court's statement in *KSR* that where a skilled artisan merely pursues 'known options' from a 'finite number of identified, predictable solutions,' obviousness under § 103 arises.'" *Id,* quoting 550 U.S. at 421, 127 S.Ct. at 1727. "The second class of *O'Farrell*'s impermissible 'obvious to try' situation occurs where 'what was "obvious to try" was to explore a new technology or general approach that seemed to be a promising field of experimentation, where the prior art gave only general guidance as to the particular form of the claimed invention or how to achieve it.'" *Id.*, quoting 853 F.2d at 903. "Again, *KSR* affirmed the logical inverse of this statement by stating that § 103 bars patentability unless 'the improvement is more than the predictable use of prior art elements according to their established functions.'" *Id.*, at 1359, 1360, quoting 550 U.S. at 417, 127 S.Ct. at 1727. Accord, see *In re Cyclobenzaprine Hydrochloride Extended-Release Capsule Patent Litigation*, 676 F.3d 1063 (Fed. Cir. 2012).

"*KSR* did not create a presumption that all experimentation in fields where it is already a background of useful knowledge is 'obvious to try,' without considering the nature of the science or technology." *Leo Pharmaceutical Products, Ltd. v. Stanek*, 726 F.3d 1346, 1356 (Fed. Cir. 2013)(*inter partes reexamination*), quoting *Abbott Labs. v. Sandoz, Inc.*, 544 F.3d 1341, 1352 (Fed. Cir. 2008). "The problem was not known, the possible solutions to solving the problem were not known or finite, and the solution was not predictable. Therefore, the claimed invention would not have been obvious to try to one of ordinary skill in the art. Indeed ordinary artisans

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would not have thought to try all because they would not have recognized the problem." *Leo Pharmaceutical Products, Ltd.*, 726 F.3d at 1356-1357. "As an initial matter, an invention can often be the recognition of a problem itself." *Id.* at 1353. "Without a reasonable expectation of success or clues pointing to the most promising combinations, an artisan could have spent years experimenting without success." *Id.*

D. Analysis

As explained in detail below, with all due respect, the Examiner's rejections of the claims as being *prima facie* anticipated or *prima facie* obvious are all based upon clear error of law and/or errors of fact.

1. The rejection of claims 1-13 on the ground of nonstatutory double patenting as being unpatentable over claims 1-23 of U.S. Patent No. 8,206,892 to Keszler et al. (hereinafter Keszler '892).

With all due respect, claims 1-13 are not obvious over claims 1-23 of Keszler '892. Both independent claim 1 and independent claim 11 of the present application claim a ratio of ligand to metal suboxide cations of at least about 2. Respectfully, as discussed in further detail in light of the Stowers reference, the high molar ratio of peroxide ligands to metal suboxide cations would not have been obvious to a person of skill in the art at the time of the invention. The claims of Keszler '892 do not teach a particular ratio of ligands to metal suboxide cations. Similarly, the claims of Keszler are silent with respect to stability of the precursor solutions. With respect to claim 11, the claims of Keszler '892 does not teach the separate formation and combination of a solution with metal suboxide cations and a solution with peroxide ligands. Claims 1-13, therefore, are not obvious over claims 1-23 of Keszler '892.

2. The rejection of claims 1-5 and 7-10 under pre-AIA 35 U.S.C. § 103(a) as being unpatentable over Stowers, et al., "High Resolution, High Sensitivity Inorganic Resists", (2009) (hereinafter Stowers) as evidenced by JP 2006/284947 to Nakamura (hereinafter Nakamura).

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With all due respect, Stowers does not render Appellant's claimed invention *prima facie* unpatentable since it does not teach or suggest all of the features of Appellant's claimed invention. Suggestions that Stowers renders the missing elements obvious with no basis in its teachings to so modify the compositions is based on clear errors of fact and law. Furthermore, Stowers does not provide a reasonable expectation of success with respect to forming a usable composition or with respect to believing that a high ligand to metal suboxide cations ratio would result in the high performance found by Appellant. Additionally, Stowers does not teach or suggest precursor solutions that are stable for at least about 2 hours without additional mixing. Stability of precursor solutions is not mentioned in Stowers. Appellant notes that the authors of Stowers are present inventors. Stowers does not discuss how to address the stability issue. Even if Stowers rendered Applicant's claimed invention *prima facie* obvious, which it clearly does not, Applicant has presented clear unexpected results, which are the subject of US 8,415,000, which is a child application related to the present case. With all due respect, on the record as a whole, the Examiner has failed to establish obviousness by a preponderance of the evidence, and the analysis follows.

a. Prima Facie Obvious

Claims 2-5 and 7-10 depend from claim 1. With respect to claim 1, Appellant's claimed precursor solution differs from the composition of Stowers by the high ligand to metal suboxide cations ratio. In particular, Stowers discloses a ligand to metal suboxide cation molar ratio of 1:2. Stowers, page 730. Stowers, therefore, does not cite overlapping values of the parameters of the claimed invention. As discussed above, all elements of the claim must be taught. As the particular ligand range cited in claim 1 is not cited in Stowers, and as it does not overlap with the present range, under the law, *prima facie* obviousness has not been established.

b. Discovery of Optimum Values

The Examiner has stated that the ratio of the ligand to metal suboxide cation "is optimizable." Office Action at page 3. However, Stowers does not suggest that his parameter is a results effect variable, and therefore Stowers does not suggest that the parameter can be optimized

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to arrive at the presently claimed range. Respectfully, however, while discovery of optimum values of a results effective variable can be the basis for an obviousness rejection, courts have repeatedly held that it is not proper to use that doctrine when the ranges do not overlap, and there is no suggestion to vary the parameter in a way leading to the claimed range. Therefore, as the high ratio in the claims does not overlap with the ratio disclosed in Stowers, the peroxide concentration in Stowers cannot be used as a basis of an obviousness rejection without a further suggestion indicating the higher ratio. No such teaching is present in Stowers. Therefore, it would not have been obvious to optimize the compositional ratio in Stowers to reach Applicant's claimed range of values. The Office Action asserts on page 4 that "Stowers et al. discloses that peroxide inhibits condensation of metal oxides (please see page 732, lines 4-7 of left column.)" With all due respect, the statement in Stowers still does not indicate a concentration dependence related to the amount of peroxide. In summary, since Stowers does not suggest in any way that ligand concentration is a result effective variable, the Examiner's assertions on this point respectfully are a clear error of law.

Nonetheless, the Examiner has stated that, because peroxide inhibits the condensation of metal oxides, it would have been predictable that increasing the peroxide concentration would stabilize the phases and would predictably result in the qualitative improvement described in the specification. Respectfully, however, seemingly the Examiner's only basis for this assertion is Applicant's own specification. The ligand concentration proposed in Stowers is an integer ratio that suggests a particular desired stoichiometry of the stabilized composition in solution. With this perspective in mind, a person of skill in the art would not expect a ratio of ligands to metal suboxide cations of at least about two to be useful, and in particular there is no basis for expecting a result with the high performance discovered by Applicant.

The improved performance discovered by Applicant would seem to be based on the unexpected effect of peroxide that is not bound to the metal in solution. With this in mind, Stowers used what seemingly would have been understood at the time to have been the appropriate value based on the understanding of the chemistry. While Stowers itself represents a significant advance on the state of the art, the present work involves another important advance beyond the work of Stowers. Furthermore, there seems to be a misunderstanding regarding Stowers, since the reference itself does not seem to comment in any way on the purpose of the peroxide reactant. Based on Appellant's work, there seems to be hindsight attribution to Stowers

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that Stowers itself comments on the value of peroxides with respect to stabilizing the solution. With all due respect, this seems to be a clear error of fact. Thus, the high peroxide to metal suboxide cation ratio described in claim 1, results in unexpected improvement in the properties over Stowers. Thus, Stowers does not render the presently claimed invention *prima facie* obvious.

c. Obvious to Try

Additionally, since Stowers does not suggest in any way that ligand concentration is a result effective variable and since Stowers uses a stoichiometric amount of ligand suggesting that no variation in ligand would be useful it would not even be obvious to try increasing the peroxide to metal suboxide cation ratio. Even if it were obvious to try, as discussed above, the courts have stated that "obvious to try" does not equate with obviousness when the experimentation involves varying all parameters until a successful result is reached without any indication of which parameters are critical or could be varied successfully. While Stowers uses peroxide in their formulation, it sets the peroxide ratio at the expected stoichiometric binding, does not vary it, and does not suggest that it could or should be varied for any purpose, let alone that varying the concentration of ligand could improve results. See Stowers, page 730, experimental and page 732, column 1. In order to come to the high peroxide to metal suboxide cation ratio present in claim 1, one would have to vary all parameters without any indication in the references that increasing the peroxide to metal suboxide cation ratio would be successful. Therefore, even though not obvious to try, even assuming it were obvious to try, it would not be obvious to vary the peroxide to metal suboxide cation ratio to arrive at the presently claimed high ratio.

d. Unexpected Results Rebut any Finding of *Prima Facie* Obviousness

Appellant has provided a clear explanation of the errors of fact and errors of law involved in the rejection such that *prima facie* obviousness clearly has not been established. Nevertheless, Appellant has also established clear unexpected results commensurate with the present claim scope. Specifically, the resulting coating materials provide previously unobtainable radiation patterning capability. The clear unexpected nature of these results is the subject of a separate

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patent application, child patent 8,415,000. Respectfully, the USPTO has already opined on the unexpected nature of the materials formed with the precursor compositions through the issuance of the '000 patent. To the extent that *prima facie* obviousness has been established, which it clearly has not, such a showing has been clearly and soundly rebutted by the USPTO issuance of the '000 patent. With all due respect, the record clearly established that the Examiner has failed to establish obviousness by a preponderance of the evidence on record.

3. The rejection of claim 6 under pre-AIA 35 U.S.C. § 103(a) as being unpatentable over Stowers as evidenced by Nakamura in further view of WO 2009/120169 to Keszler et al (hereinafter Keszler '169).

Claim 6 depends from claim 1. The Examiner cited Keszler '169 for its teaching related to particular polyatomic anions. The deficiencies of Stowers with respect to claim 1 are presented in detail above. Keszler '169 is also discussed below in the context of a distinct obviousness rejection. With all due respect, the combination of Stowers and Keszler '169 does not teach or suggest the high ligand to metal suboxide cation ratio. As discussed above, Stowers discloses a ligand to metal suboxide cation ratio of 1:2 and the high ligand to metal suboxide cation ratio leads to unexpected improvement in the properties over Stowers. Keszler '169 does not make up for the deficiencies of Stowers. Keszler '169 only discusses adding peroxide to the solution as an option and does not discuss any particular ratios. See Keszler '169, page 26, lines 12-14. Thus, Stowers and Kezler '169 does not render the presently claimed invention *prima facie* obvious.

4. The rejection of claims 1-13 under pre-AIA 35 U.S.C. § 103(a) as being unpatentable over U.S. Publication No. 2005/0242330 to Herman et al. (hereinafter Herman) in view of KR 2008/0090383 to Keszler et al. (citations to US Pub. No. 2011/0045406) (hereinafter Keszler '383).

Claims 1-10

With regard to claim 1, as stated by the Examiner, Herman does not teach radiation sensitive ligands comprising peroxide groups, or the claimed precursor solution stability. Keszler '383 does not teach or snggest a molar concentration ratio of ligands to metal suboxide

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cations of at least about two, or the claimed stability of the precursor solution. Keszler '383, therefore, does not make up for the deficiencies of Herman. Nevertheless, the Examiner asserts that it would be obvious to "optimize" the content of ligands relative to the metal suboxide cations. The Examiner cites *In re Boesch* for support for this position. With all due respect *Boesch* does not support the Examiner's position. *In re Boesch*, 617 F.2d 272, 275 (CCPA 1980)("Each of the ranges of constituents in appellant's claimed alloys overlaps ranges disclosed by Pohlman et al. and Lamb)." The optimization found in *Boesch* was within boundaries explicitly provided in the prior art references along with suggestions of "the kind of experimentation necessary to achieve the claimed composition" with the desired target structure. *Id.* at 276. Both of these circumstances are missing under the facts of the present case, so respectfully the Examiner's position is based on clear error of law.

Herman in view of Keszler '383 does not teach or suggest each and every element of claim 1. Neither of the cited references suggest in any way that the concentration of peroxide ligands is a results effective variable. The combination of Herman and Keszler '383 therefore does not render claims 1-10 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious. Also, as discussed in detail above, Appellant has presented clear evidence of unexpected results that would rebut any *prima* facie case, although such a *prima facie* case has not been established.

Claim 11

With regard to claim 11, as stated by the Examiner, Herman does not teach radiation sensitive ligands comprising peroxide groups. Office Action, page 7. Keszler '383 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two. Office Action, page 7. Keszler '383, therefore, does not make up for the deficiencies of Herman. As discussed above, a person of skill in the art would not have expected unbound ligand in the precursor solution to result in improved stability and patterning properties. Herman in view of Keszler '383 does not teach or suggest each and every element of claim 11.

Furthermore, the combination of Herman and Keszler '383 does not teach or suggest the mixing method discussed in claim 11. Herman teaches a solution containing both a metal containing cation and an polyatomic anion. Herman [0009]. The solution does not contain a

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complexing solution. Keszler '383 teaches forming the film from aqueous solutions containing the metal suboxide cation and the polyatomic anion. Keszler [0078]. By contrast, claim 11 discusses combining a first aqueous solution, a complexing solution, and an additional composition. Appellant's specification discusses the significance of processing order in forming the precursor solutions. The combination of Herman and Keszler '383 therefore does not render claim 11 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious. Furthermore, unexpected results are presented with respect to the processing approaches.

Claim 12

With regard to claim 12, as stated by the Examiner, Herman does not teach radiation sensitive ligands comprising peroxide groups. Office Action, page 8. Keszler '383 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two. Office Action, page 8. Keszler '383, therefore, does not make up for the deficiencies of Herman. As discussed above, a person of skill in the art would not have expected unbound ligand in the precursor solution to result in improved stability and patterning properties. The combination of Herman and Keszler '383 does not teach or suggest the mixing method discussed in claim 12.

Furthermore, the combination of Herman and Keszler does not teach for suggest mixing the complexing solution with an aqueous solution comprising metal suboxide cations before introducing polyatomic anions. Keszler uses hydrogen peroxide to adjust the pH of the solution without complexing with the compounds after the cations and anions have been mixed. Keszler [0103]. Herman does not use a complexing ligand. In contrast, claim 12 mixes the aqueous solution with the complexing solution prior to the introduction of the polyatomic anion. The combination of Herman and Keszler '383 therefore does not render claim 12 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious. Furthermore, unexpected results are presented with respect to the processing approaches.

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Claim 13

With regard to claim 13, as stated by the Examiner, Herman does not teach radiation sensitive ligands comprising peroxide groups. Office Action, page 8. Keszler '383 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two. Office Action, page 8. Keszler '383, therefore, does not make up for the deficiencies of Herman. As discussed above, a person of skill in the art would not have expected unbound ligand in the precursor solution to result in improved stability and patterning properties. The combination of Herman and Keszler '383 does not teach or suggest the mixing method discussed in claim 12. And, the combination of Herman and Keszler does not teach for suggest mixing the complexing solution with an aqueous solution comprising metal suboxide cations before introducing polyatomic anions.

Furthermore, neither Keszler nor Herman teaches or suggests allowing the ligand-cation mixture to age for at least about 5 minutes before adding the polyatomic anion. As previously discussed, Herman does not teach a complexing ligand. Keszler does not teach adding hydrogen peroxide before the polyatomic cation, and therefore it is impossible for Keszler to teach a ligand-cation mixture that has been aged for at least 5 minutes. In contrast, claim 13 discloses aging the ligand-cation mixture solution for at least about 5 minutes prior to the addition of the polyatomic anion. The combination of Herman and Keszler '383 therefore does not render claim 13 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious. Furthermore, unexpected results are presented with respect to the processing approaches.

5. The rejection of claims 1-13 under pre-AIA 35 U.S.C. § 103(a) as being unpatentable over Keszler '169.

Claims 1-10

With regard to claim 1, Keszler '169 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two. Similarly, Keszler '169 does not teaqch the claimed stability of the solution. Keszler '169 does not teach or suggest each and every element of claim 1. Keszler '169 recognized an important advance through the introduction of radiation sensitive ligands. See paragraphs [0103], [0116] and [0124] as well as

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US 8,206,892. However, Keszler '169 does not exemplify these compositions or determine the improved approach to achieve desired compositions and corresponding patterning as described and claimed in the present application. The present rejection is deficient for all of the reasons discussed in detail for Stowers. Keszler '169 therefore does not render claims 1-10 *prima facie* obvious. Furthermore, as discussed in detail above, Appellant has presented clear evidence of unexpected results, and this evidence clearly rebuts any showing of *prima facie* obviousness, although such a showing has not been made. Thus, the Kesler '169 does not render the presently claimed invention obvious by a preponderance of the evidence.

Claim 11

With regard to claim 11, Keszler '169 does not teach or suggest every element of claim 11. As discussed above, Keszler '169 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two, and person of skill in the art would not have expected unbound ligand in the precursor solution to result in improved stability and patterning properties.

Furthermore, Keszler '169 does not teach or suggest combining a first aqueous solution comprising metal suboxide cations, a complexing solution, and a composition comprising a polyatomic inorganic anion to form the coating precursor solution. As acknowledged by the Examiner, Keslzer '169 does not teach or suggest "the mixing method of dissolving $HfOCl_2$ in water followed by mixing it with H_2O_2 and H_2SO_4". The Examiner has stated that the order of mixing and the state of the components can be optimized. Office Action, page 11. Respectfully, however, as discussed above, optimization only applies when the reference motivation the needed experimentation. As this particular deficiency does not relate to any suggestion of experimentation in the reference, it is an error of law to use the optimization argument to find obviousness. The reference does not even make the line of experimentation obvious to try. Claim 11 combines a first aqueous solution comprising metal suboxide cations, a complexing solution, and a composition comprising a polyatomic inorganic anion to form the coating precursor solution. Therefore, Keszler '169 does not teach or suggest each and every element of claim 11. Keszler '169 does not render claim 11 *prima facie* obvious. Furthermore, unexpected results are presented with respect to the processing approaches.

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Claim 12

With regard to claim 12, Keszler '169 does not teach or suggest every element of claim 12. As discussed above, Keszler '169 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two, and person of skill in the art would not have expected unbound ligand in the precursor solution to result in improved stability and patterning properties. Additionally, Keszler '169 does not teach or suggest combining a first aqueous solution comprising metal suboxide cations, a complexing solution, and a composition comprising a polyatomic inorganic anion to form the coating precursor solution, and it is an error of law to use the optimization argument to find obviousness in these circumstances.

Furthermore, Keszler '169 does not teach or suggest mixing the aqueous solution with the complexing solution prior to introduction of the inorganic anions. As implied by the Examiner, Keszler '169 does not teach or suggest mixing the aqueous solution with the complexing solution prior to introduction of the inorganic anions. The Examiner has argued that the method and the mixing order can be "easily derived by persons skilled in the art by simply adjusting or optimizing the compounds". Office Action, page 11. Respectfully, however, as discussed above, Keszler '169 does not suggest any experimentation along the proposed lines. As the order of mixing does not relate to the methodology discussed by Keszler '169, it is an error of law to use the optimization argument to find obviousness. Claim 12 mixes the aqueous solution with the complexing solution prior to the introduction of the inorganic anions. Therefore, Keszler '169 does not teach or suggest each and every element of claim 12. Keszler '169 does not render claim 12 *prima facie* obvious. Furthermore, unexpected results are presented with respect to the processing approaches.

Claim 13

With regard to claim 13, Keszler '169 does not teach or suggest every element of claim 13. As discussed above, Keszler '169 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two, and person of skill in the art would not have expected unbound ligand in the precursor solution to result in improved stability and patterning properties. Additionally, Keszler '169 does not teach or suggest mixing the aqueous

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solution with the complexing solution prior to introduction of the inorganic anions, and it is an error of law to use the optimization argument to find obviousness in these circumstances.

Furthermore, Keszler '169 does not teach or suggest aging the ligand-cation solution for at least about 5 minutes prior to the introduction of the inorganic anions. As implied by the Examiner, Keszler '169 does not teach or suggest mixing the aqueous solution with the complexing solution prior to introduction of the inorganic anions. The Examiner has argued that the aging time is optimizable. Office Action, page 11. Respectfully, however, as discussed above, Keszler '169 does not suggest any experimentation along such lines. So the claimed method is not even obvious to try over Keszler '169. As Keszler '169 does not teach aging a ligand-cation mixture, let alone a particular time frame, it is an error of law to use the optimization argument to find obviousness. Claim 13 refers to aging the ligand-cation solution for at least about 5 minutes prior to the introduction of the inorganic anions. Therefore, Keszler '169 does not teach or suggest each and every element of claim 13. Keszler '169 does not render claim 13 *prima facie* obvious. Thus, the combination does not render the presently claimed invention *prima facie* obvious. Furthermore, unexpected results are presented with respect to the processing approaches.

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REQUEST FOR RELIEF

Applicants believe that the Patent Office has failed to meet its burden of persuasion with respect to unpatentability of any of the claims on the present record. Thus, Appellant respectfully requests the reversal of the rejections of claims.

Respectfully submitted,

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CLAIMS APPENDIX

1. An aqueous inorganic patterning precursor solution comprising a mixture of water, metal suboxide cations, polyatomic inorganic anions and radiation sensitive ligands comprising peroxide groups, wherein the solution has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours without additional mixing.

2. The aqueous inorganic patterning precursor solution of claim 1 having a metal suboxide cation concentration from about 0.01 M to about 1.4 M.

3. The aqueous inorganic patterning precursor solution of claim 2 having a polyatomic anion concentration from about 0.75 to about 1.5 times the metal suboxide cation concentration.

4. The aqueous inorganic patterning precursor solution of claim 1 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof.

5. The aqueous inorganic patterning precursor solution of claim 1 wherein the polyatomic anions comprise sulfate.

6. The aqueous inorganic patterning precursor solution of claim 1 wherein the polyatomic anions comprise borate, phosphate, tungstate, silicate or combinations thereof.

7. The aqueous inorganic patterning precursor solution of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

8. The aqueous inorganic patterning precursor solution of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 7.

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9. The aqueous inorganic patterning precursor solution of claim 1 having a stability of at least 24 hours without additional mixing.

10. The aqueous inorganic patterning precursor solution of claim 1 wherein the metal suboxide cations comprise Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or a combination thereof.

11. A method for formation of a radiation sensitive inorganic coating precursor solution, the method comprising:

combining a first aqueous solution comprising metal suboxide cations, a complexing solution comprising a ligand having a peroxide group and a composition comprising a polyatomic inorganic anion to form the coating precursor solution, wherein the molar concentration ratio of ligands to metal suboxide cations is at least about 2.

12. The method of claim 11 wherein the first aqueous solution is mixed with the complexing solution to form a ligand-cation mixture solution prior to introduction of the inorganic anions.

13. The method of claim 12 wherein the ligand-cation mixture solution is aged at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion.

14. The method of claim 11 further comprising:

forming a layer of a radiation patternable coating material comprising the coating precursor solution to form a coated substrate;

heating the coated substrate to remove at least a portion of the solvent;

irradiating the coated substrate with a pattern of radiation to condense a coating at the irradiated locations; and

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heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the coating with a developer.

15. The method of claim 14 wherein the radiation is ultraviolet light.

16. The method of claim 14 wherein the radiation is light having a wavelength of about 193 nm.

17. The method of claim 14 wherein the radiation is extreme ultraviolet light.

18. The method of claim 14 wherein the radiation comprises an electron beam.

19. The method of claim 14 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof and wherein the polyatomic anions comprise sulfate anions.

20. The method of claim 14 wherein the coating material comprises a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

21. The method of claim 14 wherein the formation of the coated substrate is performed using spin coating, spray coating, dip coating or knife edge coating.

22. The method of claim 14 wherein the layer of coating material has an average thickness from about 1 nm to about 40 nm.

23. The method of claim 14 wherein the radiation is directed through a mask to expose selected portions of the coated substrate.

24. The method of claim 14 wherein a laser beam or an electron beam is scanned over the coated substrate to expose selected portions of the coated substrate.

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25. The method of claim 14 further comprising exposing the coated substrate with a developing composition to at least partially remove the coating composition at unexposed locations.

26. The method of claim 25 wherein the developing composition is contacted with the coated substrate for no more than about 75 seconds.

27. The method of claim 25 wherein the developing composition comprises tetramethyl ammonium hydroxide.

28. The method of claim 27 wherein the developing composition has a concentration of tetramethyl ammonium hydroxide of about 2.38 weight percent.

29. The method of claim 14 wherein the substrate is treated along a surface with a hydrophilic surface treatment prior to the forming of the radiation patternable coating material.

30. The method of claim 14 wherein the forming of the radiation patternable coating material comprises a plurality of coating steps to form a coating material of a selected thickness.

31.-38. (Cancelled)

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EVIDENCE APPENDIX

1. Japaenese Patent Application No. JP 2006/284947 to Nakamura.

2. PCT Application No. WO 2009/120169 to Keszler et al..

3. Korean Application No. KR 2008/0090383 to Keszler et al..

4. Stowers et al., "High Resolution, High Sensitivity Inorganic Resists", 86 MICROELECTRONIC ENGINEERING 730-733, (2009).

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RELATED PROCEEDINGS APPENDIX

None.

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No documents available for this priority number.

Espacenet

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PHOTOSENSITIVE RESIN COMPOSITION FOR LIGHT SHIELDING FILM, METHOD FOR FABRICATING LIGHT SHIELDING FILM, TRANSFER MATERIAL, AND METHOD FOR MANUFACTURING TRANSFER MATERIAL

Inventor(s): NAKAMURA HIDEYUKI ± (NAKAMURA HIDEYUKI)

Applicant(s): FUJI PHOTO FILM CO LTD ± (FUJI PHOTO FILM CO LTD)

Classification: **- international:** ***B05D1/26; G02B5/20; G03F7/004; G03F7/038***
- cooperative:

Application number: JP20050105150 20050331

Priority number(s): JP20050105150 20050331

Abstract of JP2006284947 (A)

PROBLEM TO BE SOLVED: To provide a photosensitive resin composition for a light shielding film, with which high black density is obtained in a thin film state, which is excellent in a light shielding property and in a heat curing property after exposure, and with which high resolution image can be formed. ; SOLUTION: The photosensitive resin composition for the light shielding film contains metal particles and/or metal compound particles as a black colorant, together with a binder resin, a photo-acid generator and a cross-linking agent. ; COPYRIGHT: (C)2007,JPO&INPIT

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最終頁に続く

(54)【発明の名称】遮光膜用感光性樹脂組成物、遮光膜の作製方法、転写材料及びその製造方法

(57)【要約】
【課題】　薄膜で高い黒濃度を得、遮光性に優れると共に、露光後の加熱硬化性に優れ、高解像度の像の形成が可能な遮光膜用感光性樹脂組成物を提供する。
【解決手段】　バインダー樹脂、光酸発生剤及び架橋剤と共に、黒色剤として金属粒子及び／又は金属化合物粒子を含有している。
【選択図】　なし

【特許請求の範囲】
【請求項1】
バインダー樹脂と、光を吸収して酸を発生する光酸発生剤と、前記光酸発生剤の作用により架橋する架橋剤と、金属粒子及び／又は金属化合物粒子とを含有することを特徴とする遮光膜用感光性樹脂組成物。
【請求項2】
顔料を更に含む請求項１に記載の遮光膜用感光性樹脂組成物。
【請求項3】
前記顔料がカーボンブラック又は黒鉛である請求項２に記載の遮光膜用感光性樹脂組成物。
【請求項4】
膜厚１．０μｍの遮光膜を形成した際の光学濃度が４．０以上である請求項１～３のいずれか１項に記載の遮光膜用感光性樹脂組成物。
【請求項5】
表示装置を構成する遮光膜の形成に用いられる請求項１～４のいずれか１項に記載の遮光膜用感光性樹脂組成物。
【請求項6】
仮支持体上に、少なくとも１層の、バインダー樹脂と、光を吸収して酸を発生する光酸発生剤と、前記光酸発生剤の作用により架橋する架橋剤と、金属粒子及び／又は金属化合物粒子とを含有する感光性樹脂層を有することを特徴とする転写材料。
【請求項7】
遮光膜の形成に用いられる請求項６に記載の転写材料。
【請求項8】
表示装置を構成する遮光膜の形成に用いられる請求項６又は７に記載の転写材料。
【請求項9】
基板上に、請求項１～５のいずれか１項に記載の遮光膜用感光性樹脂組成物を塗布し、乾燥させて感光性樹脂層を形成する工程と、
形成された前記感光性樹脂層をパターン状に露光する工程と、
形成された前記感光性樹脂層を加熱する工程と、
少なくとも前記露光後の前記感光性樹脂層を現像して未露光部を除去する工程と、
を含むことを特徴とする遮光膜の作製方法。
【請求項10】
前記塗布は、スリット状ノズルを有する塗布装置を用いて行なう請求項９に記載の遮光膜の作製方法。
【請求項11】
請求項６～８のいずれか１項に記載の転写材料を用いて、仮支持体上の少なくとも１層の感光性樹脂層を基板に転写する工程と、
転写された前記感光性樹脂層をパターン状に露光する工程と、
転写された前記感光性樹脂層を加熱する工程と、
少なくとも前記露光後の前記感光性樹脂層を現像して未露光部を除去する工程と、
を含むことを特徴とする遮光膜の作製方法。
【請求項12】
請求項６～８のいずれか１項に記載の転写材料の製造方法であって、
仮支持体上に、スリット状ノズルを有する塗布装置を用いた塗布により感光性樹脂層を塗設することを特徴とする転写材料の製造方法。

【発明の詳細な説明】
【技術分野】
【0001】
本発明は、遮光性の膜形成に好適な遮光膜用感光性樹脂組成物、並びにこれを用いた遮光膜の作製方法、転写材料及びその製造方法に関する。

【背景技術】
【0002】
近年、例えば液晶表示素子や固体撮像素子として組み合わせ、カラー画像を得ることを目的としたカラーフィルタが注目を浴びている。このカラーフィルタは、二種以上の画素（Ｒ（赤）、Ｇ（緑）、Ｂ（青）、遮光膜（ブラックマトリクスなど）や、透明部分、透明画素などが組み合わされてなるカラー画像層で構成される。
【0003】
カラーフィルタの製造方法としては、従来は、カラーフィルタを設置する対象面に着色剤を含有する感光性樹脂溶液を塗布し、その塗布膜をパターン状に露光して画素層を形成し、次いでその画素層の上に、他の色の着色剤を含有する感光性樹脂溶液を塗布し、この塗布膜をパターン状に露光して最初の画素層と着色の異なる画素層を形成する工程を繰り返し行なう方法が一般的に利用されてきた。
【0004】
これに対し、別に用意した支持体シート（仮支持体）の上に、着色剤を含有する感光性樹脂溶液を塗布して着色感光性樹脂層を形成して構成された、色が異なる複数枚の感光性転写シート（転写材料）を用意し、まず一枚の感光性転写シートをカラーフィルタ設置対象面に載せて着色感光性樹脂層を転写し、これをパターン状に露光して画素層を形成し、次いでその画素層を覆うようにして更に、他の色の感光性転写シートを重ねて着色感光性樹脂層を転写し、これをパターン状に露光して最初の画素層と着色の異なる画素層を形成する工程を繰り返し行なう方法が提案され、近年ではかかる方法の利用が増えている。この方法による場合、高い均質性と高精度の膜厚均一性を有する着色感光性樹脂層で構成された画素層を形成することができる。
【0005】
上記のいずれの方法でも、カラーフィルタを構成する着色画素の作製には、画素形成用のパターン状に切り抜かれたフォトマスクを用い、その開口部分を通過させて感光性樹脂層を露光し、その露光部分を硬化させ、次いで未露光部（未硬化部）を現像液で現像処理して除去する方法が利用される。
【0006】
しかしながら、従来の転写材料の場合、感光性樹脂層は、光重合開始剤、光重合性モノマー、アクリル系重合バインダー、光重合禁止剤、顔料等を含んでラジカル重合系に構成されており、このような感光性樹脂層を有する面を露光すると、感光性樹脂層の深さ方向（厚み方向）で深さに伴なう光の減衰により反応率が異なり、層表面から離れたガラス等の基板側、具体的には基板と感光性樹脂層との界面付近では著しく反応率が低下してほとんど重合硬化しないため、現像処理した際に細線画像にサイドエッチが入りやすく、細線ができない、あるいは現像ラチチュードが狭いという問題があった。
特に、遮光膜（ブラックマトリクスなど）の用途では高い遮光性能が要求されるが、黒濃度が高くなるほど層厚に伴なう光の減衰は大きくなり、サイドエッチの発生や現像ラチチュードの低下はより顕著となる。
【0007】
かかる問題に対して、バインダー、光酸発生剤、及び光酸発生剤の作用により架橋する架橋剤（メラミン系樹脂など）等を含む感光性樹脂組成物が提案されている（例えば、特許文献１参照）。これは、光を受けて光酸発生剤から生成する酸（$I \rightarrow I^- + H^+$）の触媒作用によって酸反応性分子（架橋剤）から架橋体を生成して重合硬化するものである（ＰＡＧ；Photo Acid Generator）。
【0008】
この場合、感光性樹脂層の黒濃度が高いときには、やはり露光時に発生する酸の発生量は層表面付近で多く、層表面から離れた基板との界面付近では少なくなるため、さらに加熱処理を施すことによって酸の拡散を促進し、層表面から厚み方向に向かって架橋反応が促され、基板との界面近傍に至るまで感光性樹脂層の重合硬化を良好に行なうことができる。
【特許文献1】

特開２００２－３５１０７５号公報
【発明の開示】
【発明が解決しようとする課題】
【0009】
しかしながら、酸の触媒作用を利用したＰＡＧでは、加熱処理により拡散（加熱拡散）する酸（H^+）は、層の厚み方向のみならず、あらゆる方向（厚み方向である縦方向に対する横方向など）に拡散していくため、高濃度で高硬度の膜が得られても細線を形成するのは難しい。また、現像ラチチュードの点でも不充分である。結果的に、ボケた画像しか得られない。特に高い黒濃度の膜に構成しようとする場合には、感光性樹脂層はある程度の厚みが必要であり、充分な重合硬化性を得るには露光後の加熱に長時間を要するばかりか、加熱時間が長くなると層内に酸が広く拡散し、ボケの程度も悪化してしまう。
【0010】
本発明は、上記に鑑みなされたものであり、薄膜で高い黒濃度が得られ、遮光性に優れると共に、短時間での加熱硬化性に優れ、高解像度の像を形成することができる遮光膜用感光性樹脂組成物、薄膜で黒濃度が高く、遮光性及び短時間での加熱硬化性に優れた膜の形成を可能とする転写材料及びその製造方法、並びに、薄膜で黒濃度が高く遮光性能に優れた遮光膜を高解像度に形成し得、加熱拡散による硬化をより短い時間で行ない得る遮光膜の作製方法を提供することを目的とし、該目的を達成することを課題とする。
【課題を解決するための手段】
【0011】
本発明は、前記ＰＡＧを利用して高解像度で高濃度の黒パターンを形成する場合において、高濃度化と光酸発生剤から生成する酸の層厚方向以外の方向への拡散の抑制には、金属系粒子が有効であるとの知見を得、かかる知見に基づいて達成されたものである。
前記課題を達成するための具体的手段は以下の通りである。
【0012】
＜１＞　バインダー樹脂と、光を吸収して酸を発生する光酸発生剤と、前記光酸発生剤の作用により架橋する架橋剤と、金属粒子及び／又は金属化合物粒子とを含有することを特徴とする遮光膜用感光性樹脂組成物である。
＜２＞　顔料を更に含む前記＜１＞に記載の遮光膜用感光性樹脂組成物である。
【0013】
＜３＞　前記顔料がカーボンブラック又は黒鉛である前記＜２＞に記載の遮光膜用感光性樹脂組成物である。
＜４＞　膜厚１．０μｍの遮光膜を形成した際の光学濃度が４．０以上である前記＜１＞～＜３＞のいずれか１つに記載の遮光膜用感光性樹脂組成物である。
＜５＞　表示装置を構成する遮光膜の形成に用いられる前記＜１＞～＜４＞のいずれか１つに記載の遮光膜用感光性樹脂組成物である。
【0014】
＜６＞　仮支持体上に、少なくとも１層の、バインダー樹脂と、光を吸収して酸を発生する光酸発生剤と、前記光酸発生剤の作用により架橋する架橋剤と、金属粒子及び／又は金属化合物粒子とを含有する感光性樹脂層を有することを特徴とする転写材料である。
＜７＞　遮光膜の形成に用いられる前記＜６＞に記載の転写材料である。
＜８＞　表示装置を構成する遮光膜の形成に用いられる前記＜６＞又は＜７＞に記載の転写材料である。
【0015】
＜９＞　基板上に、前記＜１＞～＜５＞のいずれか１つに記載の遮光膜用感光性樹脂組成物を塗布し、乾燥させて感光性樹脂層を形成する工程と、形成された前記感光性樹脂層をパターン状に露光する工程と、形成された前記感光性樹脂層を加熱する工程と、少なくとも前記露光後の前記感光性樹脂層を現像して未露光部を除去する工程とを含むことを特徴とする遮光膜の作製方法である。
＜１０＞　前記塗布は、スリット状ノズルを有する塗布装置を用いて行なう前記＜９＞

に記載の遮光膜の作製方法である。
【0016】
＜１１＞　前記＜６＞～＜８＞のいずれか１つに記載の転写材料を用いて、仮支持体上の少なくとも１層の感光性樹脂層を基板に転写する工程と、転写された前記感光性樹脂層をパターン状に露光する工程と、転写された前記感光性樹脂層を加熱する工程と、少なくとも前記露光後の前記感光性樹脂層を現像して未露光部を除去する工程とを含むことを特徴とする遮光膜の作製方法である。
＜１２＞　前記＜６＞～＜８＞のいずれか１つに記載の転写材料の製造方法であって、仮支持体上に、スリット状ノズルを有する塗布装置を用いた塗布により感光性樹脂層を塗設することを特徴とする転写材料の製造方法である。
【発明の効果】
【0017】
本発明によれば、薄膜で高い黒濃度が得られ、遮光性に優れると共に、短時間での加熱硬化性に優れ、高解像度の像を形成することができる遮光膜用感光性樹脂組成物、薄膜で黒濃度が高く、遮光性及び短時間での加熱硬化性に優れた膜の形成を可能とする転写材料及びその製造方法、並びに、薄膜で黒濃度が高く遮光性能に優れた遮光膜を高解像度に形成し得、加熱拡散による硬化をより短い時間で行ない得る遮光膜の作製方法を提供することができる。
【発明を実施するための最良の形態】
【0018】
以下、本発明の遮光膜用感光性樹脂組成物、遮光膜の作製方法、並びに転写材料及びその製造方法について詳細に説明する。
【0019】
＜遮光膜用感光性樹脂組成物＞
本発明の遮光膜用感光性樹脂組成物は、バインダー樹脂と、光酸発生剤と、架橋剤と、金属粒子及び／又は金属化合物粒子とを少なくとも含んでなり、必要に応じて、着色剤や界面活性剤等のその他の成分を用いて構成することができる。
【0020】
本発明の遮光膜用感光性樹脂組成物においては、光を受けて光酸発生剤から生成する酸（H^+）の触媒作用によって後述のバインダー樹脂と架橋剤（例えば酸架橋性のメチロール化メラミン樹脂）との間で架橋反応を起こさせると共に、さらに加熱処理を加えることにより酸の拡散を促進させることで、層の表面から基板界面付近の層深部に向かって架橋反応が促され、表面から厚み方向の層深部に至る感光性樹脂層が充分に重合硬化する（ＰＡＧ）。そのため、黒濃度が高濃度であっても基板界面まで充分に架橋反応させ得ると共に、現像の許容度が広く、一方で成分の混合、塗布、乾燥工程での架橋反応は抑えられ、露光部と未露光部の現像液に対する溶解性のコントラストを充分に大きくとることができる。したがって、薄膜で高濃度、高精細な遮光膜（ブラックマトリックスなど）を得ることができる。
さらに、本発明の遮光膜用感光性樹脂組成物は、後述するように、金属粒子や金属化合物粒子を黒色剤として含み、薄膜で高濃度が得られるので、前記ＰＡＧによる場合に、酸の拡散は薄い層中で起こることから加熱拡散による硬化を短時間で行なえると共にパターンの線太りも生じ難い。したがって、薄膜で高濃度を有しかつ高解像度の遮光膜（ブラックマトリックスなど）が得られる。
【0021】
－バインダー樹脂－
本発明の遮光膜用感光性樹脂組成物は、バインダー樹脂の少なくとも１種を含有する。このバインダー樹脂は、パターン露光で後述の光酸発生剤から生成する酸の触媒作用で後述の架橋剤と架橋体（ポリマー）をつくって硬化させるものである。
【0022】
バインダー樹脂としては、例えば、（メタ）アクリル系樹脂、ポリエステル樹脂、ビニ

ル系樹脂、ノボラック樹脂（フェノールノボラック樹脂、クレゾールノボラック樹脂等）、ポリヒドロキシスチレン等の公知のバインダー樹脂の中から適宜選択することができる。

【0023】

本発明では特に、（メタ）アクリル系のモノマーの共重合によって得られるビニル系共重合体が好ましく、メタクリル酸アルキルエステル、アクリル酸アルキルエステル、又はカルボキシル基含有モノマーを構成単位として含む共重合体がより好ましい。柔軟さを付与する点で、（メタ）アクリル系が好ましく、弱アルカリ現像適正の付与の点で、カルボキシル基を含有することが好ましい。

なお、（メタ）アクリルは、アクリル又はメタクリルの両方をとり得ることを示す。以下同様である。

【0024】

上記の中でも、特にメタクリル酸メチル及びベンジルメタクリレートの少なくとも１つを含む共重合体が好ましい。メタクリル酸メチル及びベンジルメタクリレートの少なくとも１つを含む共重合体には、メタクリル酸メチルを含む共重合体、ベンジルメタクリレートを含む共重合体、メタクリル酸メチル及びベンジルメタクリレートを含む共重合体等が挙げられる。

【0025】

前記メタクリル酸メチルを含む共重合体には、メタクリル酸／メタクリル酸メチル共重合体（共重合比：１４～１７．６モル％／８２．４～８６モル％、重量平均分子量２０，０００～１４０，０００）、メタクリル酸／メタクリル酸メチル／エチルアクリレート共重合体（共重合比：５～１０モル％／７０～６０モル％／２５～３０モル％、重量平均分子量２０，０００～１４０，０００）等が挙げられる。

【0026】

前記ベンジルメタクリレートを含む共重合体には、メタクリル酸／ベンジルメタクリレート共重合体（共重合比：２５～３７モル％／７５～６３モル％、重量平均分子量２０，０００～１５０，０００）、メタクリル酸／ベンジルメタクリレート／スチレン共重合体（共重合比：２０モル％／１７．８モル％／６２．２モル％、重量平均分子量２０，０００～１４０，０００）等が挙げられる。

【0027】

前記メタクリル酸メチル及びベンジルメタクリレートを含む共重合体には、メタクリル酸／メタクリル酸メチル／ベンジルメタクリレート共重合体（共重合比：１４．６～２７．２モル％／７９．１～３２．７モル％／１６．３～４０モル％、重量平均分子量２０，０００～１５０，０００）、メタクリル酸／メタクリル酸メチル／ベンジルメタクリレート／２－エチルヘキシルアクリレート共重合体（共重合比：１０～１５モル％／７０～６５モル％／１０モル％／１０モル％、重量平均分子量２０，０００～１５０，０００）等が挙げられる。

【0028】

従来より市販のネガ型レジスト組成物によく使用されているクレゾールノボラック樹脂やポリヒドロキシスチレン及びその誘導体は露光後、ベーク後に着色してしまうが、このような露光後、ベーク処理時での着色が少なく、光透過率が低下しない点で、上記したメタクリル酸／ベンジルメタクリレート共重合体、メタクリル酸／メタクリル酸メチル／ベンジルメタクリレート共重合体等が特に好ましい。

【0029】

前記バインダー樹脂の遮光膜用感光性樹脂組成物における含有量としては、該組成物の全固形分に対して、１０～９０質量％が好ましく、２０～７０質量％がより好ましい。

【0030】

－光酸発生剤－

本発明の遮光膜用感光性樹脂組成物は、光酸発生剤の少なくとも１種を含有する。この光酸発生剤は、パターン状に露光した際に酸（H^+）を発生し、架橋反応による重合硬化

を促進させるものである。

【0031】

光の照射により酸を発生する光酸発生剤には、有機ハロゲン化合物、オニウム塩、スルホン酸エステル等が挙げられる。これらの中では、有機ハロゲン化合物が好ましく、特にハロメチル化トリアジン化合物、ハロメチル化オキサジアゾール化合物が好ましい。

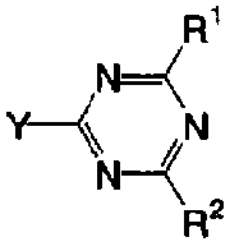
【0032】

前記ハロメチル化トリアジン化合物としては、下記一般式（１）で表される化合物が挙げられる。但し、本発明においては、これらに限定されるものではない。

【0033】

【化1】

(1)



【0034】

前記一般式（１）中、R^1及びR^2は、各々独立にハロメチル基を表し、Ｙは炭素数５以上の有機基を表す。

【0035】

前記ハロメチル基としては、例えば、トリクロロメチル基、トリブロモメチル基、ジクロロメチル基、ジブロモメチル基などが挙げられ、前記炭素数５以上の有機基としては、例えば、置換基を有していてもよい、フェニル基、ナフチル基、スチリル基、スチリルフェニル基、フリルビニル基、四級化アミノエチルアミノ基などが挙げられる。

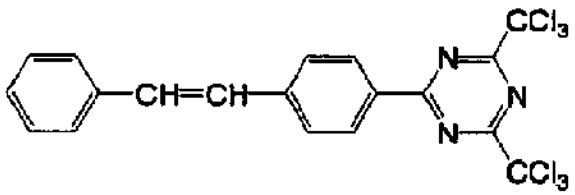
【0036】

以下、ハロメチル化トリアジン化合物の具体例〔例示化合物（２）～（２３）〕を列挙する。

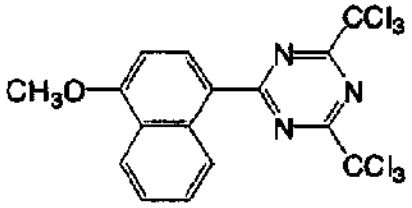
【0037】

【化2】

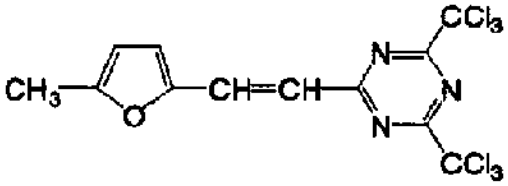
(2)



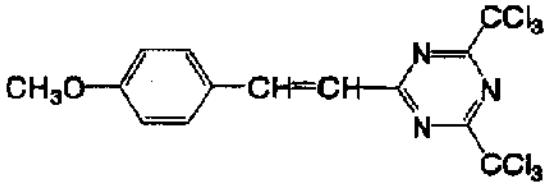
(3)



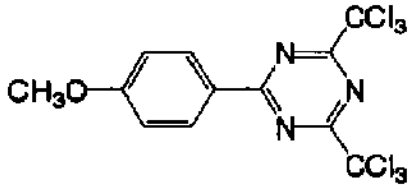
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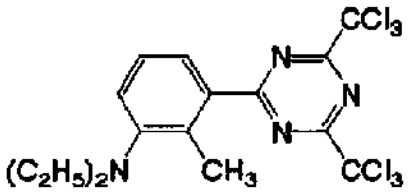
(5)



(6)



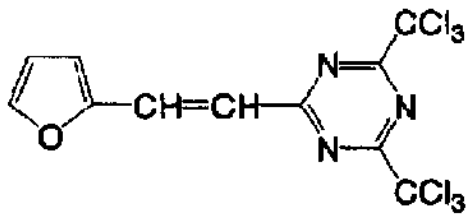
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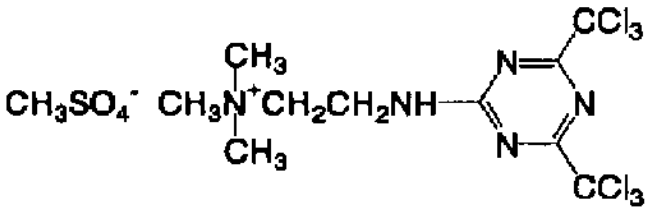
【0038】

【化3】

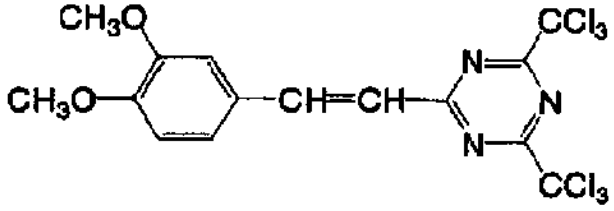
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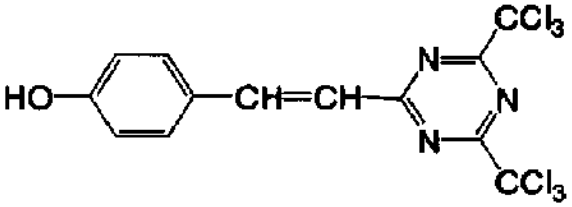
(9)



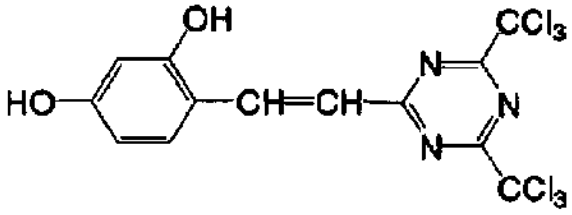
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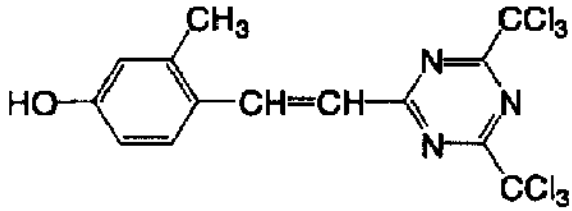
(11)



(12)



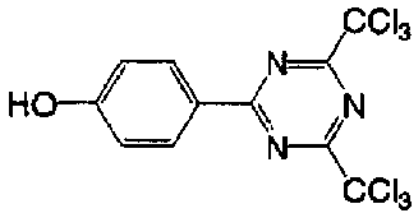
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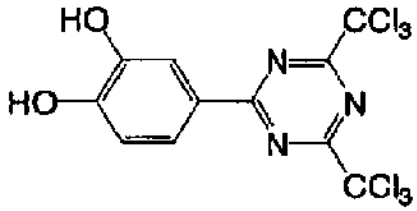
【0039】

【化4】

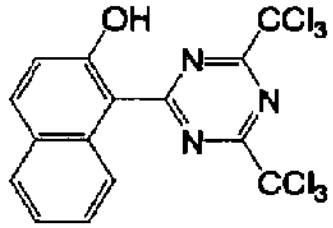
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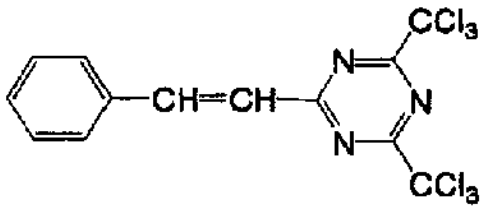
(15)



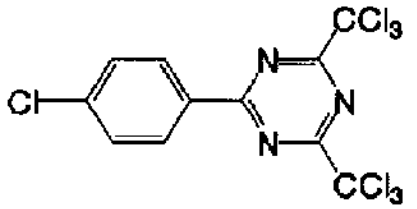
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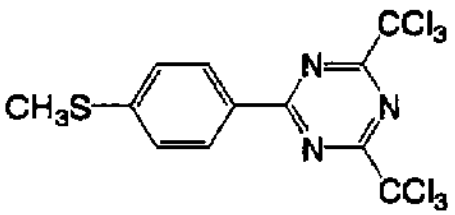
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(18)



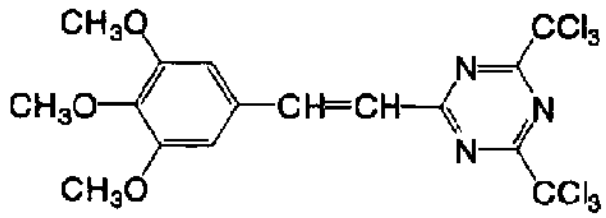
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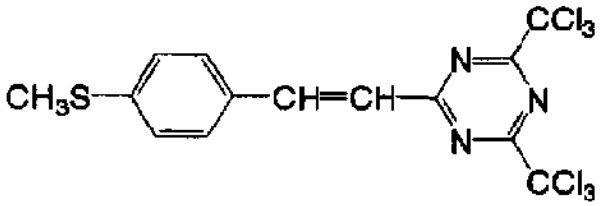
【0040】

【化5】

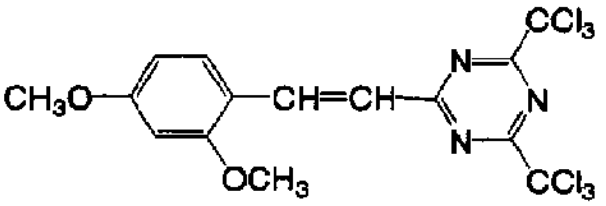
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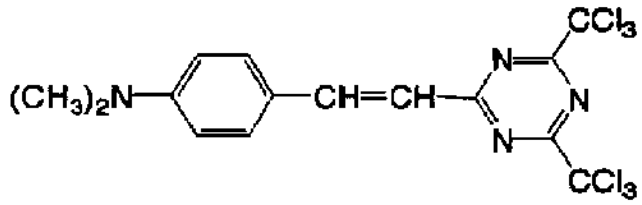
(21)



(22)

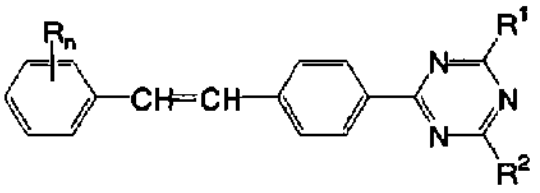


(23)



【0041】
前記一般式（１）で表されるハロメチル化トリアジン化合物の中でも、好ましいものは下記一般式（２４）、（２５）、又は（２６）で表される化合物である。
【0042】
【化6】

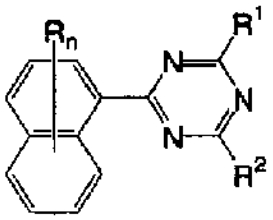
(24)



【0043】
前記一般式（２４）中のR^1及びR^2は、各々独立にハロメチル基を表し、Ｒは炭素数１～４のアルキル基又は炭素数１～４のアルコキシ基を表す。ｎは、Ｒの個数を表すものであり、０～３の整数である。
【0044】

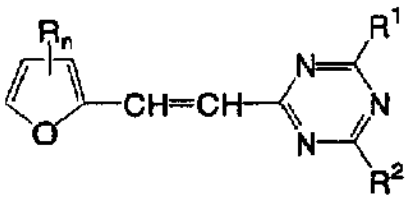
【化7】

(25)



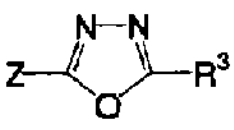
【0045】
前記一般式（２５）中のR¹及びR²は、各々独立にハロメチル基を表し、Rは炭素数１～４のアルキル基又は炭素数１～４のアルコキシ基を表す。nは、Rの個数を表すものであり、０～３の整数である。
【0046】
【化8】

(26)



【0047】
前記一般式（２６）中のR¹及びR²は、各々独立にハロメチル基を表し、Rは炭素数１～４のアルキル基を表す。nは、Rの個数を表すものであり、０～１の整数である。
【0048】
上記の一般式（２４）～（２６）で表される化合物の中でも、好ましいものは各々の一般式において、R¹及びR²がトリクロロメチル基であって、Rが炭素数１～２のアルキル基であって、更に一般式（２４）及び（２５）ではnが０～２の整数、一般式（２６）では０～１の整数である化合物である。
【0049】
前記ハロメチル化オキサジアゾール化合物としては、下記一般式（２７）で表される化合物が挙げられる。
【0050】
【化9】

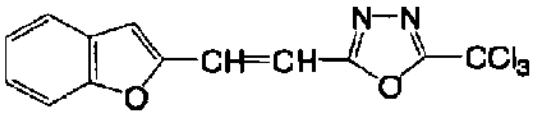
(27)



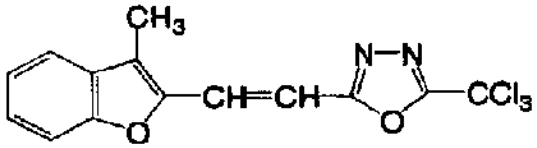
【0051】
前記一般式（２７）中、R³はハロメチル基を表し、Zは置換基を有していてもよいベンゾフリル基又はベンゾフリルビニル基を表す。
【0052】
以下、ハロメチル化オキサジアゾール化合物の具体例〔例示化合物（２８）～（４５）〕を列挙する。
【0053】

【化10】

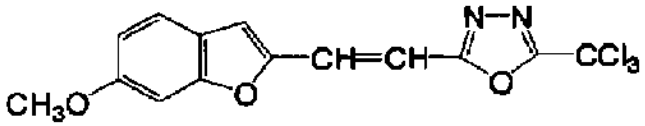
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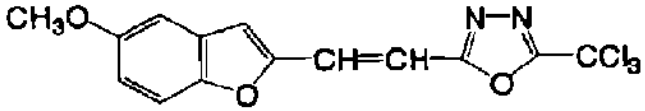
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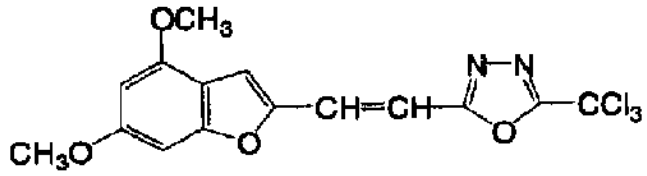
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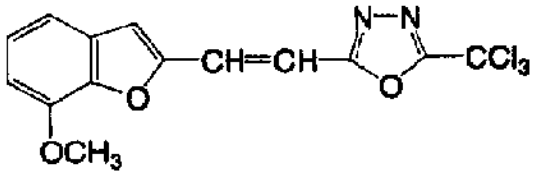
(31)



(32)



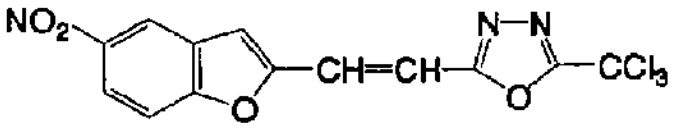
(33)



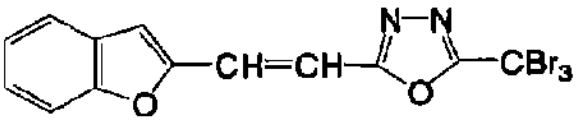
【0054】

【化11】

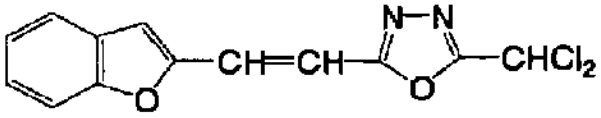
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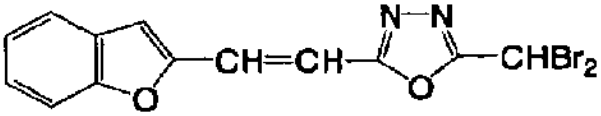
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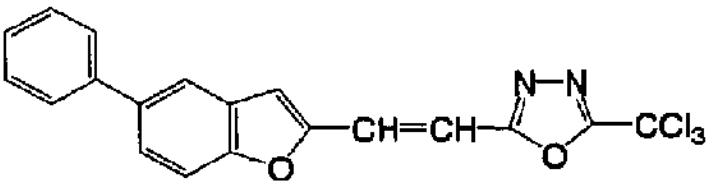
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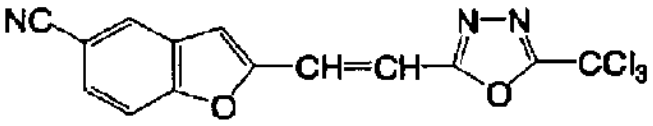
(37)



(38)



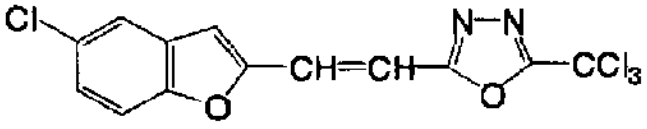
(39)



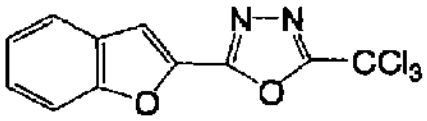
【0055】

【化12】

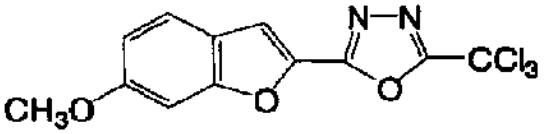
(40)



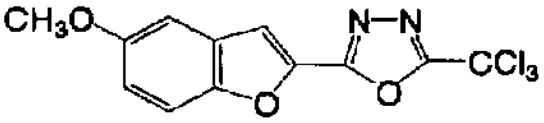
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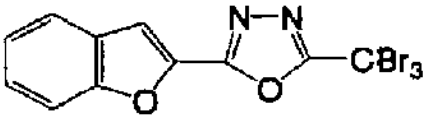
(42)



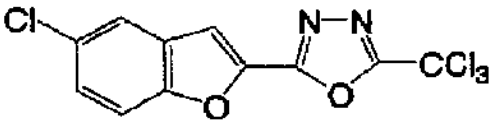
(43)



(44)



(45)



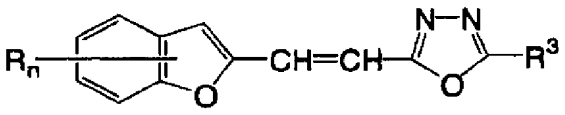
【0056】

前記一般式（２７）で表されるハロメチル化オキサジアゾール化合物の中でも、好ましいのは下記一般式（４６）で表される化合物である。

【0057】

【化13】

(46)



【0058】
前記一般式（４６）中のR³はハロメチル基を表し、Ｒは炭素数１～４のアルキル基又は炭素数１～４のアルコキシ基を表す。ｎは、Ｒの個数を表すものであり、０～２の整数である。更に好ましいのは、R³がトリクロロメチル基であって、Ｒが炭素数１～２のアルキル基又はアルコキシ基であって、ｎが０～１の整数である化合物である。
【0059】
光酸発生剤の遮光膜用感光性樹脂組成物中における含有量としては、該組成物の固形分に対して、０．０５～１５質量％、好ましくは５～１５質量％である。光酸発生剤の量が前記範囲であると、露光により充分な酸を発生してバインダー樹脂と後述の架橋剤との架橋反応が良好に行なえ、現像後の残膜率が高く、耐熱性、耐薬品性等を具えた画像を形成することができる。
【0060】
－架橋剤－
本発明の遮光膜用感光性樹脂組成物は、架橋剤の少なくとも１種を含有する。この架橋剤は、露光時に前記光酸発生剤から生成する酸の触媒作用により架橋反応を起こして硬化する作用を有する。すなわち、既述のバインダー樹脂との間で架橋反応して架橋体を形成し、露光部を硬化して画像化することができる。
【0061】
架橋剤としては、架橋性基を少なくとも１種含む置換基（以下、「架橋性置換基」と称する。）を有する化合物が挙げられる。
【0062】
前記架橋性置換基の具体例としては、下記（ｉ）～（vi）が挙げられる。
（ｉ）ヒドロキシアルキル基、アルコキシアルキル基、アセトキシアルキル基等のヒドロキシアルキル基又はその誘導体；
（ii）ホルミル基、カルボキシアルキル基等のカルボニル基又はその誘導体；
（iii）ジメチルアミノメチル基、ジエチルアミノメチル基、ジメチロールアミノメチル基、ジエチロールアミノメチル基、モルホリノメチル基等の含窒素基含有置換基；
（iv）グリシジルエーテル基、グリシジルエステル基、グリシジルアミノ基等のグリシジル基含有置換基；
（ｖ）ベンジルオキシメチル基、ベンゾイロキシメチル基等のアリルオキシアルキル基やアラルキルオキシアルキル基等の芳香族誘導体；
（vi）ビニル基、イソプロペニル基等の重合性多重結合含有置換基；
等を挙げることができる。
上記のうち、本発明における架橋剤の架橋性置換基としては、ヒドロキシアルキル基、アルコキシアルキル基等が好ましく、特にアルコキシメチル基が好ましい。
【0063】
前記架橋性置換基を有する架橋剤としては、例えば、
（ｉ）メチロール基含有メラミン化合物、メチロール基含有ベンゾグアナミン化合物、メチロール基含有ウレア化合物、メチロール基含有グリコールウリル化合物、メチロール基含有フェノール化合物等のメチロール基含有化合物；
（ii）アルコキシアルキル基含有メラミン化合物、アルコキシアルキル基含有ベンゾグアナミン化合物、アルコキシアルキル基含有ウレア化合物、アルコキシアルキル基含有グリ

コールウリル化合物、アルコキシアルキル基含有フェノール化合物等のアルコキシアルキル基含有化合物；
（iii）カルボキシメチル基含有メラミン化合物、カルボキシメチル基含有ベンゾグアナミン化合物、カルボキシメチル基含有ウレア化合物、カルボキシメチル基含有グリコールウリル化合物、カルボキシメチル基含有フェノール化合物等のカルボキシメチル基含有化合物；
（iv）ビスフェノールＡ系エポキシ化合物、ビスフェノールＦ系エポキシ化合物、ビスフェノールＳ系エポキシ化合物、ノボラック樹脂系エポキシ化合物、レゾール樹脂系エポキシ化合物、ポリ（ヒドロキシスチレン）系エポキシ化合物等のエポキシ化合物；等を挙げることができる。

【0064】

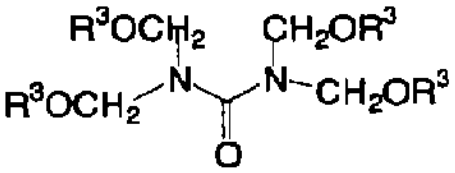
上記の架橋剤の中でも、アルコキシメチル化ウレア化合物又はその樹脂、アルコキシメチル化グリコールウリル化合物又はその樹脂が好ましい。

特に好ましい架橋剤として、下記一般式（４７）で表されるアルコキシメチル化ウレア化合物、又は下記一般式（４８）で表されるアルコキシメチル化グリコールウリル化合物を挙げることができる。

【0065】

【化14】

(47)



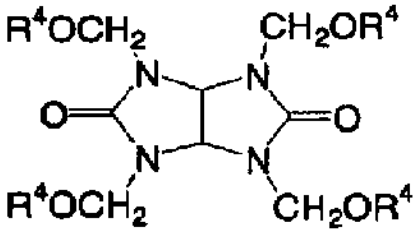
【0066】

前記一般式（４７）中のR^3は、炭素数１～４のアルキル基を表す。

【0067】

【化15】

(48)



【0068】

前記一般式（４７）中のR^4は、炭素数１～４のアルキル基を表す。

【0069】

前記一般式（４７）、（４８）において、R^3又はR^4で表されるアルキル基としては、メチル基、エチル基、プロピル基、ブチル基等を挙げることができる。

【0070】

上記のアルコキシメチル化ウレア化合物、アルコキシメチル化グリコールウリル化合物は、例えば、尿素化合物やグリコールウリル化合物とホルマリンとを縮合反応させてメチロール基を導入した後、更にメチルアルコール、エチルアルコール、プロピルアルコール、ブチルアルコール等の低級アルコール類でエーテル化し、次いで反応液を冷却して析出

する化合物又はその樹脂を回収することで得られる。また、ＣＹＭＥＬ（商品名；三井サイアナミッド社製）、ニカラッド（三和ケミカル社製）等の市販品として入手することもできる。

【0071】

架橋剤としては、メラミン、ベンゾグアナミン、グリコールウリル、又は尿素にホルムアルデヒドを作用させた化合物、又はそれらのアルキル変性化合物、エポキシ化合物、レゾール化合物等が有効であり、その具体例には以下のものが挙げられる。

【0072】

具体的な例として、三井サイアナミド社製のサイメル（登録商標）３００、同３０１、同３０３、同３５０、同７３６、同７３８、同３７０、同７７１、同３２５、同３２７、同７０３、同７０１、同２６６、同２６７、同２８５、同２３２、同２３５、同２３８、同１１４１、同２７２、同２５４、同２０２、同１１５６、同１１５８は、メラミンにホルムアルデヒドを作用させた化合物又はそのアルキル変性物の例である。また、サイメル（登録商標）１１２３、同１１２５、同１１２８は、ベンゾグアナミンにホルムアルデヒドを作用させた化合物又はそのアルキル変性物の例である。また、サイメル（登録商標）１１７０、同１１７１、同１１７４、同１１７２は、グリコールウリルにホルムアルデヒドを作用させた化合物又はそのアルキル変性物の例である。更に、尿素にホルムアルデヒドを作用させた化合物又はそのアルキル変性物の例として、三井サイアナミド社製のＵＦＲ（登録商標）６５、同３００を挙げることができる。

【0073】

また、前記エポキシ化合物の例としては、ノボラックエポキシ樹脂（東都化成社製のＹＤＰＮ－６３８、同７０１、同７０２、同７０３、同７０４等）、アミンエポキシ樹脂（東都化成社製のＹＨ－４３４等）、ビスフェノールＡエポキシ樹脂、ソルビトール（ポリ）グリシジルエーテル、（ポリ）グリセロール（ポリ）グリシジルエーテル、ペンタエリスリトール（ポリ）グリシジルエーテル、トリグリシジルトリスヒドロキシエチルイソシアヌレート、アリルグリシジルエーテル、エチルヘキシルグリシジルエーテル、フェニルグリシジルエーテル、フェノールグリシジルエーテル、ラウリルアルコールグリシジルエーテル、アジピン酸グリシジルエーテル、フタル酸グリシジルエーテル、ジブロモフェニルグリシジルエーテル、ジブロモネオペンチルグリコールジグリシジルエーテル、グリシジルフタルイミド、（ポリ）エチレングリコールグリシジルエーテル、ポリプロピレングリコールジグリシジルエーテル、ネオペンチルグリコールジグリシジルエーテル、グリセリンポリグリシジルエーテル、トリメチロールプロパンポリグリシジルエーテル、ブチルグリシジルエーテル、等を挙げることができる。

【0074】

特に好ましい化合物として、分子中に－Ｎ$(CH_2OR)_2$基を有する化合物（Ｒは水素原子又はアルキル基を表す。）が挙げられる。詳しくは、尿素あるいはメラミンにホルムアルデヒドを作用させた化合物又はそのアルキル変性物が特に好ましい。

【0075】

また、前記レゾール化合物の例としては、群栄化学社製のＰＰ－３０００ｓ、ＰＰ－３０００Ａ、ＲＰ－２９７８、ＳＰ－１９７４、ＳＰ－１９７５、ＳＰ－１９７６、ＳＰ－１９７７、ＲＰ－３９７３等が挙げられる。

【0076】

架橋剤の遮光膜用感光性樹脂組成物中における含有量としては、前記バインダー樹脂の量に対して、５～７０質量％が好ましく、１０～４０質量％がより好ましい。

【0077】

－金属粒子及び／又は金属化合物粒子－

本発明の遮光膜用感光性樹脂組成物は、金属粒子及び金属化合物粒子よりなる群より選択される少なくとも１種（以下、「本発明に係る金属粒子」ともいう。）を含有する。遮光用の黒色材料として本発明に係る金属粒子を選択的に用いるので、高い黒濃度が得られ、薄い形態で高度の遮光性が得られると共に、薄い形態に構成されるので、ＰＡＧによる

場合の加熱時の酸の拡散に伴なうパターンの線太りを防止することができ、加熱拡散による硬化時間の短縮も図れる。
なお、本発明に係る金属粒子には、後述の複合粒子、コア・シェル複合粒子が含まれる。

【0078】
〈金属粒子〉
金属粒子としては、長周期周期表（ＩＵＰＡＣ　１９９１）の例えば、元素周期表の第３周期、第４周期、第５周期、及び第６周期からなる群から選ばれる金属を主成分として含むことが好ましく、また、第２族、第８族、第９族、第１０族、第１１族、第１２族、第１３族、及び第１４族からなる群から選ばれる金属を主成分として含むことが好ましい。これらの金属のうち、本発明に係る金属粒子としては第４周期、第５周期、又は第６周期の金属であって、第２族、第１０族、第１１族、第１２族、又は第１４族の金属がさらに好ましい。

【0079】
本発明における金属粒子は、球状、立方体を含む正側面体状などのほか、縦、横、高さの比の少なくとも１つが異なる形状異方性の形（例えば、形状異方性を有する球状、あんパン状、ジャガイモ状、棒状（針状、円柱形、直方体等の角柱形、ラグビーボール型等）、平板状（鱗片状、楕円板状、板状）、繊維状、金平糖状、コイル状等）のいずれであってもよい。
また、後述する金属化合物粒子、複合粒子、コアシエル複合粒子の場合も同様である。

【0080】
前記金属粒子として好ましい例は、銅、銀、金、白金、パラジウム、ニッケル、錫、コバルト、ロジウム、イリジウム、鉄、ルテニウム、カルシウム、オスミウム、マンガン、モリブデン、タングステン、ニオブ、タンテル、チタン、ビスマス、アンチモン、鉛、又はこれらの合金、から選ばれる少なくとも一種を挙げることができる。さらに好ましい金属は、銅、銀、金、白金、パラジウム、ニッケル、錫、コバルト、ロジウム、イリジウム又はこれらの合金、より好ましい金属は、銅、銀、金、白金、錫又はこれらの合金から選ばれる少なくとも一種である。これらのうち、金、銀、銅、錫が好ましく、とりわけ銀が好ましい。銀としては、棒状をした銀やコロイド銀も好適である。金属粒子の製造には、前記金属を２種以上組合せてもよく、合金として用いることも可能である。

また、金属化合物と金属との複合微粒子として用いることもできる。

【0081】
〈金属化合物粒子〉
金属化合物粒子は、前記金属と金属以外の他の元素との化合物の粒子であり、「金属と他の元素との化合物」としては、金属の酸化物、硫化物、硫酸塩、炭酸塩などがある。このうち、硫化物が色調や微粒子形成のしやすさから特に好ましい。これら金属化合物の例としては、酸化銅(II)、硫化鉄、硫化銀、硫化銅(II)、チタンブラックなどが挙げられるが、硫化銀は色調、微粒子形成のしやすさや安定性の観点から特に好ましい。

【0082】
〈複合粒子〉
本発明においては、前記金属粒子と前記金属化合物粒子とを用い、これらが結合して１つの粒子になった複合粒子も用いることができる。複合粒子の形状には特に制限はない。例えば、粒子の内部と表面で組成の異なるもの、２種類の粒子が合一したもの等を挙げることができる。また、金属化合物と金属は、それぞれ１種でも２種以上であってもよい。金属化合物と金属との複合粒子の具体例としては、銀と硫化銀との複合粒子、銀と酸化銅(II)との複合粒子などがある。

【0083】
〈コア・シェル複合粒子〉
本発明においては、コア・シェル型の複合粒子（コア・シェル複合粒子）も用いること

ができる。コア・シェル型の複合粒子とは、コア材料の表面をシェル材料でコートしたものである。

【0084】

前記コア材料をコートするシェル材料としては、例えば、Ｓｉ、Ｇｅ、ＡｌＳｂ、ＩｎＰ、Ｇａ、Ａｓ、ＧａＰ、ＺｎＳ、ＺｎＳｅ、ＺｎＴｅ、ＣｄＳ、ＣｄＳｅ、ＣｄＴｅ、ＰｂＳ、ＰｂＳｅ、ＰｂＴｅ、Ｓｅ、Ｔｅ、ＣｕＣｌ、ＣｕＢｒ、ＣｕＩ、ＴｌＣｌ、ＴｌＢｒ、ＴｌＩ、及びこれらの固溶体、又はこれらを９０ｍｏｌ％以上含む固溶体から選ばれる少なくとも一種の半導体、あるいは銅、銀、金、白金、パラジウム、ニッケル、錫、コバルト、ロジウム、イリジウム、鉄、ルテニウム、オスミウム、マンガン、モリブデン、タングステン、ニオブ、タンテル、チタン、ビスマス、アンチモン、鉛、又はこれらの合金から選ばれる少なくとも一種の金属を用いることができる。

【0085】

好ましいシェル材料としては、銅、銀、金、パラジウム、ニッケル、錫、ビスマス、アンモチン、鉛、又はこれらの合金から選ばれる少なくとも１種を挙げることができる。

前記シェル材料は、反射率を低下させる目的で屈折率の調整剤としても好適に用いられる。

【0086】

また、コア・シェル複合粒子を構成するコア材料としては、例えば、銅、銀、金、パラジウム、又はこれらの合金から選ばれる少なくとも一種の金属を用いることができる。

【0087】

コアシェル構造を有するコア・シェル複合粒子の作製方法には、特に制限はなく、代表的な方法として以下の方法が挙げられる。

（１）公知の方法で作製した金属粒子の表面に、酸化、硫化などにより、金属化合物のシェルを形成する方法であり、例えば、金属粒子を水などの分散媒に分散させて、硫化ナトリウムや硫化アンモニウムなどの硫化物を添加する方法がある。この方法により粒子の表面が硫化されてコアシェル複合粒子が形成される。

この場合、用いる金属粒子は、気相法、液相法などの公知の方法で作製することができる。金属粒子の作製方法については、例えば「超微粒子の技術と応用における最新動向II」（住べテクノリサーチ（株）、２００２年発行）に記載されている。

（２）金属粒子を作製する過程で連続的に表面に金属化合物のシェルを形成する方法であり、例えば、金属塩溶液に還元剤を添加して、金属イオンの一部を還元して金属粒子を作製し、次いで硫化物を添加して、作製した金属粒子の周囲に金属硫化物を形成する方法がある。

【0088】

～金属粒子の作製～

金属粒子は市販のものを用いることができる他、金属イオンの化学的還元法、無電解メッキ法、金属の蒸発法等により調製することが可能である。

形状異方性の形に構成された粒子の場合、特に棒状の銀粒子（銀ロッド）の場合は、球形銀粒子を種粒子としてその後、銀塩をさらに添加し、CTAB（セチルトリメチルアンモニウムブロマイド）等の界面活性剤存在下、アスコルビン酸など比較的還元力の弱い還元剤を用いることにより銀ロッドやワイヤーが得られる。これは、Ａｄｖ．Ｍａｔｅｒ．２００２，１４，８０－８２に記載がある。また、同様の記載がＭａｔｅｒ．Ｃｈｅｍ．Ｐｈｙｓ．２００４，８４，１９７－２０４、Ａｄｖ．Ｆｕｎｃｔ．Ｍａｔｅｒ．２００４，１４，１８３－１８９にもなされている。また、電気分解を用いた方法として、Ｍａｔｅｒ．Ｌｅｔｔ．２００１，４９，９１－９５に記載の方法、マイクロ波を照射することにより銀ロッドを生成する方法として、Ｊ．Ｍａｔｅｒ．Ｒｅｓ．２００４，１９，４６９－４７３に記載の方法がある。逆ミセルと超音波の併用した例として、Ｊ．Ｐｈｙｓ．Ｃｈｅｍ．Ｂ，２００３，１０７，３６７９－３６８３が挙げられる。

金に関しても同様に、Ｊ．Ｐｈｙｓ．Ｃｈｅｍ．Ｂ　１９９９，１０３、３０７３－３０７７及びＬａｎｇｍｕｉｒ１９９９，１５，７０１－７０９、Ｊ．Ａｍ．Ｃｈｅｍ．Ｓ

ｏｃ．２００２，１２４，１４３１６－１４３１７に記載されている。
ロッド状の粒子の形成方法は上記の方法を改良（添加量調整、ＰＨ制御）しても調製できる。
【0089】
～粒子径～
本発明に係る金属粒子（複合粒子、コア・シェル複合粒子を含む。）が真球もしくは球形である場合、その粒子径としては、２～６００ｎｍが好ましく、１０～３００ｎｍがより好ましい。
【0090】
また、形状異方性の粒子である場合、粒子径は三軸径とする。すなわち、１個の金属粒子がちょうど（きっちりと）収まる箱（直方体）を考え、この箱の長さＬ、幅ｂ、高さ又は厚みｔをもってこの金属粒子の寸法と定義する仕方である。金属粒子を箱に収める場合、いくつかの仕方があるが、本発明では以下の方法を採用する。
まず、平面上に金属粒子を、最も重心が低くて安定に静止するように置く。次に、平面に対し直角に立てた２枚の平行な平板により金属粒子を挟み、その平板間隔が最も短くなる位置の平板間隔を「幅ｂ」とする。次に、前記幅ｂを決する２枚の平板に対し直角で前記平面に対しても直角の２枚の平行な平板により金属粒子を挟み、この２枚の平板間隔を「長さＬ」とする。最後に金属粒子の最も高い位置に接触するように天板を前記平面に平行に載せ、天板と平面との間隔を高さ又は厚みｔとする（この方法により平面、各２枚の平板及び天板によって画される直方体が形成される。）。また、金属粒子の三軸径ｂ、Ｌ及びｔの最も長いものに該当する軸を「長軸」と定義し、長軸方向における長さを「長軸長」と、また、長軸に平行な光を金属粒子に照射して得られる投影面積を真円換算した場合の直径を「短軸長」と定義する。
【0091】
～アスペクト比～
本発明に係る金属粒子（複合粒子、コア・シェル複合粒子を含む。）のアスペクト比とは、金属粒子又は金属化合物粒子の、上記のように定義した長軸長を短軸長で割った値を意味し、１００個の金属粒子について測定した値の平均値と定義する。なお、粒子の投影面積は電子顕微鏡写真上での面積を測定し、撮影倍率を補正することにより得られる。
【0092】
粒子のアスペクト比（粒子の長軸長／粒子の短軸長の比）は、2以上であることが好ましく、4以上であることがより好ましい。アスペクト比の上限は、１００程度である。この範囲では、黒色粒子が得られ易く、大きすぎて可視光域の吸収が小さくなることもなく、高解像化に効果的である。さらに好ましくは、４～８０であり、最も好ましくは１０～６０である。粒子の短軸長は、４～５０ｎｍが好ましく、１５～５０ｎｍがより好ましく、１５～３０ｎｍが最も好ましい。粒子の長軸長（最大長）は、１０～１０００ｎｍが好ましく、１００～１０００ｎｍがより好ましく、４００～８００ｎｍが更に好ましく、可視光波長より短いことが最も好ましい。
【0093】
また、粒子径と形状の異なる粒子を混合することによって、吸収スペクトル制御でき、色相を無彩色に近づけることもできる。
【0094】
～粒度分布～
粒度分布は、長軸長の平均粒径の、粒度分布幅Ｄ９０／Ｄ１０が2以上２０未満であることが好ましい。ここで、Ｄ９０は粒子の９０％が見出される最大直径であり、Ｄ１０は粒子の１０％が見出される最大直径である。粒度分布は、色調の観点から、より好ましくは2以上１５以下であり、さらに好ましくは4以上１０以下である。粒度分布が前記範囲であると、粗大粒子による散乱による濁りが生じるのを防止できる。
【0095】
「金属粒子及び／又は金属化合物粒子」の遮光膜用感光性樹脂組成物中における含有量

としては、用いる粒子の種類や性状により異なるが、２～４０体積％が好ましく、５～３０体積％がより好ましい。

【0096】

着色剤

本発明の遮光膜用感光性樹脂組成物は、前記金属粒子及び／又は金属化合物粒子と共に、さらに顔料及び／又は染料を併用して好適に構成することができる。

【0097】

前記顔料としては、例えば、硫酸バリウム、硫酸鉛、酸化チタン、黄色鉛、ベンガラ、酸化クロム、カーボンブラック等の無機顔料、アントラキノン系顔料、ペリレン系顔料、ジスアゾ顔料、フタロシアニン顔料、イソインドリン顔料、ジオキサジン顔料、キナクリドン顔料、ペリノン系顔料、トリフェニルメタン系顔料、チオインジゴ顔料等の有機顔料などが挙げられる。これらは、１種単独で又は２種以上を混合して用いることができる。

前記顔料の中でも、アントラキノン系顔料、フタロシアニン顔料、ジオキサジン顔料、カーボンブラックが特に好ましい。

【0098】

以下、具体的にカラーインデックス（Ｃ．Ｉ．）ナンバーで示す。

Ｃ．Ｉ．赤：９，９７，１２２，１２３，１４９，１６８，１７７，１８０，１９２，２１５，２１６，２１７，２２０，２２３，２２４，２２６，２２７，２２８，２４０；

Ｃ．Ｉ．青：１５、１５：６、２２、６０、６４；

Ｃ．Ｉ．緑：７，３６；

Ｃ．Ｉ．黒：７；

Ｃ．Ｉ．黄色：１２，２０，２４，８６，９３，１０９，１１０，１１７，１２５，１３７，１３８，１４７，１４８，１５３，１５４，１６６，１６８；

Ｃ．Ｉ．オレンジ：３６，４３，５１，５５，５９，６１；

Ｃ．Ｉ．バイオレット：１９，２３，２９，３０，３７，４０，５０；

Ｃ．Ｉ．茶：２３，２５，２６；

【0099】

顔料の平均粒径は０．００５～３μｍの範囲にあるのが好ましい。より好ましくは０．０１～１μｍである。この範囲の粒径にするには、ボールミル、サンドミル、ビーズミル、３本ロール、ペイントシェーカー、超音波などの分散処理が有効である。

【0100】

前記染料としては、例えば、クリスタルバイオレット、メチルバイオレット、エチルバイオレット、オイルブルー＃６０３、ビクトリアピュアーブルーＢＯＨ、マラカイトグリーン、ダイモンドグリーン等が挙げられる。

上記以外に、黒鉛も好適に用いることができる。

【0101】

なお、用途等に応じて、前記顔料及び染料は併用してもよく、また、顔料及び／又は染料は必ずしも含有する必要はない。

本発明においては、カーボンブラック及び／又は黒鉛を既述の本発明に係る金属粒子と共に併用する態様が最も好ましい。

【0102】

上記において、カーボンブラック等の炭素系の黒色顔料は、窒素ガス吸着法で測定した比表面積が５０m^2／ｇ以下のものが好ましい。中でも、５０～１０m^2／ｇの範囲内が好ましく、更に好ましくは３０～１５m^2／ｇの範囲内である。比表面積が前記範囲内であると、良好な遮光性能が得られると共に、分散時の分散安定性が良好である。

【0103】

着色剤（特にカーボンブラック、黒鉛）を併用する場合、着色剤の量としては、本発明に係る金属粒子の総量に対して、１０～９０体積％が好ましく、より好ましくは２０～５０体積％である。本発明に係る金属粒子と共に着色剤を併用することで、形成された遮光膜の反射率等をコントロールするのに有効であり、特に着色剤の量を前記範囲内とすると

、薄膜で高い遮光性を有すると同時に、光リークがなく表面の平坦性に優れた遮光膜を形成するのに効果的である。また、基板単独でも、また両面から偏光板で挟んでこの２枚の偏光板の偏光軸を直交したときにも光漏れがなく高い遮光性が得られ、高性能のカラーフィルタを得ることができ、高画質画像の表示が可能な液晶表示素子の製造に寄与する。また、工業的に有利な電着法によるカラーフィルタの製造において、遮光膜を背面露光法で形成する場合にも充分な増膜性、遮光性を得ることができる。

【0104】

－その他の成分－

本発明の遮光膜用感光性樹脂組成物には、種々の目的や用途に応じて、各種添加剤を含有することができる。添加剤としては、例えば、界面活性剤、密着促進剤、可塑剤等が挙げられる。

【0105】

前記界面活性剤は、遮光膜用感光性樹脂組成物を塗布液として用いる場合の塗布性、得られる塗膜の平滑性を向上させる目的で用いることができ、具体例として、ＢＭ－１０００（ＢＭ Ｃｈｅｍｉｅ社製）、メガファックスＦ１４２Ｄ、同Ｆ１７２、同Ｆ１７３、同Ｆ１８３、同Ｆ１７６ＰＦ、同Ｆ１７７ＰＦ（いずれも大日本インキ化学工業（株）製）、フロラードＦＣ－１３５、同ＦＣ－１７０Ｃ、フロラードＦＣ－４３０、同ＦＣ－４３１（いずれも住友スリーエム（株）製）、サーフロンＳ－１１２、同Ｓ－１１３、同Ｓ－１３１、同Ｓ－１４１、同Ｓ－１４５（いずれも旭硝子（株）製）、ＳＨ－２８ＰＡ、ＳＨ－１９０、ＳＨ－１９３、ＳＺ－６０３２、ＳＦ－８４２８、ＤＣ－５７、ＤＣ－１９０（いずれも東レ・シリコーン（株）製）の商品名で市販されている、フッ素系又はシリコン系界面活性剤が挙げられる。

【0106】

界面活性剤を含有する場合の含有量としては、遮光膜用感光性樹脂組成物の全固形分に対して、０．０５～１０質量％が好ましい。この範囲で含有すると、特に基板へのパターン密着性の点で有効である。更には、０．０８～５質量％の範囲が好ましく、０．１～３質量％の範囲が特に好ましい。

【0107】

本発明の遮光膜用感光性樹脂組成物は、例えばアセトン、メチルエチルケトン、メチルブチルケトン等のケトン、各種エーテル、エステルなどの有機溶剤を用いて塗布液として調製することができる。この塗布液は、塗布により被塗物となる仮支持体（シート等）や液晶表示素子などの表面に感光性樹脂層を形成するために好適に用いることができる（以下、この塗布液を「感光性樹脂層用塗布液」ということがある。）。この感光性樹脂層の厚みには特に制限はなく、適宜選択することができるが、０．２～１．３μｍが好適であり、０．３～０．８μｍがより好適である。この範囲の薄膜に構成しても高い黒濃度が得られる。

【0108】

すなわち、本発明の遮光膜用感光性樹脂組成物は、上記のような塗布による塗膜など、膜厚１．０μｍの遮光膜を形成した際に該遮光膜の光学濃度が４．０以上となるように構成された態様が好適である。カラーフィルタを構成する遮光膜（ブラックマトリクスなど）をはじめプルーフなどの印刷材料や、ＰＤＰ（Plasma Display Panel）用の隔壁材料、インクジェットインク、レジストインクなど、高度の遮光性能と薄膜形成性とが要求される用途においては、薄膜にしつつ高い黒濃度が得られることが重要であり、かかる場合に本発明の遮光膜用感光性樹脂組成物を好適に用いることができる。本発明の遮光膜用感光性樹脂組成物は、液晶表示装置等を構成するカラーフィルタの遮光膜（ブラックマトリクスなど）の形成に特に好適であり、ブラックマトリクスの形成に最適である。

【0109】

本発明の遮光膜用感光性樹脂組成物は、上記した塗布液の塗布による方法以外に、下記方法を適用して遮光膜を形成するようにすることもできる。

～インクジェット法～

インクジェット法を利用して、本発明の遮光膜用感光性樹脂組成物を吐出して遮光膜を形成することができる。これは、コストダウンの点で好ましい。このインクジェット法としては、エネルギー発生素子として電気熱変換体を用いたバブルジェット（登録商標）タイプ、あるいは圧電素子を用いたピエゾジェットタイプ等が使用可能であり、着色面積及び着色パターンは任意に設定することができる。インクジェット法には、インクが充分に拡散しにくい傾向があり、白抜けを生じて色ムラやコントラスト低下を招来する原因となりやすいが、この場合には有機溶剤に顔料を組成物（インク）全体の質量に対して少なくとも１０質量%以上の濃度で分散させたものに調製することが好ましい。詳細については、特開２００４－３２５７３６号公報の記載を参照できる。

【0110】

また、遮光膜用感光性樹脂組成物を吐出した際の濡れ広がりを制御し、濃度均一性に優れた遮光膜を作製するには、用いる溶剤種としてはインクジェット印刷における適性の表面張力が３５ｍＮ／ｍ以下で、かつ沸点が１３０℃以上のものが好ましい。表面張力が３５ｍＮ／ｍ以下であると吐出時のドット形状の安定性が良好であり、沸点が１３０℃以上であるとノズル近傍での乾燥性が抑えられ、ノズル詰まり等の吐出不良を回避することができる。濡れ広がりを制御することにより、着色画素を形成した際の混色、遮光膜中の白抜け等の欠陥のない、均一な高濃度で、膜形状が鮮明でエッヂのシャープな遮光膜が得られる。

【0111】

さらに、特開２００２－３７２６１５号公報に記載されているような、インキが瞬時に硬化し、顔料の分散安定性の確保や基材との密着性の確保も併せて向上させる手段を適用することによって、遮光膜を作製する際の生産性を向上させることも可能である。

【0112】

～印刷法～

印刷法を利用して、遮光膜を短時間に作製するようにすることができる。印刷法として、版胴と圧胴との間に透明基材を通して該透明基材に遮光パターンを印刷形成するにあたり、前記版胴は前記遮光パターンに対応する凸版の版面を備え、前記版面を構成する凸版部に、光膜用感光性樹脂組成物（転写インキ）を備えた転写シートから、前記凸版部に相対して遮光パターンとした凸版を備えた凸版体により遮光パターンで転写インキを転写して、前記版胴の版面に転写インキを遮光パターンに設け、遮光パターンに設けられた前記転写インキを、版胴の版面から前記透明基板に転写する方法がある。版胴の版面は撥インキ性を備えていることが良好である。版面における転写開始位置と転写終了位置とに粘着剤を塗布することが良好である。転写インキが版胴の版面で遮光パターンに設けられ、この転写インキを一度に透明基材に転写するため、印刷による遮光膜の作製に要する時間が短縮されると共に、透明基材に形成される遮光膜を形成する転写インキの見当ズレがなく、転写シートを用いた印刷手法により適正な遮光膜が得られる。そして、版胴の版面における凸版部の凸版が撥インキ性を備えれば、版面から透明基材への転写インキの転写が良好になると共に、版面の洗浄も容易になる。

【0113】

前記印刷方法のほか、版胴と圧胴との間に透明基材を通して該透明基材に遮光パターンを印刷形成するにあたり、前記版胴は前記遮光パターンに対応する凸版の版面を備え、前記版面を構成するセルに遮光膜用感光性樹脂組成物（黒インキ）をインキジェット供給手段にて充填し、前記版胴の版面に黒インキを遮光パターンにて設け、これを乾燥させた後、版胴の版面から前記透明基板に転写する印刷方法がある。この場合、版胴は凹版の版面を備え、版面を構成するセルに遮光膜用感光性樹脂組成物（黒インキ）をインキジェット供給手段にて充填し、前記版面に黒インキを遮光パターンにて設け、これを乾燥させた後、版胴の版面から前記透明基板に転写する構成とするので、工程時間が更に大幅に短縮されると共に見当ズレがなく、セル中でインキ形状が安定し、セル形状に透明基材側に転写できることから、遮光膜を精度よく形成できる。

【0114】

＜転写材料及びその製造方法＞
～転写材料～
本発明の転写材料は、仮支持体上に少なくとも１層の感光性樹脂層を設けて構成したものであり、更に必要に応じて中間層や熱可塑性樹脂層、保護フィルム等の他の層を設けて構成することもできる。
【0115】
前記感光性樹脂層は、バインダー樹脂と、光を吸収して酸を発生する光酸発生剤と、前記光酸発生剤の作用により架橋する架橋剤と、金属粒子及び／又は金属化合物粒子とを含んでなる層であり、これら各成分を含む態様で公知の方法により形成することができ、既述の本発明の遮光膜用感光性樹脂組成物を用いて（好ましくは塗布液の塗布により仮支持体（シート等）の表面に塗設することにより）最も好適に形成することができる。バインダー樹脂等の各成分の詳細については既述の通りである。
【0116】
本発明の転写材料を構成する感光性樹脂層の層厚は、用途や目的に応じて選択することができるが、ブラックマトリクス等の遮光膜などの薄膜が要求される用途では薄い程よく、０．２～１．３μｍの範囲とするのが好ましく、０．３～０．８μｍの範囲とするのがより好ましい。この感光性樹脂層は被転写体に転写されて黒色画像（例えばブラックマトリクス）を構成するものであり、前記範囲の薄い層に構成しても高い黒濃度、遮光性を満足することができる。
【0117】
次に、本発明の転写材料を構成する仮支持体並びに他の層について述べる。
－仮支持体－
仮支持体には、プラスチックスフィルムが好ましい。例えば、ポリエチレンテレフタレート、ポリエチレンナフタレート、セルローストリアセテート、セルロースアセテートブチレート、セルロースアセテートプロピオネート、ポリカーボネート、ポリスチレン、ポリエチレン等のフィルムを挙げることができる。中でも、ポリエチレンテレフタレートフィルムが好ましく、特に２軸延伸、熱固定されたポリエチレンテレフタレートフィルムが、安定性、強靭さなどの点から特に好ましい。
【0118】
仮支持体の厚さには特に制限はないが、５～２００μｍの範囲が一般的であり、特に１０～１５０μの範囲が取扱い易さ、汎用性などの点で好ましい。
【0119】
－熱可塑性樹脂層－
熱可塑性樹脂層は、アルカリ可溶性の熱可塑性樹脂層であって、この層を構成する樹脂は、実質的な軟化点が８０℃以下であることが好ましい。
軟化点が８０℃以下のアルカリ可溶性の熱可塑性樹脂としては、エチレンとアクリル酸エステル共重合体とのケン化物、スチレンと（メタ）アクリル酸エステル共重合体とのケン化物、ビニルトルエンと（メタ）アクリル酸エステル共重合体とのケン化物、ポリ（メタ）アクリル酸エステル、及び（メタ）アクリル酸ブチルと酢酸ビニル等の（メタ）アクリル酸エステル共重合体などとのケン化物、（メタ）アクリル酸とエチレン不飽和基含有モノマーとの共重合体から選ばれる少なくとも１つであることが好ましい。さらに、「プラスチック性能便覧」（日本プラスチック工業連盟、全日本プラスチック成形工業連合会編著、工業調査会、１９６８年１０月２５日発行）による、軟化点が約８０℃以下の有機高分子のうちアルカリ水溶液に可溶なものを使用することができる。
【0120】
また、軟化点が８０℃以上の有機高分子物質を、その有機高分子物質中に該有機高分子物質と相溶性のある各種可塑剤を添加することで実質的な軟化点を８０℃以下に下げて用いることも可能である。また、仮支持体との接着力を調節するために、有機高分子物質中に実質的な軟化点が８０℃を越えない範囲で各種のポリマーや過冷却物質、密着改良剤あるいは界面活性剤、離型剤等を加えることも可能である。

【0121】
特に特開平７－２８２３２号公報に記載の、（Ａ）重量平均分子量５万～５０万かつガラス転移温度Ｔｇ＝０～１４０℃のアルカリ可溶な熱可塑性樹脂と、（Ｂ）重量平均分子量３千～３万かつＴｇ＝３０～１７０℃のアルカリ可溶な熱可塑性樹脂とを、（Ａ）／（Ｂ）比＝５／９５～９５／５［質量比］の範囲で混合したものが好適である。前記（Ａ）の特に好ましい例は、メタクリル酸／２－エチルヘキシルメタクリレート／ベンジルメタクリレート／メチルメタクリレート共重合体（共重合モル比：５／１０／３０／５５、質量平均分子量：１０万、Ｔｇ：約７０℃）である。前記（Ｂ）の特に好ましい例は、スチレン／アクリル酸共重合体（共重合組成モル比：６５／３５、質量平均分子量：１万、Ｔｇ：約１００℃）である。また、前記（Ａ）／（Ｂ）比の特に好ましい範囲は、３０／７０～６０／４０である。
【0122】
前記可塑剤の好ましい具体例としては、ポリプロピレングリコール、ポリエチレングリコール、ジオクチルフタレート、ジヘプチルフタレート、ジブチルフタレート、トリクレジルホスフェート、クレジルジフェニルホスフェート、ビフェニルジフェニルホスフェート、ポリエチレングリコールモノ（メタ）アクリレート、ポリエチレングリコールジ（メタ）アクリレート、ポリプロピレングリコールモノ（メタ）アクリレート、ポリプロピレングリコールジ（メタ）アクリレート、エポキシ樹脂とポリエチレングリコールモノ（メタ）アクリレートとの付加反応生成物、有機ジイソシアナートとポリエチレングリコールモノ（メタ）アクリレートとの付加反応生成物、有機ジイソシアナートとポリプロピレングリコールモノ（メタ）アクリレートとの付加反応生成物、ビスフェノールＡ－ポリエチレンオキシド付加物のジ（メタ）アクリレートを挙げることができる。
【0123】
可塑剤の量は、熱可塑性樹脂層を構成する熱可塑性樹脂の量（好ましくは前記熱可塑性樹脂（Ａ）及び（Ｂ）の合計量）に対して、好ましくは０～２００％［質量比］であり、より好ましくは２０～１００％［質量比］である。
また、可塑剤の特に好ましい例は、ビスフェノールＡ、１モルにエチレンオキシドを合計で１０モル付加し、両末端アルコールをメタクリルエステル化した化合物である。可塑剤の特に好ましい添加量は、熱可塑性樹脂の量（好ましくは前記熱可塑性樹脂（Ａ）及び（Ｂ）の合計量）の３０～６０質量%である。
【0124】
熱可塑性樹脂層は、上記の各成分を溶剤に均一に溶解してなる塗布液の塗布、乾燥により塗設できる。前記溶剤の好ましい例は、メトキシプロピレングリコールアセテート、２－ヒドロキシプロピン酸エチル、３－メトキシプロピオン酸メチル、３－エトキシプロピオン酸エチル、乳酸メチル、乳酸エチル、シクロヘキサノン、メチルイソブチルケトン等の高沸点溶剤及びこれら高沸点溶剤の混合物、メチルエチルケトンやアセトン等の低沸点溶剤及びこれら低沸点溶剤の混合物である。高沸点溶剤と低沸点溶剤との質量組成比は、塗布乾燥速度が良好で乾燥ムラ防止の点で、１／９９～９９／１から好適に選択できる。好ましくは高沸点溶剤／低沸点溶剤の質量比が９０／１０～１０／９０の範囲であり、８０／２０～２０／８０の範囲が最も好ましい。
【0125】
熱可塑性樹脂層は、仮支持体上に、一般に知られた塗布方法、例えばディップコート法、エアーナイフコート法、カーテンコート法、ワイヤーバーコート法、グラビアコート法、エクストルージョンコート法、スリットコート法などにより、前記熱可塑性樹脂等を含む塗布液（以下、「熱可塑性樹脂層用塗布液」ということがある。）を塗布し、乾燥させることにより形成することができる。
【0126】
熱可塑性樹脂層の層厚は、感光性樹脂層を転写する際に被転写面に存在する０．５μｍ以上の凹凸を完全に吸収する観点から、１μｍ以上が好ましい。また、上限については、塗布製造適性の制限から約１００μｍ以下が一般的であり、約５０μｍ以下が好ましく、

約２０μｍ以下が特に好ましい。

【0127】

中間層

中間層（分離層ともいう。）としては、熱可塑性樹脂層と感光性樹脂層との間で互いに成分が混じり合うのを防止する目的で設けられる。

中間層は、水またはアルカリ水溶液に分散または溶解し、中間層と接して設けられる熱可塑性樹脂層用塗布液中の有機溶剤に不溶もしくは難溶であればよく、公知のもので構成できる。

例えば、特開昭４６－２１２１７公報や特公昭５６－４０８２４公報に記載のポリビニルエーテル／無水マレイン酸重合体、カルボキシアルキルセルロースの水溶性塩、水溶性セルロースエーテル類、カルボキシアルキル澱粉の塩、水塩、ポリビニルアルコール、ポリビニルピロリドン、各種のポリアクリルアミド類、各種の水溶性ポリアミド、ポリアクリル酸の水溶性塩、ゼラチン、エチレンオキサイド重合体、各種の澱粉およびその類似物からなる群の水溶性塩、スチレン／マレイン酸の共重合体、及びマレイネート樹脂、並びにこれら２種以上を組合せたものを挙げることができる。

【0128】

特に、１）水溶性ポリビニルブチラール単独や、２）ポリビニルアルコールとポリビニルピロリドンとの組合せが好ましい。

ポリビニルアルコールは、鹸化率が８０モル%以上であるものが好ましく、ポリビニルピロリドンの含有率は中間層固形分の１～７５質量%が一般的であり、１～６０質量%が好ましく、特に好ましくは１０～５０質量%である。この範囲とすると、感光性樹脂層との接着性が充分に得られ、感光性樹脂層用塗布液に対する耐溶剤性を損なうこともない。

【0129】

中間層の層厚は、約０．１～５μｍが好適であり、特に０．５～２μｍが好ましい。この範囲とすると、感光性樹脂層用塗布液に対する耐溶剤性を有し、塗布速度の任意選択と乾燥を制限なく行なうことができる。

【0130】

中間層用塗布液の溶媒は水単独か、水と混和性の有機溶剤と水との混合物から選ばれる。下層となる熱可塑性樹脂層との接着性を高めるために、熱可塑性樹脂層を若干膨潤させ得るように選択するのが好ましい。好ましい溶媒の例としては水／メタノール、水／エタノール、水／プロパノール、水／メトキシエタノール、水／メトキシプロパノール、水／アセトンなどを挙げることができる。水とこれらの有機溶剤の組成比は質量比で９９／１～５０／５０の範囲から選択できる。この範囲とすることで、溶剤の添加効果が得られると共に、水溶性樹脂の充分な溶解性を得ることができる。

【0131】

中間層は、熱可塑性樹脂層上に一般に知られた塗布方法、例えば、ディップコート法、エアーナイフコート法、カーテンコート法、ワイヤーバーコート法、グラビアコート法、エクストルージョンコート法、スリットコート法などにより、中間層用塗布液を塗布することによって形成することができる。

【0132】

－保護フィルム－

保護フィルムは、転写材料を保存する際の、感光性樹脂層への不純物の付着や損傷を避けるために設けることが好ましく、薄い保護フィルムが好ましい。

保護フィルムは、仮支持体と同一か又は類似の材料からなるものでもよいが、使用時には感光性樹脂層から容易に分離可能なもので構成する必要がある。

【0133】

また、保護フィルムは、感光性樹脂層と接触する面の平滑性が重要であり、約０．０１μｍ程度の突起があると感光性樹脂層への損傷となるので問題になりやすい。そのため、保護フィルムとする材料としては、例えば、シリコン紙、ポリオレフィンもしくはポリテトラフルオルエチレンシートが好ましい。特に好ましくは、ポリプロピレンフィルムまた

はポリエチレンフィルムである。

【0134】

保護フィルムの厚みは、１～１００μｍが好適であり、３～５０μｍが好ましく、特に好ましくは５～２０μｍである。この範囲であると、強度を維持でき、感光性樹脂層との間の接着性も維持できる。

【0135】

～転写材料の製造方法～

本発明の転写材料は、例えば、好ましくは帯電防止層と接着性表面とを有する仮支持体の前記接着性表面上に、熱可塑性樹脂層用塗布液を塗布し、乾燥させることにより、アルカリ可溶性の熱可塑性樹脂層を塗設し、その後この熱可塑性樹脂層上に該層を溶解しないがある程度膨潤させる溶媒を用いてなる中間層用塗布液を塗布し、乾燥させて中間層を積層した後、更に該中間層を溶解しない溶剤を用いて調製された感光性樹脂層用塗布液を塗布し、乾燥させて感光性樹脂層を積層する。その後、保護フィルムを感光性樹脂層上にラミネートして作製できる。

上記の各層を形成するための塗布液は、既述のように一般に知られた塗布方法により塗布することができる。

【0136】

上記のうち、本発明の転写材料の製造方法は、既述の本発明の転写材料を作製するものであって、仮支持体上への感光性樹脂層の塗設をスリット状ノズルを有する塗布装置を用いた塗布により行なうことを特徴するものである。すなわち、感光性樹脂層は、液を吐出する部分にスリット状の穴を有するスリット状ノズルを用いて行なうスリットコート法により形成される。スリット状ノズルを用いることによって、より均一厚の層形成が可能である。

【0137】

具体的には、特開２００４－８９８５１号公報、特開２００４－１７０４３号公報、特開２００３－１７００９８号公報、特開２００３－１６４７８７号公報、特開２００３－１０７６７号公報、特開２００２－７９１６３号公報、特開２００１－３１０１４７号公報等に記載のスリット状ノズル、及びスリットコーターが好適に用いられる。

【0138】

上記による以外に、仮支持体上に該仮支持体側から順に熱可塑性樹脂層及び中間層を設けた第１シートと、保護フィルム上に感光性樹脂層を設けた第２シートとを用意し、第１シートの中間層表面と感光性樹脂層の表面とが接するように貼り合せることによって作製することもできる。また更に、仮支持体上に熱可塑性樹脂層を設けた第１シートと、保護フィルム上に該保護フィルム側から順に感光性樹脂層及び中間層を設けた第２シートとを用意し、第１シートの中間層表面と第２シートの熱可塑性樹脂層の表面とが接するように貼り合せることによって作製することもできる。

【0139】

本発明の転写材料は、既述したように、金属粒子及び／又は金属化合物粒子を含有して薄膜で高い黒濃度を有し、遮光性に優れた感光性樹脂層を設けてなるものであるため、高度の遮光性が要求される用途に好適であり、特にブラックマトリクスなどに代表される遮光膜の形成に好適である。

【0140】

＜遮光膜の作製方法＞

本発明の遮光膜の作製方法は、既述の本発明の遮光膜用感光性樹脂組成物を基板上に直に塗布する方法（塗布法）、又は一旦既述の本発明の遮光膜用感光性樹脂組成物を用いて構成された転写材料の感光性樹脂層を基板上に転写する方法（転写法）により遮光膜を作製するものである。

【0141】

本発明の遮光膜の作製方法により作製される遮光膜は、本発明の遮光膜用感光性樹脂組成物を用いてなるので、薄膜で黒濃度が高く遮光性に優れる。そのため、ブラックマトリ

クスなど薄膜が求められる用途に好適であり、その場合には、０．２～１．３μｍの範囲が好適であり、０．３～０．８μｍの範囲がより好適である。

【0142】

本発明の第１の遮光膜の作製方法は、塗布法によるものである。すなわち、基板上に、既述の本発明の遮光膜用感光性樹脂組成物を塗布し、乾燥させて感光性樹脂層を形成する工程（塗布工程）と、塗布工程で形成された感光性樹脂層をパターン状に露光する工程（パターン露光工程）と、塗布工程で形成された感光性樹脂層を加熱する工程（加熱工程）と、少なくとも露光後の感光性樹脂層を現像して未露光部を除去する工程（現像工程）とで構成したものである。

【0143】

また、本発明の第２の遮光膜の作製方法は、転写法によるものである。すなわち、既述の本発明の転写材料を用いて、仮支持体上の少なくとも１層の感光性樹脂層を基板に転写する工程（転写工程）と、転写工程で転写された感光性樹脂層をパターン状に露光する工程（パターン露光工程）と、転写工程で転写された感光性樹脂層を加熱する工程（加熱工程）と、少なくとも露光後の感光性樹脂層を現像して未露光部を除去する工程（現像工程）とで構成したものである。

転写法におけるパターン露光工程、加熱工程、及び現像工程は、前記塗布法の場合と同様にして行なえる。

塗布工程又は転写工程の後、パターン露光工程と加熱工程とはいずれが前工程であってもよいし、同時工程であってもよく、また、加熱工程と現像工程とはいずれが前工程であってもよいし、同時工程であってもよい。

【0144】

以下、各工程について説明する。

－塗布工程－

塗布法における塗布工程では、被塗物である基板上に、既述の本発明の遮光膜用感光性樹脂組成物を塗布し、乾燥させて感光性樹脂層を形成する。塗布には、一般に知られた塗布方法、例えば、ディップコート法、エアーナイフコート法、カーテンコート法、ワイヤーバーコート法、グラビアコート法、エクストルージョンコート法、スリットコート法などを適用することができる。

【0145】

中でも、液を吐出する部分にスリット状の穴を有するスリット状ノズルを用いて行なうスリットコート法が好ましく、スリット状ノズルを有する塗布装置（スリットコーター）を用いて好適に塗布することができる。

塗布厚は、最終的に得られる遮光膜の膜厚が前記範囲となる範囲で適宜選択すればよい。

【0146】

前記基板には、透明基板が好適であり、例えば、表面に酸化ケイ素皮膜を有するソーダガラス板、低膨張ガラス、ノンアルカリガラス、石英ガラス板等の公知のガラス板、あるいはプラスチックスフィルム等を挙げることができる。また、基板は、予めカップリング処理を施しておくことにより、本発明の組成物、又は本発明の転写材料の感光性樹脂層との間の密着を良好にすることができる。カップリング処理としては、特開２０００－３９０３３記載の方法が好適に用いられる。

【0147】

－転写工程－

転写法における転写工程では、既述の本発明の転写材料を用いて、仮支持体上に設けられている少なくとも１層の感光性樹脂層を基板に転写する。

【0148】

基板への感光性樹脂層の転写は、基板の被転写面（先行パターンや薄膜が既に形成されているときはその形成面）を洗浄後、転写材料から保護フィルムを剥離除去し、基板の洗浄面と転写材料の露出した感光性樹脂層の表面とを、ラミネーターのヒートローラーによ

り加熱加圧下で貼り合せて積層体とし、この積層体から仮支持体を剥離して基板上に転写する。ラミネーターは、市販のラミネーターを適宜選択することができる。

【0149】

転写時のヒートローラーの温度は、５０℃～１５０℃が好ましく、圧着時の線圧は、５Ｋｇ／ｃｍ～２５Ｋｇ／ｃｍが好ましい。また、ラミネート速度は、搬送速度で０．２～１ｍ／分が好ましい。

特に好ましい条件としては、加圧と共に加熱可能な加熱圧着ロールを用い、加熱圧着ロール温度１３０～１４０℃、圧着時の線圧１０～１５Ｋｇ／ｃｍ、搬送速度１～３ｍ／分である。

【0150】

－パターン露光工程－

パターン露光工程では、塗布工程又は転写工程で形成された感光性樹脂層をパターン状に露光する。本工程は、後述の加熱工程の前工程として行なってもよいし、加熱工程の後工程として行なってもよく、また、加熱工程と同時に行なうようにすることもできる。

【0151】

露光は、形成された感光性樹脂層に、所定のパターンのマスクを介して光を照射することによって行なえ、後述の現像工程を経た際に所望のパターンが得られるように潜像を形成する。すなわち、露光領域では、光酸発生剤から酸（Ｈ＋）が生成され、酸の触媒作用によりバインダー樹脂と架橋剤との間で架橋反応して架橋体を形成し、パターン状に重合硬化する。

【0152】

光源としては、例えば、ｇ線（波長４３６ｎｍ）、ｉ線（波長３６５ｎｍ）、超高圧水銀灯、キセノン灯、カーボンアーク灯、アルゴンレーザー等の公知の光源からの連続状及び／又は輝線状の紫外線、ＫｒＦエキシマレーザー等の遠紫外線、シンクロトロン放射線等のＸ線、電子線等の荷電粒子線などが挙げられる。中でも、ｇ線、ｉ線、及びこれらを含む３００～４４０ｎｍの波長領域の紫外線が好ましい。特開平６－５９１１９号公報に記載のように、４００ｎｍ以上の波長の光透過率が２％以下である光学フィルター等を併用してもよい。

【0153】

－加熱工程－

加熱工程では、前記パターン露光工程でのパターン露光後あるいはパターン露光時に、加熱（ベーク）処理を行なう。パターン露光時に発生した酸の存在下で架橋反応が開始後、更にパターン露光された露光領域を加熱することによって酸の拡散を促進し、感光性樹脂層の表面近傍から厚み方向に向かって架橋反応が促され、膜深部まで感光性樹脂層の重合硬化を良好に行なう。本発明においては、形成された感光性樹脂層は薄膜に構成されるため、酸の不要な拡散（例えば厚み方向である縦方向に対する横方向などへの拡散）が抑えられ、パターンの線太りを防止して高解像度の細線を得ることができる。

【0154】

本工程は、上記のパターン露光工程の前工程として行なうことができ、パターン露光工程の後工程として行なうこともでき、パターン露光工程と同時（パターン露光前から加熱することを含む。）に行なうようにすることもできる。また、本工程は、後述の現像工程の前工程として行なってもよいし、現像工程の後工程として行なってもよく、また、現像工程と同時に行なうようにすることもできる。なお、感光性樹脂層は、現像後には感光性を消失しているが、本明細書中では説明の簡易化の観点から感光性樹脂層と記載することがある。

【0155】

ベーク処理の条件は、光酸発生剤、架橋剤等により異なるが、８０～１４０℃、好ましくは１００～１２０℃にて１５秒～３分、好ましくは１５秒～１分が公的である。

【0156】

－現像工程－

現像工程では、露光後及び、前工程に加熱工程を設けた場合には加熱後の感光性樹脂層を現像処理して未露光部を現像除去し、パターンを顕在化させる。現像は、弱アルカリ現像液を用い、温度２６～４０℃、ｐＨ９～１１の条件下で行なうのが好ましい。

【0157】

この現像工程は、主に感光性樹脂層の現像によるパターン化を施すために設けられるが、転写法における転写工程により感光性樹脂層を形成した場合には、感光性樹脂層と共に熱可塑性樹脂層及び中間層が積層された状態にあるため、熱可塑性樹脂層及び中間層を除去するための第１のアルカリ現像と、感光性樹脂層の未露光部を除去するための第２のアルカリ現像とで構成されるのが望ましい。

【0158】

この場合、第１のアルカリ現像は、弱アルカリ現像液を用い、温度２６～４０℃、ｐＨ９～１１の条件下で行ない、第２のアルカリ現像は、上記同様に弱アルカリ現像液を用いて温度２６～４０℃、ｐＨ９～１１の条件下で行なうのが好ましい。

【0159】

感光性樹脂層現像用の現像液としては、アルカリ性物質の希薄水溶液を用いることができ、これに更に水と混和性の有機溶剤を少量添加したものを用いてもよい。

適当なアルカリ性物質としては、アルカリ金属水酸化物類（例、水酸化ナトリウム、水酸化カリウム）、アルカリ金属炭酸塩類（例、炭酸ナトリウム、炭酸カリウム）、アルカリ金属重炭酸塩類（例、炭酸水素ナトリウム、炭酸水素カリウム）、アルカリ金属ケイ酸塩類（例、ケイ酸ナトリウム、ケイ酸カリウム）、アルカリ金属メタケイ酸塩類（例、メタケイ酸ナトリウム、メタケイ酸カリウム）、アンモニア、エチルアミン、ｎ－プロピルアミン、ジエチルアミン、トリエチルアミン、メチルジエチルアミン、ジメチルエタノールアミン、トリエタノールアミン、ジエタノールアミン、モノエタノールアミン、モルホリン、テトラアルキルアンモンニウムヒドロキシド類（例えばテトラメチルアンモニウムヒドロキシド、テトラエチルアンモニウムヒドロキシド）、ピロール、ピペリジン、１，８－ジアザビシクロ〔５，４，０〕－７－ウンデセン、１，５－ジアザビシクロ〔４，３，０〕－５－ノナン、又は燐酸三ナトリウム等を挙げることができる。

【0160】

水と混和性の有機溶剤としては、例えば、メタノール、エタノール、２－プロパノール、１－プロパノール、ブタノール、ジアセトンアルコール、エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、エチレングリコールモノ－ｎ－ブチルエーテル、ベンジルアルコール、アセトン、メチルエチルケトン、シクロヘキサノン、ε－カプロラクトン、γ－ブチロラクトン、ジメチルホルムアミド、ジメチルアセトアミド、ヘキサメチルホスホルアミド、乳酸エチル、乳酸メチル、ε－カプロラクタム、Ｎ－メチルピロリドン等を好適に挙げることができる。水と混和性の有機溶剤の濃度は、０．１～３０質量％が一般的である。

【0161】

また、現像液には、さらに公知のアニオン型もしくはノニオン型の界面活性剤を添加することができる。界面活性剤の濃度は、０．０１～１０質量％が好ましい。現像液は、浴液として、あるいは噴霧液として用いることができ、現像方法については、液盛り法、ディッピング法、揺動浸漬法、スプレイ法等を利用することができる。

【0162】

本工程は、前記加熱工程の前工程として行なってもよいし、加熱工程の後工程として行なってもよく、また、加熱工程と同時に行なってもよい。

【0163】

既述のように、本発明の遮光膜用感光性樹脂組成物を用いることによって、薄膜で高濃度を有し、かつ高解像度の遮光膜を得ることができる。特に、表示装置を構成する液晶表示素子（特にカラーフィルタ）のブラックマトリクス（ここでいうブラックマトリクスは、画素間に配置される黒色部であり、ストライプ状や格子状にものなどがある。）を得るのに有用である。また、本発明の転写材料及び遮光膜の作製方法による場合も同様である

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【0164】

ブラックマトリックスは、液晶表示を行なう液晶セルに対して着色された各画素毎に電圧印加を行なう必要から、遮光性のみならず、電気絶縁性を兼ね備える必要がある。具体的には、ブラックマトリックスの体積抵抗値は、１×１０^{9}Ω・ｃｍ以上に保持することが好ましい。ＩＰＳ方式では電界が液晶層面内方向にかかるが、対向基板のブラックマトリックスの電気抵抗が前記範囲にあると電界を正常に印加し得、液晶配向に乱れや表示ムラのない表示が可能となる。したがって、ＩＰＳ方式の液晶表示装置に用いるブラックマトリックスは、高い遮光性を有するだけでなく高い抵抗値を示す必要がある。体積抵抗値を前記範囲とするには、ブラックマトリックスを体積抵抗値１Ω・ｃｍ以上の粒子とポリマーとからなり、該ブラックマトリックスの表面粗度を１００オングストローム以下にすることが好ましい。

【0165】

ここで、体積抵抗値は、単位面積、単位長さ当たりの抵抗値を示し、ポリマー体積抵抗率の測定と同様に、ガードリング付きの三端子法でブラックマトリックスをなす遮光膜用感光性樹脂組成物の塗布膜の上下に設けられた電極面に所定の電圧を印加したときの電流値から求められる。また、基板上に形成された互いに対向する対向電極を遮光膜用感光性樹脂組成物で覆い、この対向電極間に所定の電圧を印加して電流値及び電極形状をもとに求めてもよい。

【0166】

また、ブラックマトリクスの電圧保持率は８０％以上が好ましく、より好ましくは９０％以上である。電圧保持率が前記範囲内であると、イオン性物質等の不純物が液晶中に溶出して液晶層へのイオン性物質が混入する等に伴なう白ムラ等の発生がなく、良好な表示画像が得られる。電圧保持率を８０％以上とするには、ブラックマトリクスの形成時に用いる光酸発生剤の量、加熱条件等を調整して架橋度を高めることが好ましい。電圧保持率を８０％以上とすることにより、特に高温高湿等の厳しい表示条件下での長時間表示であっても、焼付きや白ムラ等の表示不良の発生が防止され、表示品質に優れた液晶表示装置が可能となる。

【実施例】

【0167】

以下、実施例により本発明を説明するが、本発明はこれらの実施例に限定されるものではない。なお、実施例中の「部」は質量基準である。

【0168】

（実施例１）

（１）感光性転写シートの作製

厚さ１００μｍのポリエチレンテレフタレートフィルム（ＰＥＴ仮支持体）を用意し、このＰＥＴ仮支持体上に、下記組成よりなる塗布液を塗布し、乾燥させて、乾燥層厚が２０μｍの熱可塑性樹脂層を形成した。

【0169】

〈熱可塑性樹脂層溶液の組成〉

・メチルメタクリレート／２－エチルヘキシルアクリレート／ベンジルメタクリレート／メタクリル酸（＝５５／１１．７／４．５／２８．８〔モル比〕）共重合体
…１５部
（重量平均分子量９００００）

・ポリプロピレングリコールジアクリレート
（平均分子量８２２）　…　６．５部

・テトラエチレングリコールジメタクリレート　…　１．５部

・ｐ－トルエンスルホンアミド　…　０．５部

・ベンゾフェノン　…　１．０部

・メチルエチルケトン　…３０部

【0170】
次いで、上記より形成された熱可塑性樹脂層の上に、下記組成よりなる塗布液を塗布し、乾燥させて、乾燥層厚が１．６μｍの中間層を形成した。
【0171】
〈中間層用塗布液の組成〉
・ポリビニルアルコール
（ＰＶＡ　２０５、鹸化率８０％、（株）クラレ製）…　１３０部
・ポリビニルピロリドン　…　６０部
（ＧＡＦコーポレション製 ＰＶＰ Ｋ－９０）
・フッ素系界面活性剤
（サーフロンＳ－１３１、旭硝子（株）製）　…　１０部
・蒸留水　…３３５０部
【0172】
次いで、下記組成よりなる黒色感光性樹脂層用塗布液を調製し、この黒色感光性樹脂層用塗布液を中間層の上に更に塗布し、乾燥させて、乾燥層厚が０．６０μｍのＡｇ粒子含有の黒色感光性樹脂層を形成した。その後、黒色感光性樹脂層の表面に保護フィルムとしてポリプロピレンフィルムを貼り付けた。得られた黒色感光性樹脂層の透過光学濃度は１．０であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は６．７であった。
以上のようにして、ＰＥＴ仮支持体／熱可塑性樹脂層／中間層／黒色感光性樹脂層／保護フィルムの積層構造に構成された本発明の感光性転写シートを作製した。
【0173】
本実施例では、透過光学濃度を以下のようにして求めた。
分光光度計ＵＶ－２１００（島津製作所（株）製）を用いて、感光性転写シート（保護フィルムなし）の透過光学濃度（ＯＤ）を波長３５５ｎｍで測定すると共に、さらに黒色感光性樹脂層形成前の、熱可塑性樹脂層及び中間層が形成されたＰＥＴ仮支持体の透過光学濃度（OD^0）を同様の方法で測定し、得られたＯＤからOD^0を差し引いた値（透過ＯＤ；＝ＯＤ－OD^0）を透過光学濃度とした。
【0174】
〈黒色感光性樹脂層用塗布液の組成〉
・メタクリル酸／ベンジルメタクリレート共重合体　…　１９．９８部
（モル比：２８／７２、重量平均分子量：３００００）
・架橋剤（ＭＷ－３０Ｍ、三和ケミカル（株）製）　…　４．７６部
・Ａｇ粒子（平均粒子径８０ｎｍ）　…　５１．３部
・界面活性剤　…　０．１７部
（大日本インキ化学工業（株）製、Ｆ１７７Ｐ）
・光酸発生剤　…　２．３８部
（２，４－ビス（トリクロロ）－６，４－［４－Ｎ，Ｎ－ジエトキシカルボメチル）－３　ブロモフェニル　ｓ　トリアジン）
・メチルエチルケトン　…１０６．８０部
・プロピレングリコールモノメチルエーテルアセテート
…　４４．７０部
【0175】
（２）転写法による画像形成
上記より得た感光性転写シートから保護フィルムを剥がし、露出した黒色感光性樹脂層の表面を、厚さ１．１ｍｍのガラス基板の表面と接するようにラミネータ（Ｌａｍｉｃｌｌ型、（株）日立インダストリイズ製）を用いて１３０℃、０．２ｍ／ｍｉｎ、１０Ｋｇ／ｃｍの条件で貼り合せ、ＰＥＴ仮支持体を剥離して黒色感光性樹脂層を熱可塑性樹脂層及び中間層と共に転写し、光学濃度４．０の黒色感光性樹脂層が転写形成されたガラス基板を得た。

【0176】
続いて、この黒色感光性樹脂層の表面に、フォトマスクを介して４００ｍｊ／ｃｍ²にてパターン状に露光を行ない、露光を修了して１分経過した後、１４０℃に加熱されたホットプレート上にガラス基板面で接するようにして載置して１２秒間加熱処理（露光後ベーク）を行なった。
【0177】
露光後ベークの後、熱可塑性樹脂層及び中間層の除去用のアルカリ現像液Ｔ　ＰＤ２（富士写真フイルム（株）製）の１０倍希釈液（３３℃、ｐＨ－１０．７）を用いて熱可塑性樹脂層及び中間層を現像除去し、さらに水洗処理した後、続けて黒色感光性樹脂層の未露光部を、アルカリ現像液Ｔ　ＣＤ（富士写真フイルム（株）製）の５倍希釈液（３３℃、ｐＨ＝９．９）を用いて現像し、水洗処理を行なって、ガラス基板上に遮光性の黒色画像を形成した。
【0178】
（３）評価
下記のようにして測定、評価を行ない、測定、評価の結果を下記表１に示す。
－１．解像度－
上記より得た感光性転写シートを用い、前記同様にしてガラス基板上に黒色感光性樹脂層を転写形成し、形成された黒色感光性樹脂層を、５０μｍ～１μｍまで２μｍ間隔毎に狭くなるライン状のパターンを有するマスクを用いて、パターン露光した。その後、前記同様に現像処理を行ない、ラインが残っている部分のライン幅（μｍ）を光学顕微鏡を用いて計測し、これを解像度とした。値の小さい方が解像度に優れることを示す。
【0179】
－２．表示ムラ－
黒色画像が形成されたガラス基板に対し、下記のようにして着色画素を形成してカラーフィルタとし、レーザー顕微鏡等を用いた膜厚測定により突起の有無を評価した。ここでの突起は、画像表示した際に表示ムラを起こす一因となるものであり、着色画素を設けたときの着色画素と黒色画像との重なり部分が角状の突起となって起きるものである。
【0180】
〈カラーフィルタの作製〉
－感光性樹脂転写材料の作製－
厚さ７５μｍのポリエチレンテレフタレートフィルム仮支持体（ＰＥＴ仮支持体）の上に、スリット状ノズルを用いて、下記処方Ｈ１からなるクッション層用塗布液を塗布、乾燥させてクッション層を形成した。次に、このクッション層上に下記処方Ｐ１からなる中間層用塗布液を塗布、乾燥させて中間層（酸素遮断膜）を積層した。この中間層上に更に、下記表１に記載の組成よりなる着色感光性樹脂組成物Ｒ２を塗布、乾燥させて感光性樹脂層を積層した。このようにして、ＰＥＴ仮支持体の上に、乾燥膜厚が１４．６μｍの熱可塑性樹脂層と乾燥膜厚が１．６μｍの中間層と乾燥膜厚が２．４μｍの感光性樹脂層を設け、感光性樹脂層上には保護フィルム（厚さ１２μｍポリプロピレンフィルム）を圧着した。
【0181】

【表1】

着色感光性樹脂組成物	R1	G1	B1	R2	G2	B2
R顔料分散物1 (C. I. P. R. 254)	44	-	-	44	-	-
R顔料分散物2 (C. I. P. R. 177)	5.0	-	-	5.0	-	-
G顔料分散物1 (C. I. P. G. 36)	-	24	-	-	24	-
Y顔料分散物1 (C. I. P. Y. 150)	-	13	-	-	13	-
B顔料分散物1 (C. I. P. B. 15:6 + C. I. P. V. 23)	-	-	8.0	-	-	7.2
B顔料分散物2 (C. I. P. B. 15:6)	-	-	14.4	-	-	13
プロピレングリコールモノメチルエーテルアセテート	7.6	29	28	7.6	29	23
メチルエチルケトン	37	26	41	37	26	35
シクロヘキサノン	-	1.3	-	-	1.3	-
バインダー1	-	2.5	-	-	3	-
バインダー2	0.7	-	-	0.8	-	-
バインダー3	-	-	19	-	-	17
DPHA液	3.8	3.5	4.2	4.4	4.3	3.8
2-トリクロロメチル-5-(p-スチリルメチル)1, 3, 4-オキサジアゾール	0.12	0.1	0.17	0.14	0.15	0.15
2, 4-ビス(トリクロロメチル)-6-[4-(N, N-ジエトキシカルボニルメチル)-3-ブロモフェニル]-s-トリアジン	0.050	0.050	-	0.058	0.060	-
フェノチアジン	0.010	0.005	0.020	0.010	0.005	0.020
添加剤1	-	-	-	0.52	-	-
界面活性剤1	0.060	0.070	0.060	0.060	0.070	0.050

質量部

【0182】
上記のようにして、仮支持体と熱可塑性樹脂層と中間層（酸素遮断膜）と赤色の感光性樹脂層とが積層されて積層体に構成された感光性樹脂転写材料を作製した（以下、感光性樹脂転写材料Ｒ２と称する）。

【0183】
〔クッション層用塗布液の処方111〕
・メタノール　…１１．１部
・プロピレングリコールモノメチルエーテルアセテート　…　６．４部
・メチルエチルケトン　…５２．４部
・メチルメタクリレート／２　エチルヘキシルアクリレート／ベンジルメタクリレート／メタクリル酸共重合体　…　５．８３部
〔共重合比（モル比）－５５／１１．７／４．５／２８．８、重量平均分子量－１０万、Ｔｇ≒７０℃〕
・スチレン／アクリル酸共重合体　…１３．６部
〔共重合比（モル比）＝６３／３７、重量平均分子量＝１万、Ｔｇ≒１００℃〕
・ビスフェノールＡにペンタエチレングリコールモノメタクリートを２当量脱水縮合した化合物（新中村化学工業（株）製、２，２－ビス［４－（メタクリロキシポリエトキシ）フェニル］プロパン）　…　９．１部
・界面活性剤１　…　０．５４部

【0184】
＊界面活性剤１：
メガファックＦ－７８０－Ｆ（大日本インキ化学工業（株）製）
〔組成〕

・$C_8F_{13}CH_2CH_2OCOCH=CH_2$（４０部）とH（O（$CH_2$）CHC$H_2$）$_7$OCOCH－$CH_2$（５５部）とH（O$CH_2CH_2$）$_7$OCOCH－$CH_2$（５部）との共重合体（重量平均分子量３万）…３０部
・メチルイソブチルケトン…７０部

【0185】
〔中間層用塗布液の処方Ｐ１〕
・ポリビニルアルコール　…　２．１部
（ＰＶＡ－２０５（鹸化率－８８％）、（株）クラレ製）
・ポリビニルピロリドン　…　０．９５部
（ＰＶＰ、Ｋ　３０；ＧＡＦコーポレーション社製）
・メタノール　…４４部
・蒸留水　…５３部

【0186】
次に、得られた感光性樹脂転写材料Ｒ２の作製において用いた前記着色感光性樹脂組成物Ｒ２を、前記表１に記載の組成よりなる着色感光性樹脂組成物Ｇ２及びＢ２に代えたこと以外は、上記と同様の方法により、感光性樹脂転写材料Ｇ２及びＢ２を作製した。

【0187】
着色感光性樹脂組成物Ｒ２、Ｇ２及びＢ２の調製方法は、それぞれ前記表１中の着色感光性樹脂組成物Ｒ１、Ｇ１及びＢ１の調製方法に準ずるものとし、着色感光性樹脂組成物Ｒ１、Ｇ１及びＢ１の調製方法は後記する。なお、着色感光性樹脂組成物Ｒ２の調製は、着色感光性樹脂組成物Ｒ１の調製方法において、フェノチアジン等の添加後、界面活性剤１の添加前に、前記表１に記載の量の添加剤１をはかり取り、温度２４℃（±２℃）で混合して１５０ｒ．ｐ．ｍ．で２０分間撹拌するようにした。
※添加剤１：燐酸エステル系特殊活性剤（ＨＩＰＬＡＡＤ　ＥＤ１５２、楠本化成（株）製）

【0188】
－レッド（Ｒ）画素の形成－
前記感光性樹脂転写材料Ｒ２の保護フィルムを剥離後、露出した感光性樹脂層が、上記より遮光膜（遮光性の黒色画像）が形成されたガラス基板の表面と接するように重ね合わせ、ラミネータＬａｍｉｃⅡ型〔（株）日立インダストリイズ製〕を用いて、ゴムローラ温度１３０℃、線圧１００Ｎ／ｃｍ、搬送速度２．２ｍ／分の条件にてラミネートした。次いで、ＰＥＴ仮支持体を剥離してガラス基板上に転写した。

【0189】
次に、超高圧水銀灯を有するプロキシミティー型露光機（日立電子エンジニアリング（株）製）を用い、マスク（画像パターンを有する石英露光マスク）と、該マスクと熱可塑性樹脂層とが向き合うように配置したガラス基板とを略平行に垂直に立てた状態で、マスク面と感光性樹脂層の中間層に接する側の表面との間の距離を２００μｍに設定し、マスクを介して熱可塑性樹脂層側から露光量４０ｍＪ／ｃｍ^{2}でパターン露光した。

【0190】
次に、トリエタノールアミン系現像液（２．５％のトリエタノールアミン、ノニオン界面活性剤、及びポリプロピレン系消泡剤含有；商品名：Ｔ－ＰＤ１、富士写真フイルム（株）製）にて３０℃で５０秒間、フラットノズル圧力０．０４ＭＰａでシャワー現像し、熱可塑性樹脂層と酸素遮断膜とを除去した。

【0191】
次に、炭酸Ｎａ系現像液（０．０６モル／リットルの炭酸水素ナトリウム、同濃度の炭酸ナトリウム、１％のジブチルナフタレンスルホン酸ナトリウム、アニオン界面活性剤、消泡剤、及び安定剤を含有；商品名：Ｔ－ＣＤ１、富士写真フイルム（株）製）を用いて、３５℃で３５秒間、コーン型ノズル圧力０．１５ＭＰａでシャワー現像し、パターン画素を得た。

【0192】

次に、洗浄剤（燐酸塩、珪酸塩、ノニオン界面活性剤、消泡剤、及び安定剤含有；商品名：Ｔ－ＳＤ１、富士写真フイルム（株）製）を用いて、３３℃で２０秒間、コーン型ノズル圧力０．０２ＭＰａでシャワーとナイロン毛を有す回転ブラシを用いて残渣除去を行なうことにより、レッド（Ｒ）画素を形成した。その後さらに、この基板に対し、Ｋ画像が形成されている側から超高圧水銀灯により５００ｍＪ／ｃｍ^{2}の光でポスト露光した後、２２０℃で１５分間熱処理した。

【0193】

Ｒ画素の厚みは２．０μｍであり、Ｃ．Ｉ．ピグメント・レッド（Ｃ．Ｉ．Ｐ．Ｒ．）２５４、Ｃ．Ｉ．Ｐ．Ｒ．１７７の塗布量はそれぞれ０．８８ｇ／ｍ^2、０．２２ｇ／ｍ^{2}であった。

その後、Ｒ画素が形成されたガラス基板を再び、上記のように洗浄剤を用いてブラシ洗浄し、純水でシャワー洗浄した後、シランカップリング液は使用せずに、基板予備加熱装置により１００℃で２分間加熱した。

【0194】

－グリーン（Ｇ）画素の形成－

次に、上記より得た感光性樹脂転写材料Ｇ２を用い、前記Ｒ画素の形成と同様の工程を行ない、ガラス基板の遮光膜及びＲ画素が形成されている側にグリーン画素（Ｇ画素）を形成した。但し、露光工程での露光量は４０ｍＪ／ｃｍ^2、炭酸Ｎａ系現像液によるシャワー現像は３４℃で４５秒間とし、熱処理は２２０℃で１５分間とした。

Ｇ画素の厚みは２．０μｍであり、Ｃ．Ｉ．ピグメント・グリーン（Ｃ．Ｉ．Ｐ．Ｇ．）３６、Ｃ．Ｉ．ピグメント・イエロー（Ｃ．Ｉ．Ｐ．Ｙ．）１５０の塗布量はそれぞれ１．１２ｇ／ｍ^2、０．４８ｇ／ｍ^{2}であった。

【0195】

その後、Ｒ画素及びＧ画素が形成されたガラス基板を再び、上記のように洗浄剤を用いてブラシ洗浄し、純水でシャワー洗浄した後、シランカップリング液は使用せずに、基板予備加熱装置により１００℃で２分間加熱した。

【0196】

－ブルー（Ｂ）画素の形成－

次に、上記より得た感光性樹脂転写材料Ｂ２を用い、前記Ｒ画素の形成と同様の工程を行ない、ガラス基板の遮光膜並びにＲ画素及びＧ画素が形成されている側にブルー画素（Ｂ画素）を形成した。但し、露光工程での露光量は３０ｍＪ／ｃｍ^2、炭酸Ｎａ系現像液によるシャワー現像は３６℃で４０秒間とした。

Ｂ画素の厚みは２．０μｍであり、Ｃ．Ｉ．ピグメント・ブルー（Ｃ．Ｉ．Ｐ．Ｂ．）１５：６、Ｃ．Ｉ．ピグメント・バイオレット（Ｃ．Ｉ．Ｐ．Ｖ．）２３の塗布量はそれぞれ０．６３ｇ／ｍ^2、０．０７ｇ／ｍ^{2}であった。

【0197】

その後、Ｒ、Ｇ、Ｂの各画素が形成されたガラス基板を２４０℃で５０分間ベークし、カラーフィルタを得た。

【0198】

（実施例２）

実施例１と同様にして、黒色感光性樹脂層用塗布液を調製した。次に、厚さ１．１ｍｍのガラス基板を用意し、このガラス基板上に、得られた黒色感光性樹脂層用塗布液を乾燥膜厚が０．６０μｍになるように、スリット＆スピンコーターを用いて塗布し、乾燥させて、黒色感光性樹脂層を塗設した。

ここで、黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は６．７であった。

【0199】

続いて、塗設した黒色感光性樹脂層の表面に、フォトマスクを介して４００ｍｊ／ｃｍ^{2}にてパターン状に露光を行ない、露光を修了して１分経過した後、１４０℃に加熱され

たホットプレート上にガラス基板面で接するようにして載置して１２秒間加熱処理（露光後ベーク）を行なった。

【0200】

露光後ベークの後、熱可塑性樹脂層及び中間層の除去用のアルカリ現像液Ｔ　ＰＤ２（富士写真フイルム（株）製）の１０倍希釈液（３３℃、ｐＨ－１０．７）を用いて熱可塑性樹脂層及び中間層を現像除去し、さらに水洗処理し、続けて黒色感光性樹脂層の未露光部を、アルカリ現像液Ｔ　ＣＤ（富士写真フイルム（株）製）の５倍希釈液（３３℃、ｐＨ－９．９）を用いて現像し、水洗処理を行なって、ガラス基板上に遮光性の黒色画像を形成した。その後、実施例１と同様の評価を行なった。但し、カラーフィルタの形成は以下のようにして行なった。

【0201】

〈カラーフィルタの作製（スリット＆スピンコーターによる塗布）〉

－レッド（Ｒ）画素の形成－

上記のように遮光膜（遮光性の黒色画像）が形成されたガラス基板の遮光膜形成面側に、スリット＆スピンコーターにて、前記表１に記載の組成よりなる着色感光性樹脂組成物Ｒ１を塗布した。引き続き、真空乾燥機ＶＣＤ（東京応化社製）を用いて３０秒間溶媒の一部を乾燥させて塗布膜の流動性をなくした後、ＥＢＲ（エッジ・ビード・リムーバー）にて基板周囲の不要な塗布液を除去し、１２０℃で３分間プリベークして膜厚２．４μｍの感光性樹脂層Ｒ１を形成した。

【0202】

次に、超高圧水銀灯を備えたプロキシミティー型露光機（日立電子エンジニアリング社製）を用い、マスク（画像パターンを有する石英露光マスク）と感光性樹脂層Ｒ１が設けられたガラス基板とを垂直に立てた状態で、マスク面と感光性樹脂層Ｒ１の表面との間の距離を２００μｍとし、露光量１５０ｍＪ／ｃｍ２でパターン露光した。

次に、純粋をシャワーノズルから噴霧し、感光性樹脂層Ｒ１の表面を均一に湿らせた後、ＫＯＨ系現像液ＣＤＫ－１（富士フイルムエレクトロニクスマテリアルズ（株）製；ＫＯＨ及びノニオン界面活性剤含有アルカリ現像液）を、フラットノズルから２３℃、ノズル圧力０．０４ＭＰａにて６０秒間噴射してシャワー現像し、レッドパターンを得た。続いて、ガラス基板のレッドパターンが形成された側に超純水を超高圧洗浄ノズルにより９．８ＭＰａの圧力で噴射して残渣を除去し、ガラス基板上にレッド（Ｒ）画素を形成した。その後、２２０℃で３０分間熱処理（ベーク）した。

【0203】

Ｒ画素の厚みは１．６μｍであり、Ｃ．Ｉ．ピグメント・レッド（Ｃ．Ｉ．Ｐ．Ｒ．）２５４、Ｃ．Ｉ．Ｐ．Ｒ．１７７の塗布量はそれぞれ０．８８ｇ／ｍ^2、０．２２ｇ／ｍ^{2}であった。

【0204】

グリーン（Ｇ）画像の形成

次に、前記遮光膜及びＲ画素が形成されたガラス基板に、前記表１に示す組成よりなる着色感光性樹脂組成物Ｇ１を用い、前記Ｒ画素の形成と同様にして塗布、露光、現像、及びベークを行ない、ガラス基板の遮光膜及びＲ画素が形成されている側にグリーン画素（Ｇ画素）を形成した。但し、露光工程での露光量は１５０ｍＪ／ｃｍ２とし、現像工程でのシャワー現像は２３℃で６０秒間とし、熱処理は２２０℃で３０分間とした。

【0205】

Ｇ画素の厚みは１．６μｍであり、Ｃ．Ｉ．ピグメント・グリーン（Ｃ．Ｉ．Ｐ．Ｇ．）３６、Ｃ．Ｉ．ピグメント・イエロー（Ｃ．Ｉ．Ｐ．Ｙ．）１５０の塗布量はそれぞれ１．１２ｇ／ｍ^2、０．４８ｇ／ｍ^{2}であった。

【0206】

－ブルー（Ｂ）画像の形成－

次に、前記遮光膜並びにＲ画素及びＧ画素が形成されたガラス基板に、前記表１に示す組成よりなる着色感光性樹脂組成物Ｂ１を用い、前記Ｒ画素の形成と同様にして塗布、露

光、現像、及びベークを行ない、ガラス基板の遮光膜並びにR画素及びG画素が形成されている側にブルー画素（B画素）を形成した。但し、露光工程での露光量は１５０ｍＪ／ｃｍ２とし、現像工程でのシャワー現像は２３℃で６０秒間とし、熱処理は２２０℃で３０分間とした。

【0207】

B画素の厚みは１．６μｍであり、Ｃ．Ｉ．ピグメント・ブルー（Ｃ．Ｉ．Ｐ．Ｂ．）１５：６及びＣ．Ｉ．ピグメント・バイオレット（Ｃ．Ｉ．Ｐ．Ｖ．）２３の塗布量はそれぞれ０．６３ｇ／ｍ２、０．０７ｇ／ｍ２であった。

【0208】

その後、R、G，Bの各画素が形成されたガラス基板を２４０℃で５０分間ベークし、カラーフィルタを得た。

【0209】

ここで、前記表１に記載の着色感光性樹脂組成物Ｒ１、Ｇ１及びＢ１の調製について説明する。

〈着色感光性樹脂組成物Ｒ１の調製〉

着色感光性樹脂組成物Ｒ１は、前記表１に記載の量のR顔料分散物１、R顔料分散物２、及びプロピレングリコールモノメチルエーテルアセテートをはかり取り、温度２４℃（＋２℃）で混合して１５０ｒ．ｐ．ｍ．で１０分間撹拌し、次いで、前記表１に記載の量のメチルエチルケトン、バインダー２、ＤＰＨＡ液、２－トリクロロメチル－５－（ｐ－スチリルメチル）－１，３，４－オキサジアゾール、２，４－ビス（トリクロロメチル）－６－［４－（Ｎ，Ｎ－ジエトキシカルボニルメチル）－３－ブロモフェニル］－ｓ－トリアジン、及びフェノチアジンをはかり取り、温度２４℃（±２℃）でこの順に添加して１５０ｒ．ｐ．ｍ．で３０分間撹拌し、更に、前記表１に記載の量の界面活性剤１をはかり取り、温度２４℃（　２℃）で添加して３０ｒ．ｐ．ｍ．で３０分間撹拌し、ナイロンメッシュ＃２００で沪過することによって得た。

【0210】

なお、前記表１に記載の組成物Ｒ１中の各組成の詳細は以下の通りである。また、界面活性剤１の組成は既述の通りである。

＊R顔料分散物１の組成

・Ｃ．Ｉ．ピグメント・レッド２５４…８．０部

・５　［３　オキソ　２　［４　［３，５-ビス（３　ジエチルアミノプロピルアミノカルボニル）フェニル]アミノカルボニル］フェニルアゾ］－ブチロイルアミノベンズイミダゾロン…０．８部

・ポリマー〔ベンジルメタクリレート／メタクリル酸（－７２／２８[モル比]）のランダム共重合物（重量平均分子量３７，０００）〕…８．０部

・プロピレングリコールモノメチルエーテルアセテート…８３．２部

【0211】

＊R顔料分散物２の組成

・Ｃ．Ｉ．ピグメント・レッド１７７…１８部

・ポリマー〔ベンジルメタクリレート／メタクリル酸（－７２／２８[モル比]）のランダム共重合物（重量平均分子量３７，０００）〕…１２部

・プロピレングリコールモノメチルエーテルアセテート…７０部

＊バインダー２の組成

・ベンジルメタクリレート／メタクリル酸／メチルメタクリレート（－３８／２５／３７[モル比]）のランダム共重合物（重量平均分子量３０，０００）…２７部

・プロピレングリコールモノメチルエーテルアセテート…７３部

＊添加剤１：燐酸エステル系特殊活性剤（ＨＩＰＬＡＡＤ　ＥＤ１５２、楠本化成（株）製）

＊ＤＰＨＡ液の組成

・ジペンタエリスリトールヘキサアクリレート（商品名：ＫＡＹＡＲＡＤ　ＤＰＨＡ、

日本化薬（株）製）…７６部
　・プロピレングリコールモノメチルエーテル…２４部
【0212】
〈着色感光性樹脂組成物Ｇ１の調製〉
　着色感光性樹脂組成物Ｇ１は、前記表１に記載の量のＧ顔料分散物１、Ｙ顔料分散物１、及びプロピレングリコールモノメチルエーテルアセテートをはかり取り、温度２４℃（±２℃）で混合して１５０ｒ.ｐ.ｍ.で１０分間攪拌し、次いで、前記表１に記載の量のメチルエチルケトン、シクロヘキサノン、バインダー１、ＤＰＨＡ液、２－トリクロロメチル－５－（ｐ－スチリルメチル）－１，３，４－オキサジアゾール、２，４－ビス（トリクロロメチル）－６－［４－（Ｎ，Ｎ－ジエトキシカルボニルメチル）－３－ブロモフェニル］－ｓ－トリアジン、及びフェノチアジンをはかり取り、温度２４℃（±２℃）でこの順に添加して１５０ｒ.ｐ.ｍ.で３０分間攪拌し、更に、前記表１に記載の量の界面活性剤１をはかり取り、温度２４℃（±２℃）で添加して３０ｒ.ｐ.ｍ.で５分間攪拌し、ナイロンメッシュ＃２００で沪過することによって得た。
【0213】
　なお、前記表１に記載の組成物Ｇ１中の各組成の詳細は以下の通りである。また、ＤＰＨＡ液及び界面活性剤１の組成については既述の通りである。
＊Ｇ顔料分散物１の組成
　・Ｃ．Ｉ．ピグメント・グリーン３６…１８部
　・ポリマー〔ベンジルメタクリレート／メタクリル酸（＝７２／２８[モル比]）のランダム共重合物（重量平均分子量３７，０００）〕…１２部
　・シクロヘキサノン…３５部
　・プロピレングリコールモノメチルエーテルアセテート…３５部
＊Ｙ顔料分散物１
　商品名：ＣＦエローＥＸ３３９３（御国色素社製）
＊バインダー１
　・ポリマー〔ベンジルメタクリレート／メタクリル酸（＝７８／２２[モル比]）のランダム共重合物（分子量４０，０００）〕…２７部
　・プロピレングリコールモノメチルエーテルアセテート…７３部
【0214】
〈着色感光性樹脂組成物Ｂ１の調製〉
　着色感光性樹脂組成物Ｂ１は、前記表１に記載の量のＢ顔料分散物１、Ｂ顔料分散物２、及びプロピレングリコールモノメチルエーテルアセテートをはかり取り、温度２４℃（±２℃）で混合して１５０ｒ.ｐ.ｍ.で１０分間攪拌し、次いで、前記表１に記載の量のメチルエチルケトン、バインダー３、ＤＰＨＡ液、２－トリクロロメチル－５－（ｐ－スチリルメチル）－１，３，４－オキサジアゾール、及びフェノチアジンをはかり取り、温度２５℃（±２℃）でこの順に添加して、温度４０℃（±２℃）で１５０ｒ.ｐ.ｍ.で３０分間攪拌し、更に、前記表１に記載の量の界面活性剤１をはかり取り、温度２４℃（±２℃）で添加して３０ｒ.ｐ.ｍ.で５分間攪拌し、ナイロンメッシュ＃２００で沪過することによって得た。
【0215】
　なお、前記表１に記載の組成物Ｂ１中の各組成の詳細は以下の通りである。また、ＤＰＨＡ液及び界面活性剤１の組成については既述の通りである。
＊Ｂ顔料分散物１
　商品名：ＣＦブルーＥＸ３３５７（御国色素社製）
＊Ｂ顔料分散物２
　商品名：ＣＦブルーＥＸ３３８３（御国色素社製）
＊バインダー３の組成
　・ベンジルメタクリレート／メタクリル酸／メチルメタクリレート（＝３６／２２／４２[モル比]）のランダム共重合物（重量平均分子量３０，０００）…２７部

・プロピレングリコールモノメチルエーテルアセテート…７３部

【0216】

（実施例３）

実施例２において、スリット＆スピンコーターを、スリット状ノズルを備えたガラス基板用コーターＭＨ－１６００（エフ・エー・エス・ジャパン社製）に代えたこと以外、実施例２と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚あたりの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は６．７であった。また、実施例１と同様の評価を行なった。但し、カラーフィルタの形成は以下のようにして行なった。

【0217】

〈カラーフィルターの作製（スリット状ノズルを用いた塗布による作製）〉

実施例２のカラーフィルタの作製において、スリット＆スピンコーターをスリット状ノズルを備えたガラス基板用コーターＭＨ－１６００（エフ・エー・エス・ジャパン社製）に代えたこと以外、実施例２と同様にして、上記より得た遮光膜（遮光性の黒色画像）が形成されたガラス基板に、カラーフィルタを形成した。

【0218】

（実施例４）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、Ａｇ粒子（平均粒子径８０ｎｍ）４１部及びカーボンブラック（ＣＢ）１．７６部（添加体積比（Ag／CB）＝８０／２０）に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を０．７０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚あたりの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は５．７であった。また、実施例１と同様の評価を行なった。

【0219】

（実施例５）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、Ａｇ粒子（平均粒子径８０ｎｍ）２５．７部及びカーボンブラック（ＣＢ）４．４部（添加体積比（Ag／CB）＝５０／５０）に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を０．９０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚あたりの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は４．４であった。また、実施例１と同様の評価を行なった。

【0220】

（実施例６）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、Ａｇ粒子（平均粒子径８０ｎｍ）１０．３部及びカーボンブラック（ＣＢ）７．０４部（添加体積比（Ag／CB）＝２０／８０）に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を１．００μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚あたりの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は４．０であった。また、実施例１と同様の評価を行なった。

【0221】

（実施例７）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、下記より得た銀／硫化銀コアシェル粒子（平均粒子径９０ｎｍ）５１．３部に代えると共

に、形成した黒色感光性樹脂層の乾燥層厚を０．８０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は３．９であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は４．９であった。また、実施例１と同様の評価を行なった。

【0222】

〈銀／硫化銀コアシェル粒子の作製〉

銀粒子のアセトン分散物（平均粒径３０ｎｍ、濃度２．５質量％）２００ｇにビニルピロリドン／酢酸ビニル共重合体（＝６０／４０［質量比］、重量平均分子量５０００）を０．９５ｇ添加して、３０分間撹拌した。次いで、これに濃度７．２質量％の硫化ナトリウム水溶液（２３℃）を、撹拌しながら金属の硫化率が３０％になるように添加し、添加終了後そのまま３０分間撹拌を行なって、硫化銀のシェルを持つ銀／硫化銀コアシェル粒子を得た。

ここで、硫化率とは、金属粒子が硫化されている割合で、硫化率０％は全く硫化されていない状態を、１００％は粒子全体が完全に硫化物になっている状態を表す。

【0223】

（実施例８）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、Ｓｎ粒子（平均粒子径３６ｎｍ、短軸２０ｎｍ、長軸５０ｎｍ）５１．３部に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を０．９０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は４．４であった。また、実施例１と同様の評価を行なった。

【0224】

（実施例９）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子５１．３部を、Ａｇ粒子（平均粒子径１１７ｎｍ、短軸６０ｎｍ、長軸１８０ｎｍ）５１．３部に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を０．８０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は４．０であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は５．０であった。また、実施例１と同様の評価を行なった。

【0225】

（比較例１）

実施例１において、〈黒色感光性樹脂層用塗布液の組成〉中のＡｇ粒子（５１．３部）をカーボンブラック（２１．１７部）に代え、メタクリル酸／ベンジルメタクリレート共重合体をアクリル樹脂に代えると共に、形成した黒色感光性樹脂層の乾燥層厚を１．５０μｍとしたこと以外、実施例１と同様にして、ガラス基板上に遮光性の黒色画像を形成した。

黒色感光性樹脂層の実施例１と同様にして測定した透過光学濃度は３．５であり、単位層厚（１μｍ）当りの透過光学濃度（透過光学濃度／黒色感光性樹脂層の層厚）は２．３であった。また、実施例１と同様の評価を行なった。

【0226】

【表2】

	金属粒子		カーボンブラック	粒子径[nm]	短軸[nm]	長軸[nm]	膜厚[μm]	ベーク時間[秒]	透過光学濃度	単位体積あたりの透過光学濃度	解像度[μm]	突起の有無（表示ムラ）
	種	添加体積比	添加体積比									
実施例1	（転写法）	Ag粒子	100%	0%	80			0.60	12	4.0	6.7	6	無
実施例2	（塗布法）スリット&スピンコート	Ag粒子	100%	0%	80			0.60	12	4.0	6.7	6	無
実施例3	（塗布法）スリットコート	Ag粒子	100%	0%	80			0.60	12	4.0	6.7	6	無
実施例4	（転写法）	Ag粒子	80%	20%	80			0.70	12	4.0	5.7	6	無
実施例5	（転写法）	Ag粒子	50%	50%	80			0.90	12	4.0	4.4	6	無
実施例6	（転写法）	Ag粒子	20%	80%	80			1.00	12	4.0	4.0	6	無
実施例7	（転写法）	銀-硫化銀コアシェル	100%	0%	90			0.80	12	3.9	4.9	6	無
実施例8	（転写法）	Sn粒子	100%	0%	36	20	50	0.90	12	4.0	4.4	6	無
実施例9	（転写法）	Ag粒子	100%	0%	117	60	180	0.80	12	4.0	5.0	6	無
比較例1	（転写法）	—	0%	100%	—			1.50	30	3.5	2.3	20	有

※　添加体積比(%)の計算は、銀の比重を10．5とし、カーボンブラックの比重を1．8とし、その他を1．0として行なった。

【0227】

前記表２に示すように、実施例では、露光後ベークを短時間で行ないながら、高解像度の黒色画像を形成することができ、形成された黒色画像は４．０の高濃度を有し、単位体

積あたりの濃度も高めることができた。また、表示ムラもなく、良好な表示画像が得られた。

これに対し、金属粒子を用いずカーボンブラックのみ構成した比較例１では、黒色画像の濃度が低いばかりか、該濃度を得るのに厚膜となって、露光後ベークに長時間を要し、形成された黒色画像の解像度、表示ムラにも劣っていた。

【0228】

上記の実施例以外に、露光前に加熱（ベーク）を行なうようにした場合も同様であり、露光後現像した後に加熱（ベーク）を行なうようにした場合も同様である。

Ｆターム(参考)
2H025 AA02 AA04 AB11 AB13 AC01 AD01 BE00 BJ00 CB00 CC08
CC17 CC20 EA04 FA12
2H048 BA02 BA11 BA55 BA64 BA66 BB01 BB02 BB42 BB46
4D075 AC02 AC43 AC92 BB20Z BB26Z BB40Y BB42Y BB46Y CA48 CB07
DA04 DA06 DB13 DB31 DB33 DB36 DB37 DB48 DC24 DC40
EA45 EB14 EB19 EB22 EB32 EB35 EB45 EC01 EC07 EC10
EC11 EC24 EC37

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CLAIMS

[Claim(s)]
[Claim 1]
A photosensitive resin composition for light-shielding films containing binder resin, a photo-oxide generating agent which absorbs light and generates acid, a cross linking agent cross-bridged by operation of the aforementioned photo-oxide generating agent, and metal particles and/or metallic-compounds particles.
[Claim 2]
The photosensitive resin composition for light-shielding films according to claim 1 which includes paints further.
[Claim 3]
The photosensitive resin composition for light-shielding films according to claim 2 whose aforementioned paints are carbon black or black lead.
[Claim 4]
A photosensitive resin composition for light-shielding films of a description in any 1 item of Claims 1-3 whose optical density at the time of forming a light-shielding film of 1.0 micrometer of thickness is 4.0 or more.
[Claim 5]
A photosensitive resin composition for light-shielding films of a description in any 1 item of Claims 1-4 used for formation of a light-shielding film which constitutes a display device.
[Claim 6]
A transfer material comprising:
On temporary support, it is binder resin of at least one layer.
A photo-oxide generating agent which absorbs light and generates acid.
A cross linking agent cross-bridged by operation of the aforementioned photo-oxide generating agent.
A photosensitive resin layer containing metal particles and/or metallic-compounds particles.

[Claim 7]
The transfer material according to claim 6 used for formation of a light-shielding film.
[Claim 8]

The transfer material according to claim 6 or 7 used for formation of a light-shielding film which constitutes a display device.
[Claim 9]
A process of making any 1 item of Claims 1-5 applying and drying a photosensitive resin composition for light-shielding films of a description, and forming a photosensitive resin layer on a substrate,
A process of exposing the formed aforementioned photosensitive resin layer to pattern form,
A process of heating the formed aforementioned photosensitive resin layer,
A process of developing the aforementioned photosensitive resin layer after the aforementioned exposure at least, and removing an unexposed part,
****** -- a manufacturing method of a light-shielding film characterized by things.
[Claim 10]
A manufacturing method of the light-shielding film according to claim 9 which performs the aforementioned application using a coater which has a slit shaped nozzle.
[Claim 11]
A process of transferring a photosensitive resin layer of at least one layer on temporary support to a substrate using a transfer material of a description in any 1 item of Claims 6-8,
A process of exposing the transferred aforementioned photosensitive resin layer to pattern form,
A process of heating the transferred aforementioned photosensitive resin layer,
A process of developing the aforementioned photosensitive resin layer after the aforementioned exposure at least, and removing an unexposed part,
****** -- a manufacturing method of a light-shielding film characterized by things.
[Claim 12]
It is a manufacturing method of a transfer material of a description in any 1 item of Claims 6-8,
A manufacturing method of a transfer material painting a photosensitive resin layer on temporary support by application using a coater which has a slit shaped nozzle.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[Field of the Invention]

[0001]
The present invention relates to a manufacturing method of the photosensitive resin composition for light-shielding films preferable for the film formation of a light sheilding, and the light-shielding film using this, a transfer material, and a manufacturing method for the same.
[Background of the Invention]
[0002]
It combines as recent years, for example, a liquid crystal display element, and a solid state image pickup device, and the color filter aiming at obtaining a color picture is capturing the spotlight. This color filter is 2 or more type of pixels (it comprises a color picture layer with which it comes to combine R (red), G (green), B (blue), light-shielding films (black matrix etc.), a transparent area, a transparent pixel, etc.).
[0003]
As a manufacturing method of a color filter, conventionally, The photopolymer solution containing colorant is applied to the object face in which a color filter is installed, The method of performing by exposing that application membrane to pattern form, forming a picture element layer, applying the photopolymer solution containing colorant of other colors subsequently to that picture element layer top, exposing this application membrane to pattern form, and repeating the process of forming a first picture element layer and the picture element layer from which coloring differs is generally used.
[0004]
On the other hand, applied the photopolymer solution containing colorant on the substrate sheet (temporary support) prepared independently, and formed the coloring photosensitive resin layer and it was constituted, Prepare the photosensitive transfer sheet (transfer material) of two or more sheets in which colors differ, put the photosensitive transfer sheet of one sheet on a color filter installation object surface first, and a coloring photosensitive resin layer is transferred, As this is exposed to pattern form, a picture element layer is formed and the picture element layer is subsequently covered, further, A coloring photosensitive resin layer is transferred for the photosensitive transfer sheet of other colors in piles, the method of performing by exposing this to pattern form and repeating the process of forming a first picture element layer and the picture element layer from which coloring differs is proposed, and use of this method is increasing in recent years. When based on this method, the picture element layer which comprised a coloring photosensitive resin layer which has high homogeneity and highly precise thickness uniformity can be formed.
[0005]
By any above-mentioned method, for production of the colored pixel which constitutes a color filter. Using the photo mask clipped by the pattern form for pixel formation, the opening part is passed, a photosensitive resin layer is exposed, the exposed part is stiffened, and the way carry out the development of the unexposed part (non-hard spot), and a developing solution subsequently removes it is used.
[0006]
However, in the case of the conventional transfer material, a photosensitive resin layer is constituted by radical polymerization system including a photopolymerization initiator, a photopolymerization nature monomer, an acrylic polymerization binder, photopolymerization inhibitor, paints, etc.
When the surface which has such a photosensitive resin layer is exposed, conversion changes with attenuation of the light accompanying the depth in the depth direction (thickness direction)

of a photosensitive resin layer, The substrate side of specifically near the interface of a substrate and a photosensitive resin layer, such as glass which is distant from a layer surface, in order for conversion to be deteriorated remarkably and to hardly carry out polymerization curing, when a development was carried out, or side etch went into a thin line image easily and a small-gage wire was not made, there was a problem that a development latitude was narrow.

Although the use of light-shielding films (black matrix etc.) requires high shielding performance especially, attenuation of the light accompanying thickness becomes largely, so that black density becomes high, and generating of side etch and deterioration of a development latitude become more remarkable.

[0007]

The photosensitive resin composition containing a binder, a photo-oxide generating agent, the cross linking agents (melamine system resin etc.) cross-bridged by operation of a photo-oxide generating agent, etc. is proposed to this problem (for example, see Patent Document 1). This generates and carries out polymerization curing of the bridging body from an acid reactivity molecule (cross linking agent) by the catalysis of the acid ($I \rightarrow I^{-} + H^{+}$) generated from a photo-oxide generating agent in response to light (PAG;Photo Acid Generator).

[0008]

In this case, when the black density of a photosensitive resin layer is high. Since the yield of the acid by which it is generated after all at the time of exposure decreases near an interface with the substrate which there were and is distant from a layer surface near a layer surface, [many] Polymerization curing of a photosensitive resin layer can be performed good until it promotes diffusion of acid, and is urged to crosslinking reaction toward a thickness direction from a layer surface and it results near the interface with a substrate by furthermore heat-treating.

[Patent document 1] JP,2002-351075,A

[Description of the Invention]

[Problem to be solved by the invention]

[0009]

However, in PAG using the catalysis of acid, In order to diffuse not only in the thickness direction of a layer but in all the directions (transverse direction to the longitudinal direction which is a thickness direction, etc.), even if the film of higher hardness is obtained at high concentration, it is difficult for the acid (H^{+}) diffused by heat-treatment (heating diffusion) to form a small-gage wire. It is insufficient also in respect of a development latitude. As a result, only the image which faded is acquired. When it is going to constitute on the film of high black density especially, a certain amount of thickness is required for a photosensitive resin layer, if heating after exposure not only taking a long time for obtaining sufficient polymerization curing nature but cooking time becomes long, in a layer, acid will diffuse widely and the degree of a Japanese quince will also get worse.

[0010]

The present invention is made in view of the above, and high black density is obtained with a thin film, and excel in a light sheilding, and. The photosensitive resin composition for light-shielding films which is excellent in the heat cure nature in a short time, and can form the image of high resolution, A transfer material which enables formation of the film whose black density was high at the thin film, and which was excellent in a light sheilding and the heat cure nature in a short time, and a manufacturing method for the same, And let it be problem to attain this purpose with a thin film for the purpose of providing the manufacturing method of the light-

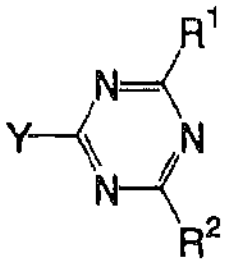
shielding film which black density can form in high resolution the light-shielding film which was highly excellent in shielding performance, and can perform hardening by heating diffusion in shorter time.
[Means for solving problem]
[0011]
When forming a high-concentration black pattern with high resolution using the aforementioned PAG, the present invention acquires the knowledge that metal system particles are effective, for inhibition of the diffusion to the direction of [other than the thickness direction of the acid generated from high-concentration-izing and a photo-oxide generating agent], and is attained based on this knowledge.
The concrete means for attaining the aforementioned problem is as follows.
[0012]
It is a photosensitive resin composition for light-shielding films containing <1> binder resin, the photo-oxide generating agent which absorbs light and generates acid, the cross linking agent cross-bridged by operation of the aforementioned photo-oxide generating agent, and metal particles and/or metallic-compounds particles.
It is a photosensitive resin composition for light-shielding films of the description to the above <1> which includes <2> paints further.
[0013]
The <3> aforementioned paints are the photosensitive resin compositions for light-shielding films of the description to the above <2> which is carbon black or black lead.
The optical density at the time of forming the light-shielding film of 1.0 micrometer of <4> thickness is a photosensitive resin composition for light-shielding films of any one description of aforementioned <1>- <3> which is 4.0 or more.
It is a photosensitive resin composition for light-shielding films of any one description of aforementioned <1>- <4> used for formation of the light-shielding film which constitutes <5> display devices.
[0014]
It is a transfer material having a photosensitive resin layer which contains binder resin of at least one layer, the photo-oxide generating agent which absorbs light and generates acid, the cross linking agent cross-bridged by operation of the aforementioned photo-oxide generating agent, and metal particles and/or metallic-compounds particles on <6> temporary support.
It is a transfer material of the description to the above <6> used for formation of <7> light-shielding films.
It is a transfer material of the description to the above <6> or <7> used for formation of the light-shielding film which constitutes <8> display devices.
[0015]
The process of applying the photosensitive resin composition for light-shielding films of any one description of aforementioned <1>- <5>, and making it drying and forming a photosensitive resin layer on <9> boards, It is a manufacturing method of a light-shielding film including the process of exposing the formed aforementioned photosensitive resin layer to pattern form, the process of heating the formed aforementioned photosensitive resin layer, and the process of developing the aforementioned photosensitive resin layer after the aforementioned exposure at least, and removing an unexposed part.
The <10> aforementioned application is a manufacturing method of the light-shielding film of the description to the above <9> performed using the coater which has a slit shaped nozzle.

[0016]
The process of transferring the photosensitive resin layer of at least one layer on temporary support to a substrate using the transfer material of any one description of <11> aforementioned <6>- <8>, It is a manufacturing method of a light-shielding film including the process of exposing the transferred aforementioned photosensitive resin layer to pattern form, the process of heating the transferred aforementioned photosensitive resin layer, and the process of developing the aforementioned photosensitive resin layer after the aforementioned exposure at least, and removing an unexposed part.
It is a manufacturing method of the transfer material of any one description of <12> aforementioned <6>- <8>, and is a manufacturing method of the transfer material painting a photosensitive resin layer by application using the coater which has a slit shaped nozzle on temporary support.
[Effect of the Invention]
[0017]
According to the present invention, high black density is obtained with a thin film, and excel in a light sheilding, and. The photosensitive resin composition for light-shielding films which is excellent in the heat cure nature in a short time, and can form the image of high resolution, A transfer material which enables formation of the film whose black density was high at the thin film, and which was excellent in a light sheilding and the heat cure nature in a short time, and a manufacturing method for the same, And black density can form in high resolution the light-shielding film which was highly excellent in shielding performance with a thin film, and the manufacturing method of the light-shielding film which can perform hardening by heating diffusion in shorter time can be provided.
[Best Mode of Carrying Out the Invention]
[0018]
Hereafter, it describes in detail about a manufacturing method of the photosensitive resin composition for light-shielding films of the present invention, and a light-shielding film, a transfer material, and a manufacturing method for the same.
[0019]
<The photosensitive resin composition for light-shielding films>
The photosensitive resin composition for light-shielding films of the present invention can be constituted using the component of others, such as colorant and a surfactant, if needed, including binder resin, a photo-oxide generating agent, a cross linking agent, and metal particles and/or metallic-compounds particles at least.
[0020]
In the photosensitive resin composition for light-shielding films of the present invention, Make crosslinking reaction cause between the below-mentioned binder resin and a cross linking agent (for example, methylol-ized melamine resin of acid cross-linking) by the catalysis of the acid (H^+) generated from a photo-oxide generating agent in response to light, and. By furthermore adding heat-treatment, by promoting diffusion of acid, it is urged to crosslinking reaction toward the layer depth part near a substrate interface from the surface of a layer, and the photosensitive resin layer from the surface to the layer depth part of a thickness direction carries out polymerization curing sufficiently (PAG). Therefore, even if black density is high concentration, crosslinking reaction can be sufficiently carried out to a substrate interface, and the tolerance of development is wide, and by one side, mixing of a component, application, and the crosslinking reaction in a drying stage are suppressed, and can take sufficient largely the soluble contrast over

the developing solution of an exposure part and an unexposed part. Therefore, high-concentration and high definition light-shielding films (black matrix etc.) can be obtained with a thin film.
The photosensitive resin composition for light-shielding films of the present invention, Since high concentration is obtained with a thin film, including metal particles and metallic-compounds particles as a black agent so that it may mention later, when based on the aforementioned PAG, since diffusion of acid takes place in a film, it can perform hardening by heating diffusion in a short time, and ****** of a pattern does not produce it easily, either. Therefore, it has high concentration with a thin film, and the light-shielding films (black matrix etc.) of high resolution are obtained.
[0021]
- Binder resin -
The photosensitive resin composition for light-shielding films of the present invention contains at least 1 type of binder resin. This binder resin builds and stiffens a below-mentioned cross linking agent and bridging body (polymer) by pattern exposure by the catalysis of the acid generated from the below-mentioned photo-oxide generating agent.
[0022]
As binder resin, it can choose suitably from publicly known binder resin, such as acrylic (meta) resin, polyester resin, vinyl system resin, novolak resin (phenol novolak resin, cresol novolak resin, etc.), and polyhydroxy styrene, for example.
[0023]
The vinyl system copolymer especially obtained by copolymerization of an acrylic (meta) monomer in the present invention is preferable, and methacrylic acid alkyl ester, acrylic acid alkyl ester, or the copolymer that contains a carboxyl group containing monomer as a constitutional unit is more preferable. acrylic (meta-) is preferable at the point which gives adaptability -- weak alkali development -- it is preferable to contain a carboxyl group in respect of proper grant.
An acrylic (meta) shows that an acrylic or methacrylic both can be taken. It is the same as that of the following.
[0024]
Also in the above, the copolymer containing especially at least one of methyl methacrylate and the benzyl methacrylate is preferable. The copolymer containing the copolymer containing methyl methacrylate, the copolymer containing benzyl methacrylate, methyl methacrylate, and benzyl methacrylate are mentioned to the copolymer containing at least one of methyl methacrylate and the benzyl methacrylate.
[0025]
In the copolymer containing the aforementioned methyl methacrylate, methacrylic acid / methyl methacrylate copolymer (copolymerization ratio: -- 14-17.6mol %/-- 82.4-86 mol %) The weight average molecular weight 20,000-140,000, methacrylic acid / methyl methacrylate / ethyl acrylate copolymer (copolymerization ratio: 5-10 mol % / 70-60 mol % / 25-30 mol %, weight average molecular weight 20,000-140,000), etc. are mentioned.
[0026]
In the copolymer containing the aforementioned benzyl methacrylate, methacrylic acid / benzyl methacrylate copolymer (copolymerization ratio: -- 25-37mol %/-- 75-63 mol %) The weight average molecular weight 20,000-150,000, methacrylic acid / benzyl methacrylate / styrene copolymer (copolymerization ratio: 20 mol %/17.8 mol % [62.2 mol %] /, weight average

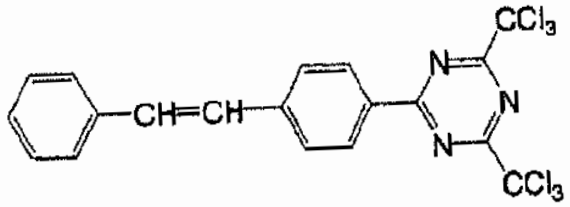
molecular weight 20,000-140,000), etc. are mentioned.
[0027]
In the copolymer containing the aforementioned methyl methacrylate and benzyl methacrylate, methacrylic acid / methyl methacrylate / benzyl methacrylate copolymer (copolymerization ratio: -- 14.6-27.2mol %/79.1-32.7mol %/-- 16.3-40 mol %) the weight average molecular weight 20,000-150,000, and methacrylic acid / methyl methacrylate / benzyl methacrylate / 2-ethylhexyl acrylate copolymer (copolymerization ratio: -- 10-15 mol % / 70-65 mol %/-- 10 mol %/10 mol %) The weight average molecular weight 20,000-150,000 etc. are mentioned.
[0028]
Although the cresol novolak resin more often [a commercial negative resist composition] than before used, polyhydroxy styrene, and its derivative will be colored after exposure and bake, There is little coloring in the time of baking treatment after such exposure, and especially methacrylic acid / benzyl methacrylate copolymer, methacrylic acid / methyl methacrylate / benzyl methacrylate copolymer, etc. above-mentioned in that light transmittance is not deteriorated is preferable.
[0029]
As content in the photosensitive resin composition for light-shielding films of the aforementioned binder resin, the 10 - 90 mass % is preferable to the total solids of this constituent, and the 20 - 70 mass % is more preferable.
[0030]
- Photo-oxide generating agent -
The photosensitive resin composition for light-shielding films of the present invention contains at least 1 type of a photo-oxide generating agent. When this photo-oxide generating agent is exposed to pattern form, it generates acid (H^+), and it promotes the polymerization curing by crosslinking reaction.
[0031]
An organic halogenated compound, onium salt, sulfonic ester, etc. are mentioned to the photo-oxide generating agent which generates acid by the exposure of light. In these, an organic halogenated compound is preferable and a halomethyl-ized triazine compound and a halomethyl-ized oxadiazole compound are especially preferable.
[0032]
As the aforementioned halomethyl-ized triazine compound, the compound denoted by a following general formula (1) is mentioned. However, in the present invention, it is not limited to these.
[0033]
[Chemical formula 1]

(1)

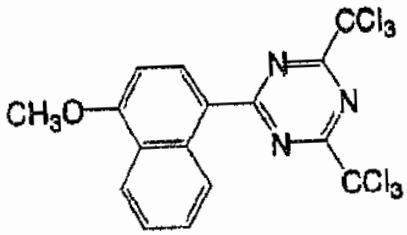


[0034]
R^1 and R^2 express a halomethyl group independently respectively among the aforementioned general formula (1), and Y expresses a with a carbon numbers of five or more organic group.
[0035]
As the aforementioned halomethyl group, they are mentioned by a trichloromethyl group, a tribromomethyl group, a dichloromethyl group, dibromomethyl group, etc., and, for example as a with an aforementioned carbon numbers of five or more organic group, For example, the phenyl group, the naphthyl group, the styryl group, styryl phenyl group and furil vinyl group which may have a substituent, the fourth class-ized aminoethyl amino group, etc. are mentioned.
[0036]
Hereafter, the examples [illustration compound (2) - (23)] of a halomethyl-ized triazine compound are enumerated.
[0037]
[Chemical formula 2]

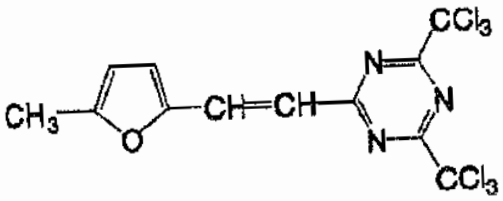
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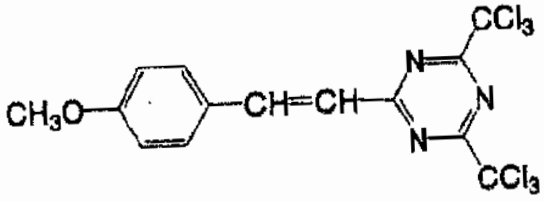
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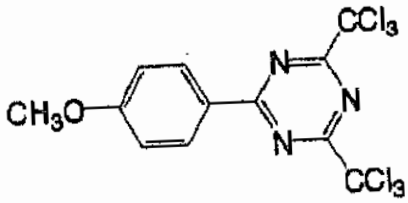
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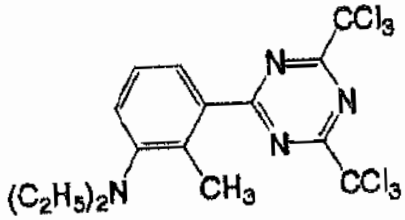
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(6)

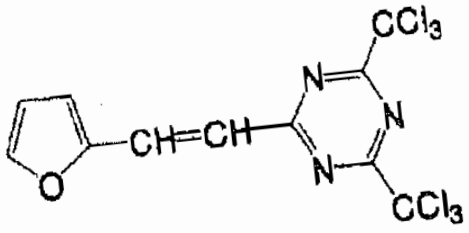


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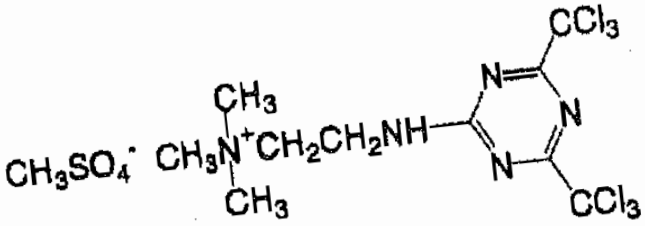


[0038]
[Chemical formula 3]

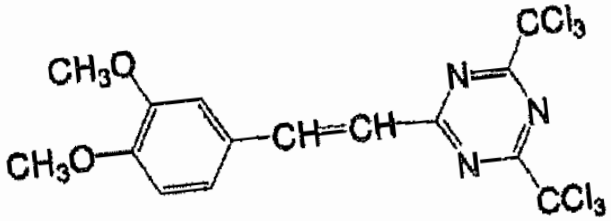
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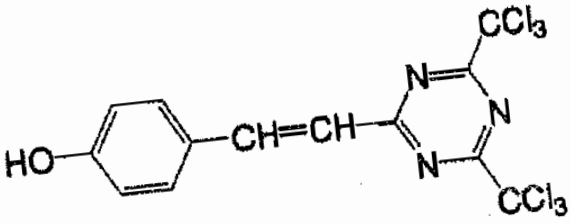
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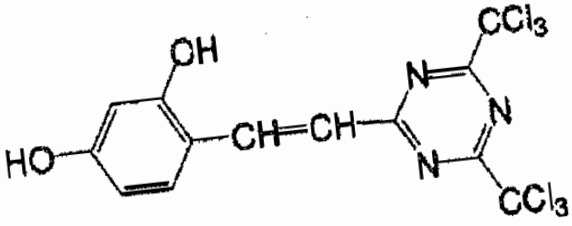
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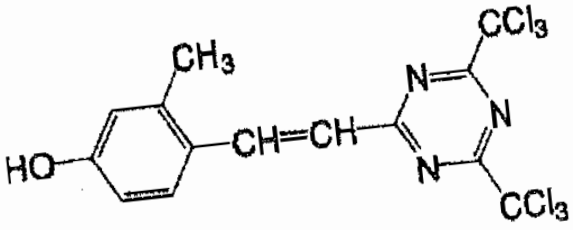
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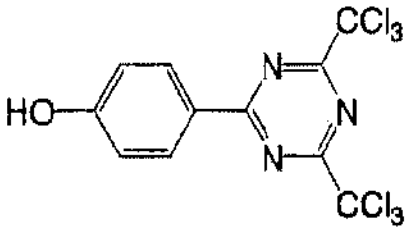


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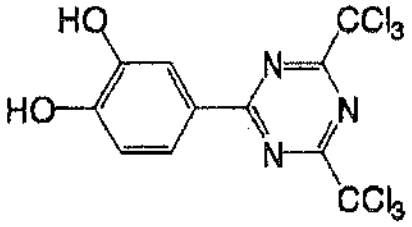


[0039]
[Chemical formula 4]

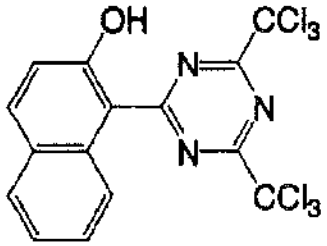
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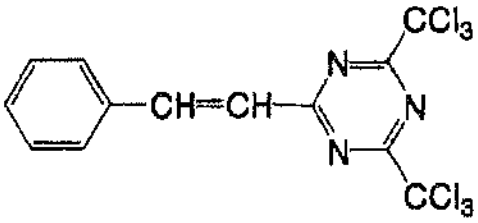
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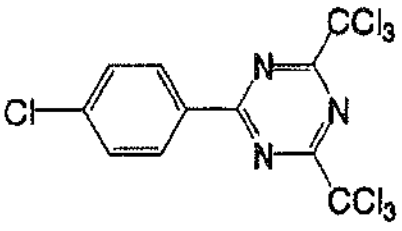
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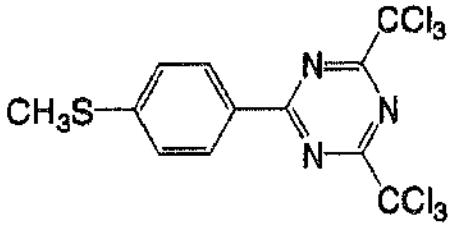
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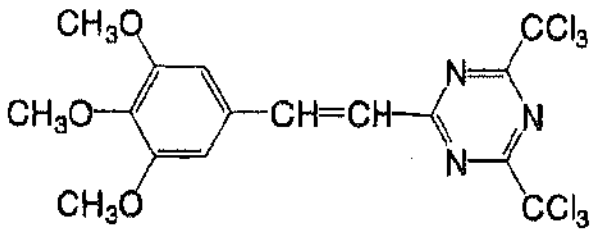


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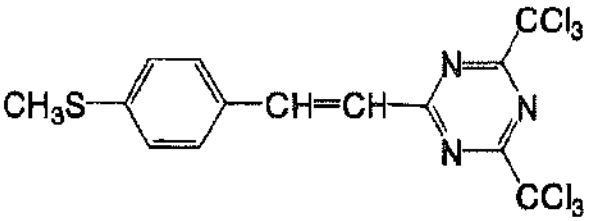


[0040]
[Chemical formula 5]

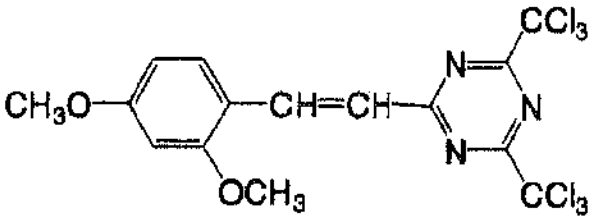
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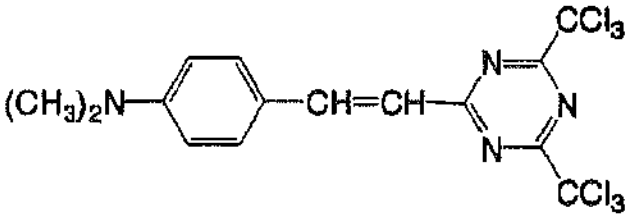
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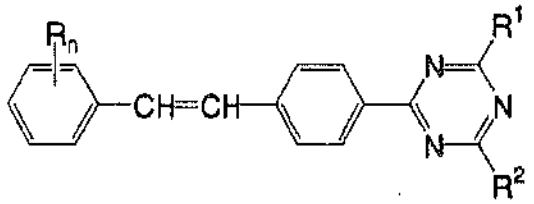


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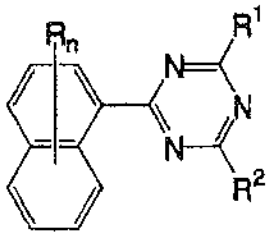
[0041]
A thing preferable also in the halomethyl-ized triazine compound denoted by the aforementioned general formula (1) is a compound denoted by (24), (25), or the following general formula (26).
[0042]
[Chemical formula 6]

(24)



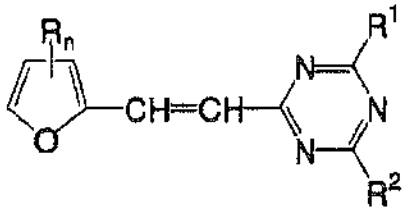
[0043]
R^1 in the aforementioned general formula (24) and R^2 express a halomethyl group independently respectively, and R expresses the alkyl group of the carbon numbers 1-4, or the alkoxy group of the carbon numbers 1-4. n expresses the number of R and is an integer of 0-3.
[0044]
[Chemical formula 7]

(25)



[0045]
R^1 in the aforementioned general formula (25) and R^2 express a halomethyl group independently respectively, and R expresses the alkyl group of the carbon numbers 1-4, or the alkoxy group of the carbon numbers 1-4. n expresses the number of R and is an integer of 0-3.
[0046]
[Chemical formula 8]

(26)



[0047]
R^1 in the aforementioned general formula (26) and R^2 express a halomethyl group independently respectively, and R expresses the alkyl group of the carbon numbers 1-4. n expresses the number of R and is an integer of 0-1.
[0048]

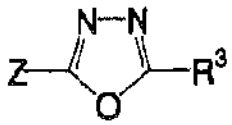
In each general formula a thing preferable also in the compound denoted by the above-mentioned general formula (24) (26) -, It is a compound which R^1 and R^2 are trichloromethyl groups, and R is an alkyl group of the carbon numbers 1-2, and also is [n are is an integer of 0-2 in the general formula (24) and (25)] an integer of 0-1 in a general formula (26).

[0049]

As the aforementioned halomethyl-ized oxadiazole compound, the compound denoted by a following general formula (27) is mentioned.

[0050]

[Chemical formula 9]

(27) 

[0051]

R^3 expresses a halomethyl group among the aforementioned general formula (27), and Z expresses the benzo furil group or benzo furil vinyl group which may have a substituent.

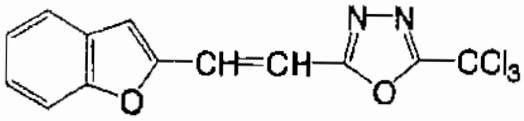
[0052]

Hereafter, the examples [illustration compound (28) - (45)] of a halomethyl-ized oxadiazole compound are enumerated.

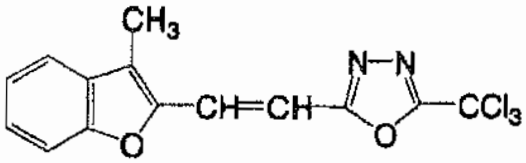
[0053]

[Chemical formula 10]

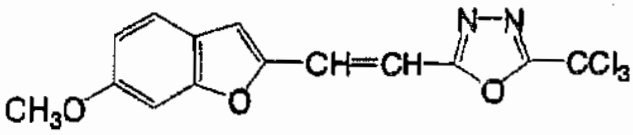
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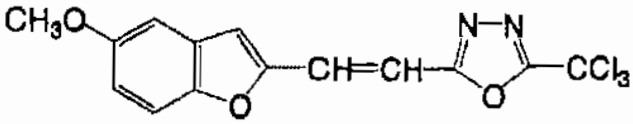
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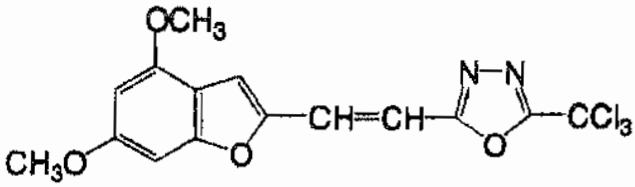
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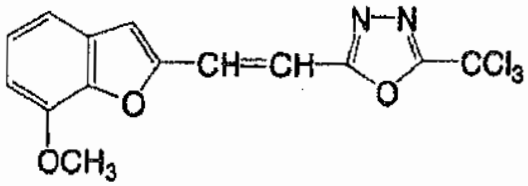
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(32)

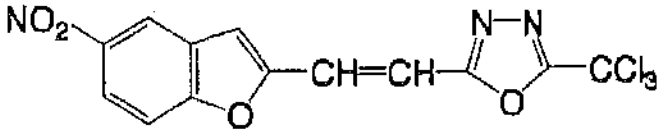


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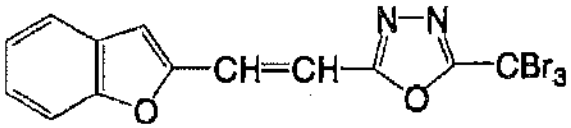


[0054]
[Chemical formula 11]

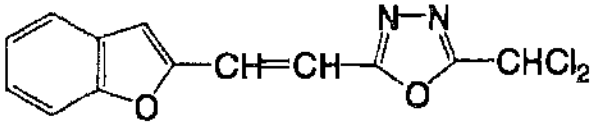
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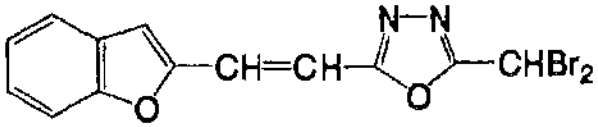
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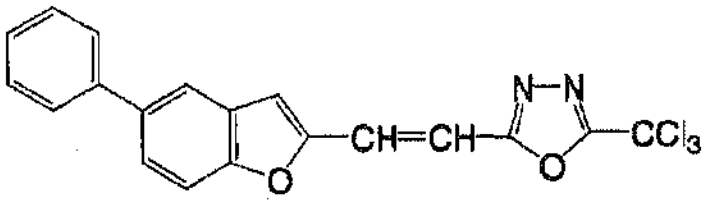
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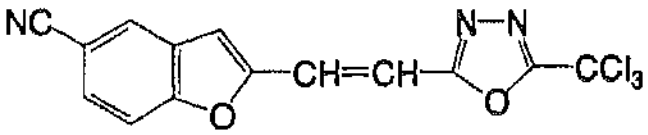
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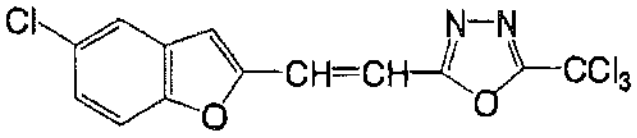


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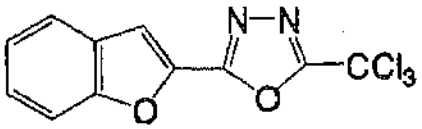


[0055]
[Chemical formula 12]

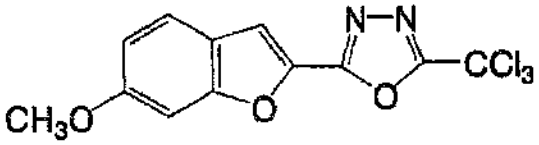
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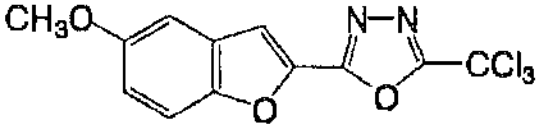
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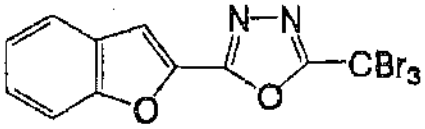
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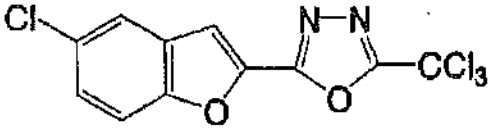
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(44)

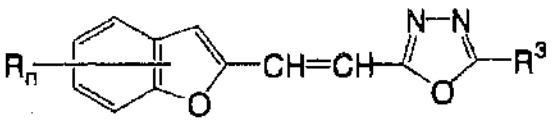


(45)



[0056]
A preferable halomethyl-ized oxadiazole compound denoted by the aforementioned general formula (27) is a compound denoted by a following general formula (46).
[0057]
[Chemical formula 13]

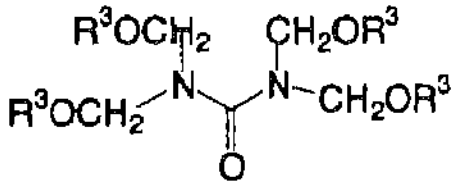
(46)



[0058]
R^3 in the aforementioned general formula (46) expresses a halomethyl group, and R expresses the alkyl group of the carbon numbers 1-4, or the alkoxy group of the carbon numbers 1-4. n expresses the number of R and is an integer of 0-2. The compound whose R^3 is a trichloromethyl group, whose R is the alkyl group or alkoxy group of the carbon numbers 1-2 and whose n is an integer of 0-1 is preferable.
[0059]
receiving the solid content of this constituent as content in the photosensitive resin composition for light-shielding films of a photo-oxide generating agent -- the 0.05 to 15 mass % -- it is the five to 15 mass % preferably. Sufficient acid is generated by exposure as the quantity of a photo-oxide generating agent is the aforementioned range, crosslinking reaction of binder resin and the below-mentioned cross linking agent can be performed good, the remaining rate of membrane after development is high, and the image provided with heat resistance, chemical resistance, etc. can be formed.
[0060]
- Cross linking agent -
The photosensitive resin composition for light-shielding films of the present invention contains at least 1 type of a cross linking agent. This cross linking agent has the operation which causes crosslinking reaction by the catalysis of the acid generated from the aforementioned photo-oxide generating agent at the time of exposure, and is hardened. That is, crosslinking reaction can be carried out between binder resin as stated above, a bridging body can be formed, and an exposure part can be hardened and imaged.
[0061]
The compound which has a substituent (a "cross-linking substituent" is called hereafter.) containing at least 1 type of cross-linking groups as a cross linking agent is mentioned.
[0062]
The following (i) - (vi) are mentioned as an example of the aforementioned cross-linking substituent.
(i) A hydroxyalkyl group or its derivatives, such as a hydroxyalkyl group, an alkoxyalkyl group, and an acetoxy alkyl group;
(ii) A carbonyl group or its derivatives, such as a formyl group and a carboxy alkyl group;

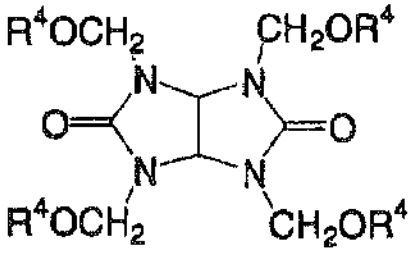
(iii) Nitrogen-containing basis content substituents, such as a dimethyl aminomethyl group, a diethyl aminomethyl group, a dimethylol aminomethyl group, a JIECHI roll aminomethyl group, and a morpholino methyl group;
(iv) Glycidyl group content substituents, such as a glycidyl ether group, a glycidyl ester group, and a glycidyl amino group;
(v) Aromatic derivatives, such as allyloxy alkyl groups, aralkyloxy alkyl groups, etc., such as a benzyloxymethyl group and a benzo yloxy methyl group;
(vi) Polymerizable multiple bond content substituents, such as a vinyl group and an isopropenyl group;
** can be mentioned.
Among the above, as a cross-linking substituent of the cross linking agent in the present invention, a hydroxyalkyl group, an alkoxyalkyl group, etc. are preferable and especially an alkoxy methyl group is preferable.
[0063]
as the cross linking agent which has the aforementioned cross-linking substituent -- for example
(i) Methylol group content compounds, such as a methylol group content melamine compound, a methylol group content benzoguanamine compound, a methylol group content urea compound, a methylol group content glycoluryl compound, and a methylol group content phenolic compound;
(ii) An alkoxyalkyl group content melamine compound, an alkoxyalkyl group content benzoguanamine compound, Alkoxyalkyl group content compounds, such as an alkoxyalkyl group content urea compound, an alkoxyalkyl group content glycoluryl compound, and an alkoxyalkyl group content phenolic compound;
(iii) Carboxymethyl group content compounds, such as a carboxymethyl group content melamine compound, a carboxymethyl group content benzoguanamine compound, a carboxymethyl group content urea compound, a carboxymethyl group content glycoluryl compound, and a carboxymethyl group content phenolic compound;
(iv) a bisphenol A system epoxy compound and bisphenol F system -- an epoxy compound -- a bisphenol S system -- epoxy compound [, such as an epoxy compound, a novolak resin system epoxy compound, a resole resin system epoxy compound, and a poly (hydroxystyrene) system epoxy compound,]; etc. can be mentioned.
[0064]
Also in the above-mentioned cross linking agent, an alkoxy methylation urea compound or its resin, an alkoxy methylation glycoluryl compound, or its resin is preferable.
As a preferable cross linking agent, the alkoxy methylation urea compound denoted by a following general formula (47) or the alkoxy methylation glycoluryl compound denoted by a following general formula (48) can be mentioned especially.
[0065]
[Chemical formula 14]

(47)



[0066]
R^3 in the aforementioned general formula (47) expresses the alkyl group of the carbon numbers 1-4.
[0067]
[Chemical formula 15]

(48)



[0068]
R^4 in the aforementioned general formula (47) expresses the alkyl group of the carbon numbers 1-4.
[0069]
In the aforementioned general formula (47) and (48), a methyl group, an ethyl group, a propyl group, a butyl group, etc. can be mentioned as an alkyl group denoted by R^3 or R^4.
[0070]
The above-mentioned alkoxy methylation urea compound and an alkoxy methylation glycoluryl compound, For example, after carrying out the condensation reaction of a urea compound, a glycoluryl compound, and the formalin and introducing a methylol group, It etherifies with lower alcohol, such as methyl alcohol, ethyl alcohol, propyl alcohol, and butyl alcohol, and is obtained by collecting the compound which subsequently cools reaction mixture and deposits, or its resin. It can also obtain as commercial items, such as CYMEL (trade name; made by Mitsui Cyanamid), and NIKARADDO (made in Sanwa Chemical).
[0071]
As a cross linking agent, the compounds on which formaldehyde was made to act or those alkyl modified compounds, an epoxy compound, a resol compound, etc. are effective in melamine, benzoguanamine, glycoluryl, or urea, and the following are mentioned as the example.
[0072]
As a specific example, Mitsui Cyanamid Cymel. (Registered trademark) 300 -- said -- 301 -- said -- 303 -- said -- 350 -- said -- 736 -- said -- 738 -- said -- 370 -- said -- 771 -- said -- 325 -- said -- 327 -- said -- 703 -- said -- 701 -- said -- 266 -- said -- 267 -- said -- 285 -- said -- 232 -- said -- 235 -- said -- 238 -- said -- 1141 -- said -- 272 -- said -- 254 -- said -- 202. said -- 1156 -- said -- 1158 is an example of the compound which made formaldehyde act on melamine, or its alkyl modified thing. Cymel (registered trademark) 1123 -- said -- 1125 -- said -- 1128 is an example of the compound on which formaldehyde was made to act at benzoguanamine, or its alkyl modified thing. Cymel (registered trademark) 1170 -- said -- 1171 -- said -- 1174 -- said -- 1172 is an example of the compound which made formaldehyde act on glycoluryl, or its alkyl

modified thing. furthermore -- as the example of the compound which made formaldehyde act on urea, or its alkyl modified thing -- Mitsui Cyanamid65 [UFR(registered trademark)] -- said -- 300 can be mentioned.
[0073]
moreover -- as the example of the aforementioned epoxy compound -- novolak epoxy resin, such as 704, VDPN-638 by Tohto Kasei Co., Ltd. -- said -- 701 -- said -- 702 -- said -- 703 -- said -- -- Amine epoxy resins (YH-434 by Tohto Kasei Co., Ltd., etc.), a bisphenol A epoxy resin, Sorbitol (poly) glycidyl ether, glycerol (poly) (poly) glycidyl ether, Pentaerythritol (poly) glycidyl ether, triglycidyl tris hydroxyethyl isocyanurate, Allyl glycidyl ether, ethylhexyl glycidyl ether, phenyl glycidyl ether, Phenol glycidyl ether, lauryl alcohol glycidyl ether, Adipic acid glycidyl ether, phthalic acid glycidyl ether, dibromo phenyl glycidyl ether, Dibromoneopentylglycol diglycidyl ether, a glycidyl phthalimide, (Poly) Ethylene glycol glycidyl ether, polypropylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, glycerin poly glycidyl ether, trimethylolpropane polyglycidyl ether, butyl glycidyl ether, ** can be mentioned.
[0074]
As a preferable compound, the compound (R expresses a hydrogen atom or an alkyl group.) which has a $-N(CH_2OR)_2$ group is especially mentioned into a molecule. In detail, the compound which made formaldehyde act on urea or melamine, or especially its alkyl modified thing is preferable.
[0075]
As an example of the aforementioned resol compound, PP-3000s by Gunei Chemical Industry Co., Ltd., PP-3000A, RP-2978, SP-1974, SP-1975, SP-1976, SP-1977, RP-3973, etc. are mentioned.
[0076]
As content in the photosensitive resin composition for light-shielding films of a cross linking agent, the 5 - 70 mass % is preferable to the quantity of the aforementioned binder resin, and the 10 - 40 mass % is more preferable.
[0077]
- Metal particles and/or metallic-compounds particles -
The photosensitive resin composition for light-shielding films of the present invention contains at least 1 type (henceforth "the metal particles concerning the present invention") chosen from the group which consists of metal particles and metallic-compounds particles. Since the metal particles concerning the present invention are selectively used as a black material for protection from light, Since high black density is obtained, and an advanced light sheilding is acquired with a thin form and it is constituted by the thin form, ****** of the pattern accompanying diffusion of acid at the time of heating in the case of being based on PAG can be prevented, and shortening of the cure time by heating diffusion can also be aimed at.
The below-mentioned composite particle and a core shell composite particle are contained in the metal particles concerning the present invention.
[0078]
<Metal particles>
as metal particles -- the long period periodic table (IUPAC 1991) -- for example, It is preferable that carry out the main component of the metal chosen from the group which consists of the 3rd cycle of the periodic table of the elements, the 4th cycle, the 5th cycle, and the 6th cycle, and it is included, It is preferable that carry out the main component of the metal chosen from the group which consists of the 2nd fellows, the 8th fellows, the 9th fellows, the 10th fellows, the 11th

fellows, the 12th fellows, the 13th fellows, and the 14th fellows, and it is included. As metal particles which start the present invention among these metal, it is metal of the 4th cycle, the 5th cycle, or the 6th cycle, and the metal of the 2nd fellows, the 10th fellows, the 11th fellows, the 12th fellows, or the 14th fellows is still more preferable.
[0079]
The others whose metal particles in the present invention have a globular shape, the shape of a right side face body containing a cube, etc., Length, width, the form of the shape anisotropy from which at least one of the ratios of height differs. They may be any, such as (for example, the globular shape which has shape anisotropy, the shape of a bean-jam bun, the shape of a potato, plate-like [rod-like] (square pillar forms, such as a needle, a cylindrical shape, and a rectangular parallelepiped, a Rugby ball type, etc.) (the shape of a scale, the shape of an elliptic plate, tabular), fibrous, the shape of konpeito, a coiled form, etc.).
The same may be said of the case of the metallic-compounds particles mentioned later, a composite particle, and a core shell composite particle.
[0080]
A preferable example as the aforementioned metal particles Copper, silver, gold, platinum, palladium, Nickel, tin, cobalt, rhodium, iridium, iron, a ruthenium, calcium, osmium, manganese, molybdenum, tungsten, niobium, Tan Tell, titanium, bismuth, antimony, lead or these alloys, and at least 1 type of ********** can be mentioned. Still more preferable metal is at least 1 type as which copper, silver, gold, platinum, palladium, nickel, tin, cobalt, rhodium, iridium or these alloys, and more preferable metal are chosen from copper, silver, gold, platinum, tin, or these alloys. Gold, silver, copper, and tin are preferable and silver is [among these] especially preferable. As silver, silver and colloidal silver which carried out rod form are also preferable. It is also possible to combine 2 or more type of aforementioned metal, and to use it for manufacture of metal particles as an alloy.

It can also use as complex particulates of metallic compounds and metal.
[0081]
<Metallic-compounds particles>
Metallic-compounds particles are particles of a compound with other elements other than the aforementioned metal and metal, and there are a metaled oxide, a sulfide, sulfate, carbonate, etc. as "a compound of metal and other elements." Among these, a sulfide is preferable especially from the ease of carrying out of a color tone or microparticle formation. As an example of these metallic compounds, although copper(II) oxide, an iron sulfide, a silver sulfide, copper sulfide (II), titanium black, etc. are mentioned, especially a silver sulfide is preferable in view of the ease of carrying out and stability of a color tone and microparticle formation.
[0082]
<Composite particle>
In the present invention, the composite particle which these joined together and turned into one particle can also be used using the aforementioned metal particles and the aforementioned metallic-compounds particles. There is no restriction in particular in the form of a composite particle. For example, that from which composition differs on the inside and the surface of particles, the thing with which two kinds of particles were united, etc. can be mentioned. Metallic compounds and at least 1 type of metal may be 2 or more type, respectively. As an example of the composite particle of metallic compounds and metal, there are a composite particle of silver and a silver sulfide, a composite particle of silver and copper(II) oxide, etc.

[0083]
<Core shell composite particle>
In the present invention, a core shell type composite particle (core shell composite particle) can also be used. The coat of the surface of core materials is carried out to a core shell type composite particle with shell material.
[0084]
As a shell material which carries out the coat of the aforementioned core materials, For example, Si, germanium, AlSb, InP, Ga, As, GaP, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, PbS, PbSe, PbTe, Se, Te, CuCl, CuBr, CuJ, TlCl, TlBr, TlI(s) and these solid solutions, or these -- more than 90mol% -- at least 1 type of semiconductors chosen from the included solid solution -- Or copper, silver, gold, platinum, palladium, nickel, tin, cobalt, At least 1 type of metal chosen from rhodium, iridium, iron, a ruthenium, osmium, manganese, molybdenum, tungsten, niobium, Tan Tell, titanium, bismuth, antimony, lead, or these alloys can be used.
[0085]
As a preferable shell material, at least 1 type chosen from copper, silver, gold, palladium, nickel, tin, bismuth, AMMOCHIN, lead, or these alloys can be mentioned.
The aforementioned shell material is preferably used also as a regulator of a refractive index the making reflectance be deteriorated purpose.
[0086]
As core materials which constitute a core shell composite particle, at least 1 type of metal chosen from copper, silver, gold, palladium, or these alloys can be used, for example.
[0087]
There is no restriction in particular in the manufacturing method of the core shell composite particle which has core shell structure, and the following methods are mentioned to it as a typical method.
(1) Are the method of forming the shell of metallic compounds, for example, dispersion media, such as water, are made to distribute metal particles on the surface of the metal particles produced by the publicly known method by oxidation, sulfuration, etc., and the method of adding sulfides, such as a sodium sulfide and ammonium sulfide, is shown in it. Are sulfuration [the surface of particles] with this method and a core shell composite particle is formed.
In this case, the metal particles to be used are producible by publicly known methods, such as a gaseous phase method and a liquid phase process. About the manufacturing method of metal particles, it describes, for example in "the newest trend II in the technology of an ultrafine particle, and application" (** BETEKUNORISACHI, Inc., 2002 issue).
(2) The circumference of the metal particles which are the methods of forming the shell of metallic compounds in the surface continuously in the process in which metal particles are produced, for example, added the reducing agent to the metal salt solution, returned some metal ion, produced metal particles, and subsequently added and produced the sulfide has the method of forming metallic sulfide.
[0088]
-Production of metal particles-
Metal particles can use a commercial thing, and also can be prepared with the chemical reduction method of metal ion, an electroless deposition method, a metaled evaporation method, etc.
In the case of the particles constituted by the form of shape anisotropy, especially in the case of a cylindrical silver granule child (silver rod), By making a globular form silver granule child into a seed particle child, after that, a silver salt is added further and a silver rod and a wire are obtained

under surfactant existence, such as CTAB (Sept lles trimethylammonium star's picture), by using reducing agents with comparatively weak reducing power, such as ascorbic acid. This has a description in Adv.Mater.2002, 14, and 80-82. The same description is made by Mater.Chem.Phys.2004, 84,197-204, Adv.Funct.Mater.2004, and 14,183-189. J.Mater.Res.2004 and 19,469-473 have the method of a description as a method using electrolysis as the method of the description to Mater.Lett.2001,49,91-95, and a method of generating a silver rod by irradiating with microwave. As an example which reversed micelle and an ultrasonic wave used together, J.Phys.Chem.B-2003, 107, and 3679-3683 are mentioned.
It deseribes in J.Phys.Chem.B 1999, 103, 3073-3077 and Langmuir1999, 15, 701-709, J.Am.Chem.Soc.2002, 124, and 14316-14317 similarly about gold.
Even if the formation method of rod-like particles improves the above-mentioned method (addition amount adjustment, PH control), it can be prepared.
[0089]
-Particle diameter-
When the metal particles (a composite particle and a core shell composite particle are included.) concerning the present invention are a real ball or a globular form, as the particle diameter, 2-600 nm is preferable and 10-300 nm is more preferable.
[0090]
When you are the particles of shape anisotropy, let the particle diameter be a diameter of the three dimensions. That is, it is a method which one metal particles consider the box (rectangular parallelepiped) settled exactly (just), and define as the dimension of these metal particles with length L [of this box], width b, height, or thickness t. When storing metal particles in a box, there are some methods, but the following methods are adopted in the present invention.
First, on a plane, metal particles are placed so that it may be stood still stably [the center of gravity is the lowest and]. Next, metal particles are inserted with the parallel plate of two sheets stood right-angled to the plane, and the plate interval makes the plate interval of the position which becomes the shortest "the width b." Next, to the plate of two sheets which settles the aforementioned width b, are right-angled, and metal particles are inserted with the parallel plate of two right-angled sheets also to the aforementioned plane, and let this plate interval of two sheets be "length L." A top plate is carried in parallel with the aforementioned plane so that the highest position of metal particles may finally be contacted, and the interval of a top plate and a plane is set to height or thickness t (the rectangular parallelepiped to draw is formed by the plane, the plate of two sheets each, and a top plate of this gentleman method.). The axis applicable to the longest thing of the diameter of the three dimensions b, L, and t of metal particles is defined as a "major axis", and the diameter at the time of carrying out perfect circle conversion of the project area produced in the length in a major axis direction by irradiating metal particles with a light parallel to a major axis with "long axis length" again is defined as "minor-axis length."
[0091]
-Aspect ratio-
The aspect ratio of the metal particles (a composite particle and a core shell composite particle are included.) concerning the present invention means the value which broke the long axis length whom metal particles or metallic-compounds particles defined as mentioned above by minor-axis length, and it is defined as the average value of the value measured about 100 metal particles. The project area of particles measures the area on an electron microscope photograph, and is obtained by correcting photographing magnification.
[0092]

As for the aspect ratio (ratio of the minor-axis length of the long axis length/particles of particles) of particles, it is preferable that it is two or more, and it is more preferable that it is four or more. The maximum of an aspect ratio is about 100. It is effective for high-resolution-izing, without black particles' being easy to be obtained, and being too large and absorption of a light region becoming small in this range. Still more preferably, it is 4-80 and is 10-60 most preferably. As for the minor-axis length of particles, 4-50 nm is preferable, it is more preferable, and is the most preferable. [of 15-30 nm] [of 15-50 nm] As for the long axis length (maximum length) of particles, 10-1000 nm is preferable, his 100-1000 nm is more preferable, his 400-800 nm is still more preferable, and it is most preferable that it is shorter than a visible light wavelength.

[0093]

By mixing the particles from which particle diameter and form differ, absorption-spectrum control can be carried out and hue can also be brought close colorless.

[0094]

-Particle size distribution-

As for particle size distribution, it is preferable that the particle-size-distribution width D90/D10 of long axis length's mean particle diameter is less than [2 or more] 20. D90 is a maximum diameter by which 90% of particles are found out here, and D10 is a maximum diameter by which 10% of particles are found out. Particle size distribution is 15 or less [2 or more] more preferably in view of a color tone, and is ten or less [4 or more] still more preferably. Muddiness by dispersion according that particle size distribution is the aforementioned range to a coarse particle can be prevented from arising.

[0095]

Although it changes with the kinds and descriptions of particles to be used as content in the photosensitive resin composition for light-shielding films of "metal particles and/or metallic-compounds particles", the 2 - 40 volume % is preferable, and the 5 - 30 volume % is more preferable.

[0096]

- Colorant -

With the aforementioned metal particles and/or metallic-compounds particles, the photosensitive resin composition for light-shielding films of the present invention can use paints and/or a color together further, and can constitute them preferably.

[0097]

As the aforementioned paints, for example Barium sulfate, lead sulfate, titanium oxide, yellow lead, Inorganic pigments, such as red ocher, chrome oxide, and carbon black, anthraquinone system paints, Organic colors, such as perylene system paints, a disazo pigment, a phthalocyanine pigment, isoindoline paints, dioxazine paints, a quinacridone pigment, peri non system paints, triphenylmethane series paints, and thioindigo paints, etc. are mentioned. A 1 type independent or 2 type or more can be mixed and used for these.

Also in the aforementioned paints, anthraquinone system paints, a phthalocyanine pigment, dioxazine paints, and especially carbon black are preferable.

[0098]

Hereafter, a Color Index (C. I.) number shows specifically.

C. I. red : 9,97,122, 123,149,168, 177,180,192, 215,216,217, 220,223,224, 226,227,228,240;

C. I. blue : 15, 15:6, 22, 60, 64;

C. I. green : 7, 36;

C. I. black : seven;
C. I. yellow : 12,20,24, 86,93,109, 110,117,125, 137,138,147, 148, 153,154,166,168;
C. I. orange : 36, 43, 51, 55, 59, 61;
C. I. violet : 19, 23, 29, 30, 37, 40, 50;
C. I. tea : 23, 25, 26;
[0099]
As for the mean particle diameter of paints, it is preferable that it is in the range of 0.005-3 micrometers. It is 0.01-1 micrometer more preferably. In order to use the particle diameter of this range, distributed processing, such as a ball mill, a sand mill, a bead mill, 3 rolls, a paint shaker, and an ultrasonic wave, is effective.
[0100]
As the aforementioned color, Crystal Violet, Methyl Violet, ethyl violet, and oil blue #603, Victoria pure blue BOH, malachite green, DAIMONDO green, etc. are mentioned, for example. In addition to the above, black lead can also be used preferably.
[0101]
According to a use etc., the aforementioned paints and a color may be used together, and it is not necessary to necessarily contain paints and/or the color.
In the present invention, the mode used together with the metal particles concerning the present invention of previous statement of carbon black and/or black lead is the most preferable.
[0102]
In the above, the black pigment of carbon systems, such as carbon black, has [the following / 50 m^2/g] the preferable specific surface area measured with the nitrogen gas adsorption process. Especially, within the limits of 50-10 m^2/g is within the limits of 30-15 m^2/g preferable still more preferably. Good shielding performance is obtained as specific surface area is [aforementioned] within the limits, and the dispersion stability at the time of distribution is good.
[0103]
When using together colorant (especially carbon black, black lead), as a quantity of colorant, the 10 - 90 volume % is preferable to the total amount of the metal particles concerning the present invention, and it is the 20 to 50 volume % more preferably. It is effective in controlling the reflectance etc. of the formed light-shielding film by using colorant together with the metal particles concerning the present invention, and when quantity of colorant is carried out especially aforementioned within the limits, while it has a high light sheilding with a thin film, it is effective for forming the light-shielding film which does not have optical leak and was excellent in surface surface smoothness. Also when a substrate independent is pinched with a polarizing plate from both sides and intersects perpendicularly the polarization axis of these two polarizing plates, there is no light leakage, a high light sheilding is acquired, a highly efficient color filter ean be obtained, and it contributes to manufacture of the liquid crystal display element which can display a high-definition image. industrially, sufficient in manufacture of the color filter by an advantageous electrodeposition process, also when forming a light-shielding film by the back face exposing method -- increase -- membranous -- a light sheilding can be acquired.
[0104]
- Other components -
In the photosensitive resin composition for light-shielding films of the present invention, various additive agents can be contained according to the various purposes and uses. As an additive agent, a surfactant, an adhesion accelerating agent, a plasticizer, etc. are mentioned, for example.
[0105]

Can use the aforementioned surfactant in order to improve the application nature in the case of using the photosensitive resin composition for light-shielding films as coating liquid, and the smooth nature of the coating film obtained, and as an example, BM-1000 (made by BM Chemie), the megger fax F142D, Said F172, said F173, said F183, the F176PF, the F177PF (all are the Dainippon Ink & Chemicals, Inc. make), Fluorad FC-135, FC-170C, and Fluorad FC-430, the FC-431 (all are the Sumitomo 3M make), The Sir chlorofluocarbon S-112, said S-113, said S-131, said S-141, said S-145 (all are the Asahi Glass Co., Ltd. make), The fluorine system or silicon system surfactant marketed with the trade name of SH-28PA, SH-190, SH-193, SZ-6032, SF-8428, DC-57, and DC-190 (all are the products made from Toray Industries Silicone) is mentioned.

[0106]

As content in the case of containing a surfactant, the 0.05 - 10 mass % is preferable to the total solids of the photosensitive resin composition for light-shielding films. If contained in this range, it is especially effective in respect of the pattern adhesion to a substrate. The range of the 0.08 - 5 mass % is preferable, and especially the range of the 0.1 - 3 mass % is preferable.

[0107]

The photosensitive resin composition for light-shielding films of the present invention can be prepared as coating liquid, for example using organic solvents, such as ketone, such as acetone, methyl ethyl ketone, and methyl butyl ketone, various ether, and ester. This coating liquid can be preferably used, in order to form a photosensitive resin layer in the surfaces which serve as a coated object by application, such as temporary support (sheet etc.) and a liquid crystal display element (this coating liquid may be hereafter called "coating liquid for photosensitive resin layers".). Although there is no restriction in particular in the thickness of this photosensitive resin layer and it can choose suitably, 0.2-1.3 micrometers is preferable and 0.3-0.8 micrometer is more nearly preferable. Even if constituted in the thin film of this range, high black density is obtained.

[0108]

That is, the mode constituted so that the optical density of this light-shielding film might become 4.0 or more, when the photosensitive resin composition for light-shielding films of the present invention formed light-shielding films of 1.0 micrometer of thickness, such as a coating film by the above application, is preferable. A color filter including the light-shielding films (black matrix etc.) to constitute Printing materials, such as a proof, In the use as which advanced shielding performance and thin-film-forming nature, such as a partitioning material for PDP (Plasma Display Panel), ink jet ink, and resist ink, are required, It is important that high black density is obtained, using a thin film, and, in this case, the photosensitive resin composition for light-shielding films of the present invention can be used preferably. The photosensitive resin composition for light-shielding films of the present invention is preferable for especially formation of the light-shielding films (black matrix etc.) of the color filter which constitutes a liquid crystal display etc., and ideal for formation of a black matrix.

[0109]

The photosensitive resin composition for light-shielding films of the present invention can form a light-shielding film with the application of the following method in addition to the method by application of the above-mentioned coating liquid.

-The ink jet method-

Using the ink jet method, the photosensitive resin composition for light-shielding films of the present invention can be discharged, and a light-shielding film can be formed. This is preferable

in respect of a cost cut. As this ink jet method, the bubble jet (registered trademark) type which used the electrothermal conversion object as an energy generation element, or the piezo jet type using a piezoelectric device is usable, and coloring area and a coloring pattern can be set up arbitrarily. Although there is a tendency for ink to be unable to diffuse sufficiently easily in the ink jet method and it is easy to become a cause which produces a blind spot and invites color unevenness and a contrast drop, In this case, it is preferable to prepare to the thing which made the organic solvent distribute paints by the concentration more than the at least 10 mass % to the mass of the whole constituent (ink). For details, the description of JP,2004-325736,A can be referred to.

[0110]

In order to produce the light-shielding film which it got wet at the time of discharging the photosensitive resin composition for light-shielding films, controlled breadth, and was excellent in concentration homogeneity, as a solvent kind to be used, the surface tension of the fitness in ink jet printing is 35 or less mN/m, and a not less than 130 degrees C thing has the preferable boiling point. The drying property near the nozzle is suppressed as the stability of the dot shape at the time of discharge is good in surface tension being 35 or less mN/m and the boiling point is not less than 130 degrees C, and discharge failures, such as nozzle plugging, can be avoided. By getting wet and controlling breadth, a light-shielding film with clear film form and edge sharp at uniform high concentration without defects, such as mixed colors at the time of forming a colored pixel and a blind spot in a light-shielding film, is obtained.

[0111]

It is also possible to improve the productivity at the time of producing a light-shielding film by applying a means which is described in JP,2002-372615,A and which ink hardens in an instant, also combines reservation of the dispersion stability of paints, and reservation of adhesion with a base material, and they improve.

[0112]

-Print processes-

A light-shielding film can be produced in a short time using print processes. As print processes, it hits carrying out print formation of the shielding pattern to this transparent base material through a transparent base material between a printing cylinder and an impression cylinder, In the letterpress part which the aforementioned printing cylinder is provided with the printing plate of the letterpress corresponding to the aforementioned shielding pattern, and constitutes the aforementioned printing plate, Transfer ink is transferred with a shielding pattern with the letterpress object provided with the letterpress which faced the aforementioned letterpress part and was used as the shielding pattern from the transfer sheet provided with the photosensitive resin composition for optical thin-film (transfer ink), There is the method of transferring the aforementioned transfer ink which provided transfer ink to the printing plate of the aforementioned printing cylinder at the shielding pattern, and was provided by the shielding pattern from the printing plate of a printing cylinder to the aforementioned transparent base. As for the printing plate of a printing cylinder, it is good to have ink repellent property. It is good to apply a binder to the transfer starting position and transfer end position in a printing plate. In order that transfer ink may be provided by the shielding pattern by the printing plate of a printing cylinder and may transfer this transfer ink to a transparent base material at once, the time which production of the light-shielding film by printing takes is shortened, and. There is no aim gap of the transfer ink which forms the light-shielding film formed in a transparent base material, and a proper light-shielding film is obtained by the printing method using a transfer sheet. And if the

letterpress of the letterpress part in the printing plate of a printing cylinder is provided with ink repellent property, transfer of the transfer ink from a printing plate to a transparent base material will become good, and washing of a printing plate also becomes easy.

[0113]

It hits carrying out print formation of the shielding pattern to this transparent base material through a transparent base material between a printing cylinder and an impression cylinder besides the aforementioned printing method, The aforementioned printing cylinder is provided with the printing plate of the letterpress corresponding to the aforementioned shielding pattern, and the photosensitive resin composition for light-shielding films (black ink) is filled up with an ink jet feeding means into the cell which constitutes the aforementioned printing plate, After providing black ink with a shielding pattern to the printing plate of the aforementioned printing cylinder and drying this, there is a printing method transferred from the printing plate of a printing cylinder to the aforementioned transparent base. In this case, a printing cylinder is provided with the printing plate of an intaglio, and the photosensitive resin composition for light-shielding films (black ink) is filled up with an ink jet feeding means into the cell which constitutes a printing plate, Since it has composition transferred from the printing plate of a printing cylinder to the aforementioned transparent base after providing black ink with a shielding pattern to the aforementioned printing plate and drying this, Since process time is shortened still more nearly substantially, and there is no aim gap, ink form is stabilized in a cell and it can transfer to cell shape at the transparent base material side, a light-shielding film can be formed precisely.

[0114]

<A transfer material and a manufacturing method for the same>

-Transfer material-

The transfer material of the present invention can provide and constitute the photosensitive resin layer of at least one layer on temporary support, and also can also provide and constitute other layers, such as an intermediate layer, a thermoplastic resin layer, and a protective film, if needed.

[0115]

The photo-oxide generating agent which the aforementioned photosensitive resin layer absorbs binder resin and light, and generates acid, It is a layer containing the cross linking agent cross-bridged by operation of the aforementioned photo-oxide generating agent, and metal particles and/or metallic-compounds particles, It can form by a publicly known method in the mode containing these each component, and can form most preferably using the photosensitive resin composition for light-shielding films of the present invention as stated above (it paints on the surface of temporary support (sheet etc.) by application of coating liquid preferably). It is as the previous statement about the details of each component, such as binder resin.

[0116]

Although the thickness of the photosensitive resin layer which constitutes the transfer material of the present invention can be chosen according to a use or the purpose, For the use as which thin films, such as light-shielding films, such as a black matrix, are required, it is so good that it is thin, and it is preferable to consider it as the range of 0.2-1.3 micrometers, and it is more preferable to consider it as the range which is 0.3-0.8 micrometer. Even if this photosensitive resin layer is transferred by the transferred object, constitutes a black image (for example, black matrix) and constitutes it in the film of the aforementioned range, it can satisfy high black density and a light sheilding.

[0117]

Next, the temporary support and other layers which constitute the transfer material of the present invention are described.

- Temporary support -

To temporary support, a plastics film is preferable. For example, films, such as polyethylene terephthalate, polyethylenenaphthalate, cellulose triacetate, cellulose acetate butylate, cellulose acetate propionate, polycarbonate, polystyrene, and polyethylene, can be mentioned. Especially, a polyethylene terephthalate film is preferable and biaxial extension and the polyethylene terephthalate film by which heat setting was carried out are preferable especially especially from points, such as stability and toughness.

[0118]

Although there is no restriction in particular in the thickness of temporary support, the range of 5-200 micrometers is common, and the range which are 10-especially 150micro is preferable in respect of the ease of dealing with it, flexibility, etc.

[0119]

- Thermoplastic resin layer -

A thermoplastic resin layer is a thermoplastic resin layer of alkali solubility, and, as for the resin which constitutes this layer, it is preferable that substantial softening temperature is 80 degrees C or less.

Softening temperature as thermoplastics of alkali solubility of 80 degrees C or less, The saponification thing of ethylene and an acrylic ester copolymer, the saponification thing of styrene and a (meth)acrylic ester copolymer, The saponification thing of vinyltoluene and a (meth)acrylic ester copolymer, It is preferable that it is at least one chosen from the copolymer of poly(meta) acrylic ester and (meta) butyl acrylate, a saponification thing with (meth)acrylic ester copolymers, such as vinyl acetate, etc. and acrylic acid (meta), and an ethylene unsaturation group containing monomer. The softening temperature by a "plastic performance manual" (Japan Plastics Industry Federation, all Japan plastic-molding industrial joint association written and edited, Kogyo Chosakai Publishing, October 25, 1968 issue) can use a meltable thing for an alkaline aqueous solution among organic high polymers of about 80 degrees C or less.

[0120]

It is also possible to lower substantial softening temperature to 80 degrees C or less, and to use it because softening temperature adds the various plasticizers which have this organic high polymer substance and compatibility in the organic high polymer substance in a not less than 80 degrees C organic high polymer substance. In order to adjust adhesive strength with temporary support, it is also possible to add various kinds of polymer, a supercooling substance, an adhesion improving agent or a surfactant, mold lubricant, etc. into an organic high polymer substance in the range in which substantial softening temperature does not exceed 80 degrees C.

[0121]

especially -- the (A) weight average molecular weight 50,000-500,000 and the glass-transition-temperature Tg=0-140 degree C alkali of the description to JP,H7-28232,A -- with meltable thermoplastics, (B) the weight average molecular weight 3000-30,000 and Tg=30-170 degree C alkali -- meltable thermoplastics -- (A)/(B) -- the thing mixed in ratio =5 / 95 - 95/5 [a mass ratio] is preferable. Especially the preferable examples of the above (A) are methacrylic acid / 2-ethylhexyl methacrylate / benzyl methacrylate / methyl methacrylate copolymer (copolymerization mole ratio: 5/10/30/55, average-molecular-weight:100,000, Tg: about 70 degrees C). Especially the preferable examples of the above (B) are styrene/acrylic acid copolymer (copolymerization-composition mole ratio: 65/35, average-molecular-weight:10,000,

Tg: about 100 degrees C). Especially the preferable ranges of the aforementioned (A) / (B) ratio are 30 / 70 - 60/40.

[0122]

As a preferable example of the aforementioned plasticizer, a polypropylene glycol, A polyethylene glycol, dioctyl phthalate, diheptylphthalate, Dibutyl phthalate, tricresyl phosphate, cresyl diphenyl phosphate, Biphenyl diphenyl phosphate, polyethylene-glycol mono- (meta) acrylate, Polyethylene glycol di(meta)acrylate, polypropylene-glycol mono- (meta) acrylate, The addition reaction product of polypropylene glycol di(meta)acrylate, and an epoxy resin and polyethylene-glycol mono- (meta) acrylate, The addition reaction product of organic diisocyanate and polyethylene-glycol mono- (meta) acrylate, Di(meth)acrylate of the addition reaction product of organic diisocyanate and polypropylene-glycol mono- (meta) acrylate and a bisphenol A-polyethylene oxide addition can be mentioned.

[0123]

The quantity of a plasticizer is 0 to 200% [mass ratio] preferably to the quantity (preferably the aforementioned thermoplastics (A) and the total quantity of (B)) of the thermoplastics which constitutes a thermoplastic resin layer, and is 20 to 100% [mass ratio] more preferably. Especially the preferable example of a plasticizer is the compound which added 10 mol of ethylene oxide to bisphenol A and 1 mol in total, and carried out methacrylic esterification of the both-ends alcohol. Especially the preferable addition amount of a plasticizer is the 30 to 60 mass % of the quantity (preferably the aforementioned thermoplastics (A) and the total quantity of (B)) of thermoplastics.

[0124]

A thermoplastic resin layer can be painted by application of the coating liquid which dissolves each of above-mentioned components in a solvent uniformly, and drying. The preferable example of the aforementioned solvent Methoxy propylene glycol acetate, 2-hydroxypropyneacid ethyl, 3-methoxy methyl propionate, It is a mixture of the mixture of retarder thinner, such as 3-ethoxyethyl propionate, methyl lactate, ethyl lactate, cyclohexanone, and methyl isobutyl ketone, and these retarder thinner, low boilers, such as methyl ethyl ketone and acetone, and these low boilers. An application drying rate is good, is a point of dry unevenness prevention, and can choose preferably the mass composition ratio of retarder thinner and a low boiler from 1 / 99 - 99/1. The ranges of the mass ratio of retarder thinner/low boiler are 90 / 10 - 10/90 preferably, and the range of 80 / 20 - 20/80 is the most preferable.

[0125]

The coating method with which the thermoplastic resin layer was generally known on temporary support, for example, a dip coating method, By the air-knife-coat method, the curtain coat method, the wire bar coat method, the gravure coating method, extrusion die coating method, the slit coat method, etc., The coating liquid (it may be hereafter called "the coating liquid for thermoplastic resin layers".) containing the aforementioned thermoplastics etc. can be applied, and it can form by making it dry.

[0126]

When the thickness of a thermoplastic resin layer transfers a photosensitive resin layer, the viewpoint of absorbing completely the unevenness of 0.5 micrometers or more which exists in a transferred surface to its 1 micrometers or more are preferable. About a maximum, about 100 micrometers or less are common from restriction of application production aptitude, about 50 micrometers or less are preferable, and especially about 20 micrometers or less are preferable.

[0127]

- Intermediate layer -
It provides in order to prevent a component from being mutually mixed between a thermoplastic resin layer and a photosensitive resin layer as an intermediate layer (it is also called a detached core.).
It distributes or dissolves in water or an alkaline aqueous solution, and if the intermediate layer is insoluble or refractory to the organic solvent in the coating liquid for thermoplastic resin layers provided in contact with an intermediate layer, he is good for it, he is publicly known, and can constitute.
For example, the polyvinyl ether / maleic anhydride polymer of the description to JP,S46-2121,A or JP,S56-40824,B, The water soluble salt of carboxy alkylcellulose, water-soluble cellulose ether, The salt of carboxy alkyl starch, a monohydrate, polyvinyl alcohol, a polyvinyl pyrrolidone, Various kinds of polyacrylamides, various kinds of water soluble polyamide, the water soluble salt of polyacrylic acid, The water soluble salt of the group which consists of gelatin, an ethyleneoxide polymer, various kinds of starch, and its prototype, the copolymer of styrene/maleic acid, MAREINETO resin, and the thing that combined these 2 or more type can be mentioned.
[0128]
In particular, the combination of 1 water-solubility polyvinyl-butyral independent, and 2 polyvinyl alcohol and a polyvinyl pyrrolidone is preferable.
That [polyvinyl alcohol's] whose saponification value is 80 mol % or more is preferable, the content of a polyvinyl pyrrolidone has the common 1 - 75 mass % of intermediate-layer solid content, and the 1 - 60 mass % is the ten to 50 mass % preferable especially preferably. If it is this range, an adhesive property with a photosensitive resin layer will be acquired sufficiently, and will not impair the solvent resistance over the coating liquid for photosensitive resin layers.
[0129]
About 0.1-5 micrometers is preferable, and, as for an intermediate layer's thickness, 0.5-2 micrometers is especially preferable. If it is this range, it has the solvent resistance over the coating liquid for photosensitive resin layers, and option of application speed and drying can be performed without restriction.
[0130]
The solvent of intermediate layer coating liquid is chosen from the mixture of a water independent, water, the organic solvent of miscibility, and water. In order to improve an adhesive property with the thermoplastic resin layer used as a lower layer, it is preferable to choose so that a thermoplastic resin layer may be swollen slightly. As an example of a preferable solvent, water/methanol, water/ethanol, water/propanol, water / methoxy ethanol, water / methoxy propanol, water/acetone, etc. can be mentioned. The composition ratio of water and these organic solvents can be chosen from the range of 99 / 1 - 50/50 with a mass ratio. By considering it as this range, the addition effect of a solvent is acquired and sufficient solubility of water soluble resin can be acquired.
[0131]
The coating method with which the intermediate layer was generally known on the thermoplastic resin layer, for example, a dip coating method, It can form by applying intermediate layer coating liquid by the air-knife-coat method, the curtain coat method, the wire bar coat method, the gravure coating method, extrusion die coating method, the slit coat method, etc.
[0132]
- Protective film

As for a protective film, it is preferable to provide in order to avoid the adhesion and damage to the impurity to the photosensitive resin layer at the time of saving a transfer material, and its thin protective film is preferable.
Although a protective film is the same as that of temporary support or consists of a similar material, at the time of use, it is easily disengageable and needs to consist of photosensitive resin layers.
[0133]
The smooth nature of a surface in contact with a photosensitive resin layer is important for a protective film, and since it will serve as damage to a photosensitive resin layer if it has the projection it is [projection] about 0.01 micrometer, it becomes a problem easily. Therefore, as a material used as a protective film, silicon paper, polyolefin, or a poly tetrafluoroethylene sheet is preferable, for example. They are a polypropylene film or a polyethylene film especially preferably.
[0134]
1-100 micrometers is preferable, 3-50 micrometers is preferable especially preferable, and the thickness of a protective film is 5-20 micrometers. Strength can be maintained as it is this range, and the adhesive property between photosensitive resin layers can also be maintained.
[0135]
-A manufacturing method of a transfer material-
The transfer material of the present invention by applying and drying the coating liquid for thermoplastic resin layers on the aforementioned adhesive surface of the temporary support which has an antistatic layer and the adhesive surface preferably, for example, The intermediate layer coating liquid which uses the solvent swollen to some extent although the thermoplastic resin layer of alkali solubility is painted and this layer is not dissolved on this thermoplastic resin layer after that is applied, After making it dry and laminating an intermediate layer, the coating liquid for photosensitive resin layers prepared using the solvent which does not dissolve this intermediate layer further is applied, it is made to dry and a photosensitive resin layer is laminated. Then, a protective film can be laminated and produced on a photosensitive resin layer. The coating liquid for forming the above-mentioned each layer can be applied with the coating method generally learned like previous statement.
[0136]
The manufacturing method of the transfer material of the present invention carries out the characteristics of producing the transfer material of the present invention as stated above, and performing painting of the photosensitive resin layer to a temporary support top by application using the coater which has a slit shaped nozzle among the above. That is, a photosensitive resin layer is formed by the slit coat method performed into the portion which discharges liquid using the slit shaped nozzle which has a slit shape hole. By using a slit shaped nozzle, the stratification of uniform thickness is more possible.
[0137]
Specifically JP,2004-89851,A, JP,2004-17043,A, The slit shaped nozzle and slit coating machine of a description are preferably used for JP,2003-170098,A, JP,2003-164787,A, JP,2003-10767,A, JP,2002-79163,A, JP,2001-310147,A, etc.
[0138]
The 1st sheet that provided the thermoplastic resin layer and the intermediate layer sequentially from this temporary support side on temporary support besides depending above, It is also producible by preparing the 2nd sheet that provided the photosensitive resin layer on a protective

film, and sticking so that the intermediate-layer surface of the 1st sheet and the surface of a photosensitive resin layer may touch. The 1st sheet that provided the thermoplastic resin layer on temporary support, and the 2nd sheet that provided the photosensitive resin layer and the intermediate layer sequentially from this protective film side on the protective film are prepared, It is also producible by sticking so that the intermediate-layer surface of the 1st sheet and the surface of the thermoplastic resin layer of the 2nd sheet may touch.

[0139]

Since the transfer material of the present invention is what provides the photosensitive resin layer which contains metal particles and/or metallic-compounds particles, has high black density with a thin film, and was excellent in the light sheilding as mentioned already, It is preferable for the use as which an advanced light sheilding is required, and preferable for formation of the light-shielding film represented by especially the black matrix etc.

[0140]

<A manufacturing method of a light-shielding film>

A way the manufacturing method of the light-shielding film of the present invention applies soon the photosensitive resin composition for light-shielding films of the present invention as stated above on a substrate (the applying method), Or a light-shielding film is produced by the method (replica method) of transferring on a substrate the photosensitive resin layer of the transfer material once constituted using the photosensitive resin composition for light-shielding films of the present invention as stated above.

[0141]

The photosensitive resin composition for light-shielding films of the present invention is used for the light-shielding film produced by the manufacturing method of the light-shielding film of the present invention, and since, black density is highly excellent in a light sheilding with a thin film. Therefore, it is preferable for the use asked for thin films, such as a black matrix, and in that case, the range of 0.2-1.3 micrometers is preferable, and the range which is 0.3-0.8 micrometer is more nearly preferable.

[0142]

The manufacturing method of the first light-shielding film of the present invention is based on the applying method. Namely, the process (application process) of applying the photosensitive resin composition for light-shielding films of the present invention as stated above, and making it drying and forming a photosensitive resin layer on a substrate, It constitutes from a process (pattern exposure process) of exposing the photosensitive resin layer formed by the application process to pattern form, a process (heating step) of heating the photosensitive resin layer formed by the application process, and a process (developing process) of developing the photosensitive resin layer after exposure at least, and removing an unexposed part.

[0143]

The manufacturing method of the second light-shielding film of the present invention is based on a replica method. Namely, the process (transfer process) of transferring the photosensitive resin layer of at least one layer on temporary support to a substrate using the transfer material of the present invention as stated above, It constitutes from a process (pattern exposure process) of exposing the photosensitive resin layer transferred by the transfer process to pattern form, a process (heating step) of heating the photosensitive resin layer transferred by the transfer process, and a process (developing process) of developing the photosensitive resin layer after exposure at least, and removing an unexposed part.

The pattern exposure process in a replica method, a heating step, and a developing process can

be performed like the case of the aforementioned applying method.
After an application process or a transfer process, any may be previous processes, a pattern exposure process and a heating step may be simultaneous processes, and any may be previous processes and a heating step and a developing process may be simultaneous processes.
[0144]
Hereafter, it describes about each process.
- Application process -
In the application process in the applying method, on the substrate which is a coated object, the photosensitive resin composition for light-shielding films of the present invention as stated above is applied, it is made to dry and a photosensitive resin layer is formed. The coating method generally learned, for example, a dip coating method, the air-knife-coat method, the curtain coat method, the wire bar coat method, the gravure coating method, an extrusion die coating method, the slit coat method, etc. are applicable to application.
[0145]
Especially, the slit coat method performed into the portion which discharges liquid using the slit shaped nozzle which has a slit shape hole is preferable, and can apply preferably using the coater (slit coating machine) which has a slit shaped nozzle.
The thickness of the light-shielding film obtained eventually should just choose the coating thickness suitably in the aforementioned range and the becoming range.
[0146]
A glass plate with a preferable for example, transparent base, publicly known soda glass board, low thermal expansion glass, non alkaline glass, quartz glass plate which have a silicon-oxide coat on the surface, etc., or a plastics film can be mentioned to the aforementioned substrate. The substrate can make good adhesion between the photosensitive resin layers of the constituent of the present invention, or the transfer material of the present invention by performing coupling processing previously. As coupling processing, the method of a JP,2000-39033,A description is used preferably.
[0147]
- Transfer process -
In the transfer process in a replica method, the photosensitive resin layer of at least one layer currently provided on temporary support is transferred to a substrate using the transfer material of the present invention as stated above.
[0148]
Transfer of the photosensitive resin layer to a substrate After washing the transferred surface (it is the forming face when the precedent pattern and the thin film are already formed) of a substrate, The strip of the protective film is carried out from a transfer material, the cleaning surface of a substrate and the surface of the photosensitive resin layer which the transfer material exposed are stuck under heat pressing by the heating roller of a laminating machine, and are made into a laminated body, temporary support is exfoliated from this laminated body, and it transfers on a substrate. The laminating machine can choose a commercial laminating machine suitably.
[0149]
As for the temperature of the heating roller at the time of transfer, 50 degrees C - 150 degrees C are preferable, and the linear pressure at the time of sticking by pressure has 5 kg/cm - preferable 25 kg/cm. As for lamination speed, the amount of 0.2-4-m/is preferable at a conveying speed.
It is a part for heat crimping roll temperature [of 130-140 degrees C], linear pressure [at the

time of sticking by pressure] 10 - 15 kg/cm, and conveying speed/of 1-3 m using the heat crimping roll which can be especially heated with application of pressure as preferable conditions.

[0150]

- Pattern exposure process -

In a pattern exposure process, the photosensitive resin layer formed by the application process or the transfer process is exposed to pattern form. This process may be performed as a previous process of the below-mentioned heating step, and may be performed as a post process of a heating step, and can be performed simultaneously with a heating step.

[0151]

Exposure can be performed by irradiating the formed photosensitive resin layer via the mask of a predetermined pattern, and it forms a latent image so that a desired pattern may be obtained, when it passes through the below-mentioned developing process. That is, in an exposure region, acid (H^+) is generated from a photo-oxide generating agent, crosslinking reaction is carried out between binder resin and a cross linking agent by the catalysis of acid, a bridging body is formed, and polymerization curing is carried out to pattern form.

[0152]

As a light source, for example g line (wavelength of 436 nm), i line (wavelength of 365 nm), Charged particle beams, such as X-rays, such as far ultraviolet rays, such as ultraviolet rays of the continuous state from publicly known light sources, such as an ultrahigh pressure mercury lamp, xenon light, a carbon arc lamp, and an argon laser, and/or the shape of a luminescent line and a KrF excimer laser, and a synchrotron radiation line, and an electron beam, etc. are mentioned. Especially, g line, i line, and the ultraviolet rays of the 300-440-nm wavelength zone containing these are preferable. Like the description to JP,H6-59119,A, light transmittance with a wavelength of not less than 400 nm may use together the light filter etc. which are 2% or less.

[0153]

- Heating step -

In a heating step, heating (bake) processing is performed at the time of pattern exposure after pattern exposing by the aforementioned pattern exposure process. By heating the exposure region by which pattern exposure was carried out after crosslinking reaction's beginning under existence of the acid by which it was generated at the time of pattern exposure, diffusion of acid is promoted, it is urged to crosslinking reaction toward a thickness direction near the surface of a photosensitive resin layer, and polymerization curing of a photosensitive resin layer is performed good to the film depths. In the present invention, since the formed photosensitive resin layer is constituted by the thin film, unnecessary diffusion (for example, diffusion to the transverse direction to the longitudinal direction which is a thickness direction, etc.) of acid can be suppressed, and it can prevent ****** of a pattern, and can obtain the small-gage wire of high resolution.

[0154]

This process can be performed as a previous process of the above-mentioned pattern exposure process, can also be performed as a post process of a pattern exposure process, and can be performed to a pattern exposure process and coincidence (it includes heating from before pattern exposure.). This process may be performed as a previous process of the below-mentioned developing process, and may be performed as a post process of a developing process, and can be performed simultaneously with a developing process. Although the photosensitive resin layer has disappeared photosensitivity after development, it may describe as a photosensitive resin layer in

view of simplification of a description in this Description.
[0155]
Although the conditions of baking treatment change with a photo-oxide generating agent, cross linking agents, etc., 15 seconds - their 1 minute are preferably public at 100-120 degrees C preferably 80-140 degrees C for 15 seconds - 3 minutes.
[0156]
- Developing process -
In a developing process, when a heating step is provided after exposure and to a previous process, the development of the photosensitive resin layer after heating is carried out, development removal of the unexposed part is carried out, and a pattern is actualized. It is preferable to perform development using a weak alkali developing solution under the temperature of 26-40 degrees C and the conditions of pH 9-11.
[0157]
This developing process is provided in order to mainly give patternizing by the development of a photosensitive resin layer, but. When a photosensitive resin layer is formed according to the transfer process in a replica method, Since it is in the state where the thermoplastic resin layer and the intermediate layer were laminated with the photosensitive resin layer, it is desirable to comprise first alkaline development for removing a thermoplastic resin layer and an intermediate layer and second alkaline development for removing the unexposed part of a photosensitive resin layer.
[0158]
In this case, first alkaline development is performed using a weak alkali developing solution under the temperature of 26-40 degrees C, and the conditions of pH 9-11, and, as for second alkaline development, it is preferable to carry out using a weak alkali developing solution under the temperature of 26-40 degrees C and the conditions of pH 9-11 like the above.
[0159]
As a developing solution for photosensitive resin layer development, the thin aqueous solution of an alkaline substance can be used and what added a little water and organic solvents of miscibility further to this may be used.
as a suitable alkaline substance -- alkali metal hydroxide (an example and sodium hydroxide --) A potassium hydrate, alkali metal carbonate (an example, sodium carbonate, potassium carbonate), Alkali metal bicarbonate (an example, sodium bicarbonate, potassium bicarbonate), Alkali metal silicates (an example, a sodium silicate, a potassium silicate), Alkaline metal metasilicates (an example, metasilicic acid sodium, metasilicic acid potassium), Ammonia, ethylamine, n-propylamine, diethylamine, Triethylamine, methyldi ethylamine, dimethylethanolamine, Triethanolamine, diethanolamine, monoethanolamine, morpholine and tetra alkyl AMMONNIUMU hydroxide (for example, tetramethylammonium hydroxide --) Tetraethylammoniumhydroxide, pyrrole, piperidine, 1,8-diazabicyclo [5,4,0]-7-undecene, 1,5-diazabicyclo [4, 3, 0]-5-nonane, or trisodium phosphate can be mentioned.
[0160]
As water and an organic solvent of miscibility, for example Methanol, ethanol, 2-propanol, 1-propanol, butanol, diacetone alcohol, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, Ethylene glycol mono-n-butyl ether, benzyl alcohol, Acetone, methyl ethyl ketone, cyclohexanone, epsilon-caprolactone, Gamma-butyrolactone, dimethylformamide, dimethylacetamide, hexamethylphosphoramide, ethyl lactate, methyl lactate, epsilon caprolactam, N-methyl pyrrolidone, etc. can be mentioned preferably. The concentration of

water and the organic solvent of miscibility has the common 0.1 - 30 mass %.
[0161]
To a developing solution, a still more publicly known anionic form or an Nonion type surfactant can be added. The concentration of a surfactant has the preferable 0.01 - 10 mass %. A developing solution can be used as bath liquid or spray liquid, and can use a liquid peak method, a dipping method, swing dip coating, a spray method, etc. about a developing method.
[0162]
This process may be performed as a previous process of the aforementioned heating step, and may be performed as a post process of a heating step, and may be performed simultaneously with a heating step.
[0163]
Like previous statement, by using the photosensitive resin composition for light-shielding films of the present invention, it has high concentration with a thin film, and the light-shielding film of high resolution can be obtained. It is useful although the black matrix (a black matrix here is a black part arranged between pixels, and there are a thing etc. stripe shape and in the shape of a lattice.) of the liquid crystal display element (especially color filter) which constitutes a display device especially is obtained. It is also the same as when based on the transfer material of the present invention, and the manufacturing method of a light-shielding film.
[0164]
The black matrix needs to have not only a light sheilding but electric insulation from the necessity colored to the liquid crystal cell which performs liquid crystal display of performing voltage impressing for every pixel. Specifically, as for the volume resistance value of a black matrix, it is preferable to hold more than $1x10^8$ omega-cm. Although electric field are built over liquid crystal layer surface inboard by an IPS system, if the electrical resistance of the black matrix of a counter substrate is in the aforementioned range, electric field can be applied normally, and the display which has neither disorder nor display unevenness in liquid crystal orientation is attained. Therefore, the black matrix used for the liquid crystal display of an IPS system not only needs to have a high light sheilding, but needs to show high resistance. In order to make a volume resistance value into the aforementioned range, it is preferable that a black matrix shall be consisted of the particles and polymer of 1 or more ohm-cm of volume resistance values, and the surface roughness of this black matrix shall be 100 A or less.
[0165]
A volume resistance value shows an unit area and the resistance per unit length here, It asks from a current value when predetermined voltage is applied to the electrode surface provided like measurement of polymer volume resistivity by the upper and lower sides of the application membrane of the photosensitive resin composition for light-shielding films which make a black matrix by a 3 terminal method with a guard ring. The counterelectrode which was formed on the substrate and which opposes mutually may be covered with the photosensitive resin composition for light-shielding films, predetermined voltage may be applied between this counterelectrode, and it may ask based on a current value and electrode shape.
[0166]
Not less than 80% of the voltage retention of a black matrix is preferable, and is not less than 90% more preferably. Impurities, such as ionic matter, elute in a liquid crystal that aforementioned voltage retention is within the limits, there is no generating of the white unevenness in accordance with the ionic matter to a liquid crystal layer mixing etc., etc., and a good display image is obtained. In order to make voltage retention into not less than 80%, it is

preferable to adjust the quantity of the photo-oxide generating agent used at the time of formation of a black matrix, heating conditions, etc., and to raise a degree of cross linking. making voltage retention into not less than 80% -- especially, even if it is the prolonged display under a display condition with severe high-humidity/temperature etc., generating of display failures, such as printing and white unevenness, is prevented, and the liquid crystal display excellent in display quality becomes possible.

[Working example]

[0167]

Hereafter, although the present invention is described according to an working example, the present invention is not limited to these working examples. The "part" in an working example is a mass basis.

[0168]

(Working example 1)

(1) Production of a photosensitive transfer sheet

The 100-micrometer-thick polyethylene terephthalate film (PET temporary support) was prepared, on this PET temporary support, the coating liquid which consists of the following composition was applied and dried, and dry layer thickness formed the thermoplastic resin layer which is 20 micrometers.

[0169]

<Composition of thermoplastic resin layer ********>

- Methyl methacrylate / 2-ethylhexyl acrylate / benzyl methacrylate / methacrylic acid (=55/11.7/4.5/28.8 [mole ratio]) copolymer -- 15 copies
(Weight average molecular weight 90000)
- Polypropylene-glycol diacrylate
(Average molecular weight 822) -- 6.5 copies
- Tetraethylene glycol dimethacrylate -- 1.5 copies
- P-toluenesulfonamide -- 0.5 copy
- Benzophenone -- 1.0 copy
- Methyl ethyl ketone -- 30 copies

[0170]

Subsequently, on the thermoplastic resin layer formed from the above, the coating liquid which consists of the following composition was applied and dried, and dry layer thickness formed the intermediate layer who is 1.6 micrometers.

[0171]

<Composition of intermediate layer coating liquid>

- Polyvinyl alcohol
(PVA-205, 80% of a saponification value, Kuraray Make) -- 130 copies
- Polyvinyl pyrrolidone -- 60 copies
(Product made from GAF condominium RESHON PVP K-90)
- Fluorochemical surfactant
(The Sir chlorofluocarbon S-131, Asahi Glass Co., Ltd. make) -- Ten copies
- Distilled water -- 3350 copies

[0172]

Subsequently, the coating liquid for black-photosensitive-resin layers which consists of the following composition was prepared, this coating liquid for black-photosensitive-resin layers is further applied on an intermediate layer, was dried, and dry layer thickness formed the black-

photosensitive-resin layer of the Ag particle content which is 0.60 micrometer. Then, the polypropylene film was stuck on the surface of a black-photosensitive-resin layer as a protective film. The transmitted light study concentration of the obtained black-photosensitive-resin layer was 4.0, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 6.7. The photosensitive transfer sheet of the present invention constituted by the laminated structure of PET temporary support / thermoplastic resin layer / intermediate layer / black-photosensitive-resin layer / protective film as mentioned above was produced.

[0173]

In this example, it asked for transmitted light study concentration as follows.

Measure the transmitted light study concentration (OD) of a photosensitive transfer sheet (with no protective film) on the wavelength of 555 nm using spectrophotometer UV-2100 (made by Shimadzu Corp.), and. The value (penetration OD;=OD-OD^0) which deducted OD^0 from OD obtained by measuring the transmitted light study concentration (OD^0) of the PET temporary support in which the thermoplastic resin layer and intermediate layer in front of the black-photosensitive-resin stratification were furthermore formed in a similar way was made into transmitted light study concentration.

[0174]

<Composition of the coating liquid for black-photosensitive-resin layers>

- Methacrylic acid / benzyl methacrylate copolymer -- 19.98 copies

(Mole ratio: 28/72, weight-average-molecular-weight:30000)

- Cross linking agent (MW-30M, made in Sanwa Chemical) -- 4.76 copies
- Ag particle (mean particle diameter of 80 nm) -- 51.3 copies
- Surfactant -- 0.17 copy

(The Dainippon Ink & Chemicals, Inc. make, F177P)

- Photo-oxide generating agent -- 2.38 copies

(2,4-bis(triehloro)-6,4-[4-N,N-diethoxycarbomethyl)-3-bromophenyl-s-triazine

- Methyl ethyl ketone -- 106.80 copies
- Propylene-glycol-monomethyl-ether acetate

-- 44.70 copies

[0175]

(2) Image formation by a replica method

A protective film from the photosensitive transfer sheet obtained from the above the surface of peel-off and the exposed black-photosensitive-resin layer, the surface of a 1.1-mm-thick glass substrate is touched -- as -- a laminator (a LamicII type --) Lamination and PET temporary support were exfoliated on condition of 130 degrees C, 0.2 m/min, and 10 kg/cm using Made in Hitachi Industries, the black-photosensitive-resin layer was transferred with the thermoplastic resin layer and the intermediate layer, and the black-photosensitive-resin layer of optical density 4.0 obtained the glass substrate by which transfer formation was carried out.

[0176]

Then, it exposes to pattern form in 400 mj/cm^2 via a photo mask on the surface of this black-photosensitive-resin layer, After it finished exposure and 1 minute passed, on the hot plate heated by 140 degrees C, as it touched, it placed in the glass substrate surface, and heat-treatment (after-exposure bake) was performed for 12 seconds.

[0177]

10 time dilution liquid of alkali developing solution T-PD2 for removal of after after-exposure

bake, a thermoplastic resin layer, and an intermediate layer (made by Fuji Photo Film Co., Ltd.) (33 degrees C) Development removal of a thermoplastic resin layer and the intermediate layer is carried out using pH=10.7, After carrying out rinsing treatment furthermore, continuously, the unexposed part of the black-photosensitive-resin layer was developed using the 5 time dilution liquid (33 degrees C, pH=9.9) of alkali developing solution T-CD (made by Fuji Photo Film Co., Ltd.), rinsing treatment was performed, and the black image of the light sheilding was formed on the glass substrate.

[0178]

(3) Evaluation

It evaluates by measuring as follows and the result of measurement and evaluation is shown in the following table 1.

-1. resolution -

Pattern exposure was carried out using the mask which has a pattern of the form line which becomes narrow for every 2-micrometer interval to 50 micrometers - 4 micrometers about the above-mentioned black-photosensitive-resin layer similarly formed by carrying out transfer formation of the black-photosensitive-resin layer on the glass substrate using the photosensitive transfer sheet obtained from the above. Then, the linewidth (micrometer) of the above-mentioned portion in which the development was similarly performed and the line remains was measured using the optieal microscope, and this was made into resolution. It is shown that the one where a value is smaller is excellent in resolution.

[0179]

-2. display Mullah

To the glass substrate in which the black image was formed, the colored pixel was formed as follows, it was considered as the color filter, and the thickness measurement using a laser beam microscope etc. estimated the existence of the projection. When image display of the projection here is carried out, it serves as a cause which starts display unevenness.

A lapped part of a colored pixel when a colored pixel is provided, and a black image serves as a corniform projection, and it occurs.

[0180]

<Production of a color filter>

- Production of a photosensitive resin transfer material -

On 75-micrometer-thick polyethylene terephthalate film temporary support (PET temporary support), the slit shaped nozzle was used, the coating liquid for cushion layers which consists of the following formula H1 was applied and dried, and the cushion layer was formed. Next, the intermediate layer coating liquid which consists of the following formula P1 was applied and dried on this cushion layer, and the intermediate layer (oxygen interception film) was laminated. The following table 1 was made to apply and dry further the coloring photosensitive resin composition R2 which consists of composition of a description on this intermediate layer, and the photosensitive resin layer was laminated. Thus, on PET temporary support, the thermoplastic resin layer whose dry membrane thickness is 14.6 micrometers, the intermediate layer whose dry membrane thickness is 1.6 micrometers, and dry membrane thickness provided the photosensitive resin layer which is 2.4 micrometers, and stuck the protective film (12-micrometer polypropylene film in thickness) by pressure on the photosensitive resin layer.

[0181]

[Table 1]

着色感光性樹脂組成物	R1	G1	B1	R2	G2	B2
R顔料分散物1 (C. I. P. R. 254)	44	-	-	44	-	-
R顔料分散物2 (C. I. P. R. 177)	5.0	-	-	5.0	-	-
G顔料分散物1 (C. I. P. G. 36)	-	24	-	-	24	-
Y顔料分散物1 (C. I. P. Y. 150)	-	13	-	-	13	-
B顔料分散物1 (C. I. P. B. 15:6 + C. I. P. V. 23)	-	-	8.0	-	-	7.2
B顔料分散物2 (C. I. P. B. 15:6)	-	-	14.4	-	-	13
プロピレングリコールモノメチルエーテルアセテート	7.6	29	28	7.6	29	23
メチルエチルケトン	37	26	41	37	26	35
シクロヘキサノン	-	1.3	-	-	1.3	-
バインダー1	-	2.5	-	-	3	-
バインダー2	0.7	-	-	0.8	-	-
バインダー3	-	-	19	-	-	17
DPHA液	3.8	3.5	4.2	4.4	4.3	3.8
2-トリクロロメチル-5-(p-スチリルメチル)1, 3, 4-オキサジアゾール	0.12	0.1	0.17	0.14	0.15	0.15
2, 4-ビス(トリクロロメチル)-6-[4-(N, N-ジエトキシカルボニルメチル)-3-ブロモフェニル]-s-トリアジン	0.050	0.050	-	0.058	0.060	-
フェノチアジン	0.010	0.005	0.020	0.010	0.005	0.020
添加剤1	-	-	-	0.52	-	-
界面活性剤1	0.060	0.070	0.060	0.060	0.070	0.050

質量部

[0182]
The photosensitive resin transfer material which temporary support, the thermoplastic resin layer, the intermediate layer (oxygen interception film), and the red photosensitive resin layer were laminated as mentioned above, and was constituted by the laminated body was produced (the photosensitive resin transfer material R2 is called hereafter).
[0183]
[The formula H1 of the coating liquid for cushion layers]
- Methanol -- 11.1 copies
- Propylene-glycol-monomethyl-ether acetate -- 6.4 copies
- Methyl ethyl ketone -- 52.4 copies
- Methyl methacrylate / 2-ethylhexyl acrylate / benzyl methacrylate / methacrylic acid copolymer -- 5.83 copies
[Copolymerization ratio (mole ratio) =55/11.7/4.5/28.8, weight-average-molecular-weight =100,000, Tgnearly equal to70 degree C]
- Styrene/acrylic acid copolymer -- 13.6 copies
[Copolymerization ratio (mole ratio) =63/37, weight-average-molecular-weight =10,000,

Tgnearly equal to100 degree C]
- Compound (the Shin-Nakamura Chemical Co., Ltd. make, 2,2-bis[4-(methacryloxy-polyethoxy) phenyl] propane) which carried out dehydration condensation of 2 Eq of the pentaethylene glycol monometer cleats to bisphenol A -- 9.1 copies
- Surfactant 1 -- 0.54 copy
[0184]
* Surfactant 1 :
Megger fuck F-780-F (made by Dainippon Ink & Chemicals, Inc.)
[Composition]
- $C_6F_{13}CH_2CH_2OCOCH=CH_2$ (40 copies), $H(O(CH_3)\ CHCH_2)_7OCOCH=CH_2$ (55 copies), and $H(OCH_2CH_2)_7OCOCH=CH_2$. Copolymer with (five copies) (weight average molecular weight 30,000) -- 30 copies
- Methyl isobutyl ketone -- 70 copies
[0185]
[The formula P1 of intermediate layer coating liquid]
- Polyvinyl alcohol -- 2.1 copies
(PVA-205 (saponification value = 88%), Kuraray Make)
- Polyvinyl pyrrolidone -- 0.95 copy
(PVP, K-30;GAF corporation company make)
- Methanol -- 44 copies
- Distilled water -- 53 copies
[0186]
Next, the photosensitive resin transfer material G2 and B-2 were produced by the same method as the above except having replaced the aforementioned coloring photosensitive resin composition R2 used in production of the obtained photosensitive resin transfer material R2 with the coloring photosensitive resin composition G2 and B-2 which consist of composition of the description to the aforementioned table 1.
[0187]
The preparing method of the coloring photosensitive resin composition R2, G2, and B-2 carries out the postscript of the preparing method of the coloring photosensitive resin composition R1, G1, and B1 according to the preparing method of the coloring photosensitive resin composition R1 in the aforementioned table 1, G1, and B1, respectively. In the preparing method of the coloring photosensitive resin composition R1 preparation of the coloring photosensitive resin composition R2, The additive agent 1 of the quantity of the description to the aforementioned table 1 is measured, and it mixes at the temperature of 24 degrees C (**2 degrees C), and was made to stir for 20 minutes in 150r.p.m. before addition of the surfactant 1 after addition of phenothiazin etc.
* Additive agent 1 : phosphoric ester system special active agent (HIPLAAD ED152, made in Kusumoto Chemicals)
[0188]
- Formation of a red (R) pixel -
The exposed photosensitive resin layer the protective film of the aforementioned photosensitive resin transfer material R2 after exfoliating, It piled up so that the surface of a glass substrate in which the light-shielding film (black image of a light sheilding) was formed from the above might be touched, and it laminated on condition of for rubber roller temperature [of 130 degrees C], linear pressure 100 N/cm, and conveying speed/of 2.2 m using the laminator LamicII type

[Made in Hitachi Industries]. Subsequently, it exfoliated and PET temporary support was transferred on the glass substrate.

[0189]

An ultrahigh pressure mercury lamp using the proximity type exposure machine (made by Hitachi Electronics Engineering) which it has Next, a mask (quartz exposure mask which has an image pattern), Where the glass substrate arranged so that this mask and a thermoplastic resin layer may face each other is stood vertically substantially parallel, The distance between the surfaces of the side which touches the intermediate layer of a mask surface and a photosensitive resin layer was set as 200 micrometers, and pattern exposure was carried out by light exposure 40 mJ/cm^2 from the thermoplastic resin layer side via the mask.

[0190]

next, a triethanolamine system developing solution (2.5% of triethanolamine --) A nonionic surface active agent and polypropylene system defoaming agent content; shower development was carried out by flat nozzle pressure 0.04MPa for 50 seconds at 30 degrees C at trade name:T-PD1 and the Fuji Photo Film Co., Ltd. make, and the thermoplastic resin layer and the oxygen interception film were removed.

[0191]

next, a carbonic acid Na system developing solution (0.06 mol/liter of sodium bicarbonate --) Sodium carbonate of the concentration, 1% of dibutyl sodium naphthalenesulfonate, Shower development of an anionic surface active agent, a defoaming agent, and the stabilizer was carried out by corn type nozzle pressure 0.15MPa for 35 seconds at 35 degrees C using content; trade name:T-CD1 and the Fuji Photo Film Co., Ltd. make, and the pattern pixel was obtained.

[0192]

Next, a detergent (phosphate, silicate, a nonionic surface active agent, a defoaming agent, and stabilizer content; trade name:T-SD1, Fuji Photo Film Co., Ltd. make) is used, The red (R) pixel was formed by performing residue removal for 20 seconds using a shower and a rotary brush with nylon hair by corn type nozzle pressure 0.02MPa at 33 degrees C. After carrying out postexposure with the light of 500 mJ/cm^2 with an ultrahigh pressure mercury lamp to this substrate from the side in which K image is formed further after that, it heat-treated for 15 minutes at 220 degrees C.

[0193]

The thickness of R pixel was 2.0 micrometers and the coverage of C.I. pigment red (C. I.P.R.) 254 and C.I.P.R.177 was 0.88g/m^2 and 0.22g/m^2, respectively.

Then, after carrying out brush washing of the glass substrate in which R pixel was formed again using the detergent as mentioned above and carrying out shower washing with pure water, silane coupling liquid was heated for 2 minutes at 100 degrees C with the substrate preheating device, without using it.

[0194]

- Formation of a green (G) pixel -

Next, using the photosensitive resin transfer material G2 obtained from the above, the same process as formation of the aforementioned R pixel was performed, and the green pixel (G pixel) was formed in the side in which the light-shielding film and R pixel of the glass substrate are formed. However, the light exposure in the exposure process carried out shower development by 40mJ/cm^2 and a carbonic acid Na system developing solution for 45 seconds at 34 degrees C, and heat treatment was carried out for 15 minutes at 220 degrees C.

The thickness of G pixel was 2.0 micrometers and the coverage of the C.I. pigment green (C.

I.P.G.) 36 and the C.I. pigment yellow (C. I.P.Y.) 150 was 1.12g/m^2 and 0.48g/m^2, respectively.
[0195]
Then, after carrying out brush washing of the glass substrate in which R pixel and G pixel were formed again using the detergent as mentioned above and carrying out shower washing with pure water, silane coupling liquid was heated for 2 minutes at 100 degrees C with the substrate preheating device, without using it.
[0196]
- Formation of a blue (B) pixel -
Next, using photosensitive resin transfer material B-2 obtained from the above, the same process as formation of the aforementioned R pixel was performed, and the blue pixel (B pixel) was formed in the side in which the light-shielding film, R pixel, and G pixel of the glass substrate are formed. However, the light exposure in the exposure process carried out shower development by 30mJ/cm^2 and a carbonic acid Na system developing solution for 40 seconds at 36 degrees C. The thickness of B pixel was 2.0 micrometers and the coverage of the C.I. pigment blue (C. I.P.B.) 15:6 and the C.I. pigment violet (C. I.P.V.) 23 was 0.63g/m^2 and 0.07g/m^2, respectively.
[0197]
Then, bake of the glass substrate in which each pixel of R, G, and B was formed was carried out for 50 minutes at 240 degrees C, and the color filter was obtained.
[0198]
(Working example 2)
The coating liquid for black-photosensitive-resin layers was prepared like the working example 1. Next, the 1.1-mm-thick glass substrate was prepared, and on this glass substrate, using the slit & spin coater, it applies and the obtained coating liquid for black-photosensitive-resin layers was dried so that dry membrane thickness might be set to 0.60 micrometer, and the black-photosensitive-resin layer was painted.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer here was 4.0, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 6.7.
[0199]
Then, it exposes to pattern form in 400 mj/cm^2 via a photo mask on the surface of the painted black-photosensitive-resin layer, After it finished exposure and 1 minute passed, on the hot plate heated by 140 degrees C, as it touched, it placed in the glass substrate surface, and heat-treatment (after-exposure bake) was performed for 12 seconds.
[0200]
10 time dilution liquid of alkali developing solution T-PD2 for removal of after after-exposure bake, a thermoplastic resin layer, and an intermediate layer (made by Fuji Photo Film Co., Ltd.) (33 degrees C) Development removal of a thermoplastic resin layer and the intermediate layer is carried out using pH=10.7, Furthermore rinsing treatment was carried out, continuously, the unexposed part of the black-photosensitive-resin layer was developed using the 5 time dilution liquid (33 degrees C, pH=9.9) of alkali developing solution T-CD (made by Fuji Photo Film Co., Ltd.), rinsing treatment was performed, and the black image of the light sheilding was formed on the glass substrate. Then, the same evaluation as the working example 1 was performed. However, formation of the color filter was performed as follows.
[0201]
<Production of a color filter (application by a slit & spin coater)>

- Formation of a red (R) pixel -
The coloring photosensitive resin composition R1 which is on the light-shielding film forming face side of the glass substrate in which the light-shielding film (black image of a light sheilding) was formed as mentioned above from composition of the description to the aforementioned table 1 in a slit & spin coater was applied. Then, after drying some solvents for 30 seconds using the vacuum dryer VCD (Tokyo adaptation shrine make) and losing the mobility of application membrane, The unnecessary coating liquid of the circumference of a substrate was removed in EBR (edge bead remover), it prebaked for 3 minutes at 120 degrees C, and the photosensitive resin layer R1 of 2.4 micrometers of thickness was formed.
[0202]
Next, where a mask (quartz exposure mask which has an image pattern), and the glass substrate in which the photosensitive resin layer R1 was provided are vertically stood using the proximity type exposure machine (made by Hitachi Electronics Engineering) provided with the ultrahigh pressure mercury lamp, The distance of Hazama of a mask surface and the surface of the photosensitive resin layer R1 was 200 micrometers, and pattern exposure was carried out by light exposure 150 mJ/cm^2.
Next, after spraying purity from the shower nozzle and making the surface of the photosensitive resin layer R1 become wet uniformly, KOH system developing solution CDK-1 (the product made from Fuji Photo Film Electronics Materials; KOH and nonionic surface active agent content alkali developing solution) was injected for 60 seconds in 23 degrees C and nozzle pressure 0.04MPa from the flat nozzle, shower development was carried out, and the red pattern was obtained. Then, ultrapure water was injected by the pressure of 9.8MPa by the ultra-high pressure washing nozzle to the side in which the red pattern of the glass substrate was formed, residue was removed, and the red (R) pixel was formed on the glass substrate. Then, it heat-treated for 30 minutes at 220 degrees C (bake).
[0203]
The thickness of R pixel was 1.6 micrometers and the coverage of C.I. pigment red (C. I.P.R.) 254 and C.I.P.R.177 was $0.88g/m^2$ and $0.22g/m^2$, respectively.
[0204]
- Formation of a green (G) image -
Next, the coloring photosensitive resin composition G1 which becomes the glass substrate in which the aforementioned light-shielding film and R pixel were formed from the composition shown in the aforementioned table 1 is used, Application, exposure, development, and bake as well as formation of the aforementioned R pixel were performed, and the green pixel (G pixel) was formed in the side in which the light-shielding film and R pixel of the glass substrate are formed. However, the light exposure in the exposure process was made into 150 mJ/cm^2, the shower development in the developing process considered it as 60-second Hazama at 23 degrees C, and heat treatment was set as 30-minute Hazama at 220 degrees C.
[0205]
The thickness of G pixel was 1.6 micrometers and the coverage of the C.I. pigment green (C. I.P.G.) 36 and the C.I. pigment yellow (C. I.P.Y.) 150 was $1.12g/m^2$ and $0.48g/m^2$, respectively.
[0206]
- Formation of a blue (B) image -
To next, the glass substrate in which the aforementioned light-shielding film, R pixel, and G pixel were formed, Using the coloring photosensitive resin composition B1 which consists of composition shown in the aforementioned table 1, application, exposure, development, and bake

as well as formation of the aforementioned R pixel were performed, and the blue pixel (B pixel) was formed in the side in which the light-shielding film, R pixel, and G pixel of the glass substrate are formed. However, the light exposure in the exposure process was made into 150 mJ/cm^2, the shower development in the developing process considered it as 60-second Hazama at 23 degrees C, and heat treatment was set as 30-minute Hazama at 220 degrees C.
[0207]
The thickness of B pixel was 1.6 micrometers and the coverage of the C.I. pigment blue (C. I.P.B.) 15:6 and the C.I. pigment violet (C. I.P.V.) 23 was $0.63g/m^2$ and $0.07g/m^2$, respectively.
[0208]
Then, bake of the glass substrate in which each pixel of R, G, and B was formed was carried out for 50 minutes at 240 degrees C, and the color filter was obtained.
[0209]
Here, it describes about preparation of the coloring photosensitive resin composition R1 of the description to the aforementioned table 1, G1, and B1.
<Preparation of the coloring photosensitive resin composition R1>
The coloring photosensitive resin composition R1 measures R pigment dispersion thing 1, R pigment dispersion thing 2, and propylene-glycol-monomethyl-ether acetate of quantity of the description to the aforementioned table 1, Mix at the temperature of 24 degrees C (**2 degrees C), and in 150r.p.m., stir for 10 minutes and it ranks second, Methyl ethyl ketone of the quantity of the description to the aforementioned table 1, the binder 2, DPHA liquid, 2-trichloromethyl 5-(p-styryl methyl)-1, 3, 4-oxadiazole, 2,4-bis(trichloromethyl)-6-[4-(N,N-diethoxy carbonylmethyl)-3-bromophenyl]-s-triazine, And measure phenothiazin, add in this order at the temperature of 24 degrees C (**2 degrees C), and it stirs for 30 minutes in 150r.p.m., The surfactant 1 of the quantity of the description to the aforementioned table 1 was measured, and it added at the temperature of 24 degrees C (**2 degrees C), stirred for 30 minutes in 30r.p.m., and obtained by filtering by nylon mesh #200.
[0210]
The details of each composition in the constituent R1 of the description to the aforementioned table 1 are as follows. Composition of the surfactant 1 is as stated above.
* Composition of R pigment dispersion thing 1
**C. 254--8.0 copies of I. pigment red
- 5-[3-oxo 2-[4-[3,5-bis(3-diethylamino propylamino carbonyl)phenyl] aminocarbonyl] phenylazo]-BUCHIRO ylamino benz imidazolone -- 0.8 copy
- Polymer [random copolymer (weight average molecular weight 37,000) of benzyl methacrylate/methacrylic acid (= 72/28 [a mole ratio])] -- 8.0 copies
- Propylene-glycol-monomethyl-ether acetate -- 83.2 copies
[0211]
* Composition of R pigment dispersion thing 2
**C. 177--18 copies of I. pigment red
- Polymer [random copolymer (weight average molecular weight 37,000) of benzyl methacrylate/methacrylic acid (= 72/28 [a mole ratio])] -- 12 copies
- Propylene-glycol-monomethyl-ether acetate -- 70 copies
* Composition of the binder 2
- Random copolymer of benzyl methacrylate / methacrylic acid / methyl methacrylate (=38/25/37 [a mole ratio]) (weight average molecular weight 30,000) -- 27 copies
- Propylene-glycol-monomethyl-ether acetate -- 73 copies

* Additive agent 1 : phosphoric ester system special active agent (HIPLAAD ED152, made in Kusumoto Chemicals)
* Composition of DPHA liquid
- Dipentaerythritol hexaacrylate (trade name: KAYARAD DPHA, Nippon Kayaku Co., Ltd. make) -- 76 copies
- Propylene glycol monomethyl ether -- 24 copies
[0212]
<Preparation of the coloring photosensitive resin composition G1>
The coloring photosensitive resin composition G1 measures G pigment dispersion thing 1, Y pigment dispersion thing 1, and propylene-glycol-monomethyl-ether acetate of quantity of the description to the aforementioned table 1, Mix at the temperature of 24 degrees C (**2 degrees C), and in 150r.p.m., stir for 10 minutes and it ranks second, Methyl ethyl ketone of the quantity of the description to the aforementioned table 1, cyclohexanone, the binder 1, DPHA liquid, 2-trichloromethyl 5-(p-styryl methyl)-1, 3, 4-oxadiazole, 2,4-bis(trichloromethyl)-6-[4-(N,N-diethoxy carbonylmethyl)-3-bromophenyl]-s-triazine, And measure phenothiazin, add in this order at the temperature of 24 degrees C (**2 degrees C), and it stirs for 30 minutes in 150r.p.m., The surfactant 1 of the quantity of the description to the aforementioned table 1 was measured, and it added at the temperature of 24 degrees C (**2 degrees C), stirred for 5 minutes in 30r.p.m., and obtained by filtering by nylon mesh #200.
[0213]
The details of each composition in the constituent G1 of the description to the aforementioned table 1 are as follows. It is as the previous statement about composition of DPHA liquid and the surfactant 1.
* Composition of G pigment dispersion thing 1
**C. 36--18 copies of I. pigment green
- Polymer [random copolymer (weight average molecular weight 37,000) of benzyl methacrylate/methacrylic acid (= 72/28 [a mole ratio])] -- 12 copies
- Cyclohexanone -- 35 copies
- Propylene-glycol-monomethyl-ether acetate -- 35 copies
* Y pigment dispersion thing 1
Trade name: CF yellow EX3393 (made by a country pigment company)
* Binder 1
- Polymer [random copolymer (molecular weight 40,000) of benzyl methacrylate/methacrylic acid (= 78/22 [a mole ratio])] -- 27 copies
- Propylene-glycol-monomethyl-ether acetate -- 73 copies
[0214]
<Preparation of the coloring photosensitive resin composition B1>
The coloring photosensitive resin composition B1 measures B pigment dispersion thing 1, B pigment dispersion thing 2, and propylene-glycol-monomethyl-ether acetate of quantity of the description to the aforementioned table 1, Mix at the temperature of 24 degrees C (**2 degrees C), and in 150r.p.m., stir for 10 minutes and it ranks second, Methyl ethyl ketone of the quantity of the description to the aforementioned table 1, the binder 3, DPHA liquid, Measure 2-trichloromethyl 5-(p-styryl methyl)-1,3,4-oxadiazole and phenothiazin, and it adds in this order at the temperature of 25 degrees C (**2 degrees C), Further, the surfactant 1 of the quantity of the description to the aforementioned table 1 was measured, and it added at the temperature of 24 degrees C (**2 degrees C), stirred [it stirred for 30 minutes in 150r.p.m. with the temperature of

40 degrees C (**2 degrees C), and] for 5 minutes in 30r.p.m., and obtained by filtering by nylon mesh #200.
[0215]
The details of each composition in the constituent B1 of the description to the aforementioned table 1 are as follows. It is as the previous statement about composition of DPHA liquid and the surfactant 1.
* B pigment dispersion thing 1
Trade name: CF blue EX3357 (made by a country pigment company)
* B pigment dispersion thing 2
Trade name: CF blue EX3383 (made by a country pigment company)
* Composition of the binder 3
- Random copolymer of benzyl methacrylate / methacrylic acid / methyl methacrylate (=36/22/42 [a mole ratio]) (weight average molecular weight 30,000) -- 27 copies
- Propylene-glycol-monomethyl-ether acetate -- 73 copies
[0216]
(Working example 3)
In the working example 2, the black image of the light sheilding was formed on the glass substrate like the working example 2 except having replaced the slit & spin coater with coating-machine MH-1600 [provided with the slit shaped nozzle] (made in F Ey S Japan) for glass substrates.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration per unit thickness (thickness of transmitted light study concentration / black-photosensitive-resin layer) was 6.7. The same evaluation as the working example 1 was performed. However, formation of the color filter was performed as follows.
[0217]
<Production of a light filter (production by the application using a slit shaped nozzle)>
It is made to be the same as that of the working example 2 except having replaced the slit & spin coater with coating-machine MH-1600 [provided with the slit shaped nozzle] (made in F Ey S Japan) for glass substrates in production of the color filter of the working example 2, The color filter was formed in the glass substrate in which the light-shielding film (black image of a light sheilding) obtained from the above was formed.
[0218]
(Working example 4)
In the working example 1, 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers>, 41 copies of Ag particles (mean particle diameter of 80 nm), and carbon black (CB) Replace with 1.76 copies (addition volume ratio (Ag/CB) = 80/20), and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 0.70 micrometer.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration per unit thickness (thickness of transmitted light study concentration / black-photosensitive-resin layer) was 5.7. The same evaluation as the working example 1 was performed.
[0219]
(Working example 5)

In the working example 1, 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers>, 25.7 copies of Ag particles (mean particle diameter of 80 nm), and carbon black (CB) Replace with 4.4 copies (addition volume ratio (Ag/CB) = 50/50), and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 0.90 micrometer.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration per unit thickness (thickness of transmitted light study concentration / black-photosensitive-resin layer) was 4.4. The same evaluation as the working example 1 was performed.
[0220]
(Working example 6)
In the working example 1, 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers>, 10.3 copies of Ag particles (mean particle diameter of 80 nm), and carbon black (CB) Replace with 7.04 copies (addition volume ratio (Ag/CB) = 20/80), and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 1.00 micrometers.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration per unit thickness (thickness of transmitted light study concentration / black-photosensitive-resin layer) was 4.0. The same evaluation as the working example 1 was performed.
[0221]
(Working example 7)
In the working example 1, replace 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers> with 51.3 copies of the silver / silver sulfide core shell particles (mean particle diameter of 90 nm) which were obtained from the following, and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 0.80 micrometer.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 3.9, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 4.9. The same evaluation as the working example 1 was performed.
[0222]
<Production of silver / silver sulfide core shell particles>
0.95g added to 200 g of the silver granule child's acetone dispersed matters (mean particle diameter of 30 nm, concentration 2.5 mass %), and vinyl pyrrolidone/vinyl acetate copolymer (= 60/40 [a mass ratio], weight average molecular weight 5000) was stirred for 30 minutes to them. Subsequently, stirring, the sodium sulfide aqueous solution (23 degrees C) of the concentration 7.2 mass % was added to this so that the metaled rate of sulfuration might be 30%, stirring was performed to it for 30 minutes as it was after the end of addition, and silver / silver sulfide core shell particles with the shell of a silver sulfide were obtained.
Here, the rate of sulfuration is the ratio, sulfuration [metal particles], and 0% of the rate of sulfuration expresses the state where the whole particle is a sulfide completely 100% about the state, sulfuration at all.

[0223]
(Working example 8)
In the working example 1, replace 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers> with 51.3 copies of Sn particles (the mean particle diameter of 36 nm, 20 nm of minor axes, 50 nm of major axes), and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 0.90 micrometer.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 4.4. The same evaluation as the working example 1 was performed.
[0224]
(Working example 9)
In the working example 1, replace 51.3 copies of Ag particles under <composition of the coating liquid for black-photosensitive-resin layers> with 51.3 copies of Ag particles (the mean particle diameter of 117 nm, 60 nm of minor axes, 180 nm of major axes), and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 0.80 micrometer.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 4.0, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 5.0. The same evaluation as the working example 1 was performed.
[0225]
(Comparative example 1)
In the working example 1, replace the Ag particle (51.3 copies) under <composition of the coating liquid for black-photosensitive-resin layers> with carbon black (21.17 copies), and replace methacrylic acid / benzyl methacrylate copolymer with an acrylic resin, and. The black image of the light sheilding was formed on the glass substrate like the working example 1 except the dry layer thickness of the formed black-photosensitive-resin layer having been 1.50 micrometers.
The transmitted light study concentration measured like the working example 1 of a black-photosensitive-resin layer was 3.5, and the transmitted light study concentration (thickness of transmitted light study concentration / black-photosensitive-resin layer) of per unit thickness (1 micrometer) was 2.3. The same evaluation as the working example 1 was performed.
[0226]
[Table 2]

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		種	添加体積比	添加体積比							光学濃度	
実施例1	（転写法）	Ag粒子	100%	0%	80			0.60	12	4.0	6.7	6
実施例2	（塗布法）スリット&スピンコート	Ag粒子	100%	0%	80			0.60	12	4.0	6.7	6
実施例3	（塗布法）スリットコート	Ag粒子	100%	0%	80			0.60	12	4.0	6.7	6
実施例4	（転写法）	Ag粒子	80%	20%	80			0.70	12	4.0	5.7	6
実施例5	（転写法）	Ag粒子	50%	50%	80			0.90	12	4.0	4.4	6
実施例6	（転写法）	Ag粒子	20%	80%	80			1.00	12	4.0	4.0	6
実施例7	（転写法）	銀-硫化銀コアシェル	100%	0%	90			0.80	12	3.9	4.9	6
実施例8	（転写法）	Sn粒子	100%	0%	36	20	50	0.90	12	4.0	4.4	6
実施例9	（転写法）	Ag粒子	100%	0%	117	60	180	0.80	12	4.0	5.0	6
比較例1	（転写法）	—	0%	100%	—			1.50	30	3.5	2.3	20

※　添加体積比（%）の計算は、銀の比重を10．5とし、カーボンブラックの比重を1．8とし、その他を1．0として行な

[0227]
As shown in the aforementioned table 2, in the working example, performing after-exposure bake for a short time, the black image of high resolution could be formed, and the formed black image has the high concentration of 4.0, and was also able to raise the concentration per unit volume. There is also no display unevenness and the good display image was obtained.
On the other hand, in the comparative example 1 which constituted only carbon black not using metal particles, it became obtaining it being not only low but this concentration with the thick film, and after-exposure bake took the long time to the concentration of the black image, and it was inferior also to the resolution of the formed black image, and display unevenness.
[0228]
In addition to the above-mentioned working example, it is also the same as when it is made to heat before exposure (bake), and it is also the same as when it is made to heat after developing negatives after exposure (bake).

[Translation done.]

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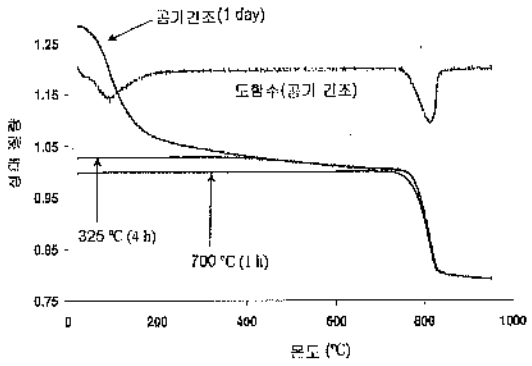
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(54) 용액 처리된 박막들 및 적층체들, 상기 박막들 및적층체들을 포함하는 장치들, 및 그들의 사용 방법 및 제조방법

(57) 요 약

하프늄 및/또는 지르코늄 옥시 하드록시 화합물들을 포함하는 박막 또는 적층체 구조물을 갖는 소자들 및 그러한 소자들의 제조 방법이 개시된다. 상기 하프늄 및 지르코늄 화합물들은 란탄과 같은, 통상 다른 금속으로 도핑될 수 있다. 제조될 수 있는 전자 소자 또는 부품의 예는, 절연체, 트랜지스터 및 캐패시터를 포함하지만 여기에 한정되지 않는다. 포지티브 또는 네거티브 레지스트를 사용하여 소자를 패터닝하기 위한 방법이 설명된다. 예를 들면, 임프린트 리소그레피에 대하여 마스터 플레이트가 사용될 수 있다. 부식 장벽을 갖는 소자를 제조하기 위한 방법의 구현에도 설명된다. 광학 기판과 코팅을 포함하는 광학 소자의 구현예들도 설명된다. 전자 현미경을 이용하여 치수를 정확하게 측정하기 위한 것과 같은 물리적 자의 구현예도 설명된다.

대 표 도 - 도1



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특허청구의 범위

청구항 1

하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) 화합물 중에서 적어도 하나를 포함하는 박막 또는 적층체 구조물을 포함하는 소자.

(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음)

청구항 2

제 1 항에 있어서,

상기 박막 또는 적층체가 약 9 내지 약 12의 범위에서 값을 갖는 유전율, 적어도 6 MV cm^{-1}까지의 항복 전계, 및 1 MV cm^{-1}의 전계 강도에서 거의 1 nA cm^{-2}의 누설 전류를 갖는 것을 특징으로 하는 소자.

청구항 3

제 1 항에 있어서,

상기 화합물이 란탄을 더 포함하고, 화학식 $M_{1-z}La_zO_{2-x-z/2}(SO_4)_x$ (MSOx:La)를 갖는 것을 특징으로 하는 소자.(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 약 3.8의 범위에서 어떤 값이든 가질 수 있음)

청구항 4

제 1 항에 있어서,

상기 화합물이 HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, 또는 ZircSOx:Ca이고, 상기 소자가 50 nA cm^{-2} 미만의 누설 전류와 약 9 내지 약 12의 값을 갖는 유전율을 갖는 것을 특징으로 하는 소자.

청구항 5

제 1 항에 있어서,

상기 소자가 HafSOx:La 및/또는 ZircSOx:La을 게이트 유전체로서, 아연 인듐 산화물 및/또는 아연 주석 산화물을 채널로서 포함하는 전계효과 트랜지스터이고, 상기 트랜지스터가 10^6보다 큰 온-투-오프 비율(on-to-off ratio) 및 pA cm^{-2} 범위의 값을 갖는 게이트 누설 전류를 갖는 것을 특징으로 하는 소자.

청구항 6

제 1 항에 있어서,

광학 기판을 더 포함하고, 상기 박막 또는 적층체 구조물이 상기 광학 기판 위에 코팅을 형성하는 것을 특징으로 하는 소자.

청구항 7

제 6 항에 있어서,

상기 코팅이 반사방지 코팅이고, 및/또는 상기 코팅이 가시광선 또는 자외선에 대하여 투명한 것을 특징으로 하는 소자.

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청구항 8

제 6 항에 있어서,

상기 광학 기판과 코팅이 유전체 거울(dielectric mirror), X-선 거울, 간섭 필터, 회절 격자, 및/또는 도파로(waveguide)를 정의하는 것을 특징으로 하는 소자.

청구항 9

제 7 항에 있어서,

상기 코팅이 Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+} 및 이들의 조합으로부터 선택되는 발광성 이온을 포함하는 도핑된 발광층을 제공하기 위하여, 선택적으로 도핑된 것을 특징으로 하는 소자.

청구항 10

제 1 항에 있어서,

상기 소자가 임프린트 리소그래피를 위한 마스터 플레이트이고, 상기 박막 또는 적층체 구조물이 가요성 또는 유리 기판 위에 증착되고, 상기 박막 또는 적층체 구조물이 상기 기판 위에 증착된 HafSOx의 제1층과 ZircSOx:Cu를 포함하는 제2층을 포함하고, 상기 제1층 및 제2층을 포함하는 적층체 구조물이 에너지 공급원에 노출됨으로써 패터닝되는 것을 특징으로 하는 소자.

청구항 11

제 10 항에 있어서,

마스크를 통해 및 또는 전자빔에 노출시키는 것이 상기 두 층들의 상호확산(interdiffuse)을 노출된 영역에서 일으키고, 그에 의하여 노출 이전에는 도핑되지 않았던 HafSOx 층을 가용하게(soluble) 만들고, 가용하게 된 상기 HafSOx 층이 제거되어 상기 마스터 플레이트의 적어도 부분적인 프린팅 구조물을 정의하는 것을 특징으로 하는 소자.

청구항 12

박막 또는 적층체 구조물을 제공하는 단계; 및

상기 구조물을 에너지 공급원에 노출시키는 단계;

를 포함하고,

상기 구조물은 기판과 상기 기판 위에 증착된 하나 또는 그 이상의 층들을 포함하고,

상기 하나 또는 그 이상의 층들의 적어도 하나는 하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 ($MO_{3-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-5x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) 화합물을 포함하는 소자의 제조 방법.

(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음)

청구항 13

제 12 항에 있어서,

상기 박막 또는 적층체 구조물은 기판, 패터닝을 위한 제1층, 및 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 제2층을 포함하고, 상기 제2층은 포지티브 레지스트층으로서 에너지 공급원에 노출되면 상기 레지스트층 물질이 현상액에 녹을 수 있는 물질로 전환되고,

상기 구조물을 패터닝하기 위하여 상기 레지스트층을 현상액으로 처리함으로써 상기 에너지 공급원에 노출된 레

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지스트층 물질을 제거하는 단계를 더 포함하는 것을 특징으로 하는 방법.

청구항 14

제 12 항에 있어서,

상기 박막 또는 적층체 구조물은 기판, 패터닝을 위한 제1층, 및 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 제2층을 포함하고, 상기 제2층은 네거티브 레지스트층으로서 에너지 공급원에 노출되면 상기 레지스트층이 중합되고,

상기 에너지 공급원에 노출되지 않은 물질을 제거하기 위하여 현상물질(developer)로 상기 구조물을 처리함으로써 상기 구조물을 패터닝하는 단계를 더 포함하는 것을 특징으로 하는 방법.

청구항 15

제 13 항에 있어서,

상기 포지티브 레지스트가 이중층(bilayer)을 포함하고, 상기 이중층의 제2층이 불용성 하프늄 옥사이드 설페이드(HafSOx) 막 위에 증착되고 산에 녹을 수 있으며 Cu-도핑된 지르코늄 옥사이드 설페이트(ZircSOx:Cu) 막을 포함하고,

마스크를 통해 빛 또는 전자빔을 포함하는 에너지 공급원에 노출시키는 것이 상기 ZircSOx:Cu 막과 상기 HafSOx 막의 상호확산을 노출된 영역에서 일으키고, 그에 의하여 HafSOx 막을 가용하게 만드는 것을 특징으로 하는 방법.

청구항 16

제 12 항에 있어서,

상기 하프늄 및/또는 지르코늄 옥시 히드록시 화합물이 설페이드를 포함하고, 상기 설페이트가 염기성 수용액과의 이온 교환에 의하여 후속 제거되고, 상기 염기성 용액이 1족 금속 히드록사이드, 가용성 2족 금속 히드록사이드, 가용성 3족 금속 히드록사이드, 가용성 란탄계 히드록사이드, 암모늄 히드록사이드 및/또는 수성(aqueous) 3차 아민, 또는 이들의 조합을 포함하는 것을 특징으로 하는 방법.

청구항 17

제 12 항에 있어서,

반도체 물질, 금속, 유리, 실리카, 고분자 물질, 또는 이들의 조합을 포함하는 적절한 기판을 제공하는 단계;

상기 기판 위에 HafSOx의 제 1 막을 용액 증착하는 단계;

적층체 구조물을 형성하기 위하여, 상기 제 1 막 위에 ZircSOx:Cu의 제 2 막을 용액 증착하는 단계;

상기 HafSOx 막과 상기 ZircSOx:Cu 막이 노출된 영역에서 상호확산하고 그에 의하여 노출 이전에는 도핑되지 않았던 HafSOx 막을 가용하게 만들기 위해, 상기 적층체 구조물을 에너지 공급원에 노출시키는 단계; 및

HafSOx 막을 제거하기 위하여 상기 노출된 구조물을 현상하는 단계;

를 포함하는 것을 특징으로 하는 방법.

청구항 18

제 12 항에 있어서,

상기 박막 또는 적층체 구조물이 기판, 상기 기판 위에 증착된 불용성 하프늄 옥사이드 설페이트(HafSOx)의 제 1 층, 및 상기 제 1 층 위에 증착되고 포름산 구리염(copper formate)을 포함하는 제 2 층을 포함하고,

상기 포름산 구리염의 분해와 상기 HafSOx 층과의 상호확산을 유발하고 그에 의하여 가용성 생성물을 생성하고 상기 가용성 생성물을 제거하기 위해, 상기 제 1 층 및 제 2 층을 포함하는 상기 적층체 구조물이 약 50 ℃ 내지 약 200 ℃의 온도로 가열되는 것을 특징으로 하는 방법.

청구항 19

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제 12 항에 있어서,

상기 박막 또는 적층체 구조물이 기판 및 고체 무기 산 또는 염기를 포함하는 제 1 층을 포함하고, 상기 고체 무기 산 또는 염기가 21번 내지 78번 범위의 원자 번호를 갖는 금속을 포함하고, 상기 제 1 층이 과산화물 또는 다른 배위 음이온을 더 포함하고, 상기 제 1 층이 산 또는 염기에 가용하며,

구조적으로 단단한 막을 제조하기 위하여 약 50 ℃ 내지 약 125 ℃의 온도로 상기 제 1 층이 가열되고, 마스크를 통하여 레이저, 전자빔 및/또는 빛에 노출시키는 것이 상기 막의 노출된 영역이 노출되지 않은 영역에 비하여 더 낮은 용해도를 갖도록 함으로써 노출되지 않은 영역이 제거되고 상기 막에 패턴이 생성되는 것을 특징으로 하는 방법.

청구항 20

제 19 항에 있어서,

상기 막에 패턴을 정의하기 위하여 상기 막이 0 $\mu C/cm^2$ 보다 크고 적어도 400 $\mu C/cm^2$까지의 도스 레벨, 더욱 일반적으로는 약 2 $\mu C/cm^2$ 내지 약 400 $\mu C/cm^2$의 도스 레벨로 전자빔에 노출되는 것을 특징으로 하는 방법.

청구항 21

제 19 항에 있어서,

패터닝된 상기 막이 약 3 nm 미만의 구조적 집적도(integrity)를 보이는(demonstrate) 것을 특징으로 하는 방법.

청구항 22

제 12 항에 있어서,

상기 소자가 마이크로- 또는 나노-채널 어레이를 포함하고, 상기 구조물이 기판, 제 1 층, 및 제 2 층을 포함하고, 상기 제 2 층은 금속 산화물 층이고, 상기 방법이

상기 구조물을 패터닝하는 단계; 및

상기 구조물을 패터닝함으로써 생성된 원하는 패턴을 갖는 내구성이 있는 물질을 형성하기 위하여 상기 구조물을 에너지 공급원에 노출시키는 단계;

를 더 포함하는 것을 특징으로 하는 방법.

청구항 23

제 22 항에 있어서,

스탬핑(stamping)된 층을 형성하기 위하여 반-고체(semi-solid) 하프늄 또는 지르코늄 화합물에 원하는 크기 스케일의 단위 지형물(feature)들을 스탬핑하는 단계를 더 포함하는 것을 특징으로 하는 방법.

청구항 24

상기 소자가 금속 및 금속/세라믹-계 열 보호(thermal protection) 시스템, 유기계 디스플레이 및 전자 제품, 태양 전지, 고 방사율(emissivity) 코팅, 산화물계 세라믹 매트릭스 시스템에 대한 계면 코팅, 인광체(phosphor) 위의 보호 코팅, 금속- 및 세라믹계 시스템에 대한 주변적 장벽 코팅, 복합체 및 섬유 레이저용 섬유, 용해 금속 처리에서의 부식 방지, 단열용 모노리딕 물질 및 촉매 담체로부터 선택되고, 청구항 22의 방법에 의하여 제조되는 소자.

청구항 25

소자를 제공하는 단계;

하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 ($MO_{2-3x/2-$

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$_{z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 하드록시 포스페이트 ($MO_{2-2x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 하드록시 실리케이트 ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) 화합물을 포함하는 금속 산화물 층을 포함하는 소자 위에 적어도 하나의 부식 장벽을 형성하는 단계(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음); 및

상기 부식 장벽을 형성하기 위해 상기 화합물을 에너지 공급원에 노출시키는 단계;

를 포함하는 부식 장벽을 갖는 소자의 제조 방법.

청구항 26

하프늄 및/또는 지르코늄 옥시 하드록시 설페이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 하드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 하드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 하드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 하드록시 실리케이트 ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) 화합물을 포함하는 조성물을 제공하는 단계(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음);

상기 화합물을 포함하는 용액을 형성하는 단계;

상기 용액을 섬유들(fibers) 내부로 인입시키는 단계; 및

상기 섬유들을 고체로 전환시켜 안정한 섬유로 만드는 단계;

를 포함하는 섬유의 제조 방법.

청구항 27

적어도 두 금속을 포함하는 금속 산화물 막의 제조 방법으로서,

용액을 제조하는 단계로서, 금속 양이온 및 하나 또는 그 이상의 음이온으로 필수적으로 구성되는 하나 또는 그 이상의 가용성 염을 착화합물을 형성하지 않는(non-complexing) 비수계 극성 용매에 용해시키는 단계를 포함하고, 금속 양이온들의 적어도 하나가 3+보다 큰 형식 전하를 갖고, 3+보다 큰 형식 전하를 갖는 금속 양이온들의 농도가 상기 금속 산화물 막 내의 금속 양이온들의 50 몰%를 초과하고, 상기 용매가 150 ℃ 미만의 끓는점을 갖는, 용액을 제조하는 단계;

상기 용액의 pH를 증가시키되, 상기 pH를 증가시키는 단계는 염기성 수용액을 첨가하는 단계, 가용성 염기 산화물을 소량 첨가하는 단계, 염기성 수용액을 형성할 수 있는 기체 화합물을 첨가하는 단계, 양성자를 소비할 수 있고 상기 막 내에 통합되는 양전성(electropositive) 금속을 첨가하는 단계, 양성자를 소비하거나 상대 이온(counter ion)을 분해하지만 상기 막 내에 통합되지 않는 수계 또는 기체 산화제를 첨가하는 단계, 또는 이들 단계들의 조합을 포함하는, 상기 용액의 pH를 증가시키는 단계;

상기 비수계 용매를 증발시킴으로써 고체를 제조하는 단계;

상기 고체를 물에 용해시키는 단계;

패터닝된 또는 블랭킷 액막을 형성하기 위해 상기 용해된 고체를 기판 위에 증착하는 단계; 및

상기 막을 열적으로 경화하는 단계;

를 포함하는 금속 산화물 막의 제조 방법.

명 세 서

기 술 분 야

<I> 본 개시는 전자 및 광학적 응용을 포함하는 목적들에 대하여 공간적으로-정의되는 구조물을 만드는 데 유용한

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무기 금속 산화물 물질을 포함하는 소자들 및 특징들의 구현예들 및 그들의 제조 방법 및 사용 방법의 구현예들에 관한 것이다.

<2> <관련 출원의 상호 참조>

<3> 본 출원은 2006년 11월 1일에 출원되었고, 그 전부가 여기에 인용되어 통합되는 미합중국 비정규출원 제60/856,070호의 선행 출원일의 이익을 주장한다.

<4> <정부 지원의 감사>

<5> 본 개시의 구현예들은 DARPA 보조금 번호 HR0011-06-1-0045의 연방 기금을 이용하여 개발되었다. 미합중국 정부는 본 발명의 특정 권리를 갖는다.

배경 기술

<6> 전자 소자들은 일반적으로 물질의 순차적인 증착 및 식각과 같은 반복적인 공정 단계들을 이용하여 제조된다. 무기 물질들을 포함하는 소자들에 있어서, 금속-유기 전구체들이 무기 산화물들의 용액-기반(solution-based) 증착에 대하여 널리 사용되어 왔다. 유기 모이어티(moiety)의 존재는 유기 물질의 제거를 위해 고온 소각(burnout) 단계가 필요하게 한다. 이 단계는 상당한 부피 변화, 결정화 및 "머드 크래킹(mud cracking)"이라고 하는 현상을 일으킬 수 있다. 이와 관련된 결함들이 이 물질들의 피복으로서의 그리고 소자들 내에서의 성능을 저해한다.

<7> 전자 소자 응용에 있어서 용액 처리 물질을 위한 방법들이 특허받아 왔다. 예를 들면, Ostergard의 미합중국 특허 제6,946,677호 "Pre-Patterned Substrate for Organic Thin Film Transistor Structures and Circuits and Related Method for Making Same"은 원하는 회로구성을 기판의 표면에 형성하는 단계, 및 그에 의하여 유기박막 트랜지스터(OTFT: organic thin film transistor) 구조 및 상호 연결하는 도전성 경로들을 형성하기에 유용한 물질을 수용하기 위해 상기 영역을 예비-패터닝(pre-patterning)하는 단계를 설명한다. 상기 미합중국 특허 제6,946,677호에 따르면, OTFT 물질은 잉크젯 프린팅과 같은 프린팅 기술을 이용하여 예비-패터닝된 영역에 증착된다.

<8> Weng 등의 미합중국 특허 제6,927,108호는 트랜지스터를 형성하기 위한 박막 물질들의 용액 처리를 설명한다. 상기 미합중국 특허 제6,927,108호는 "트랜지스터 동작이 가능한 용액-처리된 박막 구조를 형성하기 위해 순차적으로 조작화된 도전성 용액-처리된 박막 물질 콘택들, 반도체 용액-처리된 박막 물질 활성 영역들, 및 유전 용액-처리된 박막 물질 절연들"을 형성하는 단계를 설명한다.

<9> 미합중국 특허공개 제2005/0242330A1호는 전자 응용에 유용한 하프늄 및 지르코늄 화합물들에 관한 것으로서, 여기에 인용되어 통합된다. 미합중국 특허공개 제2005/0242330A1호는 발명자로서 Douglas Keszler 박사를 지명하고 있으며 그는 여기에 개시된 구현예들의 발명자이기도 하다.

발명의 상세한 설명

<10> 미합중국 특허공개 제2005/0242330A1호는 선행 기술의 결함을 해결하는 방식으로 무기 화합물의 용액 증착과 화합물을 개시한다. 예를 들면, 본 발명에 따른 용액 증착은 금속-유기 증착 기술에 대하여 요구되는 유기 물질의 사용을 피할 수 있고, 따라서 유기물질의 소각(burnout)을 피할 수 있고, 소각에 따라 관련되는 크래킹 문제를 피할 수 있다.

<11> 본 발명의 일 구현예는 하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-5x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{3-2x-z/2}(OH)_z(SiO_4)_x$) 화합물 중에서 적어도 하나를 포함하는 박막 또는 적층체 구조물을 포함하는, 전자 소자와 같은, 소자에 관한 것이다. 여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있다. x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있다. 예를 들면, 옥시 히드록시 설페이트 화합물들과 같이 전하가 2인 다원자 이온에 대해서는 x는 약 0.1 내지 약 1.75의 범위 내에서 어떠한 값이든 가질 수 있다. z는 0.0 내지 약 3.8의 범위에서 어떤 값이든 가질 수 있다.

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<12> 특정 구현예들은 화학식 $(MO_{2-x-z/2}(OH)_z(SO_4)_x)$를 갖는 하프늄 또는 지르코늄 옥시 히드록시 설페이트 화합물을 포함하는 박막 또는 적층체에 관한 것이다. (여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 1.75의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 약 3.8의 범위에서 어떤 값이든 가질 수 있음) 이들 화합물들은 HafSOx 및 ZircSOx로 불리기도 한다. 상기 하프늄 및 지르코늄 화합물들은 통상 칼슘, 세륨, 란탄, 또는 이들의 조합과 같은 다른 금속들로 도핑될 수도 있다. 특정 구현예들은 화학식 $M_{1-x}La_yO_{2-x-z/2-y/2}(OH)_z(SO_4)_x$ (MSOx:La)를 갖는 화합물을 제조하기 위해 도펀트로서 란탄을 사용하였다. 여기서, 조성과 양론은 위에서 언급한 바와 같다. 란탄-도핑된 화합물의 특정 예는 $Hf_{0.63}La_{0.32}O_{1.04}(SO_4)_{0.36}$이다. 추가적인 예시적인 화합물들은 HafSOx:La, ZircSOx:La, HafSOx:Ce, 또는 ZircSOx:Ca를 포함한다. 특정 구현예에서, 설페이트는 수성 염기와의 이온 교환을 통해 후속적으로 제거되고, M(OH)x 또는 MOx 막을 가져오게 된다. 적합한 수성 염기들은, 무엇보다도, 1족 금속 히드록사이드들, 2족 금속 히드록사이드들, 3족 금속 히드록사이드들, 란탄화 히드록사이드들, 암모늄 히드록사이드, 및/또는 수성 3차 아민류를 포함한다.

<13> 특정 구현예들은 둘 또는 그 이상의 금속을 갖는 착체(complex) 조성물을 포함하는 얇은 산화물 막 또는 적층체들에 관한 것이다. 상기 금속 양이온들의 적어도 하나는 3+보다 큰 전하를 갖고, 3+보다 큰 전하를 갖는 양이온들의 총 농도는 목표 산화물 내의 금속 양이온들의 50 몰%를 넘는다. 용해된 염들과 소정량의 물을 포함하는 비-수계 용액이 제조된다. 물의 양은 비-수계 용매의 20 몰% 미만이다. 상기 용액의 pH는 염기를 첨가함에 의하여 또는 산화-환원 메커니즘을 통한 자유 양성자의 반응에 의하며 최초 용액에 비하여 증가된다. 최종 용액의 pH는 사용되는 금속 양이온에 의존하지만, 약 2 내지 9의 범위에 있을 것이다. 증가된 pH는 양이온에 결합된 물 분자들의 가수분해와 그 결과로서 얻어지는 이들 히드록소-양이온들의 응축을 가져온다. 상기 용매는 증발되고, 그 결과 교체는 물에 용해 또는 분산되게 되고 이어서 기판에 액체 막으로서 적용된다. 그런 후, 상기 액체 막은 100 ℃ 내지 600 ℃ 사이의 온도에서 약 5 분 내지 240 분 동안 열적으로 경화된다.

<14> 본 발명에 따라 제조될 수 있는 전자 소자들 또는 소자 부품들의 예는 전계 효과 트랜지스터에서 게이트 절연막과 같은 절연체류, 전계 효과 트랜지스터와 같은 트랜지스터류, 및 MIM 캐패시터와 같은 캐패시터류를 포함하지만 여기에 한정되지 않는다. 본 구현예에 따라 제조된 박막들 및 적층체들은 약 9 내지 약 12의 범위에서 유전률 값을 갖고, 적어도 3 MV cm^{-1}에서 약 6 MV cm^{-1}까지의 항복 전계를 갖고, 1 MV cm^{-1}의 전계 강도에서 거의 1 nA cm^{-2}의 누설 전류를 가졌다. ZircSOx:Ca를 이용하여 제조한 소자들은 약 3.6 MV cm^{-1}의 항복 전계, 약 50 nA cm^{-2} 미만, 더욱 전형적으로는 약 10 nA cm^{-2} 미만의 누설 전류를 가졌다.

<15> HafSOx:La 및/또는 ZircSOx:La를 게이트 유전체 물질로서 이용하여 전계 효과 트랜지스터들을 제조할 수 있다. 개시된 특정 구현예들은 채널로서 아연 인듐 산화물 및/또는 아연 주석 산화물을 사용하였다. 특정 전계 효과 트랜지스터들은 10^6보다 큰 온-투-오프 비율(on-to-off ratio), 및 nA cm^{-2}의 게이트 누설 전류를 가졌다.

<16> 본 발명의 또 다른 구현예는 포토레지스트를 이용하여 소자를 패터닝하는 방법에 관한 것이다. 본 방법의 특정 구현예는 먼저 패터닝된 구조물을 제공하는 단계를 포함한다. 상기 구조물은 통상 반도체 물질, 금속, 유리, 고분자 물질, 또는 이들의 조합과 같은 기판; 실리카와 같이, 패터닝을 위한 물질층; 및 레지스트 층을 포함한다. 상기 레지스트 층은 통상 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함한다. 상기 구조물은 전자빔 또는 빛, 특히 예를 들면 자외선 광과 같은 에너지 공급원에 노출된다. 그런 후, 상기 소자를 패터닝하기 위해 물질이 제거되거나 소자의 활성, 패터닝된 부품으로서 유지된다.

<17> 상기 레지스트는 포지티브 레지스트 또는 네거티브 레지스트일 수 있다. 예를 들면, 상기 방법은 상기 레지스트층을 에너지 공급원에 노출시켜 상기 레지스트 층 물질을 현상액(developer)에 용해될 수 있는 물질로 전환시키는 단계를 포함할 수 있다. 상기 현상액에 용해될 수 있는 물질은 그 후 현상액을 이용하여 제거된다. 적합한 현상액들은, 무엇보다도, 산, 염기, 및/또는 초음파 교반(ultrasonic agitation)을 포함할 수 있다. 다시 예로서, 상기 방법은 에너지 공급원에 노출된 레지스트층 물질을 제거하는 단계를 포함할 수 있다. 본 발명을 특정 작동 이론에 한정됨이 없이, 적어도 특정 구현예에 대하여, 에너지 공급원에 대한 노출은 레지스트 층의 중합을 일으킬 수 있고, 에너지 공급원에 노출되기 전에 비하여 현상액에 상대적으로 덜 용해되게 만들 수 있다.

<18> 포지티브 레지스트의 한 구현예는 이중층을 포함한다. 상기 이중층의 제1층은 하프늄 옥사이드 설페이트(HafSOx) 막 위에 증착된 포름산 구리의 막을 포함한다. 상기 포름산 구리의 막은 산에 가용성이고, 도핑되지 않은 HafSOx 박은 산에 불용성이다. 상기 이중층을 마스크를 통해 빛에 노출시키거나 포커스를 맞춘 전자빔에

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노출시키는 것은 노출된 영역에서 두 막들이 상호확산하도록 하며, 그에 의하여 그 이전에 도핑되지 않았던 HafSOx 막을 가용성이 되게 한다.

<19> 레지스트를 제조하기 위한 이중층 공정의 다른 구현에는 고체 산 또는 염기의 제 1 층을 기판 위에 증착하는 단계를 포함하고, 상기 산 또는 염기는 하나 또는 그 이상의 금속 원자를 포함한다. 포름산 구리와 같은 산화물 전구체를 포함하는 현탁액을 상기 제 1 층 위에 원하는 패턴으로 적용한다. 가열 조건 하에서, 상기 전구체는 분해되어 옥사이드가 된다. 이어서 상기 산화물은 상기 제 1 층과 반응 및 상호확산하여 식각을 통해 패턴을 드러낼 수 있는 생성물을 형성한다. 선택적인 구현에는 산화물 입자를 가열과 함께, 또는 가열하지 없이 상기 제 1 층 위에 증착하고, 식각될 수 있는 생성물을 형성하는 직접 반응을 가져오는 단계를 포함한다. 추가적인 구현에는 산화물 전구체의 박층을 상기 제 1 층 위에 증착하는 단계를 포함한다. 그런 후, 포토마스크를 통해 빛에 노출시키거나 또는 포커스를 맞춘 레이저 또는 전자빔으로 직접 기록함으로써 활성화된 전구체의 패턴이 형성된다.

<20> 본 발명의 또 다른 구현에는 임프린트 리소그래피를 위한 마스터 플레이트에 관한 것이다. 상기 마스터 플레이트는 가요성 또는 유리 기판과 같은 기판을 포함하고, 박막 또는 적층체 구조물의 적어도 한 층이 적어도 하나의 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함한다. 마스터 플레이트의 특정 구현에는 상기 기판 위에 증착된 HafSOx의 층과 ZircSOx:Cu 층과 같은 제 2 층을 포함한다. 상기 마스터 플레이트는 노출된 영역에서 두 막들이 상호확산하도록 하기 위하여 마스크를 통해 빛 또는 전자빔에 노출시키는 것과 같이 에너지 공급원에 노출시킴으로써 패턴될 수 있다. 이것은 이전에 도핑되지 않았던 HafSOx 막이 가용성이 되어, 제거됨으로써 마스터 플레이트의 프린팅 피처들을 적어도 부분적으로 정의한다.

<21> 또 다른 구현에서, 단일층 공정에서 본 발명의 막들을 이용하여 마스크 또는 템플릿을 제조할 수 있다. 고체 산 또는 염기와 같은, 무기 전구체의 박막이 퍼옥사이드 또는 유사한 옴이온과 함께 기판 위에 증착된다. 상기 막은 구조적으로 감식한 막을 생성하기 위해 가열된다. 그런 후, 노출된 영역에서 응축/가교를 유발하기 위해 포토마스크를 통해 또는 레이저 또는 전자빔을 통해 노출된다. 노출된 영역의 용해도는 노출되지 않은 영역에 비하여 감소된다. 그런 후, 노출되지 않은 영역은 선택적으로 식각되어 막 내에 네거티브-톤의 이미지를 생성할 수 있다. 노출시키기 전에 상기 막을 더 높은 온도로 예열함으로써 포지티브-톤의 이미지들도 형성될 수 있다. 일부 구현예들에서, HafSOx와 같은 막을 수산화나트륨과 과산화수소의 혼합물로 처리함으로써 $M(OH)_x/H_2O_2$ 막이 형성된다. 그런 후, 그 결과로서 얻어지는 막은 빛에 또는 전자빔에 노출시킴으로써 패터닝된다.

<22> 기판, 패터닝을 위한 물질층, 및 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 금속 산화물층을 포함하는 패터닝될 구조물을 제공하는 단계를 포함하는 소자의 형성 방법이 또한 설명된다. 상기 구조물은 패터닝되고 그런 후 에너지 공급원에 노출되어, 상기 구조물을 패터닝함으로써 생성된 원하는 패턴을 갖는 내구성이 있는 물질을 형성한다. 상기 방법에 따라 제조된 소자의 일구현에는 마이크로- 또는 나노-채널 어레이와 같은 채널 어레이를 포함할 수 있다. 그러한 구현예들에 대하여, 상기 소자를 만들기 위한 방법은 반-고체 하프늄 또는 지르코늄 화합물에 원하는 크기 스케일의 단위 패치들을 스탬핑하여 스탬핑된 층을 형성하는 단계를 포함할 수 있다.

<23> 부식 장벽을 갖는 소자를 제조하기 위한 방법의 구현에도 설명된다. 상기 방법의 개시된 구현예들은 소자를 제공하는 단계 및 상기 소자 위에 적어도 하나의 부식 장벽을 형성하는 단계를 포함한다. 부식 장벽은 통상 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 금속 산화물층을 포함한다. 상기 방법은 부식 장벽을 형성하기 위해 상기 화합물을 에너지 공급원에 노출시키는 단계를 포함할 수도 있다. 그러한 소자들의 예는 금속 및 금속/세라믹-계 열 보호(thermal protection) 시스템, 유기계 디스플레이 및 전자 제품, 태양 전지, 고 방사율(emissivity) 코팅, 산화물계 세라믹 매트릭스 시스템에 대한 계면 코팅, 인광체(phosphor) 위의 보호 코팅, 금속- 및 세라믹계 시스템에 대한 주변적 장벽 코팅, 복합체 및 섬유 레이저용 섬유, 용해 금속 처리에서의 부식 방지, 단열용 모노리딕 물질 및 촉매 담체를 포함한다.

<24> 섬유를 형성하기 위한 방법의 구현예도 설명된다. 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 용액이 형성된다. 그런 후, 상기 용액은 섬유 내부로 인입된다. 상기 섬유는 가수분해, 어닐링, 공기 열분해 및 이들의 조합과 같이 적절한 어떠한 방법에 의해서든 고체, 안정한 형태로 전환될 수 있다.

<25> 광학 소자의 구현예들도 또한 설명된다. 상기 소자의 특히 개시된 구현예들은 광학 기판과, 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물을 포함하는 기판 코팅을 포함한다. 상기 층은 반사방지 코팅일 수 있다. 상기 광학 기판 및 코팅은, 예를 들면, 유전체 거울(dielectric mirror), X-선 거울, 간섭 필터, 회절 격자, 및/또는 도파로(waveguide)를 정의할 수 있다. 상기 광학 소자는 시각적으로 투명하거나 또는 자외선 빛에 투명

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한 것과 같이 투명한 층을 포함할 수도 있다. 상기 층은 Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+} 및 이들의 조합으로부터 선택되는 발광 이온들을 갖는 도핑된 층을 제공하기 위해 선택적으로 도핑될 수 있다. 상기 층을 도핑하는 단계는 발광층을 생성하기 위해 사용될 수 있다.

<26> 물리적 자를 제조하기 위한 방법의 구현예들도 개시된다. 특정 구현예들은 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물의 용액 증착에 의하여 적어도 하나의 산-가용성 층을 형성하는 단계를 포함한다. 적어도 하나의 산-불용성 층이 상기 산-가용성 층에 인접하여 형성되고, 상기 산-불용성 층은 개시된 하프늄 및/또는 지르코늄 옥시 히드록시 화합물의 용액 증착에 의하여 형성된다. 이들 단계들의 반복은 교호하는 층들을 생성하고, 상기 방법은 교호하는 산-불용성 및 산-가용성 층들의 폭들을 정확하게 결정하는 단계를 포함한다. 폭의 결정은 X-선 반사와 같이 적절한 어떠한 방법을 이용해서든 달성될 수 있다. 게다가, 적어도 하나의 층이 식각되어 측정하는 목적물에 대하여 손가락 모양의 2차 참조 패턴을 정의한다. 그러한 소자의 특정 구현예들은 전자 현미경을 이용하여 치수를 정확하게 측정하는 데 유용하다.

<27> 본 발명의 위에서의 그리고 다른 목적들, 피처들 및 장점들은 첨부된 도면을 참조하여 진행되는 다음의 상세한 설명으로부터 더욱 명백해질 것이다.

<28> 본 발명의 개시된 구현예들은 무기 물질들의 용액 증착(solution deposition)에 의하여 제조될 수 있는, 전자 소자들 또는 전자 소자들의 부품들을 포함하는 소자들에 관한 것이다. 본 개시에 걸쳐서, 단수를 나타내는 "하나의(a, an)" 및 "상기"는 문맥상 명백히 달리 표시되지 않는 한 복수의 피지칭물(referent)도 포함한다. 유사하게, "또는"이라는 단어는 문맥상 명백히 달리 표시되지 않는 한 "및"을 포함함을 의도한다. "포함한다(include)"라는 표현은 "포함한다(comprise)"를 의미한다. 여기에 표시된 모든 백분율은 달리 표시되지 않는 한 원자 백분율(atomic percentage)이다. 여기에서 언급된 모든 특허들 및 공개문헌들은, 달리 표시되지 않는 한, 그 전부가 여기에 인용되어 통합된다. 상충되는 경우에는, 용어의 설명을 포함하여 본 명세서가 우선될 것이다. 여기에 언급된 물질들, 방법들 및 실시예들은 예시적인 것일 뿐이고, 한정의 의도는 아니다.

<29> **I. 금속 산화물 설페이트(sulfate) 물질들 일반 및 미합중국 특허공개 제2005/0242330A1호**

<30> 본 개시는, 통상 전자 응용에 유용한 금속 산화물 설페이트 무기 물질들의 용액 증착인, 무기 물질들의 용액 증착을 위한 방법의 구현예들에 관한 것이다. 이들 물질들의 구현예들은 미합중국 특허공개 제2005/0242330A1호에 설명되어 있다. 공개된 상기 출원의 특정 부분, 문단 0009 내지 문단 014가 아래에 부연된다. 부연된 이 본문에서 도면에 대한 참조부호는 미합중국 특허공개 제2005/0242330A1호에 공개된 도면들을 참조한다.

<31> 도 1은 유전 전구체 물질의 제조 공정의 일 구현예를 나타낸다. 일반적으로, 공정(10)은 금속-함유 양이온과 같은 제 1 반응물(12)을 제공하는 단계, 다원자(polyatomic) 음이온과 같은 제 2 반응물(14)을 제공하는 단계, 및 그런 후 상기 다원자 음이온과 상기 금속-함유 양이온을 반응시키는 단계를 포함한다. 상기 금속-함유 양이온 및 상기 다원자 음이온은 함께 반응하였을 때 수용액과 같은 용액으로 될 수 있다. 일 구현예에서, 상기 금속-함유 양이온은 하프늄 옥시 염화물($HfOCl_2(aq)$)와 같은 하프늄 옥시 할로겐화물의 수용액을 이용하여 제공될 수 있다. 설페이트(SO_4^{2-})와 같은 상기 다원자 음이온은 황산($H_2SO_4(aq)$)과 같은 수용액을 이용하여 제공될 수 있다. 이들 두 반응물들은 원하는 물질들을 만들기에 적합한 공정들과 상대적인 양들을 이용하여 함께 혼합될 수 있다.

<32> 상기 반응은 전구체 용액(16)을 생성할 수 있다. 전구체 용액(16)은 기판에 적용함으로써와 같이 원하는 대로 즉시 사용될 수 있다. 선택적으로, 전구체 용액(16)은 적어도 부분적으로 탈수된(dehydrated) 후 적용될 수 있다. 그런 후 위에서 주어진 예에서, 상기 전구체 용액은 하프늄 옥시-히드록시 설페이트($HfO_{2-x-z/2}(OH)_z(SO_4)_x$)를 형성할 수 있다. 본 화학식에서의 변수들에 있어서, x 및 z는 고정되거나 변화할 수 있으며, 어떤 값이든 가질 수 있다. 예를 들면, x의 값은 통상 약 0.1 내지 약 1.9이고, z의 값은 0.0 내지 약 2.0이다. 일 구현예에 대하여, 이 값들은 x=0.5이고 z=0이었다. 히드록시 기는 금속-함유 양이온의 일부일 수 있고, 이 화학물은 하프늄 옥시-히드록시 설페이트($HfO_{2-x-z/2}(OH)_z(SO_4)_x$)를 포함할 수 있다.

<33> 다른 구현예들에서, 상기 다원자 음이온은 하나 또는 그 이상의 설페이트(SO_4^{2-}), 보레이트(BO_3^{3-}), 포스페이트(PO_4^{3-}), 텅스테이트(WO_4^{2-}) 및 실리케이트(SiO_4^{4-})를 포함할 수 있다. 상기 금속-함유 양이온은 금속 아산화물(suboxide)을 포함할 수 있고, 하나 또는 그 이상의 하프늄 (Hf^{4+}), 티타늄 (Ti^{4+}), 지르코늄 (Zr^{4+}), 세륨

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(Ce^{4+}), 주석 (Sn^{4+}), 탄탈륨 (Ta^{5+}), 니오븀 (Nb^{5+}), 이트륨 (Y^{3+}), 몰리브데늄 (Mo^{4+}), 텅스텐 (W^{6+}), 알루미늄 (Al^{3+}), 갈륨 (Ga^{3+}), 아연 (Zn^{2+}), 크로뮴 (Cr^{3+}), 철 (Fe^{3+}), 비스무트 (Bi^{3+}), 란탄화물(lanthanides), 하프늄 옥시-하드록사이드 ($HfO_y(OH)_z^{(4-2y-z)+}$), 지르코늄 옥시-히드록사이드 ($ZrO_y(OH)_z^{(4-2y-z)+}$), 티타늄 옥시-히드록사이드 ($TiO_y(OH)_z^{(4-2y-z)+}$), 탄탈륨 옥시-히드록사이드 ($TaO_y(OH)_z^{(5-2y-z)+}$), 이트륨 옥시-히드록사이드 ($YO_y(OH)_z^{(3-2y-z)+}$), 니오븀 옥시-히드록사이드 ($NbO_y(OH)_z^{(4-2y-z)+}$), 몰리브데늄 옥시-히드록사이드 ($MoO_y(OH)_z^{(4-2y-z)+}$), 텅스텐 옥시-히드록사이드 ($WO_y(OH)_z^{(6-2y-z)+}$), 알루미늄 옥시-히드록사이드 ($AlO_y(OH)_z^{(3-2y-z)+}$), 갈륨 옥시-히드록사이드 ($GaO_y(OH)_z^{(3-2y-z)+}$), 아연 옥시-히드록사이드 ($ZnO_y(OH)_z^{(2-2y-z)+}$), 크로뮴 옥시-히드록사이드 ($CrO_y(OH)_z^{(3-2y-z)+}$), 철 옥시-히드록사이드 ($FeO_y(OH)_z^{(3-2y-z)+}$), 비스무트 옥시-히드록사이드 ($BiO_y(OH)_z^{(3-2y-z)+}$), 및 란탄 계열의 옥시-히드록사이드들을 포함할 수 있다. y의 값은 상기 금속 양이온의 전하와 상기 금속 양이온에 결합된 히드록사이드 및 다른 다원자 음이온의 양과 관련된다.

<34> 여기에 개시된 다원자 음이온들 및 금속-함유 양이온들을 이용하는 방법의 구현예들은 착화합물을 형성하기 위한 유기물질의 이용을 필요로 하지 않는, 즉, 음이온 및 양이온의 공급원이 유기물질을 포함하지 않는 유전 전구체 물질의 형성을 가져올 수도 있다. 그러나, 특정 구현예에 대하여 원하거나 필요한 경우에는 유기물질이 사용될 수 있다. 예를 들면, 에탄올과 같이 착화합물을 형성하지 않는(non-complexing) 유기물질이 전구체 용액의 부분적 용매로서 사용될 수 있다. 만일 전구체 물질에 착화합물을 형성하는(complexing) 유기물질이 포함되어 있지 않다면, 일단 상기 전구체 용액이 기판에 적용되면 통상 상기 전구체 용액은 유기 물질들을 분해/연소시키기 위해 400 ℃ 또는 그 이상의 온도에서 가열되거나 어닐링될 필요가 없다. 가열 및/또는 건조로 인한 전구체 용액의 증합은 다결정질 물질(polycrystalline material)이 아닌 비결정질막의 형성을 가져오고 그에 의하여 기판 위에 유전 물질의 용액-기반-응용을 가능하게 한다.

<35> 일반적으로, 본 공정에서 개시된 구현예들은 공기 내의 대기압과 같은 주위 환경 조건에서 수행될 수 있다. 따라서, 진공 공정은 불필요하다. 그러나, 원한다면 진공 공정이 이용될 수 있다. 상기 공정은 주위 환경보다 높은 온도에서, 예를 들면 약 80 ℃ 내지 약 350 ℃의 범위, 통상 80 ℃ 내지 높아야 350 ℃의 온도 범위에서, 그리고 종종 높아야 100 ℃의 온도에서 수행될 수 있다. 이들 저압 및 저온 공정 단계들은 개시된 공정들에 대하여 요구되는 에너지를 감소시킬 수 있다. 유전막의 처리에 유용한 낮은 온도로 인하여, 상기 막들은 플라스틱 기판들과 같은 저온 기판들 위에 처리되거나 또는 저온 기판들에 용액으로서 적용될 수 있다. 제조된 상기 결정질이 아닌 비정질(amorphous)의 유전 전구체(dielectric precursor) 용액은 웨이퍼 위와 같은 기판 위에 전구체 용액의 콘포말(conformal)한 도포성을 가능하게 한다. 상기 용액은 마스킹 또는 식각 단계들이 사용되지 않도록, 잉크젯 프린팅을 이용함에 의해서와 같이, 소정의 특정한 패턴으로 적용될 수도 있다. 따라서, 본 개시의 공정은 기판들 위에 포토리소그래피 공정을 수행하는 동안 물질의 형성 및 제거를 위해 사용될 수 있는 유해하거나 또는 독성을 갖는 물질들의 사용을 제거하거나 감소시킬 수 있다. 그러므로, 본 공정은 알려진 공정들에 비하여 시간의 측면에서 효율적이고, 환경적으로도 친환경적(green)이다. 게다가, 본 개시의 예시적 일 구현예에서 사용된 하프늄 옥사이드 및 설페이트 물질들은 독성 물질들이 아닐 수 있다.

<36> 본 개시의 공정에 사용되는 물질들의 예는 하프늄 옥시 히드록시 실페이트류($Hf_{O_{2-x-z/2}}(OH)_z(SO_4)_x$), 하프늄 옥시 히드록시 텅스테이트류($HfO_{2-x-z/2}(OH)_z(WO_4)_x$), 하프늄 옥시 히드록시 보레이트류($HfO_{2-x-z/2}(OH)_z(BO_3)_x$), 하프늄 옥시 히드록시 포스페이트류($HfO_{2-x-z/3}OH_z(PO_4)_x$), 및 하프늄 옥시 히드록시 실라케이트류($Hf_{O_{2-x-z/2}}OH_z(SiO_4)_x$)를 포함하는 화합물들의 군에 속하는 화합물들을 포함한다. 이들 물질들은 80 ℃ 정도의 낮은 온도에서 증합될 수 있고, 약 740 ℃까지, 심지어는 1,200 ℃ 정도의 높은 온도에서도 비결정질을 유지할 수 있다. 물질의 증합은 가열 속도를 조절함으로써, 공-용매(co-solvent)를 사용함으로써, 다른 적절한 방법들에 의하여 및 여러한 방법들의 모든 조합들 및 어떤 조합들에 의하여 제어될 수 있다. 본 개시의 비결정질 막들은 조직(grain) 경계에서의 결함 형성을 감소시킬 수 있고, 비정질-결정질(amorphous-to-crystalline) 전이에서 크랙이 형성되는 것을 감소시킬 수 있다. 게다가, 본 개시의 유전박막은 상당히 높은 유전 상수, 즉, 유기 화합물들의 유전 상수보다 더 높은 유전 상수를 가질 수 있다. 잉크젯 프린팅 응용과 같은 용액-기반 처리에 의하여 고품질의 유전체를 형성할 수 있는 능력은 저렴한 가격의, 전계 효과 트랜지스터들 또는 캐패시터들과 같은 전자 부품의 형성을 가능하게 한다.

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<37> 도 2는 유전 물질을 형성하기 위하여 전구체 용액(16)을 적용하기 위한 공정의 일 구현예를 개념적으로 나타낸다. 하프늄 옥시 실페이트와 같은 전구체 용액(16)이 적용자(applicator)(20)에 의하여 웨이퍼와 같은 기판(18)에 적용될 수 있다. 일 구현예에서, 적용자(20)는 노즐들(22)을 갖는 잉크젯 프린터를 포함할수 있다. 전구체 수용액(16)은 상기 잉크젯 프린터의 노즐들(22)을 통하여 분출된다. 다른 구현예들에서, 적용자(20)는 상기 전구체 용액의 적용 방법이 스핀-코팅, 딥(dip)-코팅, 또는 스프레이-코팅을 포함할 수 있도록 각각 스핀-코터, 딥-코터, 또는 스프레이-코터를 포함할 수 있다. 전구체 용액(16)의 비결정질의 용액-기반 성질들로 인하여 전구체 용액(16)은 적용되었을 때 우수한 콘포말(conformal) 도포성을 가능하게 할 수 있다. 일단 기판 표면에 또는 상기 기판 위에 증착된 막 또는 막들에 적용되면 상기 전구체 용액 내의 수분 함량을 제거하거나 감소시키기 위하여 상기 전구체 용액은 히터(24)로 가열함으로써 또는 다른 탈수(dehydration) 장치에 의하는 것과 같이 탈수될 수 있다. 상기 탈수 단계는 웨이퍼(18) 위에 하프늄 옥시 설페이트 박막과 같은 비결정질 유전 물질(26)의 침전을 가져올 수 있다.

<38> 도 3은 유전 물질 전구체 용액(16)(도 1 참조)의 일 구현예에 있어서, 특히, 황산(H_2SO_4)과 하프늄 옥시 클로라이드($HfOCl_2$)의 반응에 있어서, 상이한 전구체 농도들에 따른 가능한 용액 농도들을 나타내는 그래프이다. 더욱 구체적으로, 도 3은 전체 하프늄 농도(클 농도(M))에 대한 전체 설페이트 농도(M)의 그래프를 나타낸다. 영역(28)은 투명한 용액, 즉, 시각적으로 감지할 수 있는 침전물이 그 안에 없는 용액을 나타내고, 영역(28)은 과량 황산(H_2SO_4)의 영역이다. 영역(30)은 투명한 용액, 즉, 시각적으로 감지할 수 있는 침전물이 그 안에 없는 용액을 나타낸다. 영역(30)은 과량 하프늄 옥시 클로라이드($HfOCl_2$)의 영역이다. 선분(32)은 황산과 하프늄 옥시 클로라이드가 일 대 일의 비율(1:1의 양론비)로 각각 존재하는 양론(stoichiometric) 선을 나타낸다. 영역(34)은 침전 영역, 즉, 시각적으로 감지할 수 있는 침전물이 그 안에 있는 용액을 나타낸다. 따라서, 영역(34) 또는 그의 일부는 잉크젯 프린팅 응용에 의하여 매끈하고도 실질적인 결함이 없는 막들을 형성하기에 가장 적합한 것은 아닌 용액들을 나타낼 수 있지만, 그의 사용이 배제되는 것은 아니다. 따라서, 전구체 용액(16)(도 2 참조)이 잉크젯 프린터 응용 장치(20)(도 2 참조)를 통해 적용될 때, 제 1 반응물 및 제 2 반응물의 농도가 영역(28) 또는 영역(30)의 어느 하나 안에 있고, 고체 영역(34) 안에 있지 않는 것이 바람직하다. 영역(34)의 용액에 존재하는 고체들은 노즐들(22)을 막거나, 매끈하지 않은 막을 형성할 수 있거나, 또는 바람직하지 않은 전구체 용액 적용을 가져올 수 있다. 다시 말하면, 상기 영역들(28 및 30)의 용액은 잉크젯 프린트헤드를 통해 또는 드롭퍼(dropper) 방법에 의하여 적용될 수 있는 가능한 "잉크" 전구체 용액을 나타낼 수 있다.

<39> II. 일반 논의

<40> 새로운 박막 유전체들 및 나노적층체들(nanolaminates)은 매끈하고 조밀한 막의 용액 증착을 이용하여, 풍상 수용액 증착을 이용하여 개발되어 왔다. 용액 증착 기술들은 스핀 코팅 및 잉크젯 프린팅을 포함한다. 용액 증착에 이어서 적당한 열처리가 후속될 수 있다($T < 325℃$).

<41> 본 발명의 개시에 따라 분말 및 막으로서 제조된 물질 모두의 화학을 정의하기 위해 다양한 분석 기술들이 사용되어 왔다. 상기 막의 품질과 기능성은 X-선 반사도(reflectivity), 전자 현미경, 및 전자 소자들에서의 성능에 의하여 평가되었다. 유전 특성들이 작동 구현예들에 대하여 결정되었으며, 약 9 내지 약 12의 범위를 커버하는 유전율(permittivity); 적어도 6 $MVcm^{-1}$까지의 항복 전계(breakdown field); 및 1 $MV\ cm^{-1}$의 전계 강도에서 1 $nA\ cm^{-2}$ 에 가까운 누설 전류를 포함한다. 상기 막질의 표면의 매끈함 및 기공이 없는 특성은 적어도 약 2 나노미터의 얇은 개별층들을 갖는 독특한 나노적층된(nanolaminated) 구조물의 제조를 용이하게 한다. 비교적 높은 유전율 막들은 박막 금속-절연체-금속(MIM: metal-insulator-metal) 캐패시터들 및 박막 트랜지스터들(TFTs)에서 높은 항복 강도와 낮은 누설 전류를 제공하면서 본 발명의 개시된 구현예들을 이용하여 실현될 수 있다. 절연막들의 예외적인 특성들도 독특한 나노적층 구조물의 제조를 가능하게 한다.

<42> 박막 유전체로서 사용되기 위하여는 비결정질 물질들이 바람직한데, 그들은 조직(grain) 경계를 갖지 않고, 따라서 결정질과 관련된 거칠(roughness)과 전하 전도의 여지가 적다. 지르코늄과 하프늄의 수많은 산화물들, 예를 들면, 단순한 이성분계(binary), 실리케이트류, 및 알루미네이트류가 고유전율(high-permittivity) 유전체 응용의 후보들로 검증되어 왔다. 다성분 물질들에서, 순수한 이성분 산화물들에 비하여 더욱 강건한 항복(breakdown) 특성을 만들기 위하여, 유전율을 희생할 수 있음에도 불구하고 결정화가 저해될 수 있다. 이들 유전막들은 종종 다양한 유기-금속 또는 금속-염 전구체들과, 원자층 증착(ALD: atomic layer deposition), 화학기상증착(CVD: chemica vapor deposition), 졸-겔 처리, 또는 이들의 조합과 같은 기술들을 이용하여 형성된다. 그러나, 용액 증착 방법에 의하여 조밀하면서도 비결정질인 유용한 유전막을 제조하는 것은 증착 및 후속 공정

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모두가 수행되는 동안 결정화와 크래킹(cracking)을 저해할 것이 요구될 수 있다.

<43> 본 발명의 개시된 여러 구현예들은 금속 산화막의 개발에 관한 것이다. 금속 산화물들은 각각 $HfO_{2-x}(SO_4)_x$ 및 $ZrO_{2-x}(SO_4)_x$ (여기서, $0.1 \le x \le 1.5$)로 나타내어지는 화학식을 갖는 하프늄 및 지르코늄 설페이트계를 참조하여 여기에 일반적으로 예시된다. 이들 화합물들은 여기에 HafSOx 및 ZircSOx의 약어로 각각 지칭될 것이다. 이들 계의 화학과 물리적 성질을 정의하기 위하여, HafSOx 및 그의 도핑된 유사체(analog)들, 즉, La-치환된 유도체 HafSOx:La와 같은 유사체를 분말 및 박막으로 제조하였다. 캐패시터들과 TFT들을 제조함으로써 HafSOx, ZircSOx 및 선택된 유도체들의 박막 유전 특성들을 평가하였다. 이들 분석들은 매우 높은 품질의 조밀한 막이 제조될 수 있음을 나타내었다. 혼합 HafSOx/ZircSOx 나노적층체의 막 두께 및 제조가 스핀-코팅 공정에 의하여 이제 조절될 수 있다.

<44> 수많은 상(相)들 및 결정 구조들이 HfO_2-SO_3-H_2O 및 ZrO_2-SO_3-H_2O 계의 검증으로부터 보고되어왔다. 여러 구조들이 금속 원자, 설페이트 기 및 물의 응축과 관련된 구조적 차원(dimensionality)과 수화도의 변화를 보이는 화학식 $Hf(SO_4)_2 \cdot nH_2O$ 또는 $Zr(SO_4)_2 \cdot nH_2O$의 단순한 수화물들로 특성화된다. 설페이트에 비하여 금속이 풍부한 물질들이 알려져 있으며, $Zr_2(OH)_2(SO_4)_3 \cdot 4H_2O$; $Hf(OH)_2SO_4$, $Zr(OH)_2SO_4$와 이들의 수화물들; $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13} \cdot 33H_2O$ 및 $Zr_{18}O_2(OH)_{38.8}(SO_4)_{12.5} \cdot 33H_2O$; 및 $Zr_3O_2SO_4$와 그의 수화물을 포함한다. 이러한 구조들 모두는 수소 결합의 변화 또는 탈수화로 인하여 실온과 약간의 가열조건에서 공기와 접촉할 때 모두 불안정할 것으로 보인다 ($Zr_3O_2SO_4$는 예외일 수 있다). 이것은 비결정질 막을 개발하기 위해 사용될 수 있는 탈수화 및 응축 공정을 가능하게 한다.

<45> (변수 x로 나타낸) 하프늄에 대한 설페이트의 선택된 분율을 갖는 수용액으로부터 시작하여 HafSOx 침전은 가열에 의하여 유발되었다. 도 1은 공기로 건조된 HafSOx 침전물의 TGA(thermogravimetric analysis) 결과이다. TGA는 샘플의 무게(질량) 변화를 온도의 함수로 측정하기 위해 사용되는 열분석 기술이다. 공기로 건조된 HafSOx 침전물의 가열은 세 영역에서의 질량 손실을 가져온다. 다른 HafSOx 유도체들에 대하여도 유사한 특성들이 관찰되었다. 약 200 ℃의 온도 아래에서의 큰 질량 손실은 포함되었던 물의 손실에 기인한다. 약 200 ℃ 내지 약 700 ℃의 온도 범위에서의 질량 손실은 주로 물보다 더욱 강하게 결합된 히드록시 종의 제거에 기인한다. 약 700 ℃를 넘어서 시작되는 급격한 질량 손실은 $SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$에 따른 설페이트 분해에 기인한다. 탈수된 HafSOx 분말이 700 ℃와 950 ℃ 사이에서 HfO_2로 완전히 전환된다고 가정할 때, 상기 설페이트 분율은 질량 손실로부터 계산될 수 있다. 샘플의 질량 손실의 결정은 모액(mother solution)에서 설페이트의 레벨을 증가시키는 것이 침전물에서의 설페이트의 레벨의 증가를 가져옴을 밝혔다. 특히, 탈수된 화학식 $HfO_{1.54}(SO_4)_{0.46}$ 및 $HfO_{1.29}(SO_4)_{0.71}$ 각각에 대하여 하프늄에 대한 설페이트의 비율은 약 46%에서 약 71%까지 변화하였다. 설페이트 공급원으로서 $H_2SO_4(aq)$가 사용되든 $(NH_4)_2SO_4(aq)$가 사용되든, 동일한 최대 설페이트 조성이 침전되었고, 설페이트 레벨 < 46%인 생성물은 검출되지 않았다. 모든 샘플들에 대하여, 열중량 측정 프로파일에서 일부 변화가 관찰되었지만 720 ℃ 이상에서 설페이트 손실의 시작이 발생하였다. 이러한 가열 곡선들의 도함수(derivative)들에 대한 정의 가능한 값으로서의 피크 위치들은 테스트된 샘플들에 대하여 793 ℃와 817 ℃ 사이에서 분해됨을 나타낸다. 설페이트 공급원으로서 $H_2SO_4(aq)$을 사용하고 최대 설페이트 함량을 갖는 샘플들에 대하여 가장 높은 분해 온도가 관찰되었다.

<46> 다시 도 1을 참조하면, 최대 설페이트 함량을 갖는 샘플들이 TGA 측정에 앞서 가열되었다. 수분과 관련된 질량 손실들이 감소되었고, 계산된 설페이트 함량들은 에칭된 샘플들과 보통의 샘플들 모두가 비슷하였다. 이 70 내지 70%의 설페이트 함량은 보고된 결정들 $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$ 및 $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13} \cdot 33H_2O$의 조성들과 유사하다. TGA 연구로부터 Ahmed, Fjelvag, 및 Kjekhus는 그들의 연구에서의 Hf 및 Zr 디설페이트들에 대한 온도보다 더 높은 온도 및 다른 데서 보고된 염기성 설페이트들 $Hf(OH)_2SO_4 \cdot H_2O$ 및 $Zr_3O_2SO_4$에 대한 온도보다 더 높은 온도에서 $Hf_{18}O_{23}(SO_4)_{13}$ 및 $Zr_{18}O_{23}(SO_4)13$에 대하여 설페이트 분해가 일어남을 발견하였다. 향상된 열적 안정성 외에, 약 13:18의 설페이트-금속 비율은 이 계에 특별한 안정성을 보여준다. 따라서, 이 조성물은 용액처리 및 가열이 필요한 목적에 대하여 적합할 수 있다.

<47> 설페이트 $La_2O_2SO_4$는 1,300 ℃보다 큰 분해 온도를 갖는다. 란탄(La)은 변성된 탈수 성질 및 열적 성질들, 한예로서 열적 안정성과 같은 변성된 물성을 갖는 추가적인 화학물을 만들기 위해 HafSOx 모액에 첨가되었다. 혼

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합-금속계인 $Hf_{1-z}La_xO_{2-x-z/2}(SO_4)_x$ (HafSOx:La)는 이러한 화합물을 예시한다. 이러한 화합물을 제조하기 위하여, 전구체 물질과 23% La (총 금속)을 포함하는 용액을 가열하여 침전물을 형성하였다. 화학 분석 결과 생성물에 3%의 La 만이 발견되는 것으로 나타났다. TGA로부터 금속에 대한 설페이트의 비율이 71%임이 입증되었고, 820 ℃에서의 (도함수 피크로서) 분해되는 것이 최대 설페이트 함량과 일치하는 것으로 발견되었다. 그런 후 32% La을 포함하는 구성 중의 염 용액에 NH_3(aq)를 첨가함으로써 공침전(co-precipitation)을 유발하였다. 생성물의 화학 조성을 분석한 결과, 모액에 존재하는 것과 동일한 La 분율인 것으로 밝혀졌다. 본 화학식에 대한 열분해는 도핑되지 않은 HafSOx와 현저하게 상이하였다. 비록 가열 특성들이 덜 급격하였지만 설페이트에 기인한 질량 손실은 700 ℃ 위에서 현저하였고, 2 ℃(분)$^{-1}$의 더 느린 승온 속도로 가열하였을 때에도 1,000 ℃까지 가열하면서 질량이 일정하게 달성되지 않았다. 이 가열 속도에 대하여, (도함수 피크로서) 분해는, 비록 가열 조건에 달려있기는 하지만, 약 870 ℃에서 일어난다. 산화물의 완전한 분해는 1,500 ℃까지 가열함으로써 달성되었는데, 건조된 침전물에 대하여 화학식 $Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$이 수득되었다.

<48> 침전된 HafSOx 분말에 대하여 XRD 데이터를 수집하여 결정상에 대한 온도 범위를 입증하였다. 공기 건조 후, 최대 설페이트 함량과 설페이트 공급원으로서 H_2SO_4(aq)를 갖는 샘플들에 대하여 복잡한 회절 패턴이 기록되었고, 다른 샘플들은 회절이 없거나 확산되는 것을 보였다. HafSOx(x=0.7)에 대한 XRD 데이터를 도 2에 나타내었다. 공기 건조된 샘플들을 약 100 ℃ 내지 약 700 ℃ 사이의 온도에서 1시간 동안 건조시킨 후, 상기 물질은 비결정질이 되었다. 모노리딕 HfO_2의 결정성 피크 특성이 750 ℃ 이상에서 1시간 동안 가열한 후 관찰되었다. TGA에 의하여 설페이트 손실의 개시가 720 ℃에서 일어나므로, 결정화는 설페이트 손실과 일치하는 것으로 밝혀졌다. 3% La을 포함하면, 1,000 ℃의 온도까지도 유사한 회절 프로파일이 생성된다.

<49> 도 3은 HafSOx:32% La에 대한 XRD 데이터를 나타낸다. 침전된 물질과 700 ℃에서 가열된 것 모두 X-선 비결정질이다. 비치환된 HafSOx에서와 같이, 감지할만한 결정상은 설페이트가 분해되기 시작하는 온도 구간인 700 ℃와 750 ℃ (1시간 가열) 사이에서 형성된다. 그러나 32% La의 치환으로는 모노리딕 HfO_2는 감지되는 상이 아니다. 오히려, 회절 프로파일은 입방계 (또는 정방정계) HfO_2와 일치한다. HfO_2의 상은 종종 란탄계 원자를 포함함으로써 안정화된다. 적절한 상 다이어그램으로 고려하면 예측할 수 있는 바와 같이, 고온으로 가열하면 $Hf_3La_2O_7$과 모노리딕 HfO_2가 생성될 수 있다. 중간 온도 산화물 상들은, 900 ℃에서 10 내지 37%의 란탄이 입방계 지르코니아를 안정화시키고 1,050 ℃에서 상분리가 일어남을 발견한 Zhang, Kershaw, 및 Dwight의 ZrO_2-La_2O_3 시스템에 관한 업적과 일관된다.

<50> 재료들을 특성화하기 위하여 약 200 나노미터 내지 약 300 나노미터의 두께를 갖는 HafSOx 및 HafSOx:La 박막들이 제조되었다. 상기 막들에 대한 조성들은 Hf, La, Cl 및 S의 상대적인 농도에 기초하여 EMPA로 결정되었다. 이 방법에 따르면 산소 레벨이 덜 정확하므로, 탈수된 화학식으로 표현하였다. 325 ℃에서 (5분간) 가열된 대표적인 두 HafSOx 박막은 하프늄에 대한 설페이트의 비율이 각각 67%와 85%로 나타난 $HfO_{0.985}(SO_4)_{0.67}Cl_{0.69}$ 및 $HfO_{0.915}(SO_4)_{0.85}Cl_{0.47}$로 결정되었다. 상기 85% 설페이트막은 650 ℃로 (5분간) 더 가열되어 $HfO_{3.275}(SO4)_{0.71}Cl_{0.03}$으로 결정되었다. 또한, 330 ℃에서 (5분간) 가열된 상기 HafSOx:La 막은 $Hf_{0.76}La_{0.24}O_{0.73}(SO_4)_{0.96}Cl_{0.38}$인 것으로 결정되었다. 650 ℃로 가열된 HafSOx에 대하여, 설페이트 비율은 71%로 감소하였으며, 이는 최대 설페이트로 가열 침전된 HafSOxjc 대한 조성과 일치한다. HafSOx:La에 대하여, La의 측정된 분율(24%)은 전구체 용액에서의 La 농도 23%와 잘 맞는다.

<51> 선택된 온도에서 5분 동안 가열한 후 HafSOx(x~0.67 및 0.85)과 HafSOx:La 막들에 대한 무과 푸리에 변환 적외선 (FTIR: transmission Fourier transform infrared) 분석 결과들이 수집되었다. 주요한 두 개의 작용기를 감지하기 위하여 FTIR 스펙트럼들이 사용되었다. 3000 내지 3600 cm^{-1} 범위에서의 흡수는 히드록시기에 기인하고, 1000 내지 1200^{-1} 범위에서의 흡수는 설페이트 기에 기인한다. 가열과 함께, 히드록시기 흡수는 약 325 ℃ 내지 약 600 ℃의 범위에 걸쳐서 감소하는 반면, 설페이트 스트래치(stretch)는 HafSOx 막에 대하여는 약 650 ℃ 내지 700 ℃ 사이에서, HafSOx:La 막에 대하여는 약 700 ℃ 내지 750 ℃ 사이에서 거의 제거된다. (실페이트 흡수에 대한 프로파일은 기판으로부터의 SiO_2가 유사한 에너지를 흡수하기 때문에 약간 왜곡되지만, 스펙트럼들은 정성적으로 정확하다)

<52> 도 4 및 도 5에 각각 보인 바와 같이, HafSOx(x~0.67 및 0.85) 및 HafSOx:24% La 막들에 대하여 각각 표시된

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온도에서 5분간 가열한 후 박막 XRD 데이터가 수집되었다. 두 HafSOx 조성물 모두에 대하여, 막들은 약 325 ℃ 내지 약 650 ℃까지 X-선 비결정질이다. 모노리딕 HfO_2는 약 700 ℃ 또는 그 이상에서 감지된다. HafSOx:La 막들은 약 330 ℃ 내지 약 700 ℃에서 비결정질인 반면, 입방계 상은 약 750 ℃ 내지 약 1000 ℃에서 감지된다. 상기 입방계 상은 1,100 ℃에서 모노리딕 HfO_2와 $Hf_6La_2O_{17}$으로의 분리가 시작되기 때문에 외관상 불안정하다. HafSOx 및 HafSOx:La 막들에 대하여, 실페이트의 손실은 산화물 결정화와 직접 상관될 수 있으며, 이는 분말 거동과 일관된다.

<53> HafSOx, ZircSOx 및 이들의 유도체들의 박들은 유전체로서 사용되기 위한 스핀-코팅에 의하여 증착되었다. 전계 항복 강도뿐만 아니라 1 kHz에서의 손실 탄젠트와 유전율의 파라미터들을 결정하기 위하여 MIM 캐패시터들을 테스트하였다. "항복"은 전계 밀도가 10 μA cm^{-2}를 넘는 전계로서 정의된다. HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, 및 ZircSOx:Ca에 대하여 유사한 테스트들이 수행되었다. 도 6은 알루미늄 점 콘택들이 0.011 cm^2의 면적을 나타내는 HafSOx 유전막에 대한 유전 항복 특성을 나타낸다. HafSOx 및 ZircSOx 박들은 4 내지 6 MV cm^{-1}의 항복 전계를 가졌다. ZircSOx:Ca에 대한 항복 전계는 3.6 MV cm^{-1}이었다. 가해진 1 MV cm^{-1}의 전계에서, 여섯 변형 물질 모두가 50 nA cm^{-2} 미만의 누설 전류를 보였으며, 많은 조성물들에 대하여 10 nA cm^{-2} 미만의 누설 전류가 관찰되었다. 모든 변형 물질들에 대하여 약 9 내지 약 12의 유전율 값들과 손실 탄젠트 < 1%가 측정되었다.

<54> HafSOx:La 또는 ZircSOx:La를 게이트 유전체로서 이용하고, 아연 인듐 산화물 또는 아연 주석 산화물을 채널로서 이용하여 전계효과 트랜지스터(FET: field-effect transistor)를 제조하였다. 전류 변조(modulation)가 달성되었는데, 드레인-소오스 전압을 증가시킴에 따라 드레인-소오스 전류가 포화되었으며, 10^6보다 큰 온-투-오프 비율(on-to-off ratio)을 제공하고, pA cm^{-2}의 범위의 값을 갖는 게이트 누설 전류를 제공한다. 이러한 결과들은 HafSOx:La과 ZircSOx:La 막들이 소자 집적에 대하여 충분히 강건하고, 유전체/채널 계면의 품질의 요건도 만족됨을 나타낸다.

<55> 새로운 종류의 비결정질 다성분 산화물 유전막으로서, HafSOx, ZircSOx 및 이들의 유도체들은 다른 혼합 시스템, 특히 $(MO_2)_{1-x}(Al_2O_3)_x$ 및 $(MO_2)_{1-x}(SiO_2)_x$ (여기서, M = Hf 또는 Zr)로 나타내어지는 알루미네이트들 및 실리케이트들과 비교될 수 있다. 이들 시스템들 각각에 대한 다양한 막 조성물들이 통상의 기상 기술들에 의하여 증착되었다. (유전체 응용에서 통상적인 조성으로서) 20 내지 50 몰%의 Al_2O_3 또는 SiO_2를 갖는 Hf 또는 Zr 알루미네이트와 실리케이트들의 경우에 있어서, 결정화는 통상 약 800 ℃ 내지 1,000 ℃에서 상 분점(phase segregation)과 함께 일어난다. 테스트된 HafSOx 분말 및 막들에 대하여, 결정화는 실페이트가 분해됨에 따라 약 700 ℃에서 일어났다. 유전체로서, 이들 알루미네이트들과 실리케이트들은 HafSOx 및 ZircSOx에 대한 9 내지 12의 값들과 비교해 볼 때 10 내지 15의 유전율 값을 보인다. 이들 새로운 종류의 산화물 실페이트 물질들은 비결정질, 중간 온도, 중간 유전율 유전체로 고려될 수 있다.

<56> 주사 전자 현미경(SEM: scanning electron microscopy) 및 반사 X-선(XRR: X-ray reflectivity)을 이용하여 막의 성질을 더 검사하였다. HafSOx 및 HafSOx:La 막들에 대한 SEM 이미지들을 도 7 및 도 8에 나타내었다. 이들 이미지들은 유전체 테스트를 위해 전형적으로 사용된 것과 같은 약 150 나노미터 내지 약 300 나노미터의 범위의 두께들을 갖는 막들의 매끈한 표면과 조밀하고 균일한 단면을 나타낸다. 도 7은 그 위에 Ta 금속의 506-nm 층(712) 및 160 nm의 HafSOx 막(714)이 증착된 SiO_2 기판(710)을 나타낸다. 도 8은 그 위에 Ta 금속의 512-nm 층(812) 및 192 nm의 HafSOx/La 막(814)이 증착된 SiO_2 기판(810)을 나타낸다.

<57> 더 얇은 막 형성을 위한 재현성의 엄격한 측정으로서 HafSOx/ZircSOx의 반복 기조를 갖는 다층 구조물들이 적층되었고 XRR로 분석되었다. 도 9는 XRR 스캔의 한 간섭 패턴을 나타낸다. 반복되는 이중층의 두께를 찾기 위해 정상파 하모닉스를 나타내는 피크 정점의 위치가 사용되었다. HafSOx와 ZircSOx의 두께를 독립적으로 규칙적으로 변화시키면서, 개별 층들의 두께가 결정되었다. 나노적층체 스택 내에서, 약 3 나노미터 정도로 얇은 단일층이 측정되었다. 회절 패턴에서 고차 반사가 관찰됨에 따라, 각 이중층은 조도(roughness)를 포함하여 0.5 미만의 변동성(variability)으로 증착되었다.

<58> Si CMOS 기술에서 소자 크기의 축소는 유전체로서 얇고, 누설 전류가 높은 SiO_2의 교체의 필요성을 가져왔다. 교체되는 유전체들은 높은 유전율을 보여야 하고, 더 작은 누설 전류로 동일한 소자 캐패시턴스를 보이기 위해

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더 두꺼운 층을 가능하게 하여야 한다. HfO_2 및 ZrO_2는 이들의 바람직한 유전 특성 및 열적 특성으로 인하여 대체 게이트 유전체로서 상당한 주목을 끌어왔다. HfO_2 및 ZrO_2 유전체에 대한 도전의 하나는 매끈하고, 조밀하며, 핀-홀이 없고, 13 nm 이하의 두께를 갖는 초박막(ultra-thin films)을 만드는 것이다. 이전의 초박막들은 원자층 증착(ALD: atomic layer deposition)을 이용하여 형성되었다. ALD의 일부 유망한 결과들에도 불구하고, 이 방법은 긴 증착 시간(1 Å/분)과 함께 진공을 이용한 것이 요구되기 때문에 비용이 높고 생산성이 낮았다. 이로 인하여 HfO_2와 ZrO_2의 용액 기반 증착의 일부 연구가 촉발되었다. 현재까지 이들 막들은 ALD 박막들과 동일한 균일성과 조밀성에 도달하지 못하였다.

<59> 교환 반응을 이용하여, ALD 품질에 필적하고 DRAM (dynamic random access memory) 및 Si CMOS (complementary metal-oxide semiconductor) 기술에 사용하기에 적합한 $M(OH)_x$ 및 MO_x 초박막을 제조할 수 있다. 개시된 구현예들에 대하여, 상기 막들은 스핀-코팅을 이용하여 무기 응축을 통해 설페이트 형태로 증착된다. 예를 들면, 반-고체 막이 $MO_x \cdot HCl \cdot H_2SO_4$ 조성으로 형성될 수 있다. 상기 설페이트는 수산화나트륨 수용액을 이용하여 이온 교환으로 제거된다.

<60> $$MO_x \cdot HCl \cdot H_2SO_4 + OH^-(aq) \rightarrow M(OH)_{2x} + Cl^-(aq) + SO_4^{2-}(aq)$$

<61> 결과로서 얻어지는 히드록소(hydroxo) 및/또는 산화물 막들은 매끈하고, 조밀하며 핀홀이 없다. 예를 들면, 약 2 나노미터의 두께를 갖는 HfO_2 막들이 HafSOx 막들로부터 제조될 수 있다. 교환된 막들은 약 800 ℃의 온도까지 약 10 초 내지 10 분 동안 열처리될 수 있고, 그 결과, 막의 표면 조도가 약 0.1 나노미터가 된다. 이러한 막의 특성들은 값비싼 원자층 증착 방법을 저비용 스핀-온 또는 분무(misting) 기술로 대체하면서 CMOS 및 관련 기술 분야에서 금속-유전체 게이트에 대한 요건들을 만족한다.

<62> 증착된 반-고체 수화 히드록소 막들은 막의 모폴로지(morphology)를 붕괴시키지 않으면서 음이온 교환을 가능하게 한다. 예를 들면, SO_4^{2-}, WO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-}, VO_4^{3-}, AlO_4^{5-}, GaO_4^{5-}과 같은 옥소 음이온들과 이들의 프로톤화된 형태들, 예를 들면, HPO_4^{2-}, $H_2PO_4^-$ 및 할로겐들 F^-, Cl^-, Br^-, 및 I^-는, 예를 들면, $Na_2SO_4(aq)$와 같은 금속염 조(槽)에 상기 막들을 넣음으로써 선택적으로 교환될 수 있다. 이것은 전자 분야 응용 및 이온 교환 크로마토그레피 및 의과와 같은 다른 분야 응용에 대하여 막 성능을 최적화하기 위한 기회들을 제공한다.

<63> 산화물 막들의 일부 구현예들에 대하여, 착체(complex) 조성물, 예를 들면, 둘 또는 그 이상의 금속 원자들을 제공하기 위해 기판에 직접 적용될 수 있는 단일-공급원 전구체 현탁액(liquid suspensions)을 제조하기는 어렵다. 다음의 방법들은 소자 응용을 위해 적합한 품질을 갖는 막 증착을 위한 단일-공급원 전구체로서의 그러한 현탁액들의 제조와 그들의 사용을 가능하게 한다.

<64> 다음은 전구체 수용액의 합성과 상기 전구체를 이용하여 금속 산화물 막을 증착하기 위한 일반적인 방법을 설명한다. 상기 전구체 수용액은 비-수계 극성 용매 내에서 가수분해에 의하여 응축되고 이어서 증착을 위한 수성(aqueous) 환경으로 전환되는 졸리머 또는 올리고머 금속-히드록소 화합물들을 포함한다는 점에서 구분된다. 바람직한 박막 전기 및 광학 특성들 및 처리 온도들은 해로운 유기 오염물 없이 금속 수산화물들을 조밀한 고체 산화물들로 응축시킴으로써 달성된다. 합성 방법의 개시된 구현예들은 1) 극성 용매 내에 금속 염을 용해; 2) 가수분해 및 응축; 3) 용매 증발; 4) H_2O 내에 용해; 및 5) 용액 증착 및 경화의 일반 절차들을 따른다.

<65> 금속 양이온(M^{a+})과 하나 또는 그 이상의 음이온들(X^{b-})을 포함하는 하나 또는 그 이상의 가용 염들은, 지방족 알코올류 또는 니트릴류, 특히 (탄소수 10 또는 그 이하의) 저알킬(lower alkyl) 알코올류 및 니트릴류와 같은, 예를 들면, 메탄올, 에탄올, 아세토니트릴 또는 이들의 혼합물과 같이 착화합물을 형성하지 않는, 비-수계 극성 용매에 용해된다. 많은 용매 시스템들이 가능하다. 특정 응용을 위해 적합한 용매들이 의도된 용액-상 반응과 양립할 수 있는 끓는점(통상 150 ℃ 미만), 저 유독성, 및 산-염기 및 산화환원 특성들을 고려하여 선택될 수 있다. 금속 공급원들은 단순 이온 또는 분자염($Zn(NO_3)_2$, $SnCl_4$ 등); 옥시 또는 히드록시염($ZrO(NO_3)_2$, ZnOHCl 등); 또는 잠재적인 유기염들($Fe(CH_3CO_2)_2$, $Cu(CHOO)_2$ 등)을 포함할 수 있다. 금속 양이온들의 적어도 하나는 3+보다 큰 형식 전하를 가져야 하고, 그러한 이온들(M^{a+}, 여기서 a>3)의 총 농도는 목적 산화물 내의 금속 양이온들의 50 몰%보다 커야 한다. 동시에, 소정량의 H_2O가 위에서 설명한 금속염들의 수화물로서, 순수한 액체로서, 또는 아래에 상술하는 염기성 용액으로서 상기 용액 내에 도입된다. 상기 몰의 양은 선택된 양이온들에 의

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하여 결정되며, 물의 통상적인 양은 비-수계 극성 용매의 20 몰%를 넘지 않을 것이다.

<66> 그런 후, 상기 용액의 pH는 적절한 염기를 첨가함으로써 또는 산화-환원 메커니즘을 통해 자유 프로톤들의 반응에 의하여 초기 pH에 비하여 증가될 수 있다. 증가된 pH는 산성(a>3) 양이온들에 의하여 결합된 H_2O 리간드들의 가수분해와 그 결과로서 생성되는 히드록소-양이온들의 응축을 촉진한다. 최종 용액 pH는 사용된 금속 양이온들에 달려있지만 약 2 내지 약 9의 범위에 통상 있게 될 것이다. 이는 다음 기술들 중의 하나 또는 그들의 어떠한 또는 모든 조합들을 이용하여 달성될 수 있다.

<67> a) NH_4OH, $(NH_4)_3PO_4$, CsOH 또는 유사한 화합물들을 함유하는 염기성 수용액의 첨가. 후속 공정에서 분해 또는 증발시키기 위하여 특정 화합물들(NH_4OH)이 선택될 수 있다. 발수에 이어서 고유한 모폴로지, 광학적 또는 전기적 특성들을 달성하기 위해 최종 산화물 막의 일부를 이루도록 의도된다면 다른 양이온들(예를 들면, Cs) 또는 다원자 음이온들(예를 들면, PO_4^{-3})이 사용될 수 있다.

<68> b) 최종 산화막에 유사한 목적으로 포함시키기 위해 CaO 또는 SrO와 같은 염기성 산화물을 소량 첨가 또는 용해.

<69> c) H_2O 내에 염기성 용액을 형성하는 NH_3 또는 다른 기체 화합물의 첨가.

<70> d) H_2에 대한 직접 환원을 통해 또는 NO_3^-의 환원과 같이 다른 양성자 소비성 산화-환원 과정의 일부로서 양성자들을 소비할 수 있는, Zn, Al 또는 Fe와 같은 양전성(electropositive) 금속 환원제의 첨가. 결과로서 얻어지는 양성자 종들은 그 이후 최종 산화막 내에 포함된다.

<71> e) 최종 산화막 내에 포함되지 않으면서 양성자들을 소비하거나 상대 이온들을 분해하기 위한 유사한 목적으로 가용 염으로서 또는 액상의 H_2O_2, N_2H_4, 또는 H_2CO와 같은 수용액 또는 기상의 산화제 또는 환원제를 첨가.

<72> 상기 용액들은 원하는 최종 조성에 따라 열 가수분해 및 응축을 촉진하기 위해 실온, 가열, 또는 용매열(solvothermal) 조건에서 교반될 수 있다. 적절한 반응 시간이 경과한 후에 상기 용액은 하나 또는 그 이상의 가용 올리고머 또는 폴리머 금속-히드록소 양이온 종을 포함할 것이다. 이들 종들은 사실상 호모 또는 헤테로-금속 종이다. H_2O에 비하여 비-수계 용매의 감소된 극성 및 크기가 입체 장애(steric) 효과 또는 변형된 전하-차폐(charge-screening) 성질들을 통하여 추가적인 응축 및 취전 과정을 방해할 수 있는 반면, 응축의 정도는 사용될 수 있는 H_2O(수상(aquo)- 또는 히드록소- 리간드들)의 제한된 몰비에 의하여 제한된다.

<73> 가용한 금속 종들은 상기 비-수계 용매를 증발시킴으로써 분리된다. 분리된 금속-히드록소 화합물들은 솔벤트, 상대 이온, 및 가수 분해 비율(hydrolysis ratio) 등과 같은 특정 고려사항들에 따라 결정질 또는 비결정질 고체 또는 겔을 형성할 수 있다.

<74> 산화물 막을 위한 전구체 용액들은 상기 분리된 고체를 H_2O에 녹이거나 분산시킴으로써 제조된다. 결과로서 얻어지는 졸 또는 용액은 균일하고, 열역학적으로 안정할 수도 있고, 그렇지 않을 수도 있다.

<75> 전구체 용액들은 패터닝된 또는 블랭킷 액상 막을 형성하기 위해 프린팅, 스핀, 스프레이, 또는 딥-코팅을 포함하는 적합한 어떠한 기술이든 이용하여 기판에 적용된다. 액상 막은 약 100 ℃ 내지 600 ℃의 온도에서 약 5 내지 240 분 동안 대기 조건 하에서 열적으로 경화된다. 원하는 화학 또는 광전자 특성에 적합하도록 산소 양론 또는 양이온 산화 상태를 변화시키기 위해 진공 또는 형성 기체(forming gas) (예를 들면, H_2 및 흐르는 N_2 또는 Ar) 어닐링이 사용될 수 있다.

<76> 여기에 설명한 막들의 매끈함과 높은 원자 밀도는 용액 공정을 통해 순수한 무기 나노적층체들의 제조를 가능하게 한다. 이들 막들은 이하에서 더욱 상세하게 논의하는 바와 같이, 넓은 응용범위로의 개발을 위한 새로운 플랫폼을 나타낸다.

<77> III. 응용들

<78> 당 기술분야에서 통상의 지식을 가진 자는 HafSOx 및 ZircSOx 화합물들과 이러한 화합물들을 포함하는 막들이 수많은 상이한 소자들을 만들기 위해 사용될 수 있고, 그러한 화합물들을 이용하는 수많은 공정들의 실행에 사용될 수 있음을 이해할 것이다. 금속-유기 전구체들이 부가 산화물들의 용액-기반 증착에 광범위하게 채용되어 왔다. 유기 모이어티의 존재는 고온 소각(burnout) 단계를 필요로 하고, 이는 상당한 부피 변화와 일반적으로

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결정화를 가지오고 또한 "머드 크래킹(mud cracking)" 현상을 야기한다. 비결정질 HafSOx 및 ZircSOx 박들을 형성하기 위해 적절한 무기 조성물들과 본 발명에 개시된 구현예들을 사용함으로써 이들 문제점들이 제거되며, 단순한 탈수 및 증합은 막질 보존으로 이어진다. 상의 안정성을 이해하기 위하여, 대표적인 HafSOx 및 HafSOx:La 분말과 박들이 다양한 온도에서 특성화되었다. HafSOx 및 ZircSOx에 기초한 박막들은 상기 막들의 품질과 유용성을 검증하기 위하여 다양한 구성으로 증착되었다. 캐패시터 유전체를 제조하기 위해 여러 유도체들이 사용되었다. HafSOx:La 및 ZircSOx:La를 사용하여 FET 소자들의 게이트 유전체를 형성하였다. HafSOx 및 ZircSOx의 나노적층체의 층들은 주목할만한 매끈함을 2개의 원자층 이내로 재현성있게 시현하였다. 무엇보다도, HafSOx, ZircSOx 및 이들의 유도체들을 포함하는 박들의 종류는 전기 절연체, 보호 장벽, 광학 코팅, 및/또는 포토리소그래피를 위한 무기 폴리머로서 유용하다.

<79> A. 레지스트, 임프린트 리소그래피 및 프린팅을 위한 패턴된 막들

<80> 포토리소그래피는 마스크 위의 기하학적인 형태를 실리콘웨이퍼 또는 다른 반도체의 표면에 전사하기 위하여 널리 사용된다. 지난 40년간, 포토리소그래피 공정은 마이크로 전자산업에서 소자 구조물의 치수 제어 및 분해능 개선의 구동력이었다. 이러한 발전들은 고성능 개인용 컴퓨터, 휴대 전화, CD 플레이어, 및 이제 우리 삶의 필수적인 부분으로 자리잡은 다른 수많은 진보된 전자 제품들을 가능하게했다. 이들 제품들을 가능하게 하였던 포토리소그래피에서의 발전은 주로 짧은-파장으로 노광하는 도구의 개발과 폴리머 레지스트들의 해상도 및 피처(feature)-크기 능력을 비상하게 확장하는 데 중심을 두어왔다. 그러나, 더욱 작은 피처들 및 소자-수율 개선을 위한 탐색이 계속됨에 따라 폴리머계 레지스트 기술의 한계와 비효율성이 점차 더욱 명백해지고 있다.

<81> 리소그래피를 통해 구현된 가장 작은 피처 크기는 무기 물질들의 전자빔 기록에 의하여 제조되었다. 그러나, 제조 환경에서 사용되기 위한 일관성 이상의 관심을 받기에는 이러한 피처들을 제조하기 위한 빛-도스 에너지는 과도하게 너무 높았다.

<82> 여기에 설명된 막들의 증착 및 처리가 이루어지는 동안, 막들의 수화 레벨을 조절하는 것이 가능한데, 이는 적층된 막들의 상호확산(interdiffusion)과 그 결과 얻어지는 물리적 및 화학적 특성의 조절을 위한 방법을 제공한다. 이러한 조절된 상호확산은 그 결과로서 얻어진 물질 용해도에 있어서의 유도된 변성과 함께 박들의 높은 품질과 결합되어 새로운 리소그래피 패터닝 방법을 개발하기 위하여 사용되었다. 이러한 방법론은 두 개의 구별되는 막들을 적층하는 단계와 반응시키는 단계를 수반하며, 이중층 확산(bilayer diffusion)으로 지칭된다. 또한, 퍼옥사이드(O_2^{2-})와 같은 작은 배위종들은 추가적인, 새로운 리소그래피 패터닝 방법을 제공하기 위해 수계 무기 현탁액들과 막들에 통합될 수 있다. 이 기술에서, 막들에 에너지(예를 들면, 빛, 전자빔, 열)가 적용될 수 있으며, 상기 막의 용해도를 변화시키는 응축 반응을 유도하고, 그에 의하여 리소그래피 패터닝을 가능하게 한다.

<83> 포지티브 또는 네거티브 포토레지스트를 이용하여 패턴들이 형성될 수 있다. 이 공정은 실리콘 기판(1012), 실리카층(1014) 및 레지스트층(1016)을 갖는 적층체 구조물(1010)을 참조하여 도 10에 개념적으로 도시된다. 포지티브 레지스트에 있어서, 상기 레지스트층(1016)은 UV광과 같은 에너지 공급원에 노출되고, 그 아래에 있는 물질들은 제거되게 된다. 이들 레지스트들에 있어서, UV 광에의 노출은 현상액(developer)에 더욱 잘 용해되게 되도록 상기 레지스트층(1016)의 화학 구조를 변화시킨다. 그런 후, 노출된 상기 레지스트층(1016)은 아래에 있는 원래의 물질 영역을 남긴 채 현상액에 의하여 제거된다. 다시 말해, "보이는 것은 무엇이든, 간다." 따라서, 상기 마스크(1018)은 웨이퍼 상에 남게 될 패턴의 복사본을 정확히 포함한다.

<84> 네거티브 레지스트들은 정반대의 방식으로 거동한다. UV 광에 대한 노출은 상기 네거티브 레지스트의 중합을 가져오고, 따라서, 더욱 용해되기 어렵게 된다. 그 결과 상기 네거티브 레지스트(1020)는 노출된 곳이면 어디나 표면 위에 남게 되고, 현상액은 노출되지 않은 무늬 만을 제거한다. 따라서, 네거티브 포토레지스트를 위해 사용된 마스크들은 전사될 패턴의 역상(사진의 "네거티브")을 갖는다.

<85> 전자 제품 제조를 위해 현재 사용되는 레지스트 물질들은 유기 폴리머들이다. 이들 폴리머들은 패턴 해상도를 제한하는 코일링(coiling)과 모폴로지를 보인다. 본 발명의 무기 박막들은 새로운 레지스트 기술을 위한 기초를 형성한다. 여기서, 네거티브 레지스트들은 반도체 형태의 상기 무기박막들을 빛 또는 전자빔들에 노출시키고, 그에 의하여 용매를 잃도록 함으로써, 특히 탈수 과정 동안 물을 잃게 함으로써 구현될 수 있다. 이는 막을 경화시키고, 이들이 산에 녹지 않도록 한다.

<86> 포지티브 레지스트의 일 구현예는 이중층 시스템을 이용하여 제조될 수 있다. 상기 이중층의 제1층은 하프늄 옥사이드 설페이트(HafSOx) 막 위에 증착된 포름산 구리 막을 포함한다. 상기 포름산 구리 막은 산에 용해될

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수 있고, 도핑되지 않은 HafSOx 막은 산에 불용성이다. 상기 이중층을 마스크를 통해 빛에 노출시키거나 포커스를 맞춘 전자빔에 노출시키는 것은 노출된 영역에서 상기 두 막의 상호확산을 가지오고, 그에 의하여 이전의 도핑되지 않았던 HafSOx 막을 용해될 수 있게 만든다.

<87> 본 공정의 일 구현예가 도 11에 개념적으로 도시되어 있다. 도 11을 참조하면, 적절한 물질을 스핀 코팅 또는 잉크젯 코팅함으로써, 작업 소자를 정의하기 위해 요구되는 바와 같이 원하는 순서 및 두께로 적층체 구조물(1110)이 먼저 형성된다. 더욱 구체적으로, 기판 물질(1112)이 먼저 선택된다. 당 기술 분야에서 통상의 지식을 가진 자는 수많은 기판 물질의 무엇이든 본 발명의 이 구현예를 실행하기 위해 잠재적으로 사용될 수 있음을 이해할 것이다. 오직 예로서, 한정함이 없이, 적합한 기판은 반도체 물질들, 금속, 유리, 고분자 물질 및 이들의 조합을 포함한다. 그로써 레지스트 기술은 반도체 제조에서 수많은 응용에 유용할 수 있다. 일단 적합한 기판(1112)이 선택되면, HafSOx의 제1층(1114)이 상기 기판(1112) 위에 용액 증착된다. 그런 후, Cu:ZircSOx의 층(1116)과 같은 제2층이 층(1114) 위에 용액 증착된다. 상기 적층체 구조물(1110)은 그 후 마스크를 통해 전자빔 또는 빛과 같은 에너지 공급원에 조사된다. 마스크를 통해 빛 또는 전자빔에 조사되면, 상기 두 막들은 노출된 영역에서 상호확산되어, 이전에는 도핑되지 않았던 HafSOx 막을 가용하게 하여 적층체 구조물(1120)이 만들어진다. 그런 후, 노출되었던 상기 구조물(1120)은 현상된다. 이전에는 도핑되지 않았던 HafSOx 막은 가용하며, 따라서, 적층체 구조물(1130)에 표시된 바와 같이 제거된다.

<88> 가요성 또는 유리 기판 위에, 구조물(1130)로 도시된 패턴은 임프린트 리소그레피를 위한 또는 그라비어 프린팅과 같은 일반화된 프린팅 공정을 위한 마스터 플레이트로 간주될 수 있다. 이러한 방식으로 HafSOx의 경화되고 패턴된 물질을 형성하는 것은 유체 제어 및 수송을 위한 소자의 제조에서 마이크로- 및 나노-채널 이레이를 개발하기 위한 수단들을 제공할 수도 있다. 그러한 소자들은 의료 진단, 잉크 수송 및 화학 합성에 응용될 수 있다.

<89> 이중층 공정의 다른 구현예가 도 12에 도시된다. 상기 공정은 선택된 기판(1210) 위에 패턴된 산화물을 제조한다. 상기 기판은, 예를 들면, 유리, 반도체 웨이퍼, 금속, 금속 합금, 플라스틱, 또는 이들의 조합일 수 있다. 상기 공정의 첫 번째 단계는 고체 산 또는 염기, 예를 들면, 금속 Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, 또는 Lu의 하나 또는 그 이상을 포함하는 수화된 설페이트, 포스페이트, 나이트레이트, 실리케이트, 알루미네이트, 보레이트 또는 이들의 혼합물들의 박막(약 1 nm 내지 약 100 nm)을 증착하는 단계를 수반한다. 또한, 상기 고체 산/염기는 NH_3, OH, F, Cl, Br, I의 하나 또는 그 이상을 포함할 수 있다. 상기 고체 산/염기는 스핀 코팅 또는 프린팅을 통해 증착되는 것이 바람직하고, 물리 및 기상 증착은 추가적인 옵션이다. 하나의 예로서, 상기 고체 산은 $HfOCl_2$ 및 H_2SO_4(aq)의 수용액으로부터 스핀 코팅을 통해 증착될 수 있다. 상기 고체 산은 약 50 ℃에서 약 2분 동안 가열함으로써와 같이, 충분히 가열되어 구조적으로 견적한 막(1212)을 만든다. 프린팅 방식의 작업에서, 상기 기판(1210)은 가열된(약 25 내지 300 ℃) 평판(platen) 위에 위치되어질 수 있고, 예를 들면, 포름산 구리와 같은 산화물 전구체(1214)를 포함하는 잉크가 잉크젯 헤드를 통해 수송함으로써 또는 상기 전구체(1214)를 포함하는 텐플릿과 상기 기판(1210)을 접속시킴으로써 원하는 패턴으로 적용될 수 있다. 상기 템플릿은 그라비어 프린터, 활판(letterpress), 또는 마이크로콘택(microcontact)의 일부를 포함한다. 가열 조건에서(약 250 ℃보다 높은) 상기 전구체(1214)는 산화물로 분해되고, 이어서 상기 고체 산과 반응 및 상호확산하여 쉽게 세정 또는 식각되어 패턴(1218)을 드러낼 수 있는 생성물(1219)을 형성한다. 상기 산화물 전구체는 미세한 산화물 마이크로- 또는 나노-입자를 포함하는 페이스트 또는 현탁액 잉크에 의하여 대체될 수 있다. 가열과 함께 또는 가열 없이 미세한 입자들을 적용하는 것은 식각되어 패턴을 드러낼 수 있는 생성물을 형성하는 직접 반응을 가져오게 된다.

<90> 도 13에, 선택된 기판(1310) 위에 패터닝된 산화물을 제조하기 위한 선택적인 구현예를 나타내었다. 초기 단계는 상기 기판 위에 고체 산(1312) 또는 염기를 증착하는 단계를 수반한다. 그런 후, 상기 산화물 전구체(1314)는 스핀 코팅, 프린팅, 화학 기상 증착 또는 물리 기상 증착을 통해 블랭킷 코팅으로서 적용된다. 그런 후, 광 마스크를 통해 빛과 같은 에너지 공급원에 노출시킴으로써 활성화된 전구체(1316)의 패턴이 형성된다. 적절한 광원은 무엇보다도, 필터링되지 않은 중수소 램프 또는 193 nm에서 빛을 만드는 광원을 포함한다. 선택적으로, 포커스를 맞춘 레이저 또는 전자빔으로 직접 가록함에 의하여 활성 전구체(1316)의 패턴이 형성된다. 그런 후, 만일 필요하다면, 상기 활성화되고 패터닝된 구조물(1316)은 두 층들의 상호확산을 촉진하기 위해 약 125 ℃ 내지 약 350 ℃의 온도로 가열될 수 있다. 그런 후, 상기 노출된 영역들은 원하는 패턴(1318)을 생성하기 위해 식각될 수 있다. 노출 감도를 개선하기 위한 절차로서 상기 고체 산 위에 산화물 전구체의 매우 얇은(약 2 nm) 막을 사용하는 것이 수반된다. 그런 후, 상기 전구체층은 산화물 나노입자들의 용액 캐스팅에 의하여,

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또는 화학 기상 증착 또는 물리 기상 증착과 같은 적절한 어떠한 방법에 의해서든 증착된 산화물의 층으로 덮어진다. 상기 층들은 전구체 박막의 노출에 이어 상호확산된다.

<91> 위에서 설명한 공정들은 포지티브 레지스트 기술에 관련된다. 고체 산/염기 및 전구체들은 불용성 생성물을 생성하게 선택하는 것도 가능하다. 이들 생성물들은 적어도 두 가지 방법으로 포지티브 이미지들을 생성하기 위해 사용될 수 있다. 하나의 구현예에서, 상기 두 층들은 하나의 불용성 층을 형성하기 위해 완전히 상호확산된다. 프린팅 또는 노출 및 현상에 이어서, 상기 막의 가용한(soluble) 부분들은 세정 또는 식각되어 포지티브 패턴을 드러낸다. 다른 접근에서는, 상호확산이 전구체와 고체 산/염기 사이에서만 일어나, 얇은 불용성의 장벽층을 생성한다. 그 후, 이 장벽층은 포지티브 이미지를 생성하기 위한 막의 스택의 식각을 조절하기 위해 사용된다. 상기 장벽층은 감광성이다. 그것은, 빛에 노출시키기 전에, 그렇지 않았다면 접촉과 함께 즉시 상호확산하였을 상기 전구체와 상기 고체 산/염기 층 사이의 반응을 방해한다. 일단 상기 장벽층이 감광되면, 그것은 반응성 산화물이 된다. 상기 장벽이 "깨어지고", 그런 후 상기 상부 층은 하부 층과 상호확산할 수 있다.

<92> 광에 기반을 두든 임프린팅에 기반을 두든, 차세대 패터닝은 전자빔 리소그래피에 의하여 통상 제조되는 마스크 또는 템플릿들을 사용한다. 이들 템플릿들 또는 마스크들의 많은 것들은 하드마스크 HSQ (hydrogen silsesquioxane)으로 제조되고 있다. HSQ 마스크들은 다양한 전자, 데이터 저장, 및 미세전자기계 소자들의 제조에 널리 사용된다. HSQ는 또한 임프린트 리소그래피를 위한 하드 마스터/템플릿으로서 개발되고 있다.

<93> 마스크들 및 템플릿들은 도 14에 나타낸 단일층 공정에서 여기서 설명된 막들을 이용하여 제조될 수 있다. 상기 공정의 제 1 단계는 기판(1412) 위에 무기 전구체(1410)의 박막(약 1 nm 내지 약 100 nm)을 증착하는 단계를 수반한다. 상기 무기 전구체(1410)는 퍼옥사이드 또는 유사한 배위 음이온과 함께 있는 고체 산 또는 염기, 예를 들면, 금속 Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, 또는 Lu의 하나 또는 그 이상을 포함하는 수화된 설페이트, 포스페이트, 나이트레이트, 실리케이트, 알루미네이트, 보레이트 또는 이들의 혼합물일 수 있다. 또한, 상기 고체 산/염기와 퍼옥사이드 혼합물은 NH_3, OH, F, Cl, Br, I의 하나 또는 그 이상을 포함할 수 있다. 상기 고체 산/염기는 스핀 코팅, 액체 미스팅(misting) 또는 프린팅을 통해 증착되는 것이 바람직하고, 물리 및 기상 증착은 추가적인 옵션이다. 하나의 예로서, 상기 고체 산은 $HfOCl_2$, H_2SO_4(aq), 및 H_2O_2(aq)의 수용액으로부터 스핀 코팅을 통해 증착될 수 있다. 상기 고체 산은 약 50 ℃ 내지 약 125 ℃의 온도에서 약 10초 내지 약 10분 동안의 시간 동안 가열함으로써와 같이, 충분히 가열되어 구조적으로 감직한 막을 만든다. 그런 후, 상기 막은 광 마스크를 통해 또는 정의된 레이저 또는 전자빔을 통해 노출되고, 노출된 영역에서 응축을 유발한다. 노출된 영역(1414)들의 용해도는 노출되지 않은 영역들에 비하여 감소되고, 따라서 상기 노출되지 않은 영역들은 산 또는 염기에 선택적으로 식각될 수 있다. 사용될 수 있는 산 또는 염기들의 예는, 무엇보다도, 염산, 황산, 과산화수소, 수산화나트륨, 및 테저리메틸 암모늄 히드록사이드를 포함한다. 통상, 사용되는 산 또는 염기들의 농도는 약 0.1 M 내지 약 1 M의 범위 내이다. 그런 후, 약 100 ℃보다 높은 온도에서의 선택적인 열경화에 이어서 상기 막은 수성 산 또는 염기 내에서 노출되지 않은 영역들을 식각하기 위해 현상된다. 이 공정은 막 내에 네거티브-톤의 이미지를 생성한다. 적용된 막을 필드(field) 노출 시키기 전에 더 높은 온도로 예열함으로써, 포지티브-톤 이미지를 구현하도록 차별적인(differential) 식각 속도가 유발될 수 있다. 도 15는 일적으로 예열된 단일층 막에 대한 차별적인 식각 속도를 설명한다. 상기 그래프는 노출된 영역이 노출되지 않은 영역에 비하여 초기시간 이후에 더 빨리 식각되도록 열처리가 식각 속도에 영향을 미치는 것을 설명한다.

<94> 또 다른 구현예에서, HafSOx 막은 수산화나트륨과 과산화수소의 혼합물로 처리되어, 음이온 교환 및 $M(OH)_x/H_2O_2$ 막의 형성을 가져온다. 선택적으로, $M(OH)_x/H_2O_2$ 막을 형성하기 위하여, 이전에 제조한 $M(OH)_x$ 막을 과산화수소에 적실 수 있다. 결과로서 일어지는 $M(OH)_x/H_2O_2$ 막은, 그런 후, 빛 또는 전자빔에 노출됨으로써 패터닝된다. 이들 기술들은 폴리머 레지스트 없이 복합 MO_x 막의 단순한 직접 패터닝하기 위한 수단들을 제공한다. 예를 들면, HfO_2 막들은 Si CMOS 회로 및 프린트된 전자공학 응용에서 하이 k 유전체로서 사용되기 위해 직접 패터닝될 수 있다. 또 다른 예에서, 패터닝된 TiO_2 막은 H_2O_2 내에서 $Ti(OH)_4$를 용액 증착함으로써 형성된 $Ti(OH)_x/H_2O_2$ 막으로부터 제조될 수 있다.

<95> 이들 방법들은 실질적으로 2-층 구현예들에서 사용된 확산을 제거하고, 노출 도스를 낮추며, 라인-에지 조도와 임계 치수(critical dimension)를 개선한다. 도 16은 전자빔이 0 $\mu C/cm^2$ 보다 크고 적어도 400 $\mu C/cm^2$까지의 범위의 도스 레벨을 갖는 단일층, 네거티브 톤 공정을 통해 패터닝된 HafSOx 막의 AFM(atomic force

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microscope) 이미지이다. 상기 이미지의 오른쪽의 나노미터 스케일은 상기 막 내부로 식각된 피치들의 높이를 나타낸다. 도 16에 나타낸 바와 같이, 피치들은 2 $\mu C/cm^2$라는 낮은 도스 레벨로 전자빔 노출을 통해 기록되었다. 이 도스 레벨은 알려진 최고의 화학 증폭된 폴리머 레지스트들에 필적할만하며, 무기 레지스트에 대하여 이전에 입증된 것보다 1000 배나 낮다. 피치들은 약 20 nm 미만의 해상도로 제조될 수 있다. 또한, 상기 막들은 HSQ에 대하여 증명된 것보다 거의 하나의 차수(an order of magnitude)만큼 작은 3 nm 미만으로 구조적 집적도(integrity)(예를 들면, 매끈하고, 조밀하고, 핀홀이 없는)를 증명한다.

<96> 무기 물질의 진공 및 고온 처리 단계들뿐만 아니라 폴리머 레지스트와 관련된 막의 적용, 가열, 및 식각 단계들이 패터닝 과정에서 제거되었다.

<97> 결과로서 얻어지는 막은 전자 소자의 가능적인 부품, 아래에 있는 기판의 후속 패터닝을 위한 하드 마스크, 또는 임프린팅을 위한 템플릿일 수 있다. 전자빔 노출을 제외하고, 모든 처리는 공기 중의 보통의 환경에서 수행된다. 이러 처리 단계들의 제거를 고려할 때, 개시된 기술은 소자 제조 수율을 개선하고 제조 비용을 낮추기 위한 새로운 방법을 제공한다. 수심 화학의 특별한 사용에 따르면, 상기 공정은 또한 환경 친화적이며, 세정된 생성물들은 완전히 회수되어 재생될 수 있다. 상기 기술은 많은 고급 기술들에 응용성을 갖는다. 그의 사용은 여기에 설명한 시스템에만 한정되지 않는다.

<98> B. 핫 엠보싱(hot embossing) 리소그래피

<99> 핫 엠보싱 리소그래피는 HafSOx, ZircSOx 및 관련 물질에 패턴을 생성하기 위한 다른 방법이다. 도 17에 개념적으로 도시한 본 방법은 유기 폴리머로 패턴을 생성하기 위해 매우 널리 적용되어 왔다. HafSOx 및 관련 조성물의 반고체 형태는 유기 폴리머들에 비하여 훨씬 더 높은 기계적 강도, 화학적 안정성 및 고유한 전기적 및 광학적 특성을 갖는 무기 물질의 패터닝할 기회를 제공한다.

<100> 도 17을 참조하면, HafSOx 또는 관련된 무기 물질은, 유기 폴리머 대신, HafSOx 층(1714)을 형성하기 위해 적합한 기판(1712) 위에 스핀 코팅 또는 잉크젯 프린팅에 의하는 것과 같이 용액 증착된다. 기판(1712)과 HafSOx 층(1714)은 적층체 구조물(1710)을 정의한다. 나노미터, 마이크로 미터 또는 밀리미터 크기 스케일과 같은, 원하는 크기의 스케일의 단위 피처들을 갖는 스탬프(1716)가 상기 반고체 HafSOx 또는 관련된 막의 층(1714)에 프레스되어 스탬프된 층(1718)을 형성한다. 스탬프된 층(1718) 및 기판(1712)은, 그런 후, 가열되어 HafSOx를 경화시킨다. 그런 다음, 상기 스탬프가 제거되어 패터닝된 적층체 구조물(1720)에 패터닝된 HafSOx 물질을 정의한다.

<101> C. 측정 장치

<102> 위에서 설명한 이중층 포지티브 레지스트 기술을 위해 개발된 화학은 전자 현미경과 같이 적합한 분야에서 측정을 표준화하는 데 사용하기 위한 도 18에 도시한 바와 같은 물리적 자의 제조하기 위해 사용될 수도 있다. 본 응용에서, 교호하는 산-가용성 층들(1812)과 산-불용성 층들(1814)의 나노 적층체(1810)가 증착된다. 상기 산-가용성 층들은 하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 ($MO_{3-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) 화합물의 용액 증착에 의하여 형성된다. 통상 이 층은 구리로 도핑된다. 상기 산-불용성 층들은 하프늄 및/또는 지르코늄 옥시 히드록시 설페이트 ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 텅스테이트 ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 보레이트 ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) 화합물, 하프늄 및/또는 지르코늄 옥시 히드록시 포스페이트 ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) 화합물, 및/또는 하프늄 및/또는 지르코늄 옥시 히드록시 실리케이트 ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) 화합물의 용액 증착에 의하여 형성된다(여기서, M은 하프늄 또는 지르코늄이고, x와 z는 고정되거나 변화할 수 있으며 x는 약 0.1 내지 약 3.5/(다원자 이온 전하)의 범위에서 어떤 값이든 가질 수 있고, z는 0.0 내지 3.8의 범위에서 어떤 값이든 가질 수 있음).

<103> 상기 층들(1812 및 1814)의 폭들은 반사 X-선에 의하는 것과 같이, 정확하게 결정된다. 그런 후, 상기 산-가용성 층들(1812)은 식각되어 전자 현미경에서 목적물을 정확하게 측정하는 데 2차적인 척도로서 사용될 수 있는 핑거-타입 패턴(1820)을 드러낸다.

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<104> D. 부식 장벽

<105> 금속 또는 합금 또는 세라믹과 같은 적절한 기판 위에 전구체 액체가 코팅되어 부식 장벽을 형성할 수 있다. 또한, 상기 액체는 몸드 내에 위치하거나 또는 홀로 사용되는 섬유 내부로 인입될 수도 있다. 상기 액체는 공기 중에서 가수분해, 머널링 또는 열분해를 포함하는 적합한 어떠한 공정에 의하여든 고체, 안정한 형태로 전환된다. 통상, 이것은 적어도 수 초동안, 더욱 전형적으로는 적어도 수 분동안 보통 100 ℃ 이상의 온도와 같이 원하는 결과를 얻기 위해 유효한 온도로, 시간 동안 가열할 것이 요구된다.

<106> 상기 막들의 원자적으로 조밀한 성질로 인하여, 잠재적인 응용은 다른 많은 것들뿐만 아니라, 금속 및 금속/세라믹-계 열 보호(thermal protection) 시스템, 유기계 디스플레이 및 전자 제품, 태양 전지, 고 방사율(emissivity) 코팅, 산화물계 세라믹 매트릭스 시스템에 대한 계면 코팅, 인광체(phosphor) 위의 보호 코팅, 금속- 및 세라믹계 시스템에 대한 주변적 장벽 코팅, 복합체 및 섬유 레이저용 섬유, 용해 금속 처리에서의 부식 방지, 단열용 모노리딕 물질 및 촉매 담체에 대한 열, 부식 및 산화 방지를 포함하지만 여기에 한정되는 것은 아니다. 상기 막들을 적층할 수 있는 능력은 다른 층과 관련하여 한 층에서 결함의 위치를 무작위화(randomize)할 기회를 제공하여 개선된 부식 보호를 제공한다.

<107> E. 광학 코팅

<108> 상기 전구체 액체들은 반사 방지 코팅, 유전체 거울(dielectric mirror), X-선 거울, 간섭 필터, 회절 격자, 도파로(waveguide), 평면 코팅 및 내-스크래치 표면을 만들기 위해 적절한 광학 기판 위에 개별 층들로서 및 다층 형식으로 코팅될 수 있다. 적어도 두 개의 물질 조성물을 교호 적층함으로써 나층 주기성이 달성된다. 단층 주기성은 포토리소그래픽 공정에 대하여 설명한 바와 같이 식각에 의하여 달성될 수 있다. 비결정질적인 성질, 층들 사이의 명확한 계면, 및 유전 상수를 조절하는 능력은 이론적 한계에 가까운 성능을 구현하기 위한 공정을 제공한다.

<109> 선택적으로 증착되거나 식각된 다층 또는 단일층 구성에서, 주기적인 구조물은 회절 응용에 적합하다. 보이드 및/또는 단일 또는 다중 물질들의 조합은 구조물을 정의할 수 있다. 보이드 공간의 사용은 주어진 구조를 내에서 물리적 성질의 큰 대비를 가능하게 한다. 기능적인 특성들은 보이드 공간의 사용에 의하여 개선되거나 구현될 수 있다. 광학 격자도 유사하게 정의될 수 있다.

<110> 실질적으로 매끈한 표면 막들은 여기에 개시된 방법의 구현예들에 따라 증착될 수 있기 때문에, 더 큰 정도의 조도(roughness)를 보이는 금속, 세라믹, 및 플라스틱과 같은 기판 층들을 평탄화하기 위해 막들이 사용될 수 있다.

<111> F. 발광막

<112> 물질은 수많은 발광 파장들에서 에너지를 흡수하고 광자를 방출할 수 있다. 발광 현상은 지배적인 상(또는 호스트) 만을 수반할 수도 있고, 또는 첨가된 원소들을 포함할 수도 있다. 단일 물질은 수많은 발광 첨가제에 대하여 호스트로서 작용할 수 있다. 개시된 막 조성물들의 많은 수는 시각적으로 투명하고, 투명성이 스펙트럼의 자외선 부분으로 잠재적으로 연장되고 있다. 이러한 물질들은 발광 호스트 물질로서 잠재적으로 기능한다. 이들 물질들은 조명 및 디스플레이 응용을 위해 관심이 있는 발광막을 가져오기 위하여, 예를 들면, Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+} 및 이들의 조합을 포함하는 통상의 발광성 이온들로 선택적으로 도핑될 수 있으나 여기에 한정되지 않는다.

<113> G. 프린트된 전자 제품

<114> 제조업자들은 종래의 기상 증착 및 리소그래픽 공정의 한계를 제거한 새롭고, 효율적인 제조 방법들을 찾고 있다. 프린팅 및 관련 마스크리스(maskless) 기술들은 백-플레인(back-plane) 전자공학에 있어서, 제조 효율의 개선을 구현하기 위한 길로서 널리 간주되고 있다.

<115> 개시된 용액-처리된 박막들은 대부분의 발전된 기상 처리 방법에 의하여 달성되는 것들과 유사한 모폴로지 및 소자-기능적 특성들을 보인다. 개시된 조성물의 용액들은 마이크로콘택, 그라비어, 잉크젯 프린터 또는 다른 적합한 수단들에 의해서와 같이 임프린트될 수 있다. 결과로서 얻어지는 임프린트된 용액들은 약 20 nA/cm^2 미만의 유전체 누설 전류 밀도를 갖고, 약 10 cm^2/Vs의 소자 이동도를 보이는 안정한 무기 트랜지스터 어레이들을 제조하기 위해 사용될 수 있다. 유전체 및 반도체 잉크들은 또한 약 100 nA/cm^2 미만의 유전체 누설 전류 밀도

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와 약 1 cm^2/Vs의 이동도를 갖는 트랜지스터 어레이를 제조하기 위해 유리 기판 위에 프린트될 수 있다. MIM 캐패시터 어레이들은 약 5보다 큰 상대 유전 상수 및 약 50 nA/cm^2 미만의 누설 전류 밀도로 제조될 수 있다.

실 시 예

<153> **실시예들**

<154> 본 발명의 작동 및/또는 가상의 구현예들의 특정한 특징들을 예시하기 위하여 다음 실시예들이 제공된다. 당 기술분야에서 통상의 지식을 가진 자는 본 발명의 범위가 이들 실시예에서 언급된 특정한 특징들에 한정되지 않음을 이해할 것이다.

<155> **실시예 1**

<156> 본 실시예는 벌크 침전물을 위한 또는 박막 전구체들로서 사용하기 위한 공급원으로서 용액들을 제조하기 위해 사용된 일반적인 방법을 설명한다. 다음 시약들이 사용되었다. $HfOCl_2 \cdot 8H_2O$ (Alfa Aesar, 99+% (1.5%Zr 제외)); $ZrOCl_2 \cdot 8H_2O$ (Wah Chang 분광 등급(spectrographic grade)); $La_2(SO_4)_3$ (Alfa Aesar, 99.9%); $La(NO_3)_3 \cdot 6H_2O$ (Johnson Matthey, 99.9%); $Ce_2(SO_4)_3 \cdot 8H_2O$ (Strem, 99%); CaO (Alfa Aesar, 99.95%); $(NH_4)_2SO_4$ (Mallinkrodt AR); H_2SO_4(aq) (EM Science, GR ACS, 95-98%); 및 NH_3(aq) (EM Science, GR ACS, 28-30%). 모든 용액들은 $HfOCl_2$ 또는 $ZrOCl_2$를 약 0.8 M의 총 금속 농도를 위하여 필요한 만큼의 $La_2(SO_4)_3$, $Ce_2(SO_4)_3$, 또는 CaO와 결합하고, 이어서 약 0.5 M의 총 금속 농도를 위하여 설페이트 용액을 첨가함으로써 제조되었다. 이들 용액들은 열-유발된 침전 및 스핀-코팅 유전막들에 대하여 직접 사용되었다. 히드록사이드 침전 반응 또는 나노적층체 증착을 위해 전구체로서 작용하는 데 필요한 바에 따라 추가적인 변경이 이루어졌다.

<157> **실시예 2**

<158> 본 실시예는 실시예 1에 따라 제조된 용액들로부터의 벌크 침전을 위해 사용된 일반적인 방법을 설명한다. 침전은 끓는 수조에 용액의 튜브를 40분간 침지시킴으로써 유발되었다. 히드록사이드-유발된 침전에 대하여, $HfOCl_2$ 및 $La_2(SO_4)_3$는 23% La(금속 백분율)이 되도록 혼합되고, 이어서 $La(NO_3)_3$ 및 $(NH_4)_2SO_4$의 용액들을 첨가함으로써 약 0.39 M의 하프늄 농도([Hf]), 약 0.18 M의 란탄 농도([La]), 및 약 0.42 M의 설페이트 농도($[SO_4]$)를 제공하였다. 그런 후, (총 금속과 관련하여) 1.9 몰 당량의 포화 NH_3(aq)가 신속히 첨가되고, 그 결과로서 얻어지는 혼합물을 1분 동안 교반하였다. 모든 침전물들은 석션이 달린 종이 여과 및 여러 차례 탈이온수로 세척함에 의하여 상청액(supernatant)으로부터 분리되었다. 여과물은 1일 동안 실온에서 건조되었다. 이어서 샘플들을 주위 공기에서 알루미나 도가니에 넣고 약 100 ℃에서 약 1,500 ℃의 온도로 약 1 시간 내지 약 4 시간 동안 가열하였다. Siemens D5000 회절계로 Cu Kα 방사선을 이용하여 XRD 데이터를 수집하였다. 열중량분석 데이터는 Shimadzu TGA-50을 이용하여 N_2(g)를 흘리면서 Pt 도가니에서 샘플들(10-20 mg)을 통상 10 ℃ $분^{-1}$의 속도로 가열하고 최고 온도에서 15분 동안 유지함으로써 수집하였다. 유도 결합 플라스마 원자 발광 분석(ICPAES: inductively coupled plasma atomic emission spectroscopy)이 Jobin Yvon JY2000 분석 설정으로 수행되었다. 샘플들을 침지 밤(digestion bomb)에 넣고 수 시간 동안 200 ℃에서 용해시키고 측정 가능한 수준으로 희석하였다.

<159> **실시예 3**

<160> 본 실시예는 실시예 1에 따라 제조된 용액들을 이용하여 박막을 증착하기 위해 사용되는 일반적인 방법을 설명한다. HafSOx, ZircSOx 및 La, Ce 또는 Ca 첨가된 유도체들의 박막이 3,000 rpm으로 30초 동안 스핀코팅에 의하여 Si 기판 위에 증착되고, 즉시 이어서 135 ℃에서 1.5 내지 2 분 동안 열판 증착을 하였다(15초 내지 약 2 분 동안 325 ℃ 오븐 표면 위에서 추가적인 가열이 특정 도핑수에 대하여 필요할 수 있다). 이 공정은 원하는 증착 막 두께가 얻어질 때까지 반복되었다. 325 ℃에서의 최종 오븐 어닐링은 5 내지 10분 동안 사용되었다.

<161> 나노 적층체 막들을 위한 전구체들이 $HfOCl_2$ 또는 $ZrOCl_2$에 H_2SO_4를 금속에 대하여 46% 설페이드가 되도록 첨가함으로써 제조되었다. 용액은 금속 농도가 0.03 내지 0.13 M로 희석되었다. HafSOx와 ZircSOx의 교호하는 층들이 유전막에 대하여 설명한 바와 동일한 방식으로 증착되었다.

<162> 상기 실리콘 기판은 SiO_2 또는 Ta 금속의 표면을 가졌다. 유전 테스트를 위하여 500-나노미터 Ta 표면이 이용

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되었다. 모든 다른 목적으로는 200-나노미터 SiO_2 표면이 사용되었다. 상기 표면들은 45℃의 (Decon Labs, Contrad 70) 용액 내에서 45분간 초음파 세척을 한 후 증착하기 전에 Millipore 물로서 완전히 표면을 세정함으로써 증착을 위한 준비를 하였다.

<163> XRD 데이터는 50 kV 및 270 mA에서 회전 음극으로부터 생성된 Cu Kα 방사선을 채용한 Rigaku RAPID 회절계로 수집되었다. 회절된 빔이 이미지 판에 수집되는 동안 입사빔의 각도는 7.6° 이었다. Cu Kα 방사선으로 XRR 데이터가 수집되었다. 낮은 각도 반사가 10° (2θ)까지 0.005° 단위로 수집되었다. 푸과 FTIR 데이터가 코팅되지 않은 기판을 레퍼런스로 하여 Nicolet 5PC 스펙트로미터를 이용하여 수집되었다. EMPA가 수집되었다.

<164> 증착된 유전체 위의 Al의 원형 콘택(1.2 mm 직경)들을 열적으로 증발시킴으로써 MIM 캐패시터 구조물들이 완성되었다. 유전 상수 및 손실 탄젠트의 파라미터들을 얻었다. 하부-게이트 트랜지스터 구조물도 활성-영역의 가열 없이 무기 채널 물질들을 스퍼터링함으로써 제조되었다. 이어서 ZTO-채널 소자들이 325 ℃로 1 시간 동안 가열되었다. 알루미늄 소오스 및 드레인 콘택들이 열적으로 증발되었다. 트랜지스터 특성화가 수행되었다.

<165> **실시예 4**

<166> 본 실시예는 매끈하고, 조밀하며 핀홀이 없는 약 2 nm만큼 얇은 초박(ultra-thin) 나노적층체 막을 제조하기 위한 일반적인 방법을 설명한다. 미합중국 특허공개 제2005/0242330A1호에 설명된 바와 같이 $HfOCl_2 \cdot 8H_2O$ 또는 $ZrOCl_2 \cdot 8H_2O$, H_2O_2 (30%) 및 H_2SO_4(aq)를 포함하는 전구체 용액이 준비되었다. 상기 전구체 용액은 약 0.05 M 내지 0.4 M의 금속 이온 농도 및 금속에 대하여 70% H_2O_2 및 50% 설페이트를 포함하였다. 금속 이온 농도에서의 상기 차이는 코팅당 두께의 변화를 3 nm에서 25 nm로 변화시키는 것을 가능하게 하였다. 실리카 기판 위에 열성장 SiO_2의 박막이 증착되었다. 기판은 45 ℃에서 60 분간 Contrad-70 용액으로 초음파 조를 이용함으로써 세정되고, 이어서 탈이온수로 헹구어졌다. 스핀 코터를 이용하여 3000 rpm의 스핀 속도로 30초 동안 막이 증착되고, 이어서 125 ℃에서 1 내지 2 분 동안 열판(hotplate) 증합이 후속되었다. 스핀-코팅과 증합 단계는 원하는 두께에 도달할 때까지 반복되었다. 원하는 두께에 도달한 후, 일부 막들은 결정화 온도까지 가열되었다. 다른 막들은 0.1 M 내지 0.5 M NaOH 조에서 1 내지 2분 동안 1차 처리되고, 그런 후, 헹치리되기 전에 탈이온수 조에서 1 내지 2 분 동안 세정되었다.

<167> X-선 회절(XRD) 분석을 이용한 박막 특성화가 Cu Kα 방사선을 채용한 Rigaku R-axis RAPID로 수행되었다. Veeco NP-20 SiN 탐침 및 1.15 Hz의 스캔 주파수를 갖고 접촉 모드로 동작하는 Digital Instruments Nanoscope III Mulitmode AFM으로 원자력 현미경(AFM: atomic force microscopy) 측정을 수행하였다. Bruker Discover D8을 이용하여 반사 X-선 측정이 수행되었고, 상기 막의 표면과 계면 조도를 결정하기 위해 사용되었다. 4개의 튜닝가능한 파장 분산 분광기로 장착한 Cameca SX-50 전자 마이크로탐침 상에서 조성 분석이 얻어졌다. O, Cl, Na, S, 및 Si의 Kα 세기와 Zr 및 Hf의 Lα 세기를 모니터하기 위해 12, 16 및 22 kV의 가속 전압들이 사용되었고 5 점에 걸쳐 평균을 내었다. 분석을 위해 사용된 스탠다드는 MgO, Hf, Zr, FeS_2 (pyrite), $Ca_5(PO_4)_3Cl$ (apatite), Si, and Si_3AlNaO_8 (albite)이었다. Probe for Windows 자동화 및 분석 패키지를 이용하여 원본 세기(raw intensity)에 대한 수정이 이루어졌다. StrataGEM 조성 분석 소프트웨어 패키지를 사용하여 실험으로 구한 K-비율들과 모사된 값들을 비교함으로써 박막 기하구조를 수정하였다.

<168> 비결정질이고, 원자 수준에서 평탄하고, 조밀하고, 핀홀이 없는 박막들이 증착된대로의(as-deposited) 막들과 교환된 막들에 대하여 스핀 코팅을 통해 증착되었다. 도 19는 약 0.1 nm의 조도를 갖는, 교환되지 않은 HafSOx 막의 AFM 이미지이다. 도 20은 HafSOx의 이온 교환과 850 ℃에서의 열처리 다음의 HfO_2 막의 TEM 이미지이다. 교환되지 않은 막들은 Zr에 대하여는 600 ℃까지, Hf에 대하여는 650 ℃까지 매끈하고 비결정질로 남았다. 그러나, 이들 온도보다 높게 가열한 후에는, 막들이 결정화되고 표면에 화산과 같은 피처들을 형성하면서 거칠게 되었다. 도 21은 실리카 위에 증착된 HfO_2 막의 AFM 이미지이다. 상기 HfO_2 막은 HafSOx의 열분해에 의하여 형성되었다. 결과로서 얻어지는 막은 약 5 nm의 조도를 가졌고, 화산과 같은 피크들을 가져왔다. 이들 피처들은 SO_3의 손실에 의하여 야기되었을 것으로 유력하게 추정되었다. 이것은 700 ℃를 넘는 온도에서 설페이트 분해(SO_3 (g) → SO_2 (g) + ½O_2 (g))가 일어나는 Hf 설페이트 분말의 열질량 분석에 의하여 뒷받침된다. 화산 현상을 없애기 위하여, 막들은 0.1 내지 0.5 M NaOH(aq) 조 내에서 1분 내지 2분 동안 처리되고, 가열하기 전에 막으로부터 SO_4^{2-} 및 Cl^- 음이온들이 제거된다. 이전부터 NaOH는 히드록시 음이온을 지르코늄 염의 다른 음이온과 효과적으로 교환하는 것으로 알려져왔다. 상기 NaOH 처리는 40 내지 40%의 두께 감소를 가져오지만(2 내지

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15 nm의 두께의 층을 가져옴), 상기 처리는 지르코니아와 하프니아 대하여 각각 500 ℃와 550 ℃ 이하로 가열할 때 막의 매끈함(smoothness)(~1Å) 또는 비결정질 성질에는 영향이 거의 없다.

<169> 도 22는 실리카 위에 증착되고, 이어서 0.1 M NaOH로 처리되고 450 ℃에서 10분간 가열된 HafSOx 막의 AFM 이미지이다. 결과로서 얻어지는 막은 약 0.1 nm의 조도를 가졌다. 이들 온도 위로 가열된 막들은 결정화되었지만 850 ℃까지의 온도에서는 매끈함을 유지하였다.

<170> 도 23은 실리카 위에 증착되고, 이어서 0.1 M NaOH로 처리되고 850 ℃에서 10분간 가열된 HfO_2 막을 나타낸다. 결과로서 얻어지는 결정화된 막은 약 0.2 nm의 조도로 매끈하게 유지되었다.

<171> X-선 회절 그래프에서(도 24 내지 도 27) 결정화 온도의 감소가 관찰되었다. 도 24 내지 도 27에서, 기판의 피크들은 소프트웨어에 의하여 제거되었다. "*"는 주요 정방정계(tetragonal) 상의 피크들을 나타낸다. 도 24는 700 ℃에서 정방정계와 단사정계(monoclinic) 상의 혼합물로 결정화된 처리되지 않은 HfO_2 막의 XRD 그래프이다. HfO_2 그래프는 단사정계 상에 대한 기준 그래프이다. 대조적으로, 도 25는 550 ℃에서 단사정계 상에서만 결정화된 0.1 M NaOH로 처리된 하프니아 막의 XRD 그래프이다. HfO_2 그래프는 단사정계 상에 대한 기준 그래프이다. 도 26은 650 ℃에서 단사정계와 정방정계 상이 혼합되어 결정화된, 처리되지 않은 지르코니아 막의 XRD 그래프이다. ZrO_2 그래프는 단사정계 상에 대한 기준 그래프이다. 도 27에서 보는 바와 같이, 0.13 M NaOH 처리된 지르코니아 막들은 500 ℃에서 정방정계에서만 결정화되었다. 계속 가열하면, 막은 단사정계와 정방정계 상 모두로 발전되었다. HfO_2와 ZrO_2의 정방정계 상들은 이전의 박막 연구에서 관찰되었다. 더 낮은 결정화 온도, 결정화 및 두께 손실은 NaOH 처리가 박막으로부터 음이온(SO_4^{2-} 및 Cl^-)을 제거함을 가리켰다.

<172> 0.4 M Hf 용액으로부터 증착되고 350 ℃까지 5분 동안 가열된 막의 전자 탐침 미세 분석(EPMA: electron probe microanalysis)은 $HfO_{1.33}(SO_4)_{0.61}Cl_{0.15}$의 조성을 가져왔다. 상기 막 내의 염소는 급속한 물 탈수의 결과로 동적 트랩핑된 결과였다. NaOH(aq) 조 내에서의 처리된 박들은 측정 가능한 황의 레벨을 갖지 않았고(0.01 원자 퍼센트 미만), 0.3 원자 퍼센트 미만의 Cl이 관찰되었다. 이것은 황과 염소가 모두 NaOH(aq) 조 내에서 상기 막으로부터 제거되었음을 확인하였다. EMPA는 또한 상기 처리 후에 상기 막에 남은 잔류 나트륨은 0.3 원자 퍼센트 미만임을 확인하였다.

<173> **실시예 5**

<174> 위에서 설명한 접근방법들의 구체적인 구현예들에서, 수화된 인듐 및 갈륨 나이트레이드 염들($In(NO_3)_3 \cdot 0.5H_2O$ 및 $Ga(NO_3)_3 \cdot 9.5H_2O$)을 메탄올(CH_3OH) 내에 용해시켰다. 최종 농도는 [In] = 0.288 M, [Ga] = 0.170 M이었다. 그런 후, 아연 분말을 상기 용액에 첨가하고, 플라스크를 밀봉하였다. 아연의 최종 농도는 0.2 M이었다. 1일 내지 7일의 기간에 걸쳐 반응시키고, 상기 분말은 서서히 산화되고 용해되어 전체 금속 이온 농도를 0.658 M까지 민화시켰다. 상기 메탄올 용액을 공기 중에 노출시키고, 실온에서 증발할 수 있도록 하였다. 그런 후, 상기 용액 내에 잔존하는 고체 잔사물을 H_2O에 용해시켜 총 금속 농도를 0.395 M로 하였다. 이 전구체 용액은 도전성 백 콘택(back contact)을 갖는 SiO_2 기판 위에 스핀-코팅되고, 450 ℃에서 1 시간 내지 4 시간 동안 어닐링되었다. 어닐링에 이어서, 투명하고 비결정질인 $InGa_{0.5}Zn_{0.7}O_{3.15}$ 반도체 막을 도 28의 SEM 이미지에 나타낸 바와 같이 수득하였다. 알루미늄 소오스 및 드레인 콘택들은 박막 트랜지스터(TFT)를 제조하기 위해 새도우 마스크를 통해 산화물 반도체 막 위로 열 증발되었다. 이들 TFT들의 전계 효과 이동도는 8 $cm^2 V^{-1} s^{-1}$을 넘는 것으로 나타났다.

<175> **실시예 6**

<176> 본 실시예는 이중층 무기 리소그래픽 공정의 두 개의 일반적인 방법들을 설명한다. 하나의 작동 구현예에서, 약 30 nm 내지 약 60 nm의 두께를 갖는 HafSOx 막이 SiO_2/Si 기판 위에 용액 증착되었다. 상기 기판은 약 50 ℃로 설정된 열판(hot-plate)의 직접 위에 위치되고, 상기 막에 구조적 집적도를 부여하기 위해 가열되었다. 결과로서 얻어지는 박은 산에 불용성이었다. 그런 후, 상기 기판을 잉크젯 프린터의 가열된 평판(platen)(약 50 ℃ 내지 200 ℃) 위에 위치되고, 열 잉크젯 헤드를 통해서 기판 위에 포름산 구리의 선들이 프린트되었다. 포름산 구리는 가열됨에 따라 분해되고 HafSOx 막 내부로 확산되어 상기 막을 가용성으로 만들었다. 물로 세정한 후에, 약 300 ℃로 추가 가열하고, 묽은 산 내에서 현상한 결과, 도 29에 나타낸 바와 같이, 그려진 선들은

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명백히 뚜렷하였다.

<177> 다른 작동 구현예에서, 패턴이 먹시 포토리소그래피를 통해 생성되었다. 도 30에 나타낸 패턴의 후속적인 상호확산 및 현상을 위해, 허과되지 않은 중수소 램프를 이용하여 $HfO_{2-x}(SO_4)_x$ 이중층을 신자외선 광에 노출하여 포름산 구리의 분해를 촉진하였다. 패치 크기는 전자빔 가록(writing)에 따라 약 22 nm로 감소되었다. 상기 상호확산 과정은 패턴과 목적물을 나노스케일로 그리도록 전자빔 에너지를 통해 공간적으로 제어될 수 있다. 고해상도의 패턴들이 150 $\mu C/cm^2$ 근처의 전하 도스 레벨에서 생성되었는데, 밥은 폴리머 레지스트들의 그것과 유사한 민감도를 나타낸다. 도 31 및 32는 약 200 $\mu C/cm2$의 도스 레벨에서의 전자빔 기록에 의해 생성된 두 패턴들이다. 도 31에서, 전자 현미경으로 측정한 바와 같이 상기 선의 간격은 500 nm이다.

<178> 실시예 7

<179> 본 실시예는 단일층 부기막을 패터닝하기 위한 일반적인 방법들을 설명한다. 퍼옥사이드 또는 관련된 배위종들을 포함하는 단일 무기막은 적절한 기판 위에 스핀-캐스트(spin-cast), 액체 분무(misted), 또는 잉크젯 프린트된다. 상기 막은 100 ℃ 미만의 중간 정도의 온도에서 가열되어 막의 구조적 집적도를 제공한다. 그런 후, 상기 막은 패턴 또는 다른 바람직한 막 피처들을 정의하기 위해, 포토마스크를 통해 고에너지 광에 노출되거나, 공간 광 모듈레이션을 통한 마스크리스 패턴, 정의된 레이저 빔, 또는 전자빔에 노출된다. 도 33 및 도 34는 사진 공정으로 패터닝된 막들의 두 예들을 나타낸다. 도 33은 패터닝된 $ZrO_{2-x}(SO_4)_x$ 막이다. 도 34는 패터닝된 TiO_2 막이다. 상기 TiO_2 막은 약 15 내지 50 nm 두께이었다. 여과되지 않은 중수소 램프를 이용하여 패터닝하였고, 이어서 0.1 내지 0.2 M HCl로 60초 미만 동안 식각하였다. 도 35 내지 도 37은 전자빔에 의하여 패터닝된 $HfO_{2-x}(SO_4)_x$ 막들이다. 상기 막들은 약 30 내지 60 nm 두께이었다. 이들은 200 $\mu C/cm^2$의 도스 레벨로 전자빔을 이용하여 패터닝되었고, 이어서 5 내지 12 M HCl로 1 내지 4분 동안 식각되었다.

<180> 개시된 본 발명의 원리가 적용될 수 있는 가능한 많은 구현예들의 관점에서, 예시된 구현예들은 단지 본 발명의 바람직한 실시예일 뿐이고, 본 발명의 범위를 한정하는 것으로 받아들여서는 안된다. 오히려, 본 발명의 범위는 첨부된 청구항들에 의하여 정의된다. 따라서, 우리는 이들 청구항들의 범위와 정신의 범위 내에 들어오는 모든 것을 우리의 발명으로 청구한다.

도면의 간단한 설명

<116> 도 1은 다양한 전처리들과 함께 샘플들을 $N_2(g)$을 흘리면서 10℃ $분^{-1}$의 속도로 가열하면서 HafSOx (x = 0.70)에 대한 열질량 분석(TGA: thermogravimetric analysis)(온도에 따른 상대 습도) 결과를 제공한다.

<117> 도 2는 표시된 것을 제외하고는 언급된 온도로 공기 중에서 1 시간 동안 가열한 후의 HafSOx 분말에 대한 XRD 패턴이다.

<118> 도 3은 표시된 것을 제외하고는 언급된 온도로 1 시간 동안 가열한 후의 HafSOx:32% La 분말에 대한 XRD 패턴이다.

<119> 도 4는 공기 중에서 주어진 온도로 5 분 동안 가열한 후의 HafSOx 박에 대한 XRD 패턴으로, 31.8° 와 45.6° 에서의 매우 작은 피쳐(feature)들은 기판에 기인한 것이다.

<120> 도 5는 언급된 온도로 공기 중에서 5 분 동안 가열한 후의 HafSOx:24% La 박막에 대한 XRD 패턴이다.

<121> 도 6은 HafSOx 막에 대한 유전 항복 특성을 도시한다.

<122> 도 7은 이산화실리콘 기판 위와 탄탈륨(Ta) 금속 위에 증착된 HafSOx의 일 구현예를 나타낸 SEM이다.

<123> 도 8은 Ta위에 증착된 HafSOx:24% La에 대한 SEM이다.

<124> 도 9는 이중층이 17.6 nm의 두께를 갖는 14 개의 교호층들(7개의 이중층들)을 포함하는 HafSOx/ZircSOx 다층 박막에 대한 XRR 패턴이다.

<125> 도 10은 포지티브 또는 네거티브 포토레지스트 절차들을 나타낸 개념도이다.

<126> 도 11은 이중층 시스템을 이용하는 포지티브 레지스트를 도시한 개념도로서 도시된 구현예가 하프늄 산화물 설페이트 (HafSOx) 막 위에 증착된 Cu-도핑된 지르코늄 산화물 설페이트 (Cu:ZircSOx) 막을 포함한다

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<127> 도 12는 기판 위에 패터닝된 산화물을 생성하기 위한 이중층 공정을 나타낸 개념도이다.

<128> 도 13은 기판 위에 패터닝된 산화물을 생성하기 위한 이중층 공정을 나타낸 개념도이다.

<129> 도 14는 기판 위에 패터닝된 막을 생성하기 위한 단일층 공정을 나타낸 개념도이다.

<130> 도 15는 열적으로 전처리된, 단일층 막에 대한 식각 시간에 따른 두께의 그래프이다.

<131> 도 16은 전자빔에 의하여 패터닝된 막이다.

<132> 도 17은 유기 고분자에 비하여 훨씬 더 높은 기계적 강도, 화학적 안정성 및 고유의 전기 및 광학적 특성을 갖는 여기에 개시된 화합물들의 반-고체 형태로 사용되기 위한 핫 엠보싱 리소그래피를 도시한 개념도이다.

<133> 도 18은 전자 현미경과 같은 응용 분야에서 표준화 측정으로 사용되기 위한 물리적 자의 한 제조 방법을 도시한 개념도이다.

<134> 도 19는 실리카 위에 증착된, 교환되지 않은 HafSOx 막의 AFM 이미지이다.

<135> 도 20은 HafSOx의 이온 교환과 850 ℃에서의 열처리 후의 HfO_2의 TEM 이미지이다.

<136> 도 21은 700 ℃ 이상으로 가열된 후 HafSOx 열분해로부터 형성되고 실리카 위에 증착된 HfO_2 막의 AFM 이미지이다.

<137> 도 22는 0.1 M NaOH로 처리되고, 450 ℃로 10 분 동안 가열된, 실리카 위에 증착된 HafSOx 막의 AFM 이미지이다.

<138> 도 23은 0.1 M NaOH로 처리되고, 850 ℃로 10 분 동안 가열된, 실리카 위에 증착된 HfO_2 막의 AFM 이미지이다.

<139> 도 24는 처리되지 않은 하프니아 막의 XRD 그래프를 제공한다.

<140> 도 25는 처리된 하프니아 막의 XRD 그래프를 제공한다.

<141> 도 26은 처리되지 않은 지르코니아 막의 XRD 그래프를 제공한다.

<142> 도 27은 처리된 지르코니아 막의 XRD 그래프를 제공한다.

<143> 도 28은 실리카 위에 증착된 인듐 갈륨 아연 산화물 반도체 막의 SEM 이미지이다.

<144> 도 29는 무기 확산-반응과 잉크젯 프린팅을 통해 생성된 선형 패턴이다.

<145> 도 30은 이중층 막을 UV 광에 노출시킴으로써 생성된 패턴이다.

<146> 도 31은 전자빔 기록에 의하여 패터닝된 막이다.

<147> 도 32는 전자빔 기록에 의하여 패터닝된 막이다.

<148> 도 33은 사진적으로 패터닝된 막이다.

<149> 도 34는 사진적으로 패터닝된 막이다.

<150> 도 35는 전자빔에 의하여 패터닝된 $HfO_{2-x}(SO_4)_x$ 막이다.

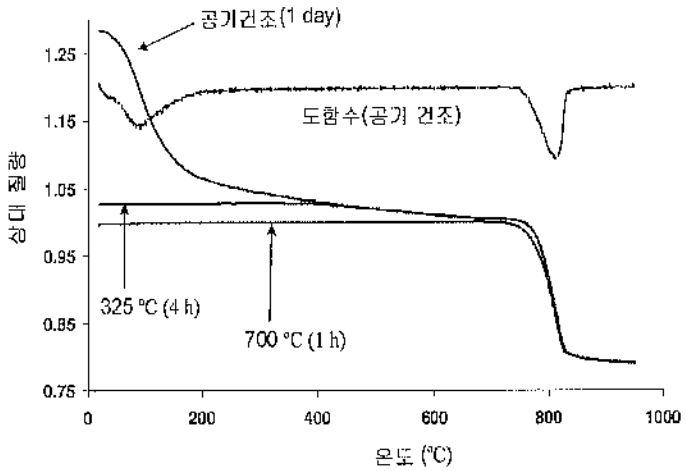
<151> 도 36은 전자빔에 의하여 패터닝된 $HfO_{2-x}(SO_4)_x$ 막이다.

<152> 도 37은 전자빔에 의하여 패터닝된 $HfO_{2-x}(SO_4)_x$ 막이다.

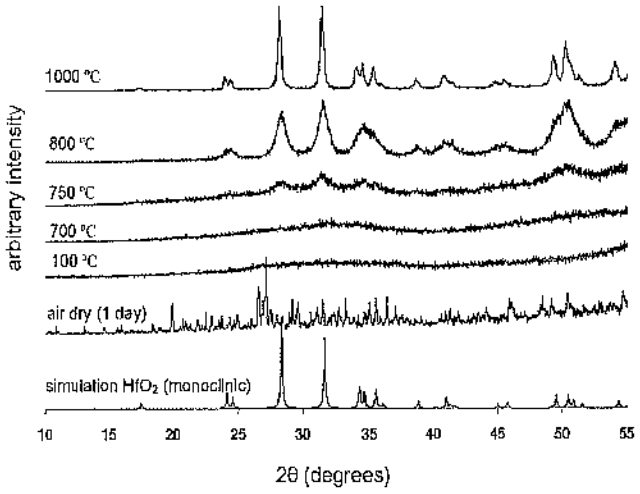
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도면

도면1

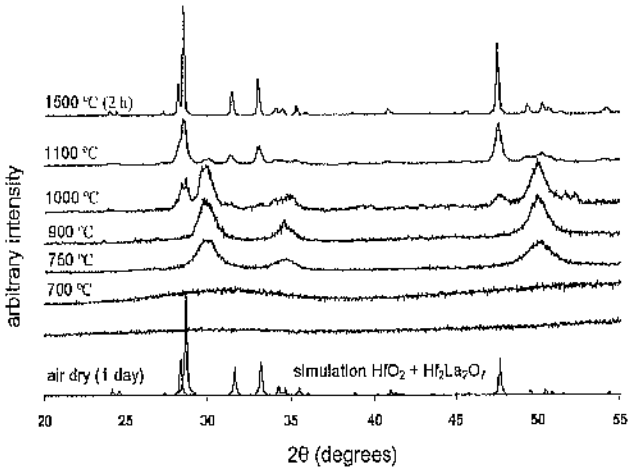


도면2

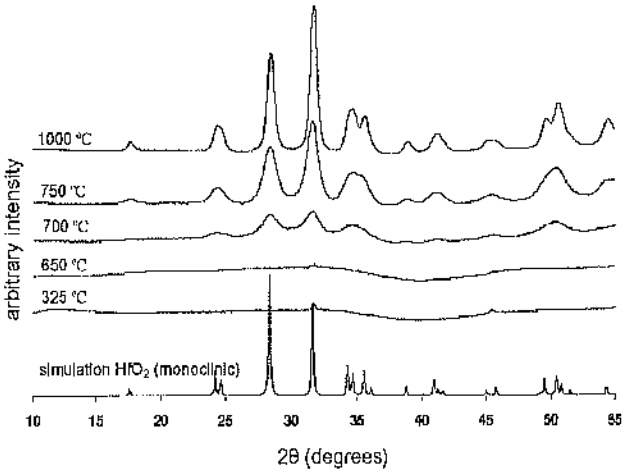


Lam Research Ex. 1004 - Page 802 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

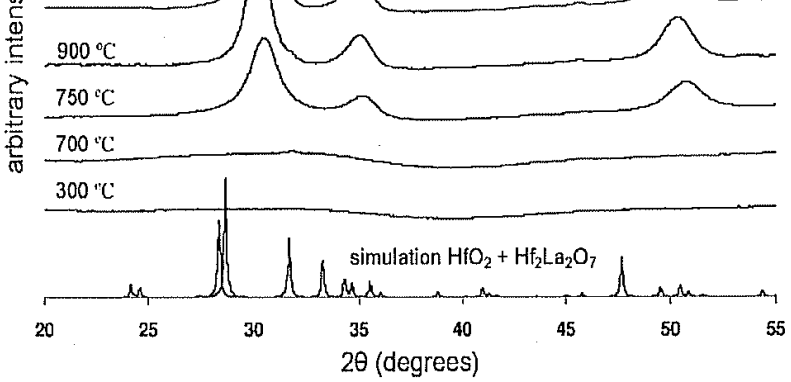
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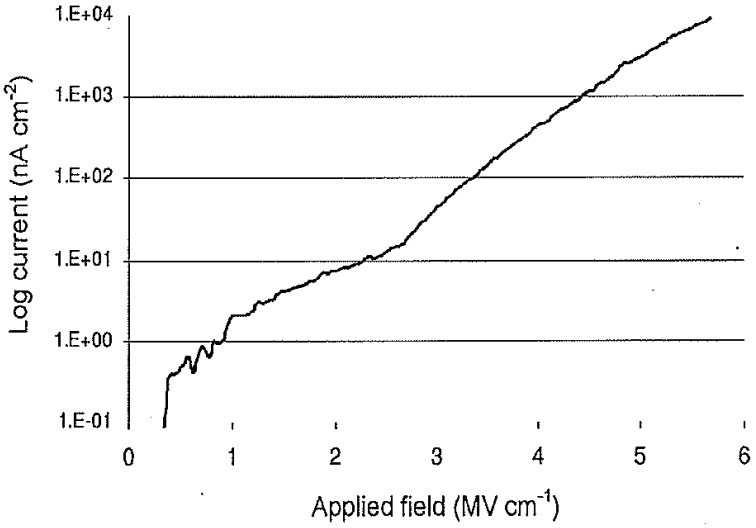


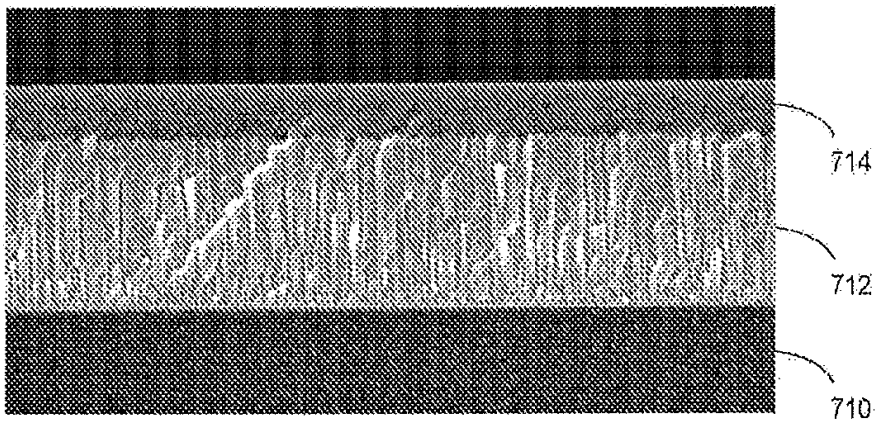
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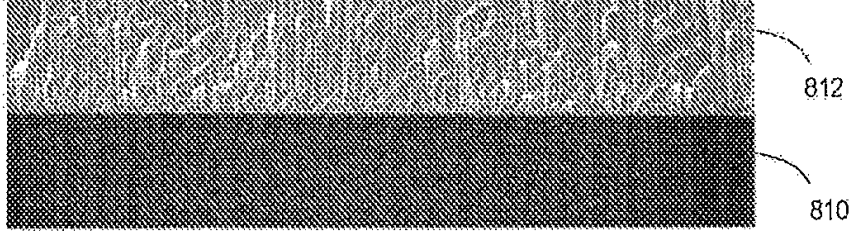


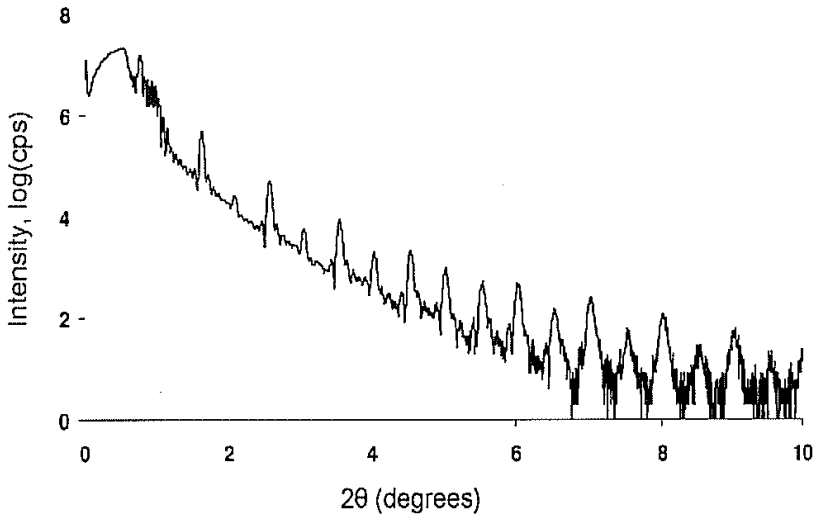
Lam Research Ex. 1004 - Page 803 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564


arbitrary intens
900 °C
750 °C
700 °C
300 °C
simulation $HfO_2 + Hf_2La_2O_7$
20
25
30
35
40
45
50
55
2θ (degrees)

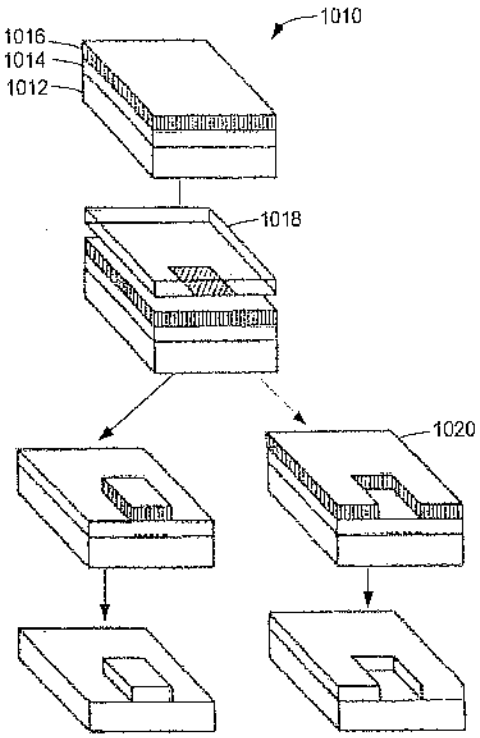

1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
Log current (nA cm^{-2})
0
1
2
3
4
5
6
Applied field (MV cm^{-1})


714
712
710

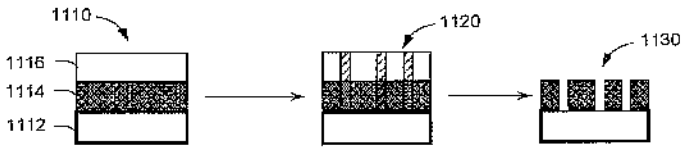

812
810


Intensity, log(cps)
8
6
4
2
0
0
2
4
6
8
10
2θ (degrees)

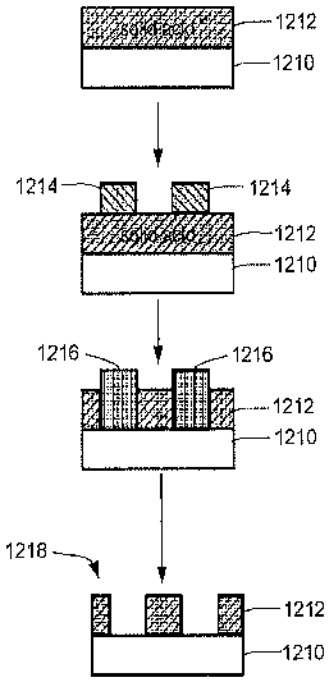
도면10



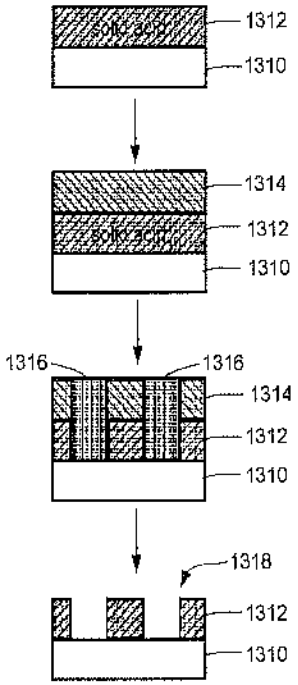
도면11



도면12

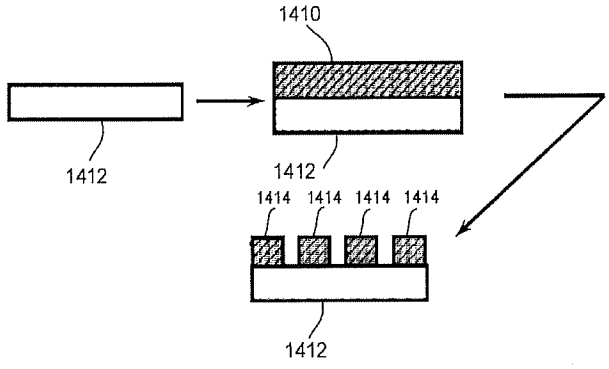


도면13

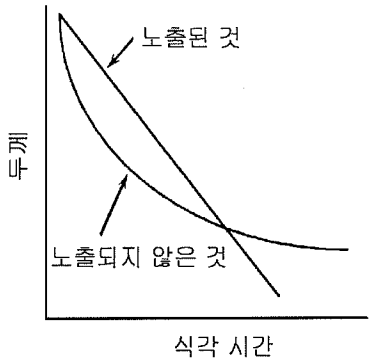


Lam Research Ex. 1004 - Page 807 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

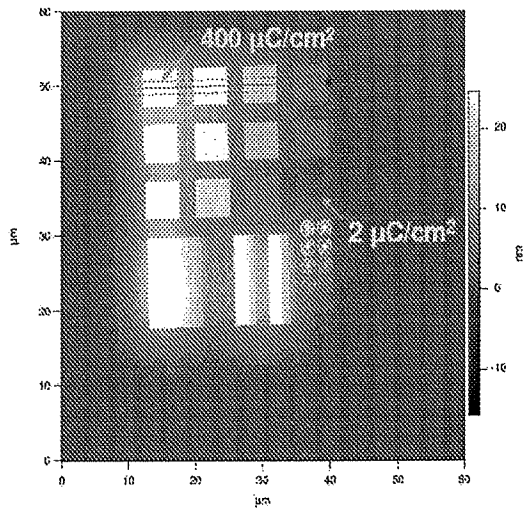
도면14



도면15

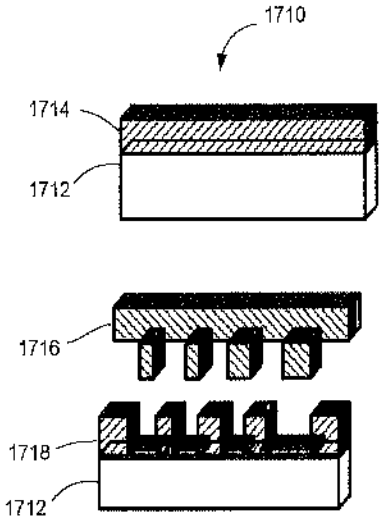


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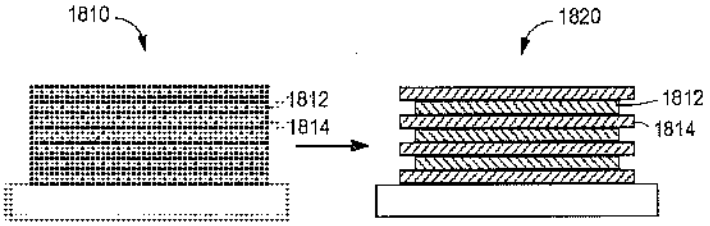


Lam Research Ex. 1004 - Page 808 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

도면17

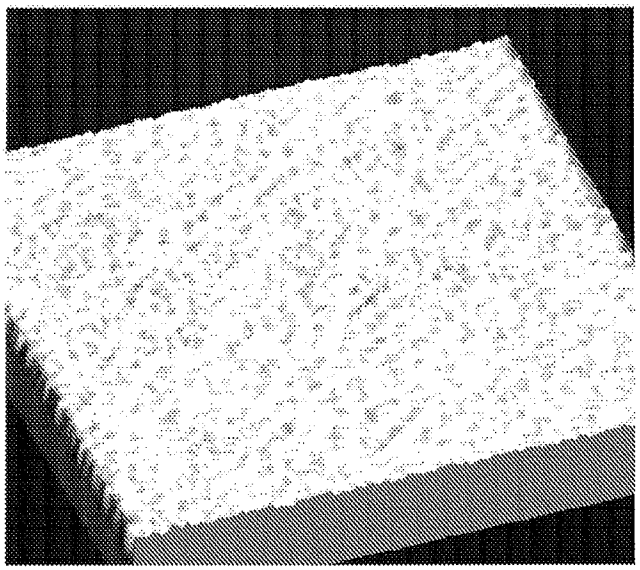


도면18

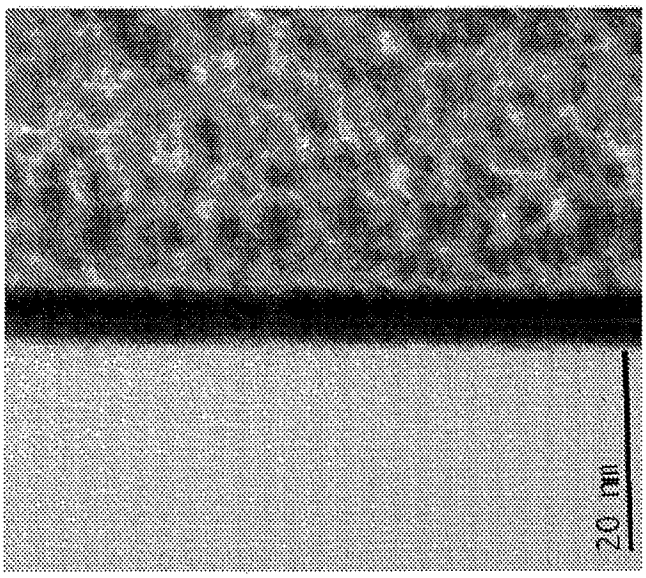


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도면19

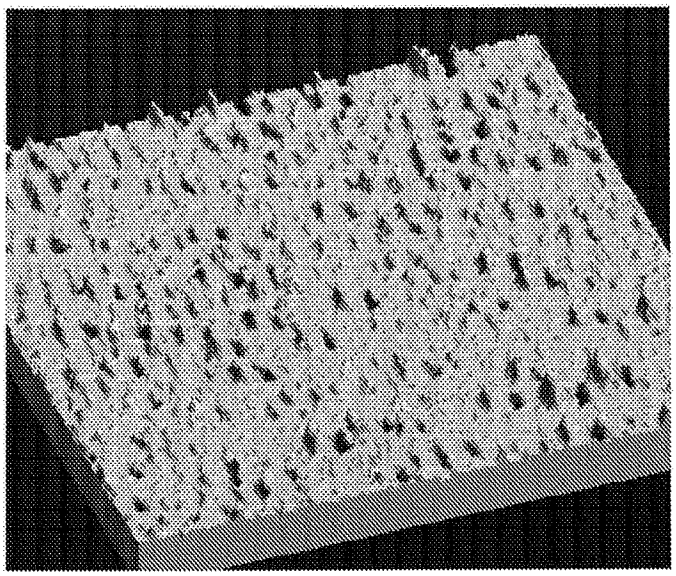


도면20

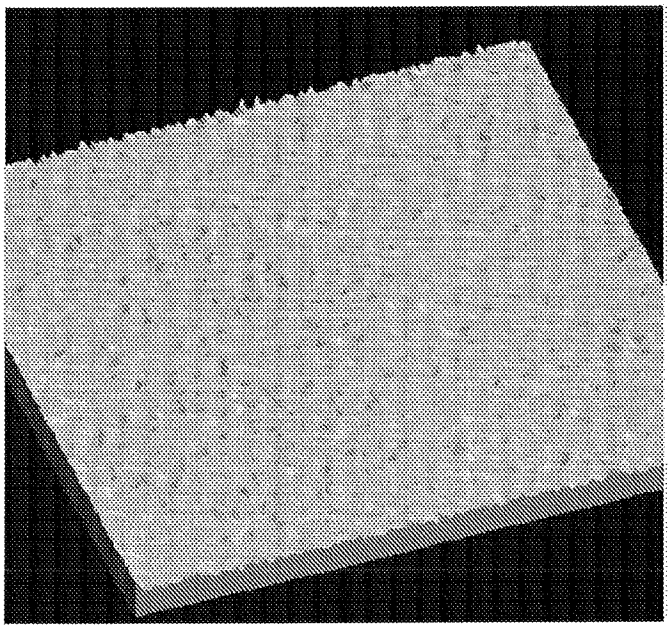


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도면21

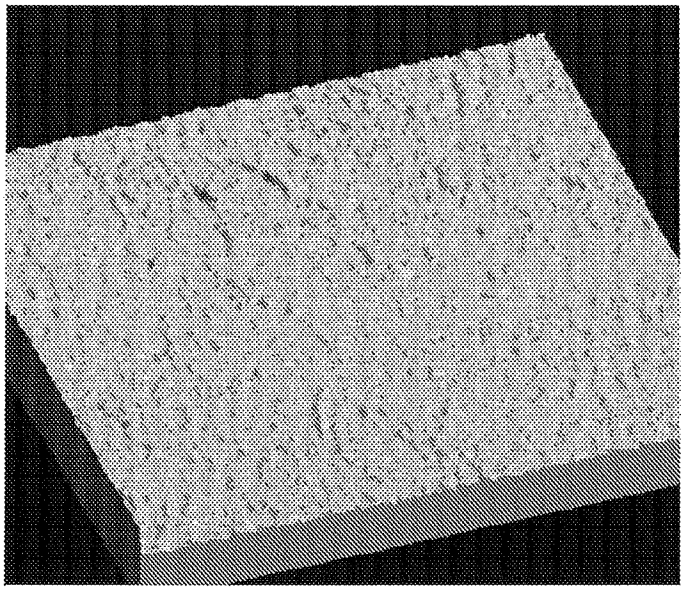


도면22

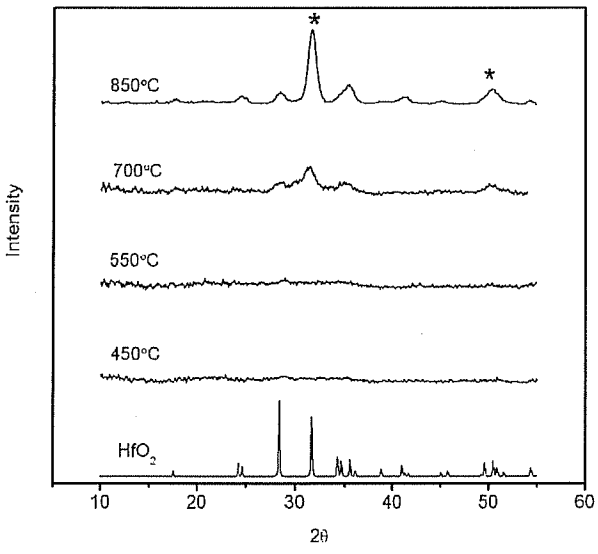


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도면23

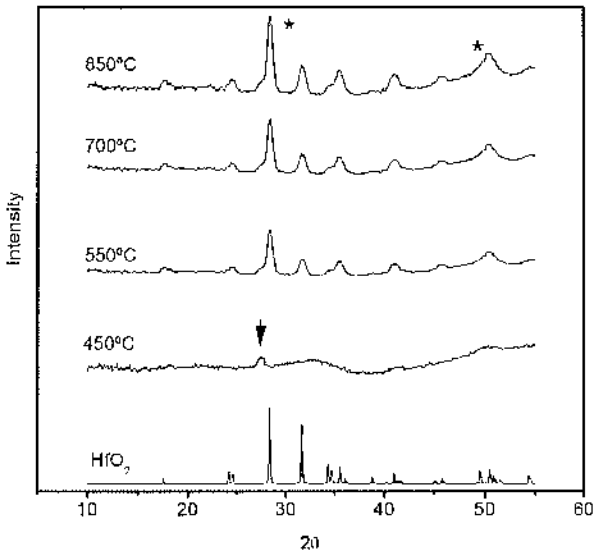


도면24

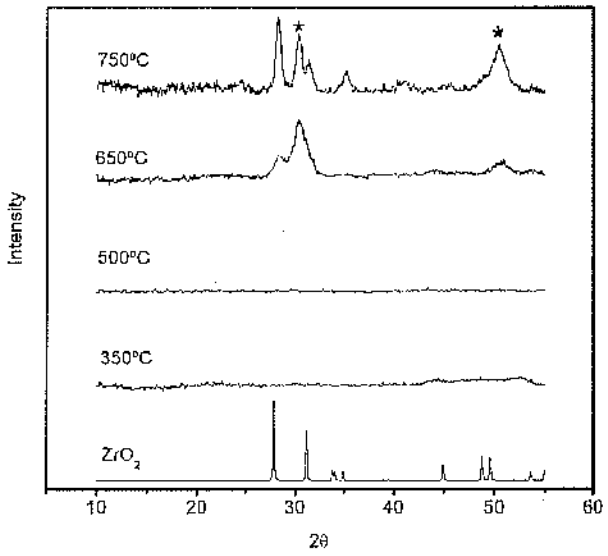


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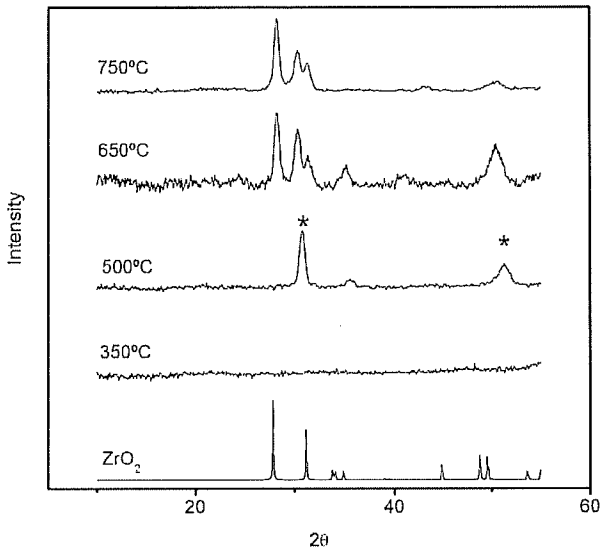
도면25


850°C
700°C
550°C
450°C
HfO2
Intensity
10
20
30
40
50
60
2θ

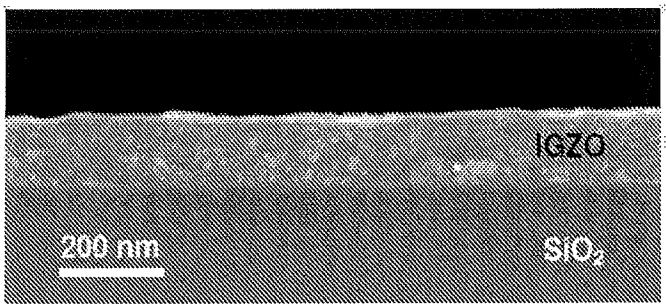
도면26


750°C
650°C
500°C
350°C
ZrO2
Intensity
10
20
30
40
50
60
2θ

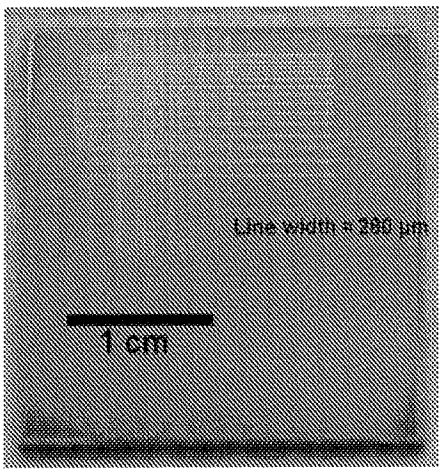
도면27



도면28

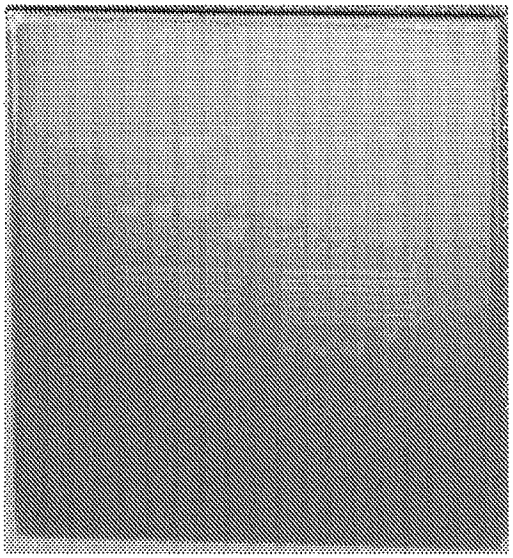


도면29

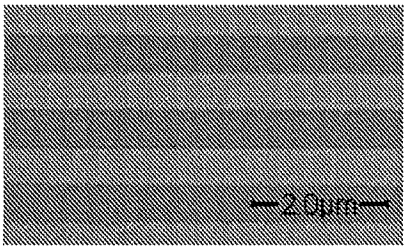


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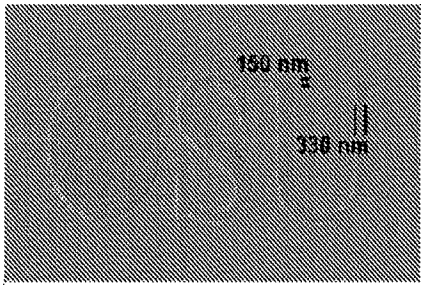
도면30



도면31

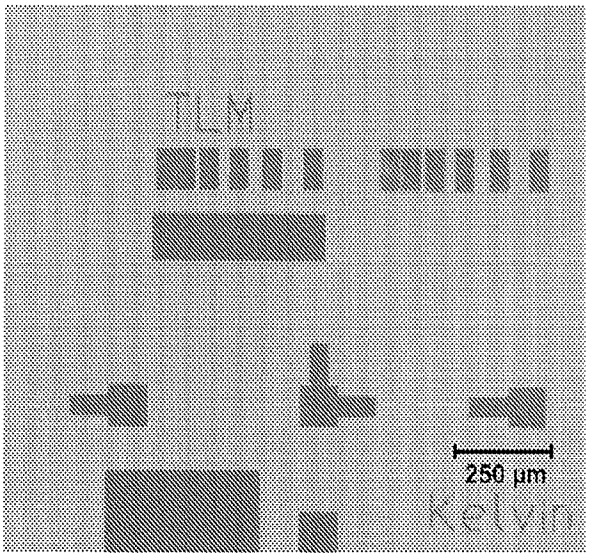


도면32

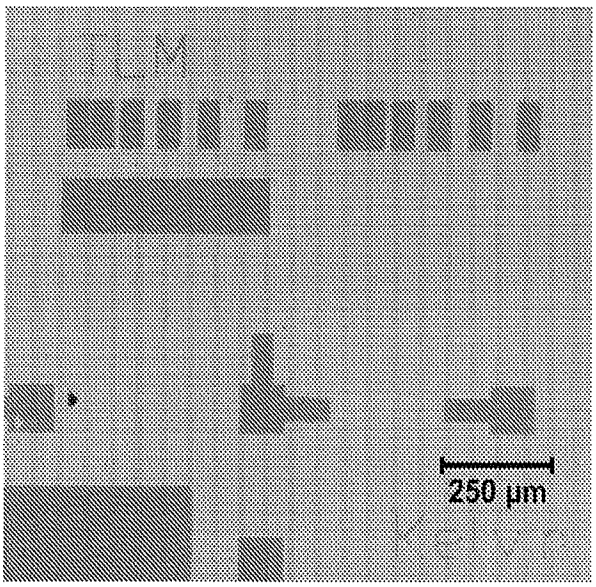


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도면33

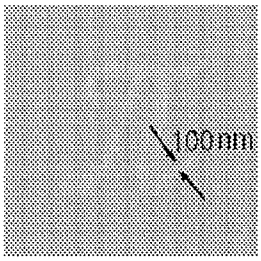


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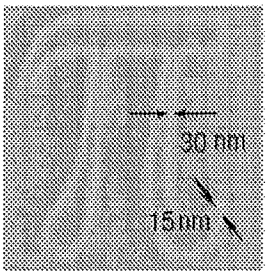


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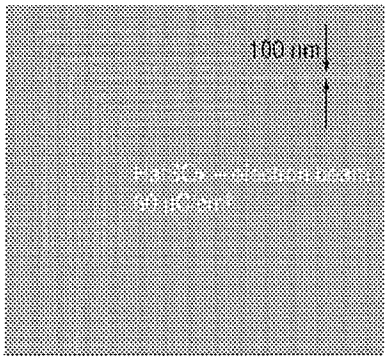
도면35



도면36



도면37



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(74) Agent: **SLATER, Stacey, C.**; Klarquist Sparkman, Llp, One World Trade Center, Suite 1600, 121 Sw Salmon Street, Portland, OR 97204 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

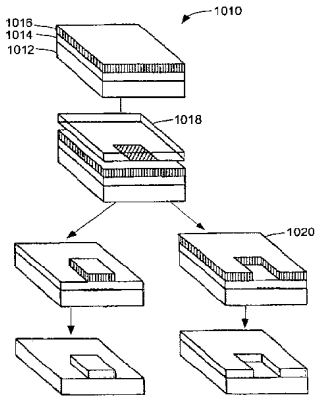
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Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report*

[Continued on next page]

(54) Title: SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THEIR USE AND MANUFACTURE



(57) Abstract: Devices having a thin film or laminate structure comprising hafnium and/or zirconium oxy hydroxy compounds, and methods for making such devices, are disclosed. The hafnium and zirconium compounds can be doped, typically with other metals, such as lanthanum. Examples of electronic devices or components that can be made include, without limitation, insulators, transistors and capacitors. A method for patterning a device using a positive or negative resist also is described. For example, a master plate for imprint lithography can be made. An embodiment of a method for making a device having a corrosion barrier also is described. Embodiments of an optical device comprising an optical substrate and coating also are described. Embodiments of a physical ruler also are disclosed, such as for accurately measuring dimensions using an electron microscope.

WO 2008/082448 A1

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THEIR USE AND MANUFACTURE

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of the earlier filing date of U.S. provisional application No. 60/856,070, filed November 1, 2006, which is incorporated in its entirety herein by reference.

FIELD

The present disclosure concerns embodiments of features and devices comprising inorganic metal oxide materials useful for creating spatially-defined structures for purposes including electronic and optical applications, and embodiments of methods for their manufacture and use.

ACKNOWLEDGMENT OF GOVERNMENT SUPPORT

Embodiments of the present disclosure have been developed using federal funding under DARPA grant number HR0011-06-0045. The United States government has certain rights in the invention.

BACKGROUND

Electronic devices currently are made using iterative process steps, such as sequential deposition and etching of materials. For devices comprising inorganic materials, metal-organic precursors have been used extensively for solution-based deposition of inorganic oxides. The presence of the organic moiety necessitates a high-temperature burnout step to remove the organic material. This step can cause significant volume change, crystallization and the phenomenon of "mud cracking." The associated defects inhibit the performance of these materials as coatings and within devices.

Methods for solution processing materials for electronic device applications have been patented. For example, Ostergard, U.S. Patent No. 6,946,677, entitled "Pre-Patterned Substrate for Organic Thin Film Transistor Structures and Circuits and Related Method for Making Same," describes forming a desired circuit

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configuration in the surface of a substrate, thereby pre-patterning the area to receive material useful for forming an organic thin film transistor (OTFT) structure and interconnecting conductive paths. According to the '677 patent, OTFT material is deposited in the pre-patterned area using printing techniques such as inkjet printing.

Weng *et al.*, U.S. Patent No. 6,927,108, describes solution processing thin-film materials to form transistors. The '108 patent describes forming "conductive solution-processed thin film material contacts, semiconductor solution-processed thin film material active regions, and dielectric solution-processed thin film material isolations in a sequence and organization to form a solution-processed thin film structure capable of transistor operation."

U.S. Patent Publication No. 2005/0242330 A1, which is incorporated herein by reference, concerns hafnium and zirconium compounds useful for electronic applications. U.S. Patent Publication No. 2005/0242330 A1 names Dr. Douglas Keszler as an inventor, who also is an inventor of embodiments disclosed herein.

SUMMARY

U.S. Patent Publication No. 2005/0242330 A1 discloses compounds and solution deposition of inorganic compounds in a manner that addresses deficiencies of prior technologies. For example, solution deposition according to the present invention avoids using organic materials required for metal-organic deposition techniques, and hence also avoids organic burnout and the cracking problems associated with burnout.

One embodiment of the present invention concerns devices, such as electronic devices, having a thin film or laminate structure comprising at least one hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, hafnium and/or zirconium oxy hydroxy phosphate ($HfO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable. X may have any value in a range of from about 0.1 to about 3.5/(polyatomic ion charge). For example, x may be any value within the

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range of from about 0.1 to about 1.75 for a polyatomic ion with a charge of 2, such as the oxy hydroxy sulfate compounds. Z may have any value range of from 0.0 to about 3.8.

Particular embodiments concern thin films or laminates comprising a hafnium or zirconium oxy hydroxy sulfate compound having a formula $(MO_{2-x-z/2}(OH)_z(SO_4)_x)$, wherein M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 1.75, and any value for z in a range of from 0.0 to about 3.8. These compounds also are referred to as HafSOx and ZircSOx. The hafnium and zirconium compounds also can be doped, typically with other metals, such as calcium, cerium, lanthanum, or combinations thereof. Certain embodiments have used lanthanum as a dopant to produce compounds having a formula $M_{1-x}La_yO_{2-x-z/2-y/z}(OH)_z(SO_4)_x$ (MSOx:La), where the composition and stoichiometry are as stated above. A particular example of a lanthanum-doped compound is $Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$. Additional exemplary compounds include HafSOx:La, ZircSOx:La, HafSOx:Ce, or ZircSOx:Ca. In certain embodiments, sulfate is subsequently removed via ion exchange with an aqueous base, resulting in $M(OH)_x$ or MO_x films. Suitable aqueous bases include group I metal hydroxides, group II metal hydroxides, group III metal hydroxides, lanthanide hydroxides, ammonium hydroxide, and/or aqueous tertiary amines, among others.

Certain embodiments concern thin oxide films or laminates comprising complex compositions with two or more metals. At least one of the metal cations has a charge greater than 3^+, and the total concentration of cations with charge greater than 3^+ exceeds 50 mol% of the metal cations in the target oxide. A non-aqueous solution comprising dissolved salts and an amount of water is prepared. The amount of water is less than 20 mol% relative to the non-aqueous solvent. The pH of the solution is increased relative to the starting solution by adding a base or by reaction of free protons via oxidation-reduction mechanisms. The final solution pH depends upon the metal cations used, but will typically be in the range of about 2-9. The increased pH results in hydrolysis of water molecules bound to the cations and condensation of these resulting hydroxo-cations. The solvent is evaporated, and the resulting solid is dissolved or dispersed in water and subsequently applied to a

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substrate as a liquid film. The liquid film is then thermally cured at a temperature between about 100 °C and 600 °C for about 5-240 minutes.

Examples of electronic devices, or components of devices, that can be made according to this invention include, without limitation, insulators, such as a gate insulator in a field effect transistor, transistors, such as a field effect transistor, and capacitors, such as a MIM capacitor. Thin films and laminates made according to this embodiment had a permittivity value within the range of from about 9 to about 12, a breakdown field from at least 3 MV cm^{-1} up to about 6 MV cm^{-1}, and a leakage current near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}. Devices made using ZircSOx:Ca had a breakdown field of about 3.6 MV cm^{-1}, a leakage current of less than about 50 nA cm^{-2}, more typically less than about 10 nA cm^{-2}.

Field effect transistors can be made using HafSOx:La and/or ZircSOx:La as gate dielectric materials. Certain disclosed embodiments used zinc indium oxide and/or zinc tin oxide as channels. Particular field effect transistors had an on-to-off ratio of greater than 10^6, and nA cm^{-2} gate leakage currents.

Another embodiment of the present invention concerns a method for patterning a device using a photoresist. A particular embodiment of the method comprises first providing a structure to be patterned. The structure typically comprises: a substrate, such as a semiconductor material, a metal, glass, a polymeric material, or combinations thereof; a material layer for patterning, such as silica; and a resist layer. The resist layer typically includes disclosed hafnium and/or zirconium oxy hydroxy compounds. The structure is exposed to an energy source, such as an electron beam or light, with particular examples using ultraviolet light. Thereafter, material is removed to pattern the device, or it is retained as an active, patterned component of the device.

The resist may be a positive resist or a negative resist. For example, the method can include exposing the resist layer to an energy source to convert the resist layer material into a developer-soluble material. The developer-soluble material is then removed using a developer. Suitable developers may includes acids, bases, and/or ultrasonic agitation, among others. Again by way of example, the method can comprise removing resist layer material exposed to the energy source. Without limiting the invention to a particular theory of operation, at least for certain

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embodiments, exposure to the energy source may cause the resist layer to polymerize, making it relatively less soluble in a developer than prior to exposure to the energy source.

One embodiment of a positive resist comprises a bilayer. A first layer of the bilayer comprises a copper formate film deposited on a hafnium oxide sulfate (HafSOx) film. The copper formate film is soluble in acid and the undoped HafSOx film is insoluble in acid. Exposing the bilayer to light through a mask or to a focused electron beam causes the two films to interdiffuse in exposed areas, thereby rendering the previously undoped HafSOx film soluble.

Another embodiment of a bilayer process for making a resist comprises depositing a first layer of a solid acid or base, where the acid or base contains one or more metal atoms, onto a substrate. A liquid suspension containing an oxide precursor, such as copper formate, is applied in a desired pattern onto the first layer. Under heated conditions, the precursor decomposes to an oxide. The oxide subsequently reacts and interdiffuses with the first layer, forming a product that can be etched to reveal a pattern. An alternate embodiment comprises depositing oxide particles onto the first layer, with or without heating, resulting in a direct reaction to form a product that can be etched. A further embodiment comprises depositing a thin layer of the oxide precursor onto the first layer. A pattern of activated precursor is then formed by light exposure through a photomask or direct writing with a focused laser or electron beam.

Another embodiment of the present invention concerns a master plate for imprint lithography. The master plate comprises a substrate, such as a flexible or glass substrate, and at least one layer of a thin film or laminate structure comprising at least one disclosed hafnium and/or zirconium oxy hydroxy compound. A particular embodiment of a master plate includes a layer of HafSOx deposited onto the substrate, and a second layer, such as a ZircSOx:Cu layer. The master plate may be patterned by exposure to an energy source, such as exposure to light or an electron beam through a mask to cause the two films to interdiffuse in exposed areas. This renders previously undoped HafSOx film soluble, which is removed to at least partially define printing features of the master plate.

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In another embodiment, masks or templates can be fabricated using the films of the present invention in a single layer process. A thin film of an inorganic precursor, such as a solid acid or base, is deposited onto a substrate in combination with a peroxide or similar anion. The film is heated to produce a structurally rigid film. It is then exposed through a photomask or via a laser or electron beam to induce condensation/crosslinking in exposed areas. The solubility of the exposed areas decreases relative to the unexposed areas. The unexposed areas can then be selectively etched, producing a negative-tone image in the film. Positive-tone images also can be formed by preheating the film to higher temperatures before exposure. In some embodiments, an $M(OH)_x/H_2O_2$ film is formed by treating a film such as HafSOx with a mixture of sodium hydroxide and hydrogen peroxide. The resulting film is then patterned by exposure to light or an electron beam.

A method for forming a device also is described, comprising providing a structure to be patterned comprising a substrate, a material layer for patterning, and a metal oxide layer comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The structure is patterned and then exposed to an energy source to form a durable material having a desired pattern produced by patterning the structure. One embodiment of a device made according to the method can include a channel array, such as a micro- or nano-channel array. For such embodiments, the method for making the device can include stamping unit features of a desired size scale into a semi-solid hafnium or zirconium compound to form a stamped layer.

An embodiment of a method for making a device having a corrosion barrier also is described. Disclosed embodiments of the method comprise providing a device, and forming at least one corrosion barrier on the device. The corrosion barrier typically comprises a metal oxide layer comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The method also can include exposing the compound to an energy source to form the corrosion barrier. Examples of such devices include metal and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal and ceramic-based systems, fibers for

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composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, and catalyst supports.

An embodiment of a method for forming fibers also is disclosed. A solution is formed comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The solution is then drawn into fibers. The fibers may be converted into solid, stable forms by any suitable process, such as hydrolysis, annealing, air pyrolysis, and combinations thereof.

Embodiments of an optical device also are described. Particular disclosed embodiments of the device comprise an optical substrate, and a substrate coating comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The layer may be an antireflective coating. The optical substrate and coating may define, for example, a dielectric mirror, an X-ray mirror, an interference filter, a diffractive grating, and/or a waveguide. The optical device also may include a layer that is transparent, such as visibly transparent or transparent to ultraviolet light. The layer may be selectively doped to provide a doped layer having luminescent ions selected from Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof. Doping the layer can be used to produce a light-emitting layer.

Embodiments of a method for making a physical ruler also are disclosed. Certain embodiments comprise forming at least one acid-soluble layer by solution deposition of disclosed hafnium and/or zirconium oxy hydroxy compounds. At least one acid-insoluble layer is formed adjacent to the acid-soluble layer, the acid-insoluble layer being formed by solution deposition of disclosed hafnium and/or zirconium oxy hydroxy compounds. Repeating these steps produces alternating layers, and the method includes accurately determining widths of alternating acid-insoluble and acid-soluble layers. Width determination can be accomplished using any suitable method, such as X-ray reflectivity. Moreover, at least one layer is etched to define a digitated secondary reference pattern for measuring objects. Certain embodiments of such a device are useful for accurately measuring dimensions using an electron microscope.

The foregoing and other objects, features, and advantages of the invention will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 provides thermogravimetric analysis (relative moisture versus temperature) (TGA) for HafSOx (x = 0.70) with various pretreatments and with samples heated under flowing N_2(g) at a rate of 10 °C minute^{-1}.

FIG. 2 is an XRD pattern for HafSOx powders after heating at stated temperatures in air for 1 hour, except as noted.

FIG. 3 is an XRD pattern for HafSOx:32% La powders after heating at stated temperatures for 1 hour, except as noted.

FIG. 4 is an XRD pattern for HafSOx films after heating at given temperatures in air for 5 minutes, where the very small features at 31.8° and 45.6° are attributed to the substrate.

FIG. 5 is an XRD pattern for HafSOx:24% La thin films after heating at stated temperatures in air for 5 minutes.

FIG. 6 illustrates dielectric breakdown characteristics for HafSOx film.

FIG. 7 is an SEM showing one embodiment of HafSOx deposited on tantalum (Ta) metal on a silicon dioxide substrate.

FIG. 8 is an SEM for HafSOx:24% La deposited on Ta.

FIG. 9 is an XRR pattern for HafSOx/ZircSOx multilayer thin-film comprising 14 alternating layers (7 bilayers) having a bilayer thickness of 17.6 nm.

FIG. 10 is a schematic diagram illustrating positive or negative photoresist procedures.

FIG. 11 is a schematic diagram illustrating a positive resist using a bilayer system, the illustrated embodiment comprising a Cu-doped zirconium oxide sulfate (Cu:ZircSOx) film deposited on a hafnium oxide sulfate (HafSOx) film.

FIG. 12 is a schematic diagram illustrating a bilayer process for producing a patterned oxide on a substrate.

FIG. 13 is a schematic diagram illustrating a bilayer process for producing a patterned oxide on a substrate.

FIG. 14 is a schematic diagram illustrating a single layer process for producing a patterned film on a substrate.

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FIG. 15 is a graph of thickness versus etch time for a thermally pre-treated, single-layer film.

FIG. 16 is a film patterned by an electron beam.

FIG. 17 is a schematic diagram illustrating hot embossing lithography for use with semi-solid forms of compounds disclosed herein having much higher mechanical strength, chemical stability, and unique electrical and optical properties relative to organic polymers.

FIG. 18 is a schematic diagram illustrating one method for making a physical ruler for use in standardizing measurements in applications, such as electron microscopy.

FIG. 19 is an AFM image of an unexchanged HafSOx film deposited on silica.

FIG. 20 is a TEM image of HfO_2 following ion exchange of HafSOx and thermal treatment at 850 °C.

FIG. 21 is an AFM image of a HfO_2 film deposited on silica and formed from HafSOx thermal decomposition after heating above 700 °C.

FIG. 22 is an AFM image of a HafSOx film deposited on silica, treated with 0.1M NaOH, and heated to 450 °C for 10 minutes.

FIG. 23 is an AFM image of a HfO_2 film deposited on silica, treated with 0.1M NaOH and heated to 850 °C for 10 minutes.

FIG. 24 provides XRD plots of untreated hafnia films.

FIG. 25 provides XRD plots of treated hafnia films.

FIG. 26 provides XRD plots of untreated zirconia films.

FIG. 27 provides XRD plots of treated zirconia films.

FIG. 28 is an SEM image of an indium gallium zinc oxide semiconductor film deposited on silica.

FIG. 29 is a line pattern produced via ink-jet printing and inorganic diffusion-reaction.

FIG. 30 is a pattern produced by exposing a bilayer film to UV light.

FIG. 31 is a film patterned by electron-beam writing.

FIG. 32 is a film patterned by electron-beam writing.

FIG. 33 is a film patterned photographically.

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FIG. 34 is a film patterned photographically.

FIG. 35 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

FIG. 36 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

FIG. 37 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

DETAILED DESCRIPTION

Disclosed embodiments of the present invention concern devices, including electronic devices or components of electronic devices, which can be made by solution deposition of inorganic materials. Throughout this disclosure, the singular terms "a," "an," and "the" include plural referents unless the context clearly indicates otherwise. Similarly, the word "or" is intended to include "and" unless the context clearly indicates otherwise. The term "includes" means "comprises." All percentages recited herein are atomic percentages unless indicated otherwise. All patents and publications mentioned herein are incorporated by reference in their entirety, unless otherwise indicated. In case of conflict, the present specification, including explanations of terms, will control. The materials, methods, and examples recited herein are illustrative only and are not intended to be limiting.

I. Metal Oxide Sulfate Materials Generally and U.S. Patent Publication No. 2005/0242330 A1

The present disclosure concerns embodiments of a method for solution deposition of inorganic materials, typically solution deposition of metal oxide sulfate inorganic materials that are useful for electronic applications. Embodiments of these materials are described in U.S. Patent Publication No. 2005/0242330 A1. Certain portions of that published application, from paragraph 009 through paragraph 014, are paraphrased below. References to figures in this paraphrased text refer to the figures as published with the '330 publication.

> FIG. 1 illustrates one embodiment of a process for manufacturing a dielectric precursor material. Process 10 generally comprises providing a first reactant 12, such as a metal-containing cation, providing a second reactant 14, such as a polyatomic anion, and then reacting the polyatomic anion and the metal-containing cation. The metal-containing cation and the polyatomic anion may be in solution, such as an aqueous solution, when reacted together. In one embodiment, the metal-containing cation may be provided using an aqueous solution of a hafnium oxy halide, such as hafnium

oxy chloride ($HfOCl_2(aq)$). The polyatomic anion, such as sulfate (SO_4^{2-}), may be provided using an aqueous solution of sulfuric acid ($H_2SO_4(aq)$). These two reactants may be mixed together using processes and relative amounts suitable for making desired materials. The mixture may be heated.

The reaction may produce a precursor solution 16. Precursor solution 16 may be immediately used as desired, such as by being applied to a substrate. Optionally, precursor solution 16 may be at least partially dehydrated and then applied. In the example given above, the precursor solution may then form hafnium oxy-hydroxy sulfate ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$). With reference to the variables in this formula, x and z may be fixed or variable, and may have any value. For example, the value of x typically is from about 0.1 to about 1.9, and a value for z is from 0.0 to about 2.0. For one embodiment the values were x=0.5 and z=0. Hydroxyl groups may be a part of the metal-containing cation, and the compound may comprise hafnium oxy-hydroxy sulfate ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$).

In other embodiments, the polyatomic anion may include one or more of sulfate (SO_4^{2-}), borate (BO_3^{3-}), phosphate (PO_4^{3-}), tungstate (WO_4^{2-}) and silicate (SiO_4^{4-}). The metal-containing cation may comprise a metal suboxide, and may include one or more of hafnium (Hf^{4+}), titanium (Ti^{4+}), zirconium (Zr^{4+}), cerium (Ce^{4+}), tin (Sn^{4+}), tantalum (Ta^{5+}), niobium (Nb^{4+}), yttrium (Y^{3+}), molybdenum (Mo^{4+}), tungsten (W^{6+}), aluminum (Al^{3+}), gallium (Ga^{3+}), zinc (Zn^{2+}), chromium (Cr^{3+}), iron (Fe^{3+}), bismuth (Bi^{3+}), lanthanides, hafnium oxy-hydroxide ($HfO_y(OH)_z^{(4-2y-z)+}$), zirconium oxy-hydroxide ($ZrO_y(OH)_z^{(4-2y-z)+}$), titanium oxy-hydroxide ($TiO_y(OH)_z^{(4-2y-z)+}$), tantalum oxy-hydroxide ($TaO_y(OH)_z^{(5-2y-z)+}$), yttrium oxy-hydroxide ($YO_y(OH)_z^{(3-2y-z)+}$), niobium oxy-hydroxide ($NbO_y(OH)z^{(4-2y-z)+}$), molybdenum oxy-hydroxide ($MoO_y(OH)_z^{(4-2y-z)+}$), tungsten oxy-hydroxide ($WO_y(OH)_z^{(6-2y-z)+}$), aluminum oxy-hydroxide ($AlO_y(OH)_z^{(3-2y-z)+}$), gallium oxy-hydroxide ($GaO_y(OH)_z^{(3-2y-z)+}$), zinc oxy-hydroxide ($ZnO_y(OH)_z^{(2-2y-z)+}$), chromium oxy-hydroxide ($CrO_y(OH)_z^{(3-2y-z)+}$), iron oxy-hydroxide ($FeO_y(OH)_z^{(3-2y-z)+}$), bismuth oxy-hydroxide ($BiO_y(OH)_z^{(3-2y-z)+}$), and oxy-hydroxides of the lanthanide series. The value of y is related to the charge on the metal cation and the amount of hydroxide and other polyatomic anion that is bound to the metal cation.

Embodiments of the method using polyatomic anions and metal-containing cations disclosed herein may result in the formation of a dielectric precursor material that does not require using organics for forming complexes, i.e., the sources of the anion and the cation do not contain organics. However, organic materials can be used, if desired or necessary for certain embodiments. For example, a non-complexing organic, such as ethanol, may be used as a partial solvent in the precursor solution. If complexing organics are not included in the precursor material, the precursor solution typically does not have to be heated or annealed at temperatures as high as 400 °C or higher, to decompose/combust any organic materials once the precursor solution is applied to a substrate. Polymerization of the

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precursor solution upon heating and/or drying results in the formation of amorphous films and not polycrystalline materials, thereby allowing solutions-based-application of the dielectric material on a substrate.

In general, disclosed embodiments of the present process may be conducted at ambient conditions, such as atmospheric pressure in air. Accordingly, vacuum processing is not required, but may be utilized if desired. The process may be conducted at a temperature above ambient, such as in a range of from about 80 °C to about 850 °C, typically in a temperature range of from about 80 °C to at most 350 °C, and often at a temperature of at most 100 °C. These low pressure and low temperature processing steps may reduce the energy requirements for disclosed processes. Due to the low temperatures useful for processing the dielectric films, the films may be processed on or applied as a solution to low-temperature substrates, such as plastic substrates. The amorphous, non-crystalline dielectric precursor solution produced allows even, conformal coverage of the precursor solution on a substrate, such as on a wafer. The solution also may be applied in a predetermined, specific pattern, such as by using inkjet printing, so that no masking or etching steps are used. Accordingly, the process of the present disclosure may eliminate or reduce the usage of hazardous or toxic materials that may be used for the formation and removal of materials during photolithography processing on substrates. Thus the present process is time efficient and environmentally "green" relative to known processes. Moreover, the hafnium oxide and sulfate materials utilized in one example embodiment of the present disclosure may not be toxic materials.

Examples of materials used in the process of the present disclosure include compounds belonging to the family of compounds including hafnium oxy hydroxy sulfates ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$), hafnium oxy hydroxy tungstates ($HfO_{2-x-z/2}(OH)_z(WO_4)_x$), hafnium oxy hydroxy borates ($HfO_{2-x-z/2}(OH)_z(BO_3)_x$), hafnium oxy hydroxy phosphates ($HfO_{2-x-z/2}OH_z(PO_4)_x$), and hafnium oxy hydroxy silicates ($HfO_{2-x-z/2}OH_z(SiO_4)_x$). These materials may be polymerized at temperatures as low as 80 °C and may remain amorphous up to approximately 740 °C, and even as high as 1,200 °C. Material polymerization may be controlled by adjusting the heating rate, by using co-solvents, by other suitable methods, and by any and all combinations of such methods. Amorphous films of the present disclosure may reduce defect formation at grain boundaries and may reduce crack formation upon an amorphous-to-crystalline transition. Moreover, the dielectric films of the present disclosure may have a reasonably high dielectric constant, i.e., a dielectric constant higher than the dielectric constant of organic compounds. The ability to form high quality dielectrics by solution-based processing, such as inkjet printing applications, allows formation of low cost electronic components, such as field effect transistors or capacitors.

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FIG. 2 schematically illustrates one embodiment of a process for applying precursor solution 16 to form a dielectric material. Precursor solution 16, such as hafnium oxy sulfate, may be applied to a substrate 18, such as a wafer, by an applicator 20. In one embodiment, applicator 20 may comprise an inkjet printer having nozzles 22. The aqueous precursor solution 16 is ejected through nozzles 22 of the inkjet printer. In other embodiments, applicator 20 may comprise a spin-coater, a dip-coater, or a spray-coater such that the method of applying the precursor solution may comprise, respectively, spin-coating, dip-coating, or spray-coating. Due to the amorphous, solution-based properties of precursor solution 16, precursor solution 16 may allow good conformal coverage when applied. Once applied to the substrate surface, or to a film or films deposited on the substrate, the precursor solution may be dehydrated, such as by heating with a heater 24, or by other dehydration devices, to remove or reduce the amount of water in the precursor solution. This dehydration step may cause precipitation of an amorphous dielectric material 26, such as a hafnium oxy sulfate thin film, on wafer 18.

FIG. 3 is a graph showing possible solution concentrations for differing precursor concentrations for one embodiment of dielectric material precursor solutions 16 (see FIG. 1), in particular, for the reaction of sulfuric acid (H_2SO_4) with hafnium oxy chloride ($HfOCl_2$). More particularly, FIG. 3 shows a graph of total sulfate concentration (molarity (M)) versus total hafnium concentration (M). Region 28 represents a clear solution, i.e., a solution with no visually detectable precipitate therein, wherein region 28 is a region of excess sulfuric acid (H_2SO_4). Region 30 represents a clear solution, i.e., a solution with no visually detectable precipitate therein. Region 30 is a region of excess hafnium oxy chloride ($HfOCl_2$). Line 32 represents a stoichiometric line wherein sulfuric acid and hafnium oxy chloride are each present in a one-to-one ratio (1:1 stoichiometric ratio). Region 34 represents a precipitation area, i.e., a solution having a visually detectable precipitate therein. Region 34, or portions thereof, therefore, may represent solutions that are not best suited for forming smooth substantially defect free films by inkjet printing applications, but its use is not foreclosed. Accordingly, when precursor solution 16 (see FIG. 2) is applied through an inkjet printer application device 20 (see FIG. 2), it may be desirable that the concentration of the first and second reactants fall within either of regions 28 or 30, but not within solids region 34. Solids present in the solutions of region 34 may occlude nozzles 22, may form an unsmooth film, or may otherwise result in unfavorable precursor solution application. In other words, the solutions of regions 28 and 30 may represent possible precursor solution "inks" that may be applied through an inkjet printhead or by a dropper method.

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II. General Discussion

New thin-film dielectrics and nanolaminates have been developed using solution deposition, typically aqueous solution deposition, of smooth, dense films. Solution deposition techniques include spin coating and inkjet printing. Solution deposition may be followed by modest thermal treatment ($T < 325\ ^{\circ}C$).

A variety of analytical techniques have been used to define the chemistry of the materials made according to the present disclosure, both as powders and films. The quality and functionality of the films have been assessed by X-ray reflectivity, electronic microscopy, and performance in electronic devices. Dielectric characteristics have been determined for working embodiments, and include permittivity values covering the range of from about 9 to about 12; breakdown fields up to at least 6 MV cm^{-1}; and leakage currents near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}. The surface smoothness and pore-free nature of the films facilitate the production of unique nanolaminated structures having individual layers at least as thin as about 2 nanometers. Relatively high permittivity films can be realized using disclosed embodiments of the present invention, while also providing high-breakdown strengths and low-leakage currents in thin-film metal-insulator-metal (MIM) capacitors and thin-film transistors (TFTs). The exceptional characteristics of the insulating films also have allowed fabrication of unique nanolaminated structures.

Amorphous materials are desirable for use as thin-film dielectrics; they do not have grain boundaries, and hence are not susceptible to roughness and charge conduction associated with crystallites. Numerous oxides of hafnium and zirconium, e.g., the simple binaries, silicates, and aluminates, have been examined as candidates for high-permittivity dielectric applications. In multiple-component materials, crystallization can be inhibited to produce more robust breakdown characteristics relative to the pure binary oxides, though permittivity may be sacrificed. These dielectric films often are formed using a variety of metal-organic or metal-salt precursors and techniques such as atomic layer deposition (ALD), chemical vapor deposition (CVD), sol-gel processing, or combinations thereof. However, making useful dielectric films by solution deposition methods that are

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both dense and amorphous may require inhibiting crystallization and cracking, both during deposition and subsequent processing.

Certain disclosed embodiments of the present invention concern the development of metal oxide films. Metal oxides are exemplified herein generally by reference to hafnium and zirconium sulfate systems having representative formulas $HfO_{2-x}(SO_4)_x$ and $ZrO_{2-x}(SO_4)_x$, respectively, where $0.1 \leq x \leq 1.5$. These compounds are referred to herein by the acronyms HafSOx and ZircSOx, respectively. To define the chemistry and physical properties of these systems, HafSOx, and doped analogs thereof, such as the La-substituted derivative HafSOx:La, have been made, both as powders and thin films. Thin-film dielectric properties of HafSOx, ZircSOx, and selected derivatives have been assessed by fabricating capacitors and TFTs. These analyses revealed that very high-quality, dense films could be produced. Film thickness and fabrication of mixed HafSOx/ZircSOx nanolaminates can now be controlled by spin-coating processes.

A number of phases and crystal structures have been reported from examination of HfO_2-SO_3-H_2O and ZrO_2-SO_3-H_2O systems. Several structures are characterized as simple hydrates of formulations $Hf(SO_4)_2 \cdot nH_2O$ or $Zr(SO_4)_2 \cdot nH_2O$, exhibiting variations in the degree of hydration and in the structural dimensionality associated with the condensation of the metal atom, sulfate groups, and water. Materials rich in metal relative to sulfate are known, including $Zr_2(OH)_2(SO_4)_3 \cdot 4H_2O$; $Hf(OH)_2SO_4$, $Zr(OH)_2SO_4$, and their hydrates; $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13} \cdot 33H_2O$ and $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$; and $Zr_3O_5SO_4$ and its hydrate. All of these structures (with the possible exception of $Zr_3O_5SO_4$) are likely unstable when subjected to air at both room temperature and under moderate heating, resulting from changes in hydrogen bonding or dehydration. This allows the dehydration and condensation processes to be used to develop amorphous films.

Starting from aqueous solutions with selected fractions of sulfate relative to hafnium (variable x), HafSOx precipitates were induced by heating. FIG. 1 is a thermogravimetric analysis (TGA) of air-dried HafSOx precipitates. TGA is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature. Heating an air-dried HafSOx precipitate leads to mass loss in three domains. Similar characteristics have been observed for other

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HafSOx derivatives as well. The large mass loss below a temperature of about 200 °C is attributed to loss of incorporated water. Mass loss in the temperature range of from about 200 °C to about 700 °C is attributed mainly to elimination of more tightly bound hydroxyl species as water. The sharp mass loss that begins above about 700 °C, is attributed to sulfate decomposition according to $SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$. Assuming dehydrated HafSOx powder is converted completely to HfO_2 between 700 °C and 950 °C, the sulfate fraction can be calculated from the mass loss. Determining mass loss of samples revealed that increasing levels of sulfate in the mother solution yielded increasing levels of sulfate in precipitates. Specifically, the sulfate-to-hafnium ratio varied from about 46% to about 71% for dehydrated formulas of $HfO_{1.54}(SO_4)_{0.46}$ and $HfO_{1.29}(SO_4)_{0.71}$, respectively. The same maximum sulfate composition precipitated whether $H_2SO_4(aq)$ or $(NH_4)_2SO_4(aq)$ was used as the sulfate source; products with sulfate levels < 46% were not examined. The onset of sulfate loss occurred above 720 °C for all samples, though some variations in the thermogravimetric profiles were observed. Peak positions for the derivatives of these heating curves, as definable values, reveal decomposition between 793 °C and 817 °C for samples tested. The highest decomposition temperatures were observed for samples having maximum sulfate content with $H_2SO_4(aq)$ as the sulfate source.

Again with reference to FIG. 1, samples with maximum sulfate content also were heated prior to TGA measurements. Mass losses associated with water were reduced, and calculated sulfate contents were similar for both preheated and regular samples. This sulfate content of 70–71% mimics the compositions of the reported crystals $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$ and $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}\cdot 33H_2O$. From TGA studies, Ahmed, Fjellvåg, and Kjekhus also found that sulfate decomposition for $Hf_{18}O_{23}(SO_4)_{13}$ and $Zr_{18}O_{23}(SO_4)_{13}$ occurs at temperatures higher than those for the Hf and Zr disulfates within their study, and higher than those for the basic sulfates $Hf(OH)_2SO_4\cdot H_2O$ and $Zr_3O_5SO_4$ reported by others. In addition to enhanced thermal stability, a sulfate-to-metal ratio of approximately 13:18 exhibits special stability within this system. As such, this composition may be suitable for purposes where solution processing and heating are required.

The sulfate $La_2O_2SO_4$ has a decomposition temperature of greater than 1,300 °C. Lanthanum (La) was added to the mother HafSOx solution to produce

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additional compounds having modified physical properties, such as modified dehydration properties and thermal characteristics, one example being thermal stability. A mixed-metal system, $Hf_{1-z}La_zO_{2-x-z/2}(SO_4)_x$ (HafSOx:La), exemplifies such compounds. To produce such compounds a solution containing the precursor materials and 23% La (total metal) was heated to form precipitates. Chemical analysis indicated that only 3% La was found in the product. From TGA, a sulfate-to-metal ratio of 71% was established, and the decomposition (as derivative peak) at 820 °C was found to be consistent with maximal sulfate content. Co-precipitation was then induced by adding NH_3(aq) to a salt solution of the constituent species containing 32% La. The chemical composition of the product was analyzed, revealing the same fraction of La as that present in the mother solution. Thermal decomposition for this formula was markedly different from undoped HafSOx. Mass loss attributed to sulfate was apparent above 700 °C, though heating features were less abrupt and no constant mass was achieved with heating to 1,000 °C, even when heating at the slower rate of 2 °C minute^{-1}. For this heating rate, decomposition (as derivative peak) occurs at approximately 870 °C, though this value depends on heating conditions. Complete decomposition to the oxides was accomplished by heating to 1,500 °C, yielding the formula $Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$ for the dried precipitate.

XRD data were collected for precipitated HafSOx powders to establish temperature ranges for crystalline phases. After air drying, a complex diffraction pattern was recorded for samples having maximum sulfate content and H_2SO_4(aq) as the sulfate source; other samples exhibited no or diffuse diffraction. XRD data for HafSOx (x = 0.70) are shown in FIG. 2. After heating air dried samples for 1 hour at temperatures between from about 100 °C to about 700 °C, the material becomes amorphous. Crystalline peaks characteristic of monoclinic HfO_2 are observed after heating at 750 °C and above for 1 hour. As the onset of sulfate loss occurs at 720 °C by TGA, crystallization is found to coincide with sulfate loss. Inclusion of 3% La generates similar diffraction profiles for temperatures up to 1,000 °C.

XRD data for HafSOx:32% La are shown in FIG. 3. Both the precipitated material and that heated to 700 °C are X-ray amorphous. Just as with unsubstituted HafSOx, a detectable crystalline phase forms between 700 °C and 750 °C (1 hour

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heating), which is the temperature interval over which sulfate begins to decompose. Yet with substitution of 32% La, monoclinic HfO_2 is not the detected phase. Rather, the diffraction profile is consistent with cubic (or tetragonal) HfO_2, the phases of HfO_2 often stabilized by lanthanide atom inclusion. High-temperature heating generates $Hf_2La_2O_7$ and monoclinic HfO_2 as predicted from consideration of the appropriate phase diagrams. Intermediate temperature oxide phases are consistent with work on the system ZrO_2-La_2O_3 by Zhang, Kershaw, and Dwight, who found that 10–37% lanthanum stabilizes cubic zirconia at 900 °C, with phase separation occurring at 1,050 °C.

HafSOx and HafSOx:La thin films having thicknesses of from about 200 nanometers to about 300 nanometers were fabricated for materials characterization. Compositions for the films were determined with EMPA, based on relative concentrations of Hf, La, Cl, and S. Oxygen levels are less precise by this method, so dehydrated formulas are expressed. Two representative HafSOx films heated at 325 °C (5 minutes) were determined to be $HfO_{0.985}(SO_4)_{0.67}Cl_{0.69}$ and $HfO_{0.915}(SO_4)_{0.85}Cl_{0.47}$, representing 67% and 85% sulfate relative to hafnium. The 85% sulfate film was further heated to 650 °C (5 minutes) and determined to be $HfO_{1.275}(SO_4)_{0.71}Cl_{0.03}$. Also, the HafSOx:La film heated at 330 °C (5 minutes) was determined to be $Hf_{0.76}La_{0.24}O_{0.73}(SO_4)_{0.96}Cl_{0.38}$. For HafSOx heated to 650 °C, the sulfate ratio was reduced to 71%, which matches the composition for heat precipitated HafSOx powders with maximal sulfate. For HafSOx:La, the measured fraction of La (24%) agrees well with the 23% La concentration in the precursor solution.

Transmission Fourier transform infrared (FTIR) analyses for HafSOx ($x \sim 0.67$ & 0.85), and HafSOx:La films were collected after heating for 5 minutes at selected temperatures. FTIR spectra were used to detect principally two functional groups. Absorption in the range 3000–3600 cm^{-1} is attributed to hydroxyl groups; and absorption in the range 1000–1200 cm^{-1} is attributed to sulfate groups. With heating, hydroxyl absorption diminishes over the range from about 325 °C to about 600 °C, while sulfate stretches are nearly eliminated between about 650 °C and 700 °C for HafSOx films, and between about 700 °C and 750 °C for the HafSOx:La

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film. (The profiles for sulfate absorption are slightly distorted since SiO_2 from the substrates absorbs at a similar energy, but spectra are qualitatively correct.)

Thin-film XRD data were collected for HafSOx (x ~ 0.67 & 0.85) and HafSOx:24% La films after heating at indicated temperatures for 5 minutes each, as shown in FIGS. 4 and 5, respectively. For both HafSOx compositions, films are X-ray amorphous from about 325 °C to about 650 °C. Monoclinic HfO_2 is detected at about 700 °C and above. HafSOx:La films are amorphous from about 330 °C to about 700 °C, while a cubic phase is detected from about 750 °C to about 1000 °C. The cubic phase is apparently unstable at 1,100 °C, as separation into monoclinic HfO_2 and $Hf_2La_2O_7$ phases commences. For HafSOx and HafSOx:La films, loss of sulfate can be directly correlated with oxide crystallization, which is consistent with powder behavior.

Films of HafSOx, ZircSOx, and derivatives thereof, were deposited by spin-coating for use as dielectrics. MIM capacitors were tested to determine the parameters of permittivity and loss tangent at 1 kHz, as well as electric-field breakdown strength. "Breakdown" is defined as the field where current density surpasses 10 $\mu A\ cm^{-2}$. Similar tests were conducted for HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, and ZircSOx:Ca. FIG. 6 illustrates dielectric breakdown characteristics for HafSOx dielectric film where the aluminum dot contacts represent an area of 0.011 cm^2. HafSOx and ZircSOx films had breakdown fields of 4–6 MV cm^{-1}. A breakdown field of 3.6 MV cm^{-1} was found for ZircSOx:Ca. At an applied field of 1 MV cm^{-1}, all six variations exhibited leakage current less than 50 nA cm^{-2}, and leakage currents less than 10 nA cm^{-2} were observed for many compositions. Permittivity values of from about 9 to about 12, and loss tangent < 1% were measured for all variations.

Field-effect transistors (FETs) were fabricated with HafSOx:La or ZircSOx:La as the gate dielectrics and zinc indium oxide or zinc tin oxide as the channels. Current modulation was achieved; drain-to-source current saturated with increasing drain-to-source voltage, providing an on-to-off ratio greater than 10^6; and gate leakage currents are in the range of pA cm^{-2}. These results clearly indicate that HafSOx:La and ZircSOx:La films are sufficiently robust for device integration; the requirement for a quality dielectric/channel interface is also met.

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As a new class of amorphous multi-component oxide dielectric films, HafSOx, ZircSOx, and their derivatives may be compared to other mixed systems, particularly aluminates and silicates, represented as $(MO_2)_{1-x}(Al_2O_3)_x$ and $(MO_2)_{1-x}(SiO_2)_x$ where M = Hf or Zr. Various film compositions for each of these systems have been deposited by conventional vapor phase techniques. In the cases of Hf or Zr aluminates and silicates with 20–50 mol% Al_2O_3 or SiO_2 (as common compositions for dielectric applications), crystallization typically occurs at about 800 °C to about 1,000 °C, in conjunction with phase segregation. For tested HafSOx powders and films, crystallization occurs at approximately 700 °C as sulfate decomposes. As dielectrics, these aluminates and silicates exhibit permittivity values of 10–15, compared to values of 9–12 for HafSOx and ZircSOx. This new class of oxide sulfate materials can be considered amorphous, moderate temperature, medium permittivity dielectrics.

Scanning electron microscopy (SEM) and X-ray reflectivity (XRR) were used to further examine film qualities. SEM images for HafSOx and HafSOx:La films are shown in FIGS. 7 and 8. These images reveal smooth surfaces and dense, uniform cross-sections for films having thicknesses in the range of from about 150 nanometers to about 300 nanometers, as typically used for dielectric testing. FIG. 7 shows a SiO_2 substrate 710 upon which a 506-nm layer of Ta metal 712 and a 160-nm HafSOx film 714 have been deposited. FIG. 8 shows a SiO_2 substrate 810 upon which a 512-nm layer of Ta metal 812 and a 192-nm HafSOx/La film 814 have been deposited.

As a stringent measure of reproducibility for thinner film fabrication, multilayer structures with a HafSOx/ZircSOx repeating motif were deposited and analyzed by XRR. The interference pattern from one XRR scan is shown in FIG. 9. Positions of peak maxima, representative of standing wave harmonics, were used to find the thickness of the repeating bilayer. By systematically varying the thicknesses of HafSOx and ZircSOx independently, the thicknesses of the individual layers were determined. Within a nanolaminate stack, single layers as thin as about 3 nanometers were measured. As high order reflections in the diffraction pattern are observed, each bilayer was deposited with a variability < 0.5, including roughness.

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Shrinking device dimensions have led to the need to replace thin, high leakage-current SiO_2 as a dielectric in Si CMOS technologies. The replacement dielectrics must exhibit a high permittivity, allowing thicker layers to exhibit the same device capacitance with smaller leakage currents. HfO_2 and ZrO_2 have attracted considerable attention as replacement gate dielectrics because of their desirable dielectric properties and thermal properties. One of the challenges for HfO_2 and ZrO_2 dielectrics is making smooth, dense, pinhole-free, ultra-thin films having a thickness less than or equal to 13 nm. Previously ultra-thin films have been formed using atomic layer deposition (ALD). Despite some promising results from ALD, the processing requires using a vacuum with long deposition times (1 Å/min), which leads to high costs and low throughput. This has driven some work on the solution based deposition of HfO_2 and ZrO_2. To date these films have not reached the same uniformity and density of the ALD films.

Using an exchange reaction, ultra-thin $M(OH)_x$ and MO_x films can be fabricated that rival ALD quality and are suitable for use in DRAM (dynamic random access memory) and Si CMOS (complementary metal-oxide semiconductor) technologies. For disclosed embodiments, the films are deposited in a sulfate form via inorganic condensation using spin-coating. For example, a semi-solid film can be formed with the composition $MO_x{\cdot}HCl{\cdot}H_2SO_4$. The sulfate is removed by ion exchange using an aqueous sodium hydroxide solution:

$$MO_x{\cdot}HCl{\cdot}H_2SO_4 + OH^-(aq) \rightarrow M(OH)_{2x} + Cl^-(aq) + SO_4^{2-}(aq)$$

The resulting hydroxo and/or oxide films are smooth, dense, and pinhole free. For example, HfO_2 films with a thickness of about 2 nanometers can fabricated from HafSOx films. Exchanged films are subjected to thermal treatments up to about 800 °C for about 10 seconds to 10 minutes, resulting in a film surface roughness of about 0.1 nanometer. Such film characteristics satisfy requirements for metal-dielectric gates in CMOS and related technologies, while replacing expensive atomic layer deposition processing with low-cost spin-on or misting techniques.

The deposited semi-solid hydrated hydroxo films allow for anion exchange without disruption of the films' morphology. For example, oxoanions such as SO_4^{2-}, WO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-}, VO_4^{3-}, AlO_4^{5-}, GaO_4^{5-}, and their protonated forms, e.g., HPO_4^{2-}, $H_2PO_4^-$, and the halides F^-, Cl^-, Br^-, and I^-, can be selectively exchanged by

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placing the films in a metal salt bath, e.g., Na_2SO_4(aq). This provides opportunities to optimize film performance for electronic applications and other applications, such as ion exchange chromatography and filtration.

For some embodiments of oxide films, it is difficult to produce single-source precursor liquid suspensions that can be directly applied to a substrate to provide a complex composition, e.g., two or more metal atoms. The following methods allow the production of the such liquid suspensions and their use as single-source precursors for deposition of films of suitable quality for device applications.

The following describes a general method for synthesizing an aqueous precursor solution and depositing metal oxide films using the precursor. The aqueous precursor is distinctive in that it comprises polymeric or oligomeric metal-hydroxo compounds condensed via hydrolysis in a non-aqueous polar solvent and subsequently transferred to an aqueous environment for deposition. Advantageous thin-film electrical and optical properties and processing temperatures are achieved by condensing metal hydroxides to dense solid oxides without deleterious organic contaminants. Disclosed embodiments of the synthetic method follow the general procedure: 1) dissolution of metal salt in polar solvent; 2) hydrolysis and condensation; 3) solvent evaporation; 4) dissolution in H_2O; and 5) solution deposition and curing.

One or more soluble salts comprising a metal cation (M^{a+}) and one or more anions (X^{b-}) are dissolved in a non-complexing, non-aqueous polar solvent such as aliphatic alcohols or nitriles, particularly lower (10 carbon atoms or fewer) alkyl alcohols and nitriles, such as methanol, ethanol, acetonitrile, or a mixture thereof. Many solvent systems are possible. Suitable solvents for a particular application can be selected by considering boiling point (typically less than 150 °C), low toxicity, and acid-base and redox properties compatible with intended solution-phase reactions. Metal sources may include simple ionic or molecular salts ($Zn(NO_3)_2$, $SnCl_4$, etc.); oxy or hydroxy salts ($ZrO(NO_3)_2$, ZnOHCl, etc.); or potentially organic salts ($Fe(CH_3CO_2)_2$, $Cu(CHOO)_2$, etc.). At least one of the metal cations must have a formal charge greater than 3^+ and the total concentration of such ions (M^{a+} where $a > 3$) should exceed 50 mol% of the metal cations in the target oxide. Concurrently, an amount of H_2O is introduced into the solution as hydrates of the metal salts

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described above, as a pure liquid, or a basic solution detailed below. The amount of water is determined by the cations chosen; typical amounts of water will not exceed 20 mol% of the non-aqueous polar solvent.

The pH of the solution is then raised relative to the starting pH by adding an appropriate base or by reaction of free protons via oxidation-reduction mechanisms. The increased pH drives hydrolysis of the H_2O ligands bound by the acidic ($a > 3$) cations and condensation of the resulting hydroxo-cations. The final solution pH depends upon the metal cations used, but will typically be in the range of about 2-9. This may be accomplished using one of the following techniques, or any and all combinations thereof:

a) Addition of a basic aqueous solution containing NH_4OH, $(NH_4)_3PO_4$, CsOH, or similar compounds. Specific compounds (NH_4OH) may be chosen to decompose or volatilize during subsequent processing. Other cations (e.g., Cs) or polyatomic anions (e.g., PO_4^{-3}) may be used if they are intended to comprise part of the final oxide film to achieve unique morphological, optical, or electrical properties following dehydration.

b) Addition and dissolution of a small amount of a basic oxide such as CaO or SrO, with a similar goal of inclusion in the final oxide film.

c) Addition of NH_3 or other gaseous compounds, which form a basic solution in H_2O.

d) Addition of electropositive metal reducing agents, such as Zn, Al or Fe, which may consume protons through direct reduction to H_2, or as part of other proton-consuming oxidation-reduction processes such as the reduction of NO_3^-. Resultant cationic species are thereafter incorporated into the final oxide film.

e) Addition of aqueous or gaseous oxidizing or reducing agents such as N_2H_4, H_2CO, or H_2O_2 in liquid form, or as soluble salts, with a similar purpose of consuming protons or decomposing counter ions but without inclusion in the final oxide film.

The solution may be stirred at room temperature, heated, or exposed to solvothermal conditions to promote thermohydrolysis and condensation, depending on the final composition desired. Following a suitable reaction period the solution

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will contain one or more soluble oligomeric or polymeric metal-hydroxo cationic species. These species may be homo or hetero-metallic in nature. The degree of condensation is limited by the restricted molar ratio of H_2O (aquo- and hydroxo-ligands) available, while the decreased polarity and size of the non-aqueous solvent relative to H_2O may prevent additional condensation and precipitation processes through steric effects or altered charge-screening properties.

Soluble metal species are isolated by evaporating the non-aqueous solvent. Isolated metal-hydroxo compounds may form crystalline or amorphous solids or gels depending on certain processing considerations, such as solvent, counterion, and hydrolysis ratio.

Precursor solutions for oxide films are prepared by dissolving or dispersing the isolated solid in H_2O. The resulting sol or solution is homogenous, and may or may not be thermodynamically stable.

Precursor solutions are applied to a substrate using any suitable technique, including printing, spin, spray, or dip-coating to form a patterned or blanket liquid film. Liquid films are thermally cured under atmospheric conditions for about 5-240 minutes at a temperature from about 100 °C to 600 °C. Vacuum or forming gas (e.g., H_2 and flowing N_2 or Ar) anneals may be used to alter oxygen stoichiometry or cation oxidation state as appropriate for the chemical or optoelectronic properties desired.

The smoothness and high atomic density of the films described herein allow fabrication of purely inorganic nanolaminates via solution processing. These films represent a new platform for developing a wide range of applications, as discussed further below.

III. Applications

A person of ordinary skill in the art will appreciate that the HafSOx and ZircSOx compounds, and films comprising such compounds, can be used to make a number of different devices, and can be used to practice a variety of processes utilizing such compounds. Metal-organic precursors have been extensively employed in the solution-based deposition of inorganic oxides. The presence of the organic moiety necessitates a high-temperature burnout step, which leads to

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significant volume change and generally to crystallization and the phenomenon of "mud cracking." These problems are eliminated by using disclosed embodiments of the present invention and suitable inorganic compositions to form amorphous HafSOx and ZircSOx films, where simple dehydration and polymerization lead to film quality preservation. To understand phase stability, representative HafSOx and HafSOx:La powders and films were characterized at various temperatures. Thin-films based on HafSOx and ZircSOx were deposited in multiple configurations in order to examine the quality and utility of the films. Several derivatives have been used to produce capacitor dielectrics. HafSOx:La and ZircSOx:La were used to form gate dielectrics in FET devices. Nanolaminate layers of HafSOx and ZircSOx exhibited remarkable smoothness with reproducibility within a couple atomic layers. Classes of films comprising HafSOx, ZircSOx, and their derivatives are useful, amongst other things, as electrical insulators, protective barriers, optical coatings, and/or as inorganic polymers for photolithography.

A. Patterned films for Resist, Imprint Lithography, and Printing

Photolithography is commonly used to transfer geometric shapes on a mask to the surface of a silicon wafer or other semiconductor. For the past four decades, photolithographic processing has been the driving force for the improvements in resolution and dimensional control of device features in the microelectronics industry. These advances have made possible the high-performance personal computers, cell phones, CD players, and other innumerable advanced electronic products that are now considered to be essential parts of our lives. The photolithographic advances that have made these products possible have largely centered on developing short-wavelength exposure tools and an extraordinary extension in the resolution and feature-size capabilities of polymer resists. As the quest for ever smaller features and device-yield improvements continue, however, the limitations and inefficiencies of polymer-based resist technology are becoming more evident.

The smallest feature sizes realized via lithography have been produced by electron-beam writing of inorganic materials. The beam-dose energies required to

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produce these features, however, have been much too high to receive more than passing interest for use in a manufacturing environment.

During the deposition and processing of the films described herein, it is possible to control the film hydration level, which provides a method for controlling the interdiffusion of stacked films and their resulting physical and chemical properties. This controlled interdiffusion with resulting induced modifications in material solubility, coupled with the high quality of the films, was used to develop a new lithographic patterning method. This methodology involves depositing and reacting two distinct films, and it is designated as bilayer diffusion. In addition, small coordinating species such as peroxide (O_2^{2-}) can be incorporated into aqueous-based inorganic liquid suspensions and films to provide an additional, new lithographic patterning method. In this technique, energy (e.g., light, electron beam, heat) can be applied to films, inducing condensation reactions that alter the solubility of the film, thereby allowing lithographic patterning.

Patterns can be formed using a positive or negative photoresist. This process is illustrated schematically in FIG. 10 with reference to a laminate structure 1010 having a silicon substrate 1012, a silica layer 1014 and a resist layer 1016. For positive resists, the resist layer 1016 is exposed to an energy source, such as UV light, wherever the underlying material is to be removed. In these resists, exposure to the UV light changes the chemical structure of the resist layer 1016 so that it becomes more soluble in the developer. The exposed resist layer 1016 is then removed by the developer solution, leaving areas of the bare underlying material. In other words, "whatever shows, goes." The mask 1018, therefore, contains an exact copy of the pattern which is to remain on the wafer.

Negative resists behave in just the opposite manner. Exposure to the UV light causes the negative resist to polymerize, and it therefore is more difficult to dissolve. As a result, the negative resist 1020 remains on the surface wherever it is exposed, and the developer solution removes only the unexposed portions. Masks used for negative photoresists, therefore, contain the inverse (or photographic "negative") of the pattern to be transferred.

Resist materials in current use for electronics manufacture are organic polymers. These polymers exhibit coiling and morphologies that limit pattern

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resolution. Inorganic thin films of the present invention form the basis for a new resist technology. Here, negative resists can be realized by exposing the inorganic films in semi-solid form to light or electron beams, causing them to lose solvent, particularly water during dehydration. This hardens the films, rendering them insoluble in acid.

One embodiment of a positive resist can be made using a bilayer system. A first layer of the bilayer comprises a copper formate film deposited on a hafnium oxide sulfate (HafSOx) film. The copper formate film is soluble in acid and the undoped HafSOx film is insoluble in acid. Exposing the bilayer to light through a mask or to a focused electron beam causes the two films to interdiffuse in exposed areas, thereby rendering the previously undoped HafSOx film soluble.

One embodiment of this process is illustrated schematically in FIG. 11. With reference to FIG. 11, a laminate structure 1110 is first formed, such as by spin coating or inkjet coating suitable materials, in desired orders and thicknesses as required to define a working device. More specifically, a substrate material 1112 is first selected. A person of ordinary skill in the art will appreciate that any of a number of substrate materials potentially can be used to practice this embodiment of the present invention. Solely by way of example, and without limitation, suitable substrates include semiconductor materials, metals, glass, polymeric materials, and combinations thereof. As such the resist technology can be useful for a variety of applications in semiconductor manufacture. Once a suitable substrate 1112 is selected, a first layer 1114 of HafSOx is solution deposited onto the substrate 1112. Thereafter, a second layer, such as a layer 1116 of Cu:ZircSOx, is solution deposited onto layer 1114. The laminate structure 1110 is then subjected to an energy source, such as an electron beam or light, through a mask. Upon exposure to light or an electron beam through a mask, the two films interdiffuse in the exposed areas to render the previously undoped HafSOx film soluble to produce a laminate structure 1120. The exposed structure 1120 is then developed. The previously undoped HafSOx film is soluble, and hence is removed as indicated in laminate structure 1130.

On a flexible or glass substrate, the pattern illustrated in structure 1130 can be considered the master plate for imprint lithography or for generalized printing

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processes such as gravure printing. Forming a hardened patterned material of HafSOx in this way also provides a means for developing micro- and nano-channel arrays in the fabrication of devices for fluid control and delivery. Such devices could be applied in medical diagnostics, ink delivery, and chemical synthesis.

Another embodiment of a bilayer process is shown in FIG. 12. The process produces a patterned oxide on a selected substrate 1210. The substrate can, for example, be a glass, semiconductor wafer, metal, metal alloy, plastic, or a combination thereof. The first step of the process involves depositing a thin film 1212 (from about 1 nm to about 100 nm) of a solid acid or base, e.g., hydrated sulfate, phosphate, nitrate, silicate, aluminate, borate, or mixtures thereof, containing one or more of the metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu. In addition the solid acid/base can contain one or more of NH_3, OH, F, Cl, Br, I. The solid acid/base is preferably deposited via spin coating or printing; physical and vapor deposition are additional options. As one example, the solid acid can be deposited from an aqueous solution of $HfOCl_2$ and H_2SO_4(aq) via spin coating. The solid acid is heated sufficiently to produce a structurally rigid film 1212, such as by heating at about 50 °C for about 2 minutes. In the printing mode of operation, the substrate 1210 can be placed on a heated platen (about 25 – 300 °C), and an ink containing an oxide precursor 1214, e.g., copper formate, can be applied in a desired pattern by delivery through an ink-jet head or by bringing the substrate 1210 into contact with a template containing the precursor 1214. The template comprises a portion of a microcontact, letterpress, or gravure printer. Under heated conditions (greater than about 250 °C), the precursor 1214 decomposes to an oxide, subsequently reacting and interdiffusing with the solid acid, forming a product 1216 that can readily be washed or etched to reveal a pattern 1218. The oxide precursor also may be replaced by an ink suspension or paste containing fine oxide micro- or nanoparticles. Application of the fine particles with or without heating results in a direct reaction to form a product that can be etched to reveal a pattern.

An alternate embodiment is shown in FIG. 13 for producing a patterned oxide on a selected substrate 1310. The initial step involves depositing a solid acid 1312 or base onto the substrate. The oxide precursor 1314 is then applied as a

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blanket coat via spin coating, printing, chemical vapor, or physical vapor deposition. A pattern of activated precursor 1316 is then formed by exposure to an energy source, such as light, via a photomask. Suitable light sources include an unfiltered deuterium lamp or a light source producing light at 193 nm, among others. Alternatively, a pattern of activated precursor 1316 is formed by directly writing with a focused laser or electron beam. If necessary, the activated and patterned structure 1316 can then be heated to a temperature from about 125 °C to about 350 °C to promote interdiffusion of the two layers. The exposed areas can then be etched to produce the desired pattern 1318. A procedure to improve exposure sensitivity involves using a very thin layer (about 2 nm) of oxide precursor on the solid acid. The precursor layer is then covered with a layer of an oxide that is deposited via any suitable technique, such as chemical or physical vapor deposition or by solution casting of oxide nanoparticles. The layers interdiffuse following exposure of the thin layer of precursor.

The processes described above correlate to a positive resist technology. It is also possible to select solid acids/bases and precursors that will produce insoluble products. These products can be used to produce positive images in at least two ways. In one embodiment, the two layers completely interdiffuse to form a single insoluble layer. Following printing or exposure and development, the soluble portions of the film are then washed or etched to reveal a positive pattern. In an alternative approach, interdiffusion occurs only at the interface between the precursor and the solid acid/base to produce a thin, insoluble barrier layer. This barrier layer is then used to control the etching of the film stack to produce a positive image. The barrier layer is photosensitive. Prior to light exposure, it prevents reaction between the precursor and solid acid/base layers that would otherwise readily interdiffuse on contact. Once the barrier layer is photosensitized, it becomes a reactive oxide. The barrier is "broken," and the top layer can then interdiffuse with the lower layer.

Next-generation patterning, whether based on photo or imprinting, uses masks or templates, typically fabricated by electron-beam lithography. Many of these templates or masks are being fabricated with the hard mask HSQ (hydrogen silsesquioxane). HSQ masks are widely used for fabricating a variety of electronic,

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data storage, and microelectromechanical devices. HSQ is also under development as a hard master/template for imprint lithography.

Masks or templates can be fabricated using the films described herein in a single layer process as shown in FIG. 14. The first step of the process involves depositing a thin film (from about 1 nm to about 100 nm) of an inorganic precursor 1410 onto a substrate 1412. The inorganic precursor1410 may be a solid acid or base, e.g., hydrated sulfate, phosphate, nitrate, silicate, aluminate, borate, or mixtures thereof, containing one or more of the metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu in combination with peroxide or similar coordinating anion. In addition the solid acid/base and peroxide mixture can contain one or more of NH_3, OH, F, Cl, Br, I. The solid acid/base is preferably deposited via spin coating, liquid misting, or printing; physical and vapor deposition are additional options. As one example, the solid acid can be deposited from an aqueous solution of $HfOCl_2$ H_2SO_4(aq), and H_2O_2(aq) via spin coating. The solid acid is heated sufficiently, such as to a temperature of from about 50 °C to about 125 °C, and for a period of time from about 10 seconds to about 10 minutes to produce a structurally rigid film. The film is then exposed through a photomask or via a defined laser or electron beam to induce condensation in the exposed areas. The solubility of exposed areas 1414 decreases relative to unexposed regions, so the unexposed regions can be selectively etched in acid or base. Examples of acids or bases that can be used include hydrochloric acid, sulfuric acid, hydroxgen peroxide, sodium hydroxide, and tetramethyl ammonium hydroxide, among others. Typically, the concentration of the acids or bases used is within the range of about 0.1 M to about 1 M. The film is then developed in aqueous acid or base to etch the unexposed regions following an optional thermal cure at a temperature greater than about 100 °C. This process produces a negative-tone image in the film. By preheating the applied film to higher temperatures prior to field exposures, differential etching rates can be induced to realize positive-tone images. FIG. 15 demonstrates differential etching rates for thermally pre-treated, single-layer film. The graph demonstrates that thermal treatment affects etching rates such that exposed regions etch faster than unexposed regions following an initial time.

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In another embodiment, a HafSOx film is treated with a mixture of sodium hydroxide and hydrogen peroxide, resulting in anion exchange and formation of a $M(OH)_x/H_2O_2$ film. Alternatively, a previously prepared $M(OH)_x$ film may be soaked in hydrogen peroxide to form a $M(OH)_x/H_2O_2$ film. The resulting $M(OH)_x/H_2O_2$ film is then patterned by exposure to light or an electron beam. These techniques provide a means for directly patterning simple of complex MO_x films without a polymer resist. For example, HfO_2 films may be directly patterned for use as high k dielectrics in Si CMOS circuits and printed electronics applications. In another example, a patterned TiO_2 film can be produced from a $Ti(OH)_x/H_2O_2$ film formed by solution deposition of $Ti(OH)_4$ in H_2O_2.

These methods substantially eliminate diffusion used in two-layer embodiments, lower exposure doses, and improve line-edge roughness and critical dimensions. FIG. 16 is an AFM (atomic force microscope) image of a HafSOx film patterned via a single-layer, negative tone process with an electron beam at dose levels ranging from greater than 0 $\mu C/cm^2$ to at least 400 $\mu C/cm^2$. The nanometer scale to the right of the image indicates the height of the features etched into the film. As shown in FIG. 16, features have been written via electron-beam exposure at dose levels as low as 2 $\mu C/cm^2$. This dose level is comparable to the best known chemically amplified polymer resists and 1000 times lower than that previously demonstrated for an inorganic resist. Features can be produced with a resolution of less than about 20 nm. In addition, the films demonstrate structural integrity (e.g., smooth, dense, pinhole-free) to less than 3 nm, nearly an order of magnitude smaller than that demonstrated for HSQ.

The film application, heating, and etching steps associated with a polymer resist, as well as the vacuum and high-temperature processing steps of the inorganic material, have been eliminated in the patterning process. The resulting patterned film could be a functional component of an electronic device, a hard mask for subsequent patterning of the underlying substrate, or a template for imprinting. Except for the electron-beam exposure, all processing is conducted in a normal environment in air. Considering the elimination of several processing steps, the disclosed technique provides a new method to improve device production yields and lower fabrication costs. Relying on the exclusive use of aqueous chemistries, the

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process is also environmentally green, and washed products can be completely recovered and recycled. The technique has applications to many advancing technologies. Its use is not restricted only to the systems described herein.

B. Hot Embossing Lithography

Hot embossing lithography is another method for producing patterns in HafSOx, ZircSOx and related materials. This process, illustrated schematically in FIG. 17, most commonly has been applied to creating patterns with organic polymers. The semi-solid form of HafSOx and related compositions provides an opportunity to pattern inorganic materials having much higher mechanical strength, chemical stability, and unique electrical and optical properties relative to organic polymers.

With reference to FIG. 17, HafSOx or related inorganic material, instead of an organic polymer, is solution deposited, such as by spin coating or inkjet printing, on a suitable substrate 1712 to form HafSOx layer 1714. Substrate 1712 and HafSOx layer 1714 define laminate structure 1710. A stamp 1716 with unit features of desired size scale, such as nanometer, micrometer or millimeter size scale, is pressed into the semi-solid HafSOx or related film layer 1714 to form stamped layer 1718. Stamped layer 1718 and substrate 1712 are then heated to harden the HafSOx. The stamp is then removed to define a patterned HafSOx material in patterned laminate structure 1720.

C. Measuring Device

The chemistry developed for the bilayer positive resist technology noted above also can be used to fabricate a physical ruler, as illustrated in FIG. 18, for use in standardizing measurements in suitable fields, such as electron microscopy. In this application, a nanolaminate 1810 of alternating acid-soluble layers 1812 and acid-insoluble layers 1814 is deposited. The acid soluble layers are formed by solution deposition of a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy

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phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8. Typically this layer is doped with copper. The acid-insoluble layers are formed by solution deposition of a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8.

The widths of the layers 1812 and 1814 are accurately determined, such as by using X-ray reflectivity. The acid-soluble layers 1812 are then etched to reveal a finger-type pattern 1820 that can be used as a secondary reference in accurately measuring objects in an electron microscope.

D. Corrosion Barriers

The precursor liquid can be coated onto a suitable substrate, such as a metal or alloy or ceramic, to form a corrosion barrier. In addition, the liquid can be drawn into fibers, placed in a mold, or used alone. The liquid is converted into solid, stable form by any suitable process, including hydrolysis, annealing, or pyrolysis in air. Typically, this requires heating to temperatures, and for a period of time, effective to achieve the desired results, such as a temperature normally above 100 °C for at least a few seconds, more typically at least a few minutes.

Because of the atomically dense nature of the films, potential applications include, but are not limited to, thermal, corrosion and oxidation protection for metals and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based

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ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal and ceramic-based systems, fibers for composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, catalyst supports, as well as many others. The ability to laminate the films provides an opportunity to randomize the location of defects in one layer relative to another, providing enhanced corrosion protection.

E. Optical Coatings

The precursor liquids can be coated as individual layers and in multilayer formats onto suitable optical substrates to produce antireflection coatings, dielectric mirrors, X-ray mirrors, interference filters, waveguides, planar coatings, and scratch-resistant surfaces. Multilayer periodicity is achieved by alternately depositing at least two material compositions. Single layer periodicity can be achieved by etching, as described for photolithography processes. The amorphous nature, sharp interfaces between layers, and abilities to control dielectric constants provides a process for realizing performance near theoretical limits.

In multilayer or single layer configurations, which have been selectively deposited or etched, the periodic structure is appropriate for diffracting applications. Combinations of single or multiple materials and/or voids may define the structures. The use of void space allows for great contrast of physical properties within given structures. Functional characteristics may be enhanced or realized by the use of void space. Optical gratings may be similarly defined.

Because substantially smooth surface films can be deposited according to embodiments of the method disclosed herein, films may be used to planarize substrate layers such as metal, ceramics, and plastics that exhibit greater degrees of roughness.

F. Luminescent Films

A material may absorb energy and emit photons in a number of luminescent processes. The luminescent events may involve only the predominant phase (or host), or also may include added elements. A single material may serve as host for numerous luminescent additives. Many of the disclosed film compositions are

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visibly transparent with transparency potentially extending into the ultraviolet portion of the spectrum. These materials potentially function well as luminescent host materials. These materials can be selectively doped with common luminescent ions, including by way of example, and without limitation, Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof, to yield light-emitting films of interest for lighting and display applications.

G. Printed Electronics

Manufacturers are seeking new, efficient fabrication methods that eliminate the limitations of conventional vapor deposition and lithographic processing. Printing and related maskless techniques are widely regarded as paths forward for realizing advancement in manufacturing efficiencies for back-plane electronics.

The disclosed solution-processed thin films exhibit morphological and device-functional characteristics similar to those achieved by the most advanced vapor-phase processing methods. Solutions of the disclosed compositions can be imprinted, such as with microcontact, gravure, an inkjet printer or other suitable means. The resulting imprinted solutions can be used to fabricate stable inorganic transistor arrays exhibiting device mobilities of about 10 cm^2/Vs with dielectric leakage current densities less than about 20 nA/cm^2. Dielectric and semiconductor inks also can be printed onto glass substrates to produce transistor arrays having mobility of about 1 cm^2/Vs and dielectric leakage currents less than about 100 nA/cm^2. MIM capacitor arrays can be fabricated with relative dielectric constants greater than about 5 and leakage current densities less than about 50 nA/cm^2.

IV. EXAMPLES

The following examples are provided to exemplify particular features of working and/or hypothetical embodiments of the present invention. A person of ordinary skill in the art will appreciate that the scope of the present invention is not limited to the particular features stated in such examples.

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Example 1

This example describes a general method that has been used to prepare solutions as sources for bulk precipitates or for use as thin film precursors. The following reagents were used: $HfOCl_2 \cdot 8H_2O$ (Alfa Aesar, 99+% excluding 1.5%Zr); $ZrOCl_2 \cdot 8H_2O$ (Wah Chang spectrographic grade); $La_2(SO_4)_3$ (Alfa Aesar, 99.9%); $La(NO_3)_3 \cdot 6H_2O$ (Johnson Matthey, 99.9%); $Ce_2(SO_4)_3 \cdot 8H_2O$ (Strem, 99%); CaO (Alfa Aesar, 99.95%); $(NH_4)_2SO_4$ (Mallinkrodt AR); H_2SO_4(aq) (EM Science, GR ACS, 95-98%); and NH_3(aq) (EM Science, GR ACS, 28-30%). All solutions were prepared by combining $HfOCl_2$ or $ZrOCl_2$ with $La_2(SO_4)_3$, $Ce_2(SO_4)_3$, or CaO as necessary for a total metal concentration of about 0.8 M, followed by addition of sulfate solution, for a total metal concentration of about 0.5 M. These solutions were directly used for heat-induced precipitation and spin-coating dielectric films. Additional modifications were made as necessary to serve as precursors for hydroxide precipitation reactions or nanolaminate depositions.

Example 2

This example describes a general method that has been used for bulk precipitation from solutions made according to Example 1. Precipitation was induced by immersing tubes of solution in a boiling water bath for 40 minutes. For hydroxide-induced precipitation, $HfOCl_2$ and $La_2(SO_4)_3$ were mixed as 23% La (metal percent), followed by addition of solutions of $La(NO_3)_3$ and $(NH_4)_2SO_4$ to provide a hafnium concentration ([Hf]) of about 0.39 M, a lanthanum concentration ([La]) of about 0.18 M, and a sulfate ($[SO_4]$) concentration of about 0.42 M. 1.9 mole equivalents (relative to total metals) of saturated NH_3(aq) were then added quickly and the resulting mixture stirred for 1 minute. All precipitates were separated from the supernatant by paper filtration with suction, including several rinses with de-ionized water. The filtrates were dried at room temperature for 1 day. Samples were subsequently heated in alumina crucibles in ambient air at temperatures from about 100 °C to about 1,500 °C for about 1 to about 4 hours. XRD data was collected with a Siemens D5000 diffractometer, utilizing Cu Kα radiation. Thermogravimetric data were collected with a Shimadzu TGA-50 by heating samples (10–20 mg) in a Pt crucible under flowing N_2(g), typically at a rate

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of 10 °C minute^{-1}, and holding for 15 minutes at the highest temperature. Inductively coupled plasma atomic emission spectroscopy (ICPAES) was conducted with a Jobin Yvon JY2000 analysis setup. Samples were dissolved in digestion bombs at 200 °C for a few hours and diluted to measurable levels.

Example 3

This example describes a general method that has been used for deposition of thins films using solutions made according to Example 1. Thin-films of HafSOx, ZircSOx, and derivatives with added La, Ce, or Ca, were deposited on Si substrates by spin-coating at 3,000 rpm for 30 seconds, followed by immediate hotplate polymerization at 135° C for 1.5–2 minutes (additional heating on a 325 °C oven surface for 15 seconds to about 2 minutes may be required for certain derivatives). This process was repeated until desired deposited film thicknesses were obtained. A final oven anneal at 325 °C for 5–10 minutes was used.

Precursors for nanolaminate films were prepared by adding H_2SO_4 to $HfOCl_2$ or $ZrOCl_2$ as 46% sulfate relative to metal. Solutions were diluted to a metal concentration of 0.03–0.13 M. Alternating layers of HafSOx and ZircSOx were deposited in the same fashion as described for dielectric films.

The silicon substrates had a surface of SiO_2 or Ta metal. A 500-nanometer Ta surface was used for dielectric testing. A 200-nanometer SiO_2 surface was used for all other purposes. The surfaces were prepared for deposition by ultrasonic cleaning in (Decon Labs, Contrad 70) solution at 45 °C for 45 minutes, then rinsing the surfaces thoroughly with Millipore water before deposition.

XRD data were collected with a Rigaku RAPID diffractometer, employing Cu Kα radiation generated from a rotating anode at 50 kV and 270 mA. The incident beam angle was 7.6°, while the diffracted beam was collected with an image plate. XRR data were collected with Cu Kα radiation. Low angle reflections up to 10° (2θ) were collected at 0.005° steps. Transmission FTIR data were collected with a Nicolet 5PC spectrometer, with an uncoated substrate as reference. EMPA was collected.

MIM capacitor structures were completed by thermally evaporating circular contacts of Al (1.2 mm diameter) on deposited dielectrics. Parameters of dielectric

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constant and loss tangent were obtained. Bottom-gate transistor structures also were fabricated by sputtering inorganic channel materials without active heating. ZTO-channel devices were subsequently heated to 325 °C for 1 hour. Aluminum source and drain contacts were thermally evaporated. Transistor characterization was performed.

Example 4

This example describes a general method for producing smooth, dense, and pinhole-free ultra-thin nanolaminate films as thin as about 2 nm. Precursor solutions containing $HfOCl_2 \cdot 8H_2O$ or $ZrOCl_2 \cdot 8H_2O$, H_2O_2 (30%) and H_2SO_4(aq) were prepared as described in U.S. Patent Publication No. 2005/0242330 A1. The precursor solutions contained a metal ion concentration of about 0.05 M to 0.4 M with 70% H_2O_2 and 50% sulfate relative to metal. The difference in metal ion concentrations allowed for thickness per coat variation from 3 nm to 25 nm. Thin films were deposited on silica substrates with thermally grown SiO_2. Substrates were cleaned by using an ultrasonic bath with Contrad-70 solution at 45 °C for 60 minutes followed by a rinse with deionized water. Films were deposited by using a spin coater with a spin rate of 3000 rpm for 30 seconds followed by hotplate polymerization at 125 °C for 1-2 minutes. Spin-coating and polymerization steps were repeated until the desired thickness was reached. After the desired thickness had been reached, some films were heated to crystallization temperature. Other films were first treated in a 0.1 M-0.5 M NaOH bath for 1-2 minutes, then rinsed in a deionized water bath for 1-2 minutes before the thermal treatment.

Thin-film characterization using X-ray diffraction (XRD) analysis was performed on a Rigaku R-axis rapid with Cu Kα radiation. Atomic force microscopy (AFM) measurements were performed using a Digital Instruments Nanoscope III Mulitmode AFM operated in contact mode with a Veeco NP-20 SiN probe and a scan frequency of 1.15 Hz. X-ray reflectivity (XRR) measurements were performed using a Bruker Discover D8 and used to determine surface and interfacial roughness of the films. Compositional analyses were acquired on a Cameca SX-50 electron microprobe equipped with 4 tunable wavelength dispersive spectrometers. Accelerating voltages of 12, 16 and 22 kV were used and averaged

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over 5 points to monitor O, Cl, Na, S, and Si Kα intensities and Zr and Hf Lα intensities. Standards used for analysis were MgO, Hf, Zr, FeS_2 (pyrite), $Ca_5(PO_4)_3Cl$ (apatite), Si, and Si_3AlNaO_8 (albite). Corrections to the raw intensity were made by using Probe for Windows automation and analysis package. The StrataGEM compositional analysis software package was used for thin film geometry corrections by comparing experimental K-ratios to simulated values.

Amorphous, atomically flat, dense, pinhole-free thin films were deposited via spin coating for the as-deposited and exchanged films. FIG. 19 is an AFM image of an unexchanged HafSOx film with a roughness of about 0.1 nm. FIG. 20 is a TEM image of an HfO_2 film following ion exchange of HafSOx and thermal treatment at 850 °C. Unexchanged films remained smooth and amorphous up to 600 °C for Zr and 650 °C for Hf. However, after heating above these temperatures, films crystallized and became rough forming volcano-like features at the surface. FIG. 21 is an AFM image of a HfO_2 film deposited on silica. The HfO_2 film was formed by thermal decomposition of $HafSO_x$. The resulting film had a roughness of about 5 nm, resulting in volcano-like peaks. These features were most likely caused by the loss of SO_3. This was supported by thermal gravimetric analysis of Hf sulfate powder, where sulfate decomposition
(SO_3 (g) → SO_2 (g) and ½ O_2 (g)) occurs above 700 °C.

To eliminate the volcano effects, films were treated in a 0.1-0.5M NaOH(aq) bath for 1-2 minutes to remove the SO_4^{2-} and Cl^- anions from the film before heating. NaOH previously has been shown to effectively exchange hydroxy anions for other anions in zirconium salts. The NaOH treatment caused a thickness reduction of 40-45% (giving layer thickness of 2-15 nm), but the treatment had little effect on the smoothness (~1Å) or amorphous nature of the films when heated below 500 °C or 550 °C for zirconia and hafnia, respectively.

FIG. 22 is an AFM image of a HafSOx film deposited on silica, subsequently treated with 0.1M NaOH and heated to 450 °C for 10 minutes. The resulting film had a roughness of approximately 0.1 nm. Films heated above these temperatures crystallized, yet remained smooth at temperatures up to 850 °C.

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FIG. 23 shows a HfO_2 film deposited on silica, subsequently treated with 0.1 M NaOH and heated to 850 °C for 10 minutes. The resulting crystallized film remained smooth with a roughness of about 0.2 nm.

A drop in crystallization temperature was seen in the X-ray diffraction plots (FIGS. 24-27). In FIGS. 24-27, the substrate peaks have been removed with software. The *'s represent the major tetragonal phase peaks. FIG. 24 is an XRD plot of the untreated HfO_2 film crystallized as a mixture of tetragonal and monoclinic phases at 700 °C. The HfO_2 plot is a reference plot for the monoclinic phase. In contrast, FIG. 25 is an XRD plot of the 0.1 M NaOH-treated hafnia film crystallized only in the monoclinic phase at 550 °C. The HfO_2 plot is a reference plot for the monoclinic phase. FIG. 26 is an XRD plot of untreated zirconia films crystallized in a mixed monoclinic and tetragonal phase at 650 °C. The ZrO_2 plot is a reference plot for the monoclinic phase. As seen in FIG. 27, the 0.13 M NaOH-treated zirconia films crystallized only in the tetragonal phase at 500 °C. Upon further heating, films developed both monoclinic and tetragonal phases. The tetragonal phases of HfO_2 and ZrO_2 have been observed in previous thin film studies. The lower crystallization temperature, crystallization and loss of thickness indicated that the NaOH treatment removed anions (SO_4^{2-} and Cl^-) from the thin films.

Electron probe microanalysis (EPMA) of a film deposited from the 0.4 M Hf solution and heated to 350 °C for 5 minutes gave a film with composition $HfO_{1.32}(SO_4)_{0.61}Cl_{0.15}$. The chlorine in the film was a result of kinetic trapping as a consequence of the rapid thermal dehydration. Films that were treated in the NaOH(aq) bath did not have measurable sulfur levels (less than 0.01 atomic percent), and less than 0.3 atomic percent Cl was observed. This confirmed that the sulfur and chlorine were both removed from the films in the NaOH(aq) bath. EPMA also verified that the residual sodium left in the film after the treatment was less than 0.3 atomic percent.

Example 5

In a specific embodiment of the approach described above, hydrated indium and gallium nitrate salts ($In(NO_3)_3 \cdot 0.5H_2O$ and $Ga(NO_3)_3 \cdot 9.5H_2O$) were dissolved in

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methanol (CH_3OH). Final concentrations were [In] = 0.288 M, [Ga] = 0.170 M. Zinc powder was then added to the solution, and the flask sealed. The final concentration of zinc was 0.2 M. Reacting over a period of 1-7 days, the powder was slowly oxidized and dissolved to bring the total metal ion concentration to 0.658 M. The methanolic solution was exposed to air, and the methanol was allowed to evaporate at room temperature. The solid residue remaining in the solution was then dissolved in H_2O to a total metal concentration of 0.395 M. This precursor solution was spin-coated on a SiO_2 substrate with a conductive back contact and annealed to 450 °C for 1-4 hours. Following annealing, a transparent, amorphous $InGa_{0.6}Zn_{0.7}O_{3.15}$ semiconductor film was obtained as shown in the SEM image of FIG. 28. Aluminum source and drain contacts were thermally evaporated onto the oxide semiconductor film through a shadow mask to produce a thin film transistor (TFT). Field effect mobility for these TFTs was shown to exceed 8 $cm^2 V^{-1} s^{-1}$.

Example 6

This example describes two general methods of bilayer inorganic lithographic processing. In one working embodiment, a HafSOx film with a thickness from about 30 nm to about 60 nm was solution deposited onto a SiO_2/Si substrate. The substrate was placed directly onto a hot-plate set at about 50 °C and heated to impart structural integrity to the film. The resulting film was acid insoluble. The substrate was then placed on a heated platen (about 50 °C to 200 °C) of an ink-jet printer, where copper formate lines were printed onto the substrate via a thermal ink-jet head. Copper formate decomposed and diffused into the HafSOx film on heating, rendering the film soluble. Following a rinse in water, additional heating to about 300 °C, and development in dilute acid, the drawn lines were clearly evident as shown in FIG. 29.

In another working embodiment, patterns also were produced via photolithography. Exposure of a $HfO_{2-x}(SO_4)_x$ bilayer film with deep UV light using an unfiltered deuterium lamp promoted copper formate decomposition for subsequent interdiffusion and development of the pattern shown in FIG. 30. Feature sizes were reduced to about 22 nm with electron beam writing. The interdiffusion process can be spatially controlled via electron-beam energies to draw patterns and

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objects on the nanoscale. Highly resolved patterns were produced at charge dose levels near 150 $\mu C/cm^2$, representing a sensitivity similar to that of many polymer resists. FIGS. 31 and 32 are two patterns produced by electron-beam writing at a dose of level of about 200 $\mu C/cm^2$. In FIG. 31, the line spacing is 500 nm as measured by an electron microscope.

Example 7

This example describes general methods for patterning a single-layer inorganic film. A single inorganic film containing peroxide or related coordinating species is spin-cast, liquid misted, or ink-jet printed onto an appropriate substrate. The film is heated at modest temperatures of less than 100°C to provide structural integrity to the film. The film is then exposed through a photomask to high-energy light, a maskless pattern via spatial light modulation, a defined laser beam, or electron beam to define a pattern or other preferred film features. Two examples of photogryaphically patterned films are shown in FIGS. 33 and 34. FIG. 33 is a patterned $ZrO_{2-x}(SO_4)_x$ film. FIG. 34 is a patterned TiO_2 film. The TiO_2 film was about 15-50 nm thick. It was patterned using an unfiltered deuterium lamp, followed by etching with 0.1-0.2 M HCl for less than 60 seconds. FIGS. 35-37 are $HfO_{2-x}(SO_4)_x$ films patterned by an electron beam. The films were about 30-60 nm thick. They were patterned using an electron beam at a dose level of 200 $\mu C/cm^2$, followed by etching with 5-12 M HCl for about 1-4 minutes.

In view of the many possible embodiments to which the principles of the disclosed invention may be applied, it should be recognized that the illustrated embodiments are only preferred examples of the invention and should not be taken as limiting the scope of the invention. Rather, the scope of the invention is defined by the following claims. We therefore claim as our invention all that comes within the scope and spirit of these claims.

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We claim:

1. A device comprising a thin film or laminate structure comprising at least one hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8.

2. The device according to claim 1 wherein the thin film or laminate has a permittivity value within the range of from about 9 to about 12, a breakdown field up to at least 6 MV cm^{-1}, and a leakage current near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}.

3. The device according to claim 1 where the compound further comprises lanthanum, and has a formula $M_{1-z}La_zO_{2-x-z/2}(SO_4)_x$ (MSOx:La), where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatombic ion charge), and any value for z in a range of from 0.0 to about 3.8.

4. The device according to claim 1 where the compound is HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, or ZircSOx:Ca, the device having leakage current less than 50 nA cm^{-2} and permittivity values of from about 9 to about 12.

5. The device according to claim 1 where the device is a field effect transistor comprising HafSOx:La and/or ZircSOx:La as a gate dielectric and zinc indium oxide and/or zinc tin oxide as channels, the transistor having an on-to-off ratio of greater than 10^6, and gate leakage currents are in the range of pA cm^{-2}.

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6. The device according to claim 1, further comprising an optical substrate where the thin film or laminate structure forms a coating on the optical substrate.

7. The device according to claim 6 where the coating is an antireflective coating and/or the coating is transparent to visible or ultraviolet light.

8. The device according to claim 6 where the optical substrate and coating define a dielectric mirror, an X-ray mirror, an interference filter, a diffractive grating, and/or a waveguide.

9. The optical device according to claim 7 where the coating is selectively doped to provide a doped light-emitting layer having luminescent ions selected from Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof.

10. The device according to claim 1 where the device is a master plate for imprint lithography and the thin film or laminate structure is deposited onto a flexible or glass substrate, the thin film or laminate structure comprises a first layer of HafSOx deposited onto the substrate and a second layer comprising ZircSOx:Cu, and where the laminate structure comprising the first and second layers is patterned by exposure to an energy source.

11. The master plate according to claim 10 where exposure to light or an electron beam through a mask causes the two layers to interdiffuse in exposed areas, thereby rendering previously undoped HafSOx layer soluble, the soluble HafSOx layer being removed to define at least partial printing features of the master plate.

12. A method for making a device, comprising:

providing a thin film or laminate structure, the structure comprising a substrate and one or more layers deposited onto the substrate;

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at least one of the one or more layers comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8; and

exposing the structure to an energy source.

13. The method according to claim 12 where the thin film or laminate structure comprises a substrate, a first layer for patterning, and a second layer comprising the hafnium and/or zirconium oxy hydroxy compound, where the second layer is a positive resist layer, exposure to an energy source converts the resist layer material into a developer-soluble material, and the method further comprises removing resist layer material exposed to the energy source by treating the resist layer with a developer solution to pattern the structure.

14. The method according to claim 12 where the thin film or laminate structure comprises a substrate, a first layer for patterning and a second layer comprising the hafnium and/or zirconium oxy hydroxy compound, where the second layer is a negative resist layer, exposure to an energy source causes the resist layer to polymerize, and the method further comprises patterning the structure by treating the structure with a developer to remove material not exposed to the energy source.

15. The method according to claim 13 where the positive resist comprises a bilayer, where a second layer of the bilayer comprises an acid-soluble Cu-doped zirconium oxide sulfate (ZircSOx:Cu) film deposited on an insoluble hafnium oxide sulfate (HafSOx) film, and where exposure to an energy source comprising light or an electron beam through a mask causes the ZircSOx:Cu film and the HafSOx film to interdiffuse in exposed areas, thereby rendering the HafSOx film soluble.

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16. The method according to claim 12 where the hafnium and/or zirconium oxy hydroxy compound comprises sulfate, and where the sulfate is subsequently removed by ion exchange with an aqueous basic solution, the basic solution comprising a Group I metal hydroxide, soluble Group II metal hydroxide, soluble Group III metal hydroxide, soluble lanthanide hydroxide, ammonium hydroxide, and/or aqueous tertiary amine, or a combination thereof.

17. The method according to claim 12 comprising:

providing a suitable substrate comprising a semiconductor material, a metal, glass, silica, a polymeric material, or combinations thereof;

solution depositing a first HafSOx film onto the substrate;

solution depositing a second ZircSOx:Cu film onto the first film to form a laminate structure;

exposing the laminate structure to an energy source to cause the HafSOx film and the ZircSOx:Cu film to interdiffuse in exposed areas, thereby rendering previously undoped HafSOx film soluble; and

developing the exposed structure to remove HafSOx film.

18. The method according to claim 12 where the thin film or laminate structure comprises a substrate, a first layer of insoluble hafnium oxide sulfate (HafSOx) deposited onto the substrate, and a second layer comprising copper formate deposited onto the first layer, and where the laminate structure comprising the first and second layers is heated to a temperature from about 50 °C to about 200 °C to cause the copper formate to decompose and interdiffuse with the HafSOx layer, thereby producing a soluble product, the soluble product being removed.

19. The method according to claim 12 where the thin film or laminate structure comprises a substrate and a first layer comprising a solid inorganic acid or base, the solid inorganic acid or base comprising a metal having an atomic number in the range of 21-78, the first layer further comprising a peroxide or other coordinating anion, where the first layer is soluble in acid or base, the first layer is

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heated to a temperature from about 50 °C to about 125 °C to produce a structurally rigid film, and exposure to a laser, an electron beam, and/or light through a mask causes exposed areas of the film to become less soluble than unexposed areas, the unexposed areas being removed to define a pattern in the film.

20. The method according to claim 19 where the film is exposed to an electron beam at a dose level of from greater than 0 $\mu C/cm^2$ to at least 400 $\mu C/cm^2$, more typically from about 2 $\mu C/cm^2$ to about 400 $\mu C/cm^2$, to define a pattern in the film.

21. The method according to claim 19 where the patterned film demonstrates structural integrity to less than about 3 nm.

22. The method according to claim 12, where the device includes a micro- or nano-channel array, and where the structure comprises a substrate, a first layer and a second layer, the second layer being a metal oxide layer, the method further comprising:

patterning the structure; and

exposing the structure to an energy source to form a durable material having a desired pattern produced by patterning the structure.

23. The method according to claim 22 further comprising stamping unit features of a desired size scale into a semi-solid hafnium or zirconium compound to form a stamped layer.

24. A device made according to the method of claim 22, the device selected from metal and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal- and ceramic-based systems, fibers for composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, and catalyst supports.

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25. A method for making a device having a corrosion barrier, comprising:

providing a device;

forming at least one corrosion barrier on the device comprising a metal oxide layer comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8; and

exposing the compound to an energy source to form the corrosion barrier.

26. A method for forming fibers, comprising:

providing a composition comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8;

forming a solution comprising the compound;

drawing the solution into fibers; and

converting the fibers into solid, stable fibers.

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27. A method for making a metal oxide film where the film comprises at least two metals, the method comprising:

making a solution comprising dissolving one or more soluble salts consisting essentially of a metal cation and one or more anions in a non-complexing, non-aqueous polar solvent, where at least one of the metal cations has a formal charge greater than 3^+ and the concentration of metal cations with a formal charge greater than 3^+ exceeds 50 mol% of the metal cations in the metal oxide film, and where the solvent has a boiling point less than about 150 °C;

raising the pH of the solution, where raising the pH comprises adding a basic aqueous solution, adding a small amount of a soluble basic oxide, adding a gaseous compound capable of forming a basic aqueous solution, adding an electropositive metal which may consume protons and is incorporated into the film, adding an aqueous or gaseous oxidizing agent which consumes protons or decomposes counter ions but is not incorporated into the film, or any combination thereof;

producing a solid by evaporating the non-aqueous solvent;

dissolving the solid in water;

depositing the dissolved solid onto a substrate to form a patterned or blanket liquid film; and

thermally curing the film.

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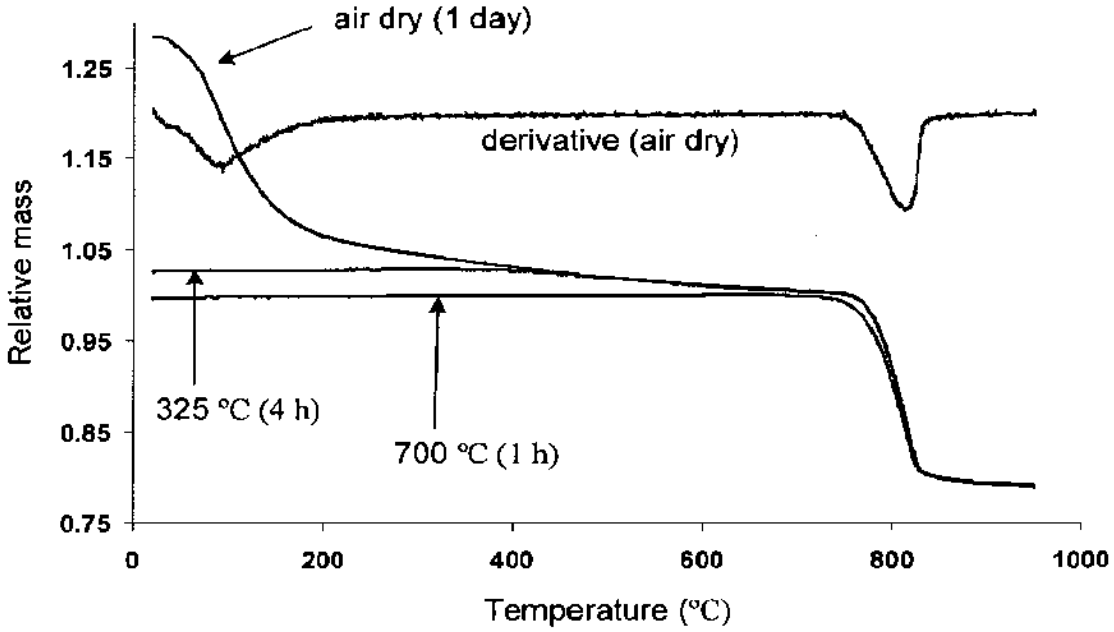


FIG. 1

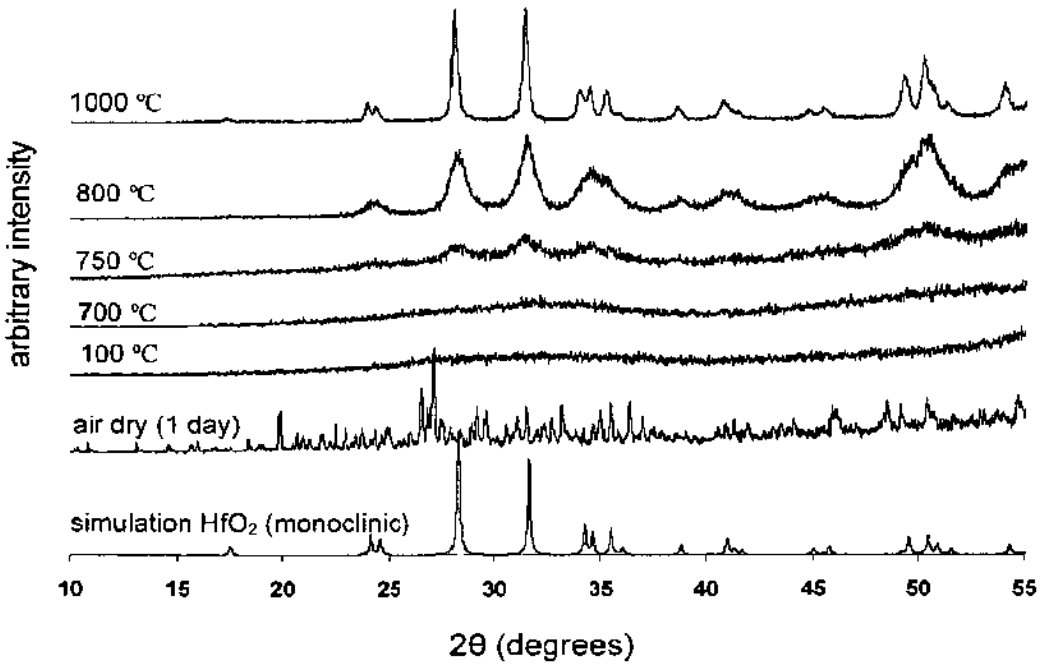


FIG. 2

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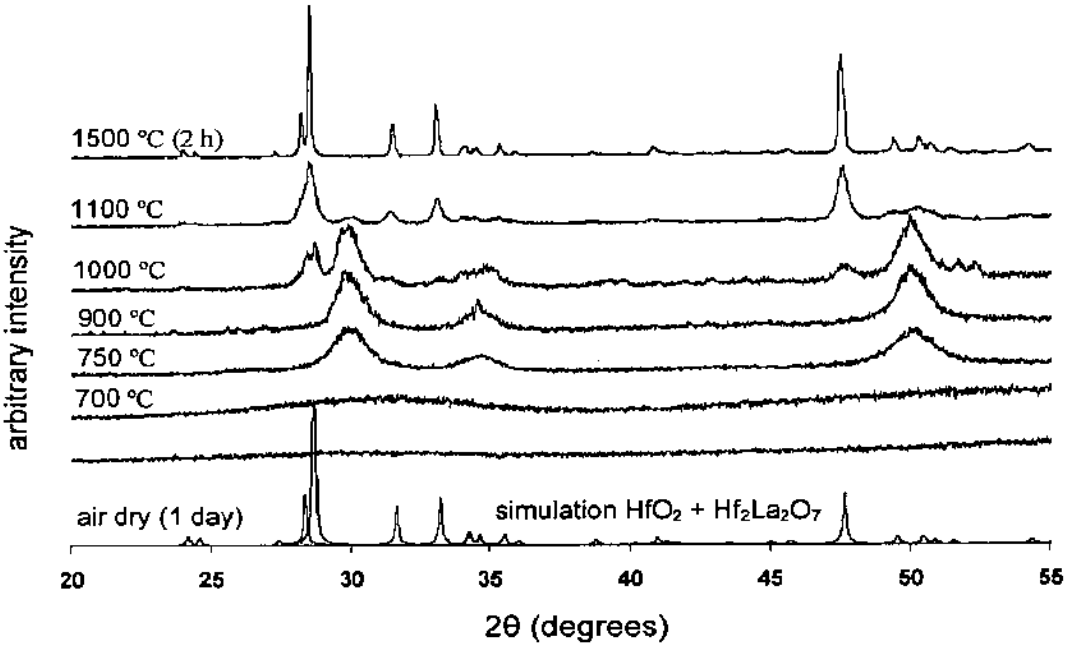


FIG. 3

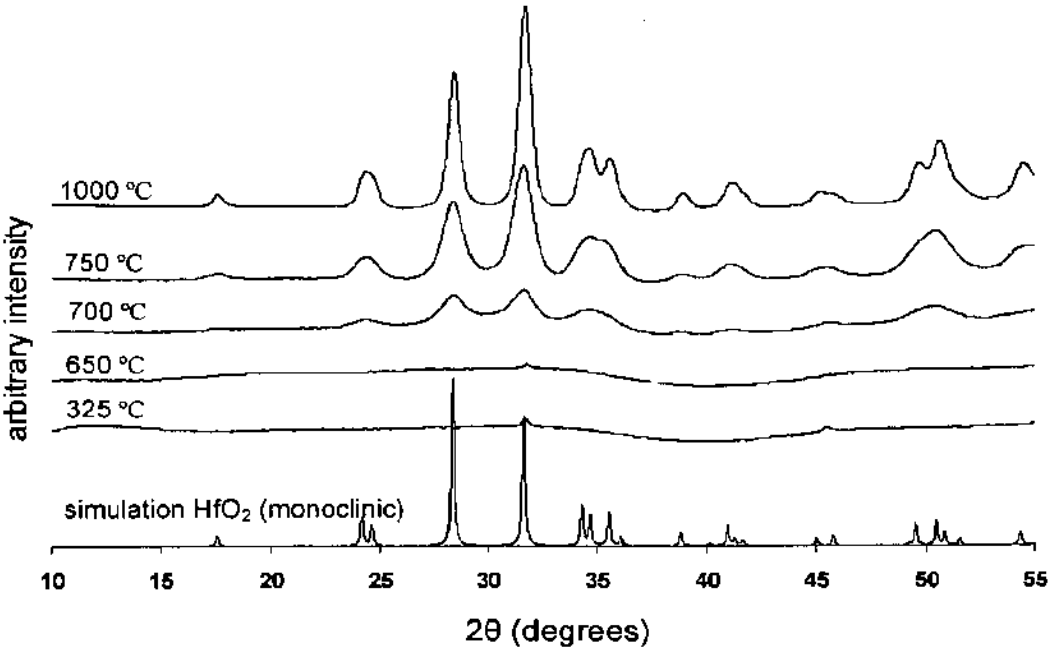


FIG. 4

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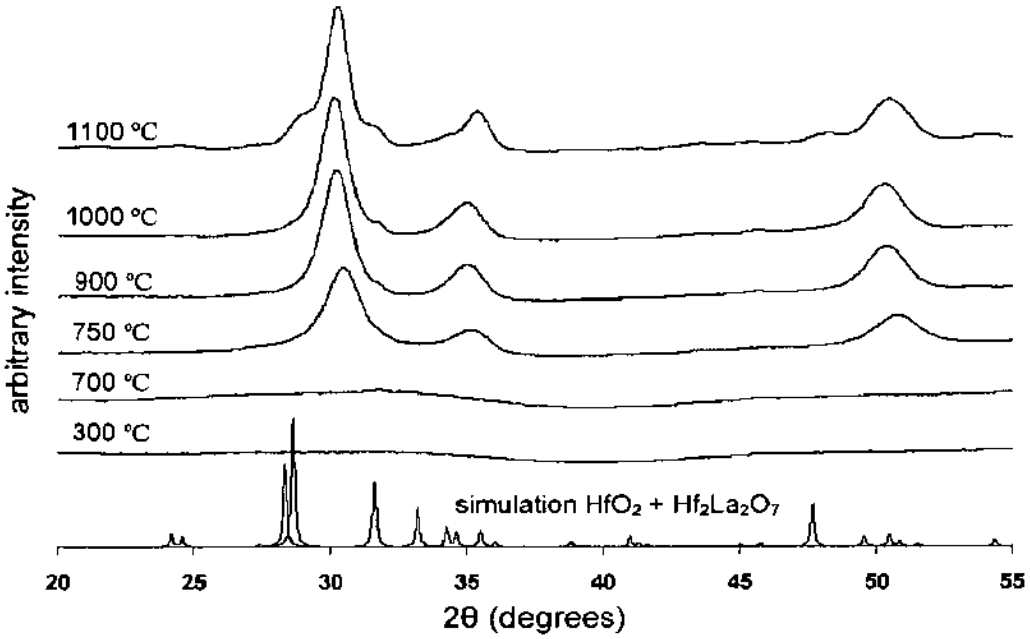


FIG. 5

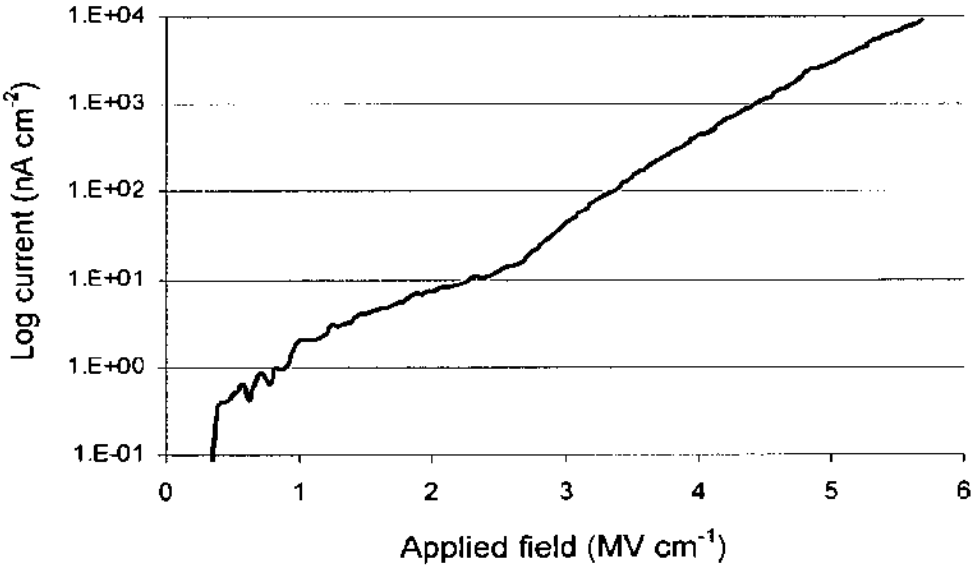


FIG. 6

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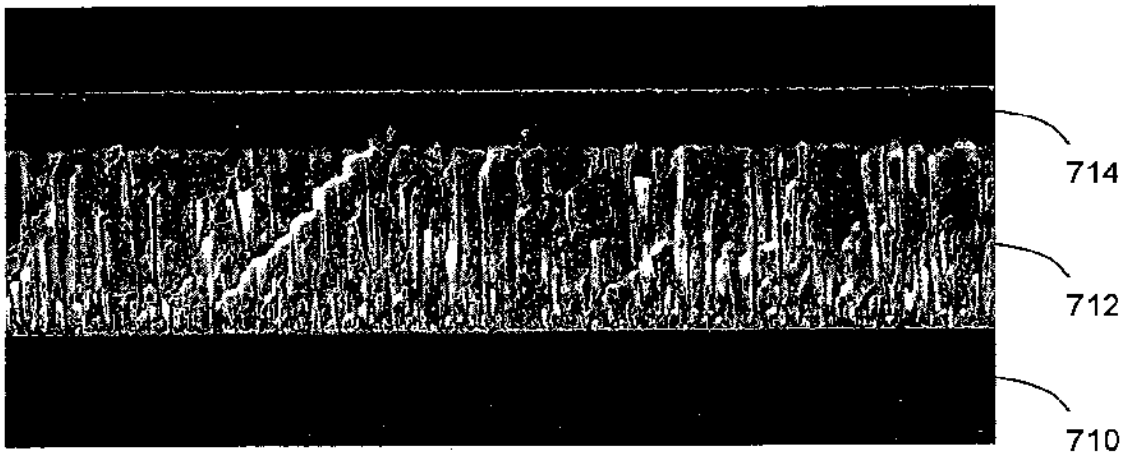


FIG. 7

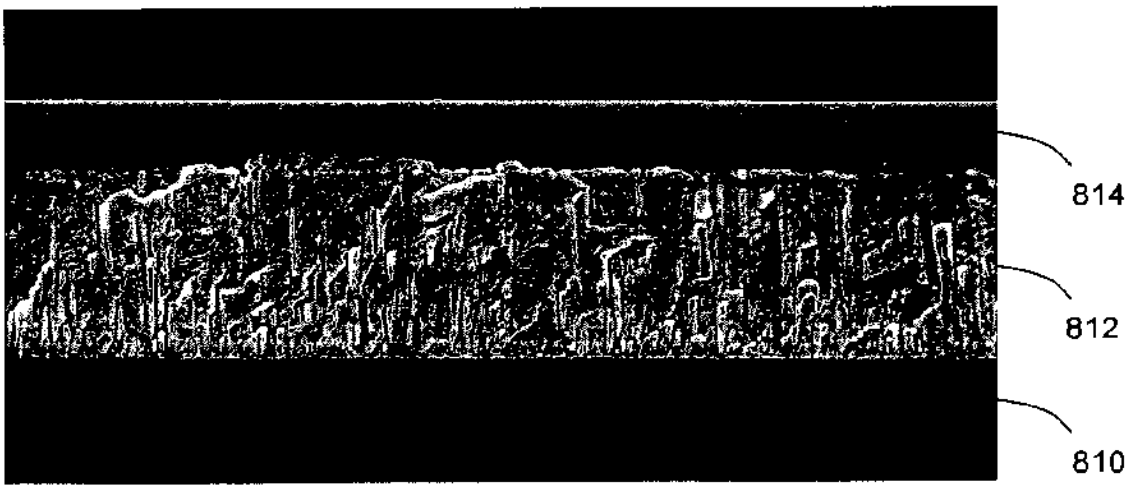


FIG. 8

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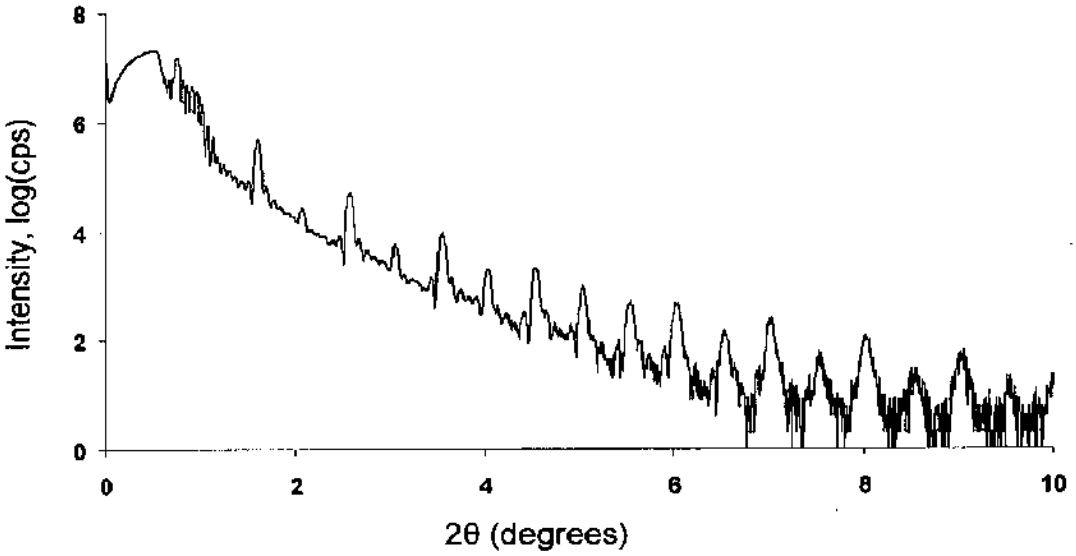


FIG. 9

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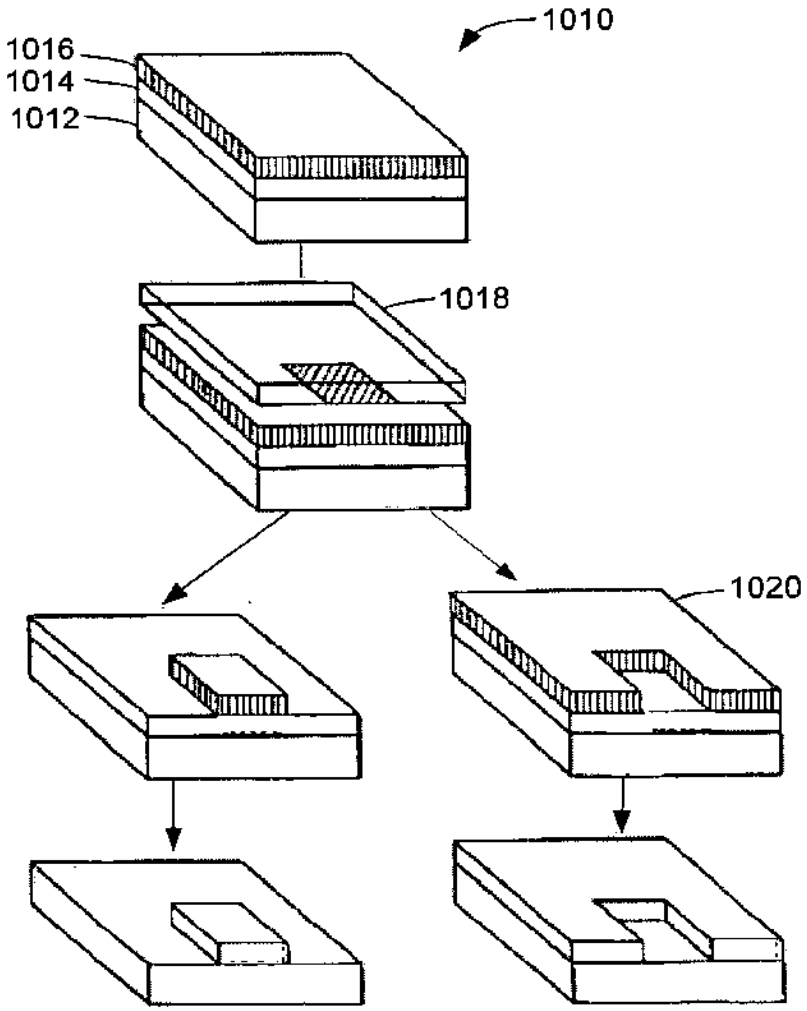


FIG. 10

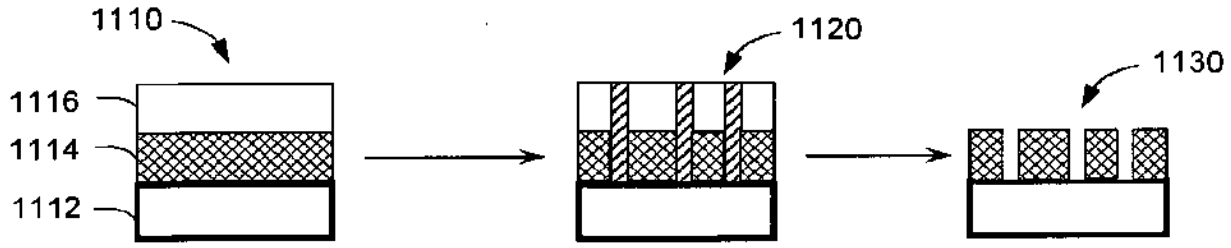


FIG. 11

SUBSTITUTE SHEET (RULE 26)

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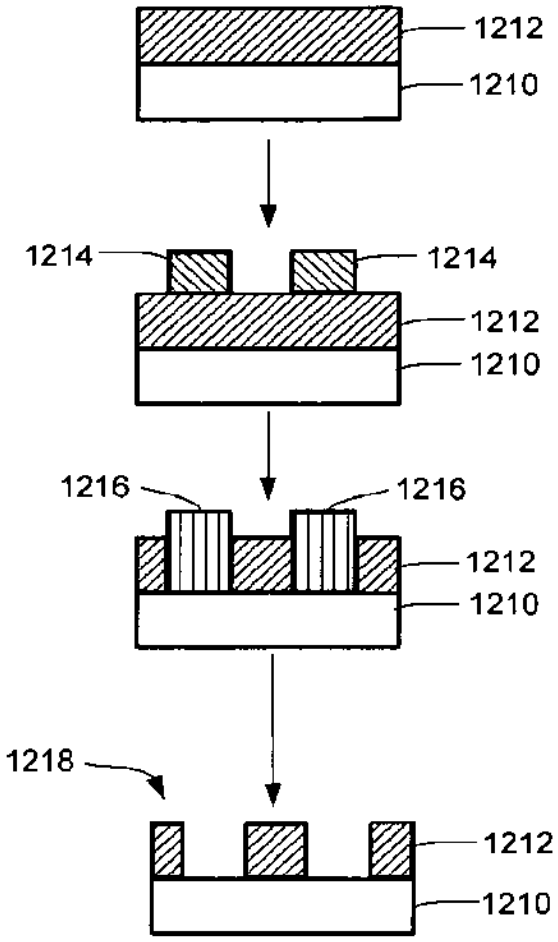


FIG. 12

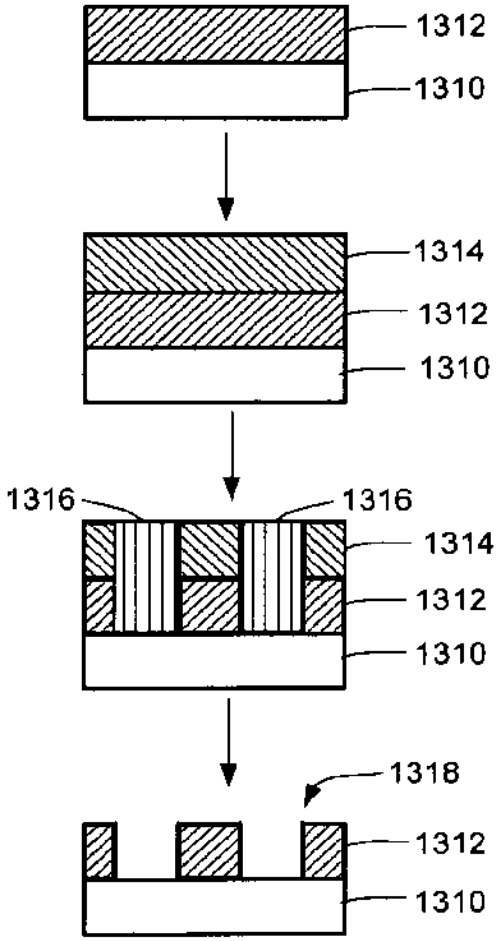


FIG. 13

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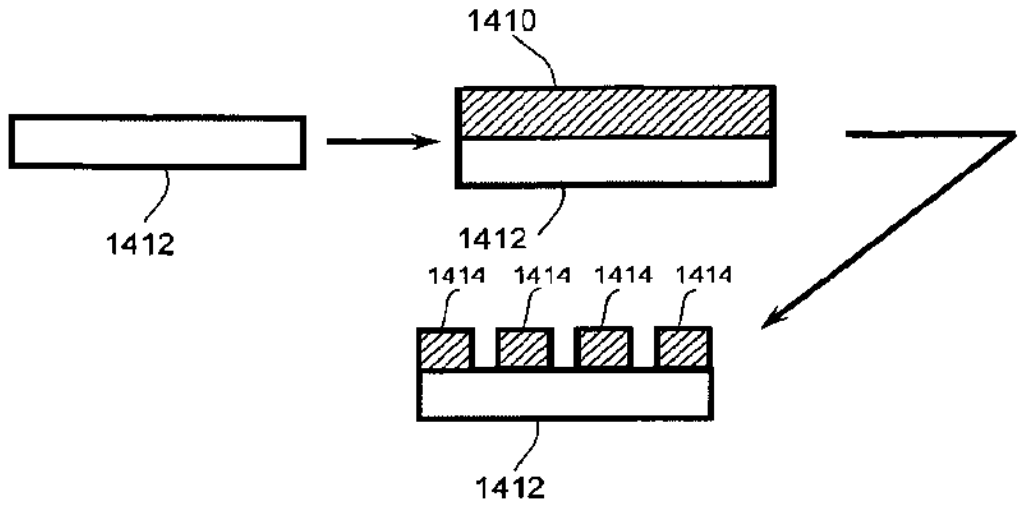


FIG. 14

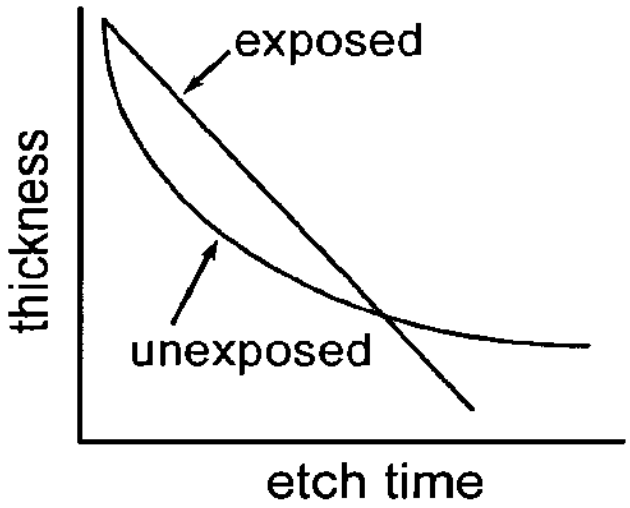


FIG. 15

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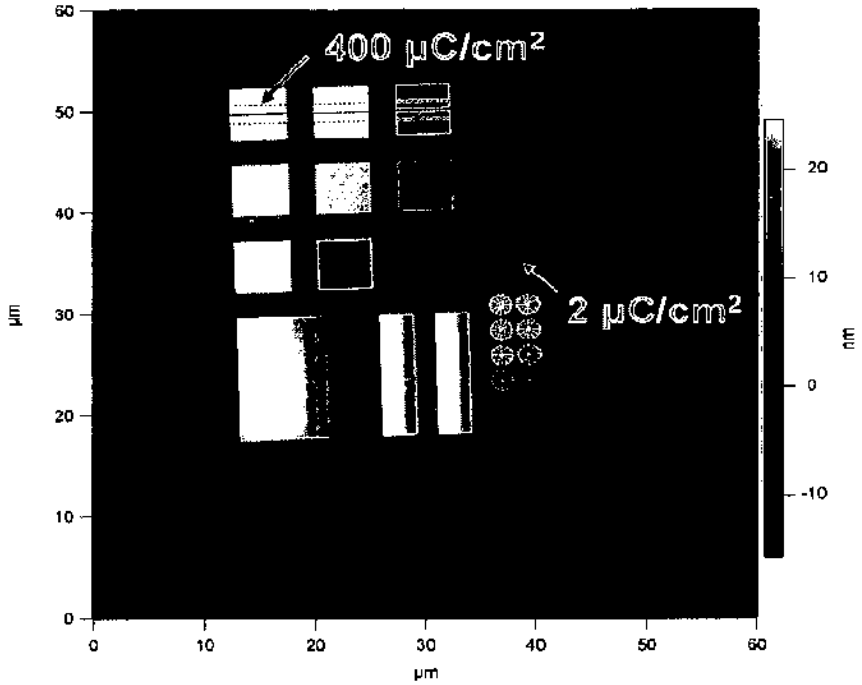


FIG. 16

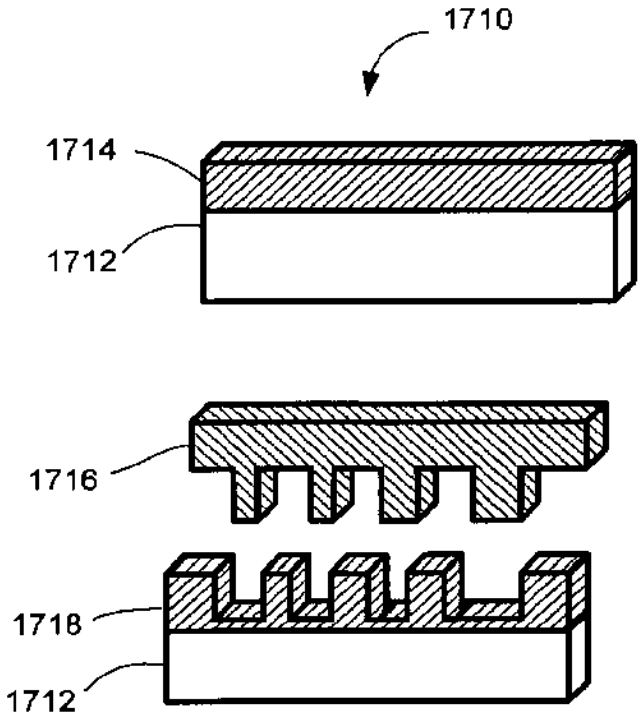


FIG. 17

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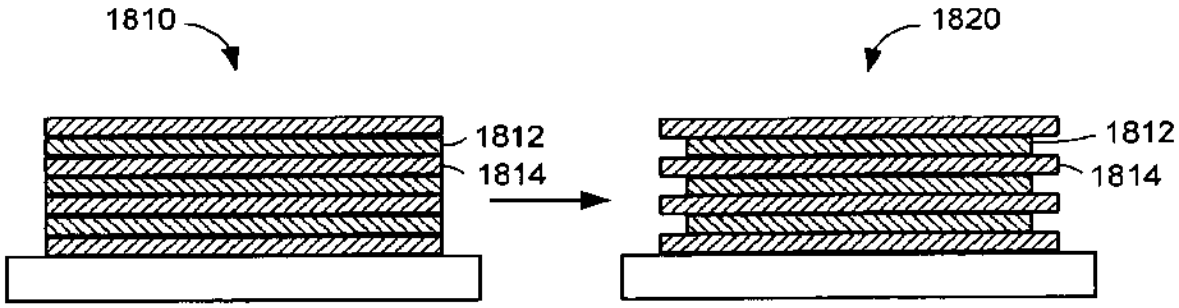


FIG. 18

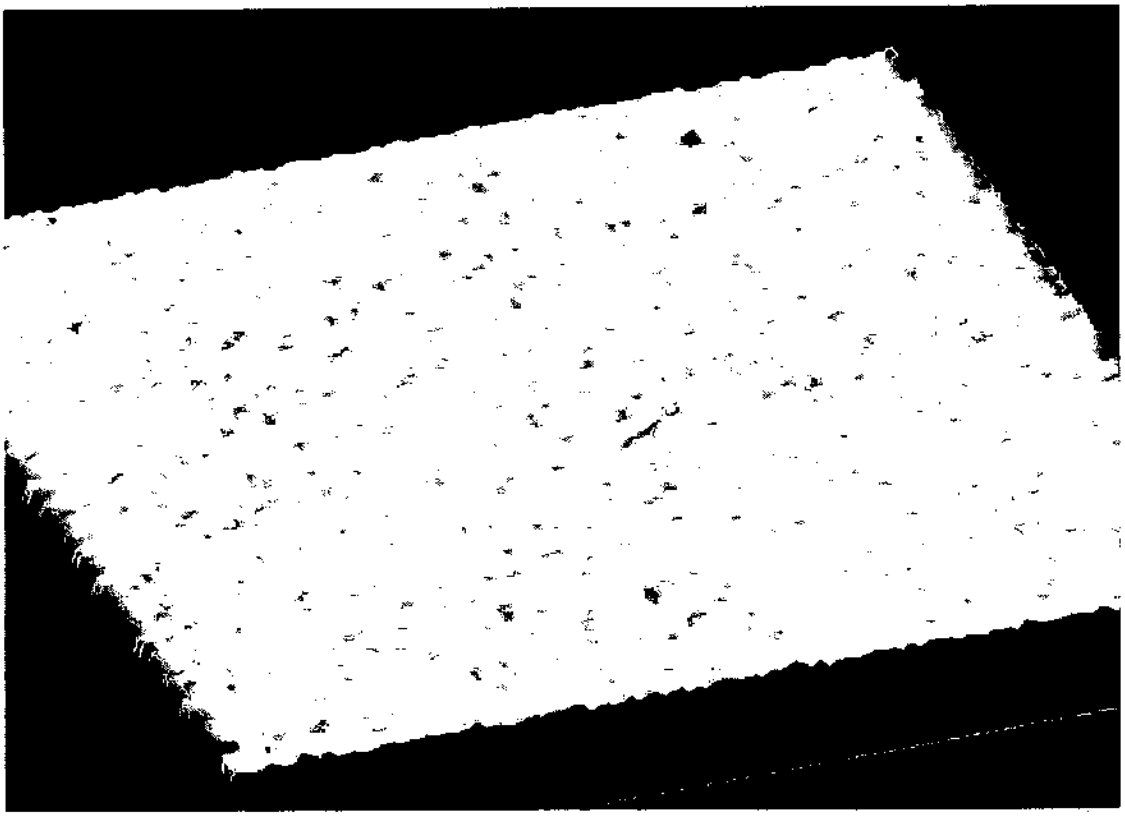


FIG. 19

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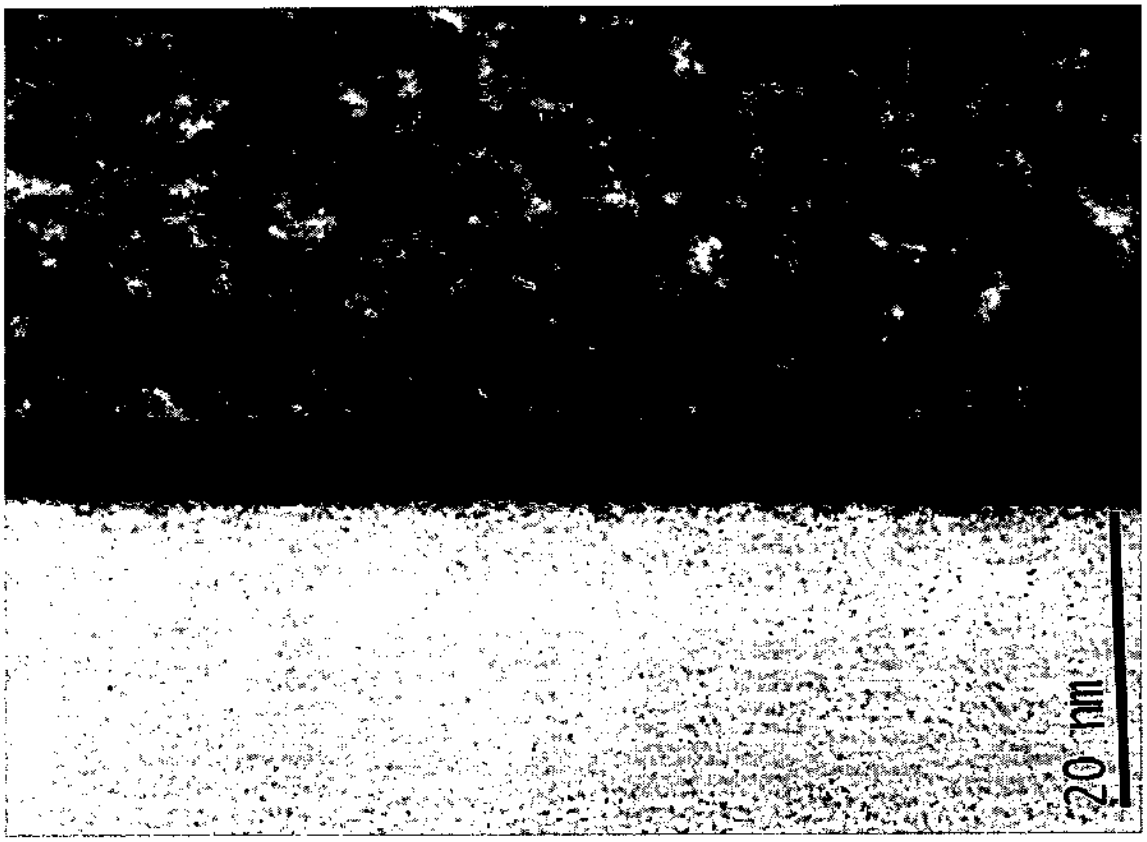


FIG. 20

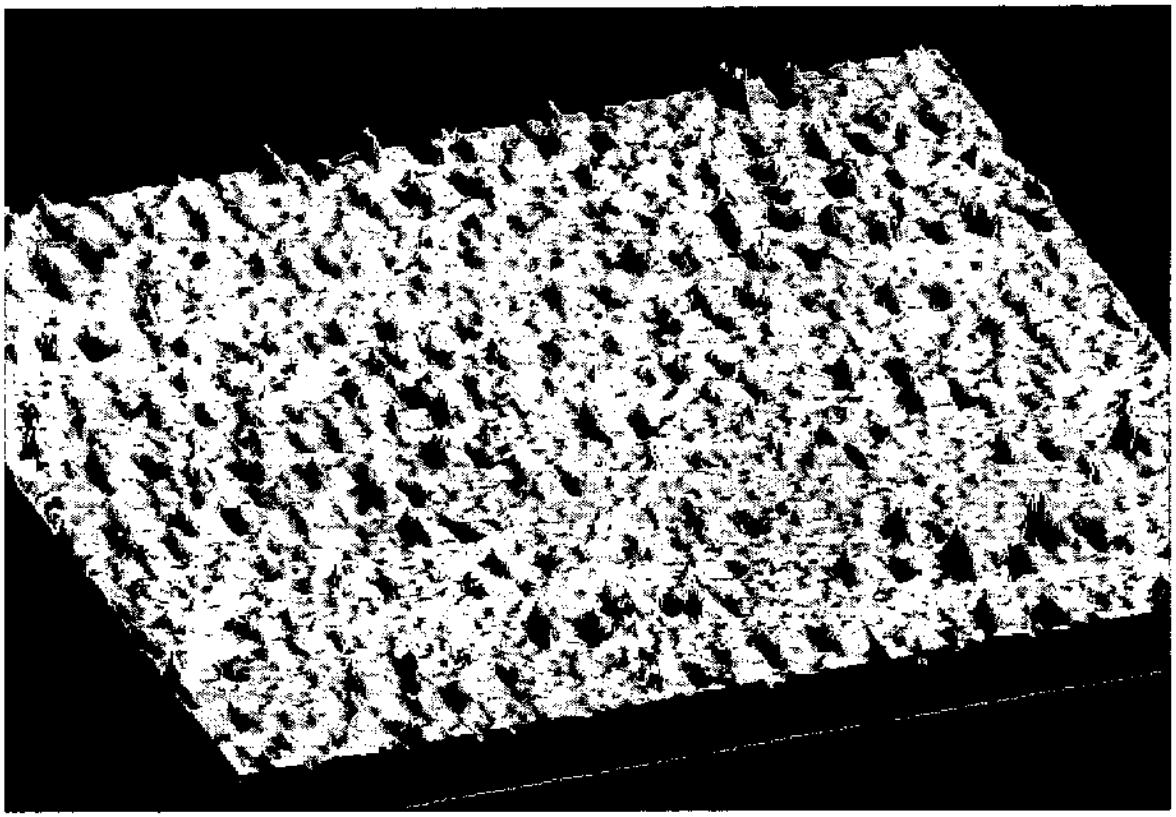


FIG. 21

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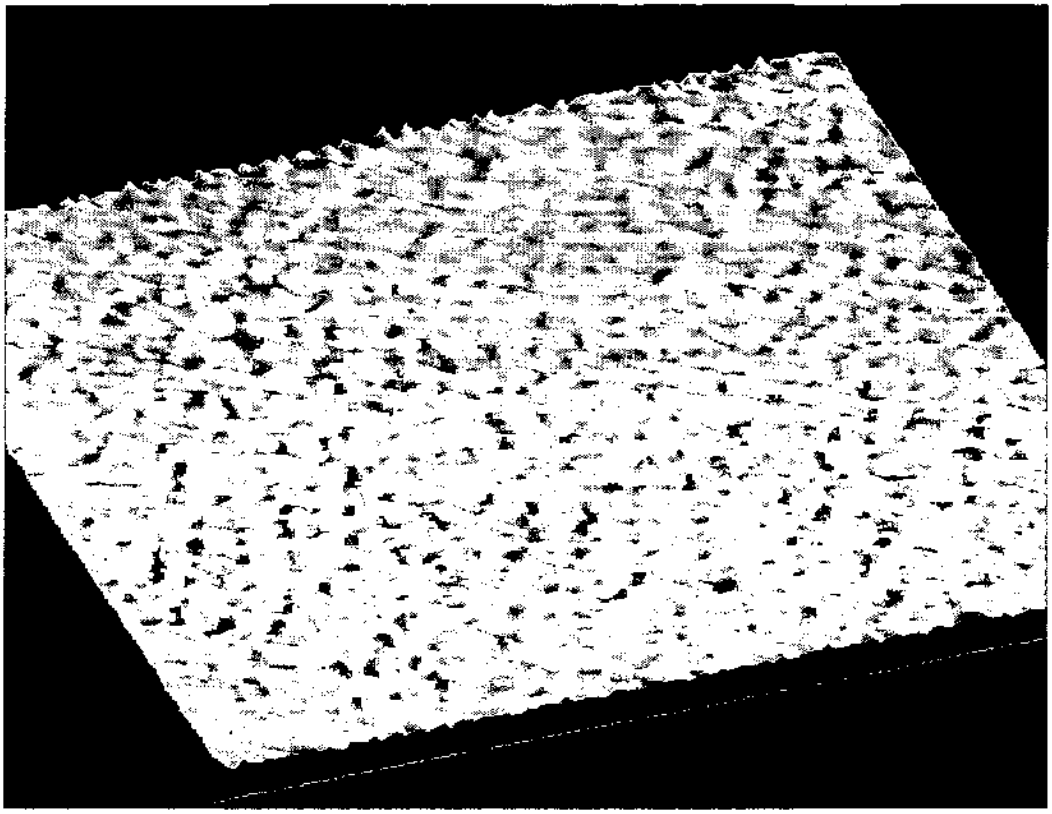


FIG. 22

Lam Research Ex. 1004 - Page 881 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

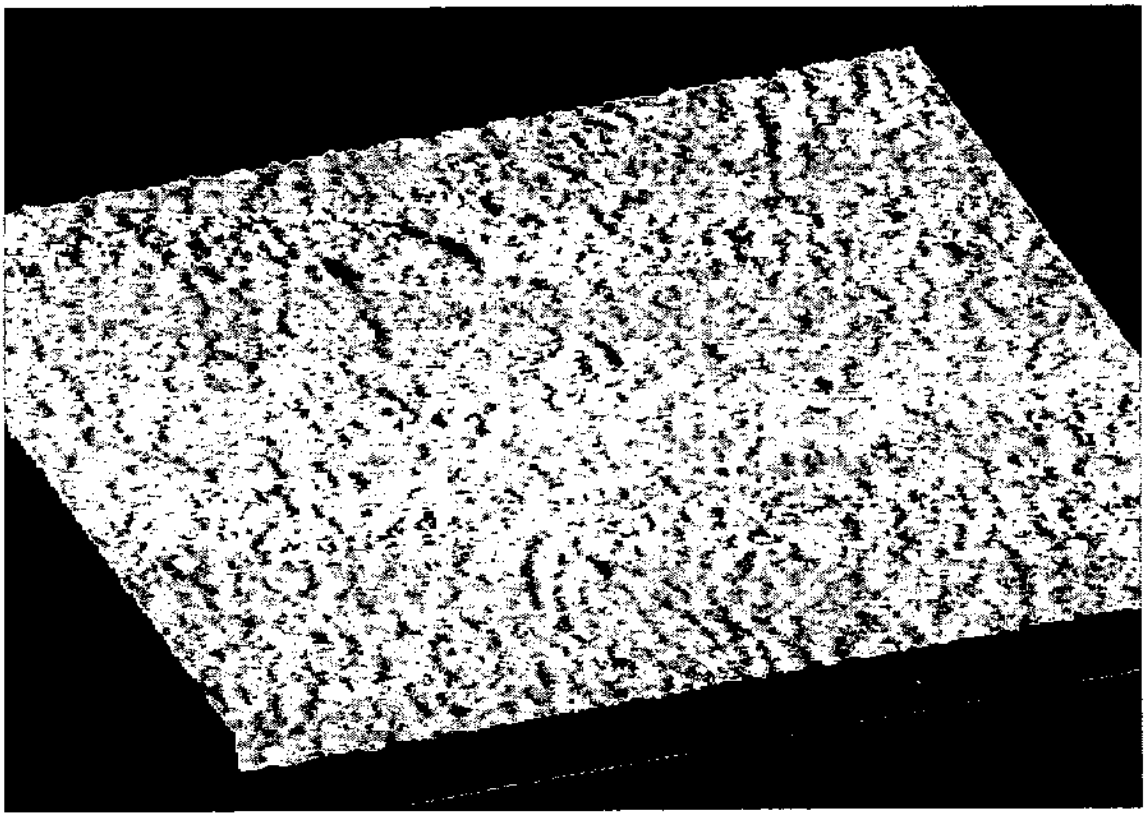


FIG. 23

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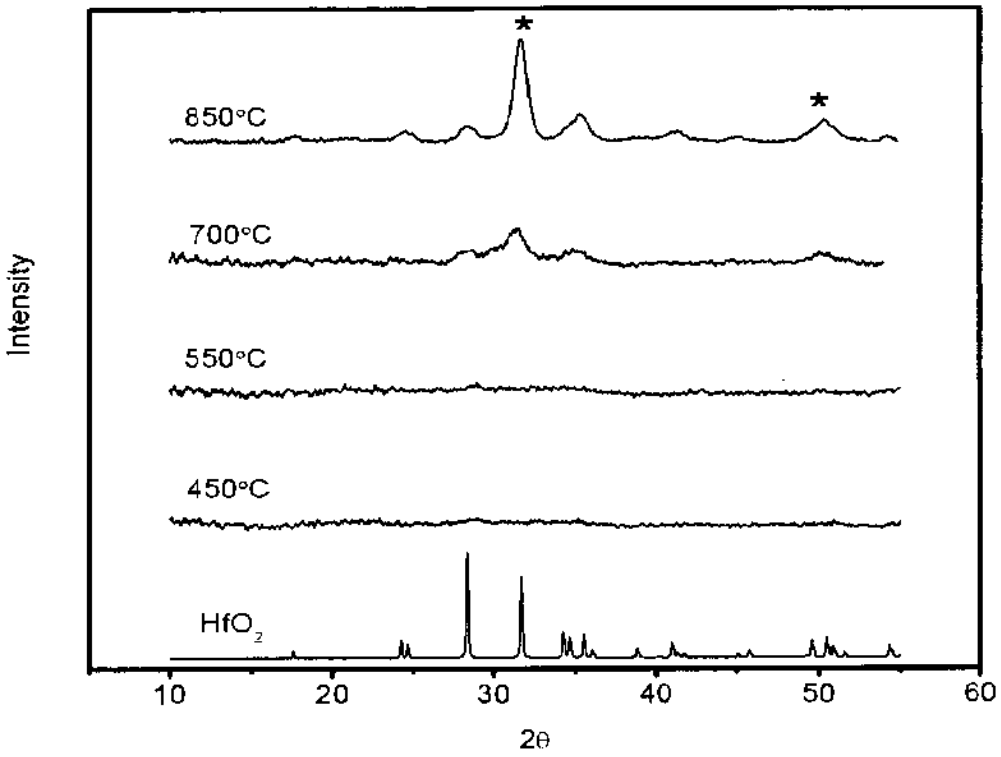


FIG. 24

Lam Research Ex. 1004 - Page 883 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

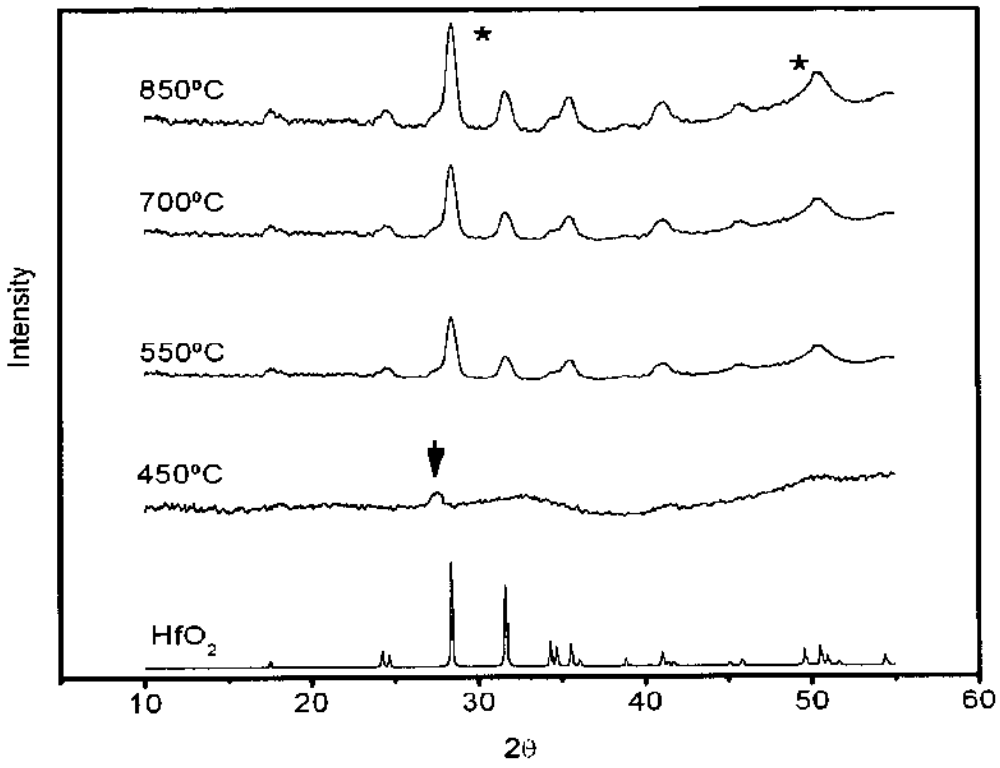


FIG. 25

Lam Research Ex. 1004 - Page 884 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

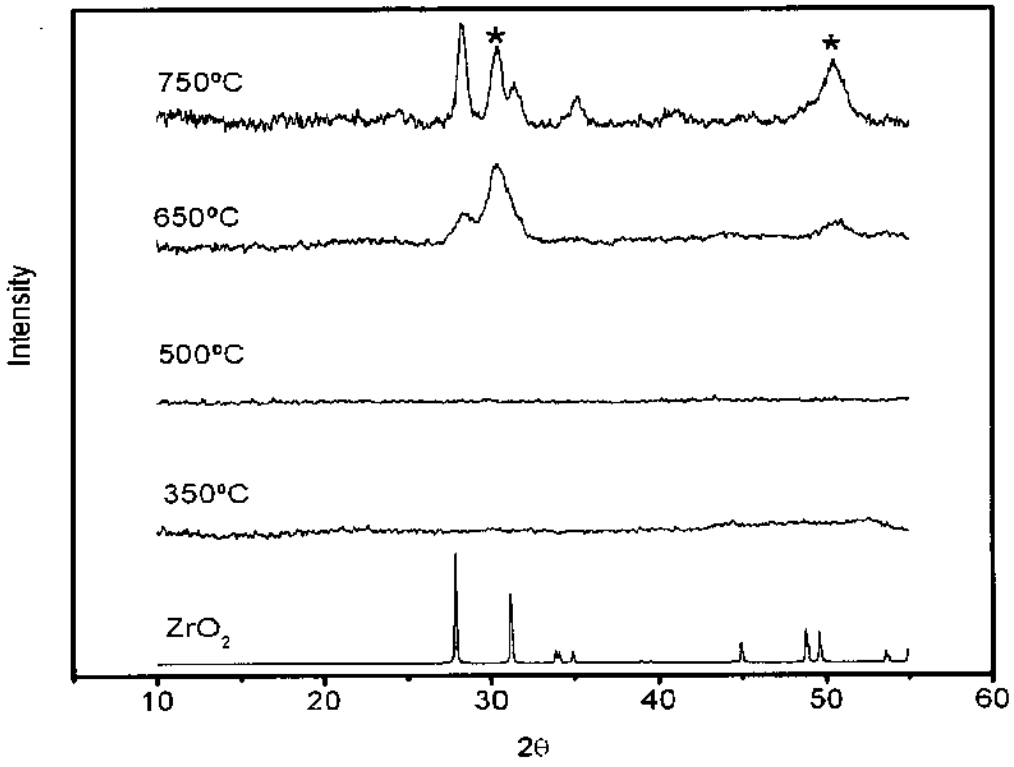


FIG. 26

Lam Research Ex. 1004 - Page 885 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

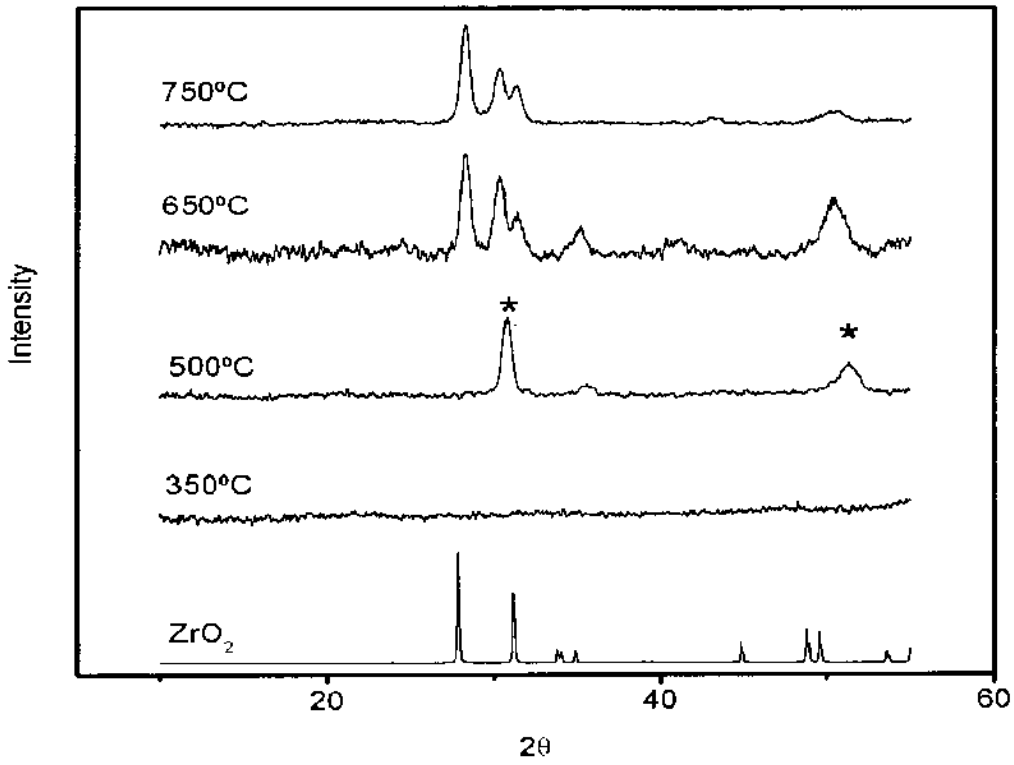


FIG. 27

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FIG. 28

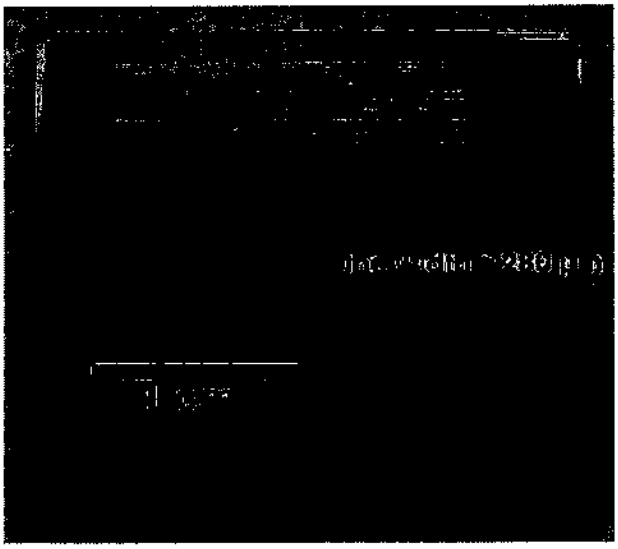


FIG. 29

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FIG. 30



FIG. 31

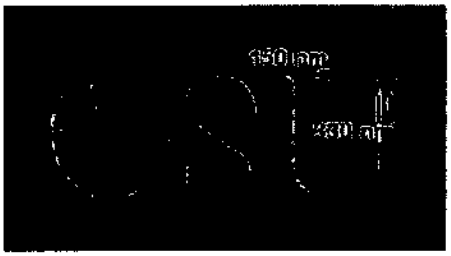


FIG. 32

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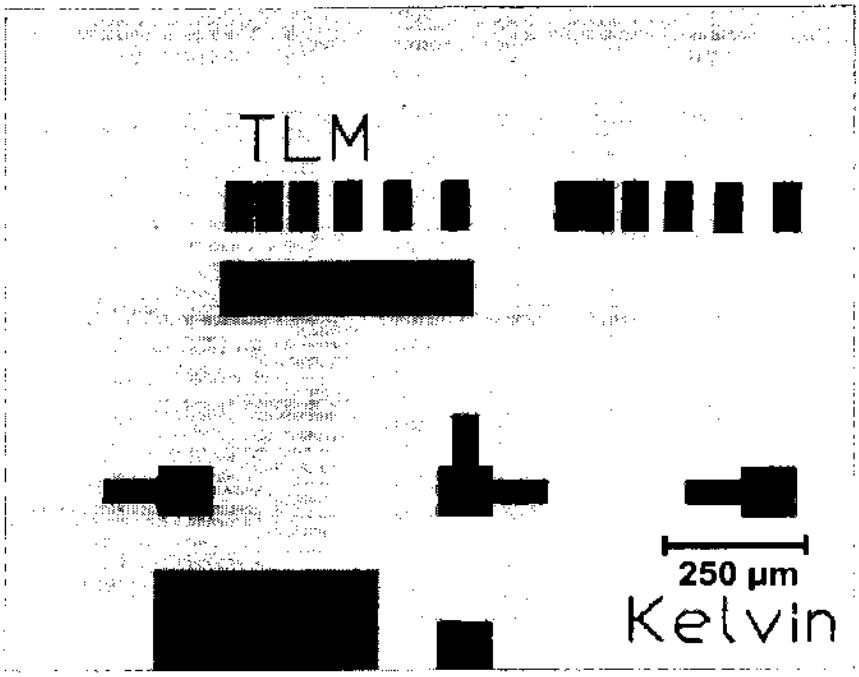


FIG. 33

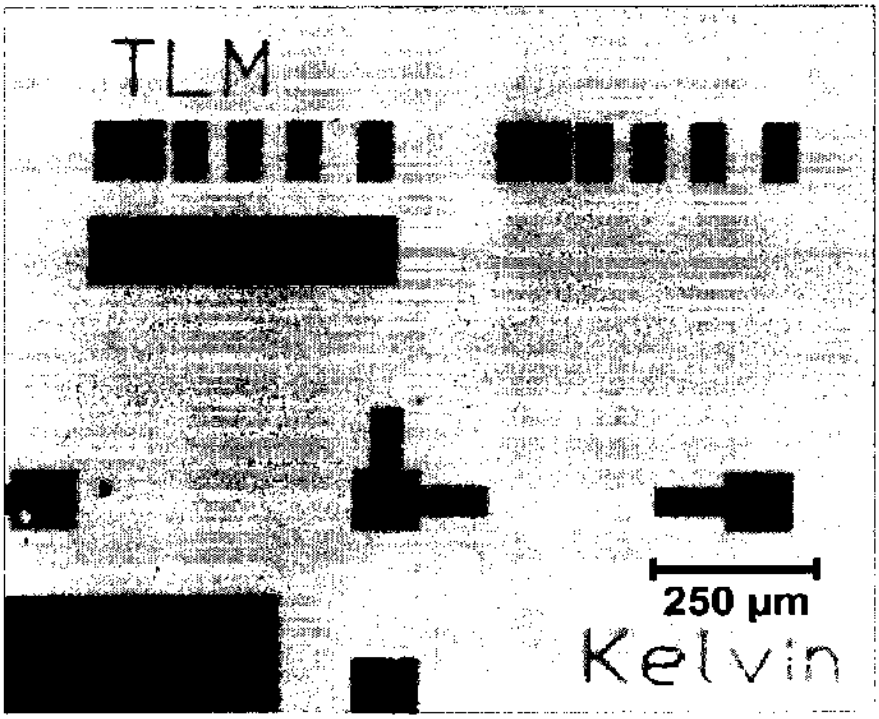


FIG. 34

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FIG. 35



FIG. 36

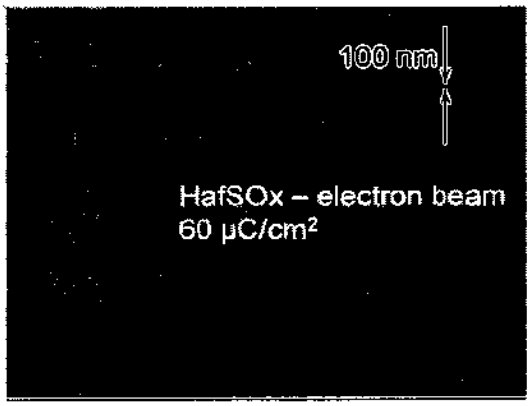


FIG. 37

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 07/23084

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08F 10/00, H01L 21/00 (2008.04)
USPC - 252/570; 438/151; 257/E21.01
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC - 252/570; 438/151; 257/E21.01

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Chemical Engineering and Biotech Research

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST: US Patents full-text; US PGPubs full-text; EPO Abstracts; and JPO Abstracts; Google
Terms: zirconium oxy hydroxy sulfate; hafnium oxy hydroxy sulfate; electronic device; photoresist; tungstate; lanthanum; photolithograph; optical and glass substrate; photo and resist.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2005/0242330 A1 (Herman et al.) 03 November 2005 (03.11.2005), para [0009] - [0012] and [0018]-[0029]; Figures	1-4, 12, 16, 25 ---------- 5-11, 13-15, 17-24, 26-27
Y	US 2006/0088962 A1 (Herman et al.) 27 April 2006 (27.04.2006), para [0006]-[0023]; Figures	5-11, 13-15, 17-24, 26
Y	US 3,385,915 A (Hamling) 28 May 1968 (28 May 1968), col 1, ln 40-45; col 2, ln 18-26	27

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 April 2008 (10.04.2008)	15 MAY 2008
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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(74) Agent: **SLATER, Stacey, C.**; Klarquist Sparkman, LLP, One World Trade Center, Suite 1600, Portland, OR 97204 (US).

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Published:

— *with international search report (Art. 21(3))*

WO 2009/120169 A1

(54) Title: SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THE USE AND MANUFACTURE

(57) Abstract: Devices having a thin film or laminate structure comprising hafnium and/or zirconium oxy hydroxy compounds, and methods for making such devices, are disclosed. The hafnium and zirconium compounds can be doped, typically with other metals, such as lanthanum. Examples of electronic devices or components that can be made include, without limitation, insulators, transistors and capacitors. A method for patterning a device using the materials as positive or negative resists or as functional device components also is described. For example, a master plate for imprint lithography can be made. An embodiment of a method for making a device having a corrosion barrier also is described. Embodiments of an optical device comprising an optical substrate and coating also are described. Embodiments of a physical ruler also are disclosed, such as for accurately measuring dimensions using an electron microscope.

SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THEIR USE AND MANUFACTURE

FIELD

The present disclosure concerns embodiments of features and devices comprising inorganic metal oxide materials useful for creating spatially-defined structures for purposes including electronic and optical applications, and embodiments of methods for their manufacture and use.

ACKNOWLEDGMENT OF GOVERNMENT SUPPORT

Embodiments of the present disclosure have been developed using federal funding under DARPA grant number HR0011-06-1-0045. The United States government has certain rights in the invention.

BACKGROUND

Electronic devices currently are made using iterative process steps, such as sequential deposition and etching of materials. For devices comprising inorganic materials, metal-organic precursors have been used extensively for solution-based deposition of inorganic oxides. The presence of the organic moiety necessitates a high-temperature burnout step to remove the organic material. This step can cause significant volume change, crystallization and the phenomenon of "mud cracking." The associated defects inhibit the performance of these materials as coatings and within devices.

Methods for solution processing materials for electronic device applications have been patented. For example, Ostergard, U.S. Patent No. 6,946,677, entitled "Pre-Patterned Substrate for Organic Thin Film Transistor Structures and Circuits and Related Method for Making Same," describes forming a desired circuit configuration in the surface of a substrate, thereby pre-patterning the area to receive material useful for forming an organic thin film transistor (OTFT) structure and interconnecting conductive paths. According to the '677 patent, OTFT material is deposited in the pre-patterned area using printing techniques such as inkjet printing.

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Weng *et al.*, U.S. Patent No. 6,927,108, describes solution processing thin-film materials to form transistors. The '108 patent describes forming "conductive solution-processed thin film material contacts, semiconductor solution-processed thin film material active regions, and dielectric solution-processed thin film material isolations in a sequence and organization to form a solution-processed thin film structure capable of transistor operation."

U.S. Patent Publication No. 2005/0242330 A1, which is incorporated herein by reference, concerns hafnium and zirconium compounds useful for electronic applications. U.S. Patent Publication No. 2005/0242330 A1 names Dr. Douglas Keszler as an inventor, who also is an inventor of embodiments disclosed herein.

SUMMARY

U.S. Patent Publication No. 2005/0242330 A1 discloses compounds and solution deposition of inorganic compounds in a manner that addresses deficiencies of prior technologies. For example, solution deposition according to the present invention avoids using organic materials required for metal-organic deposition techniques, and hence also avoids organic burnout and the cracking problems associated with burnout.

One embodiment of the present invention concerns devices, such as electronic devices, having a thin film or laminate structure comprising at least one hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable. X may have any value in a range of from about 0.1 to about 3.5/(polyatomic ion charge). For example, x may be any value within the range of from about 0.1 to about 1.75 for a polyatomic ion with a charge of 2, such as the oxy hydroxy sulfate compounds. Z may have any value range within the range of from 0.0 to about 3.8.

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Particular embodiments concern thin films or laminates comprising a hafnium or zirconium oxy hydroxy sulfate compound having a formula ($MO_{2-x-z/2}(OH)_z(SO_4)_x$), wherein M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 1.75, and any value for z in a range of from 0.0 to about 3.8. These compounds also are referred to as HafSOx and ZircSOx. The hafnium and zirconium compounds also can be doped, typically with other metals, such as calcium, cerium, lanthanum, or combinations thereof. Certain embodiments have used lanthanum as a dopant to produce compounds having a formula $M_{1-x}La_yO_{2-x-z/2-y/z}(OH)_z(SO_4)_x$ (MSOx:La), where the composition and stoichiometry are as stated above. A particular example of a lanthanum-doped compound is $Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$. Additional exemplary compounds include HafSOx:La, ZircSOx:La, HafSOx:Ce, or ZircSOx:Ca. In certain embodiments, sulfate is subsequently removed via ion exchange with an aqueous base, resulting in $M(OH)_x$ or MO_x films. Suitable aqueous bases include group I metal hydroxides, group II metal hydroxides, group III metal hydroxides, lanthanide hydroxides, ammonium hydroxide, and/or aqueous tertiary amines, among others. The absence of organic components in the $M(OH)_x$ allows the unique conversion and dehydration to metal oxide MO_x at low temperatures, using any suitable technique, such as via microwave and lamp drying or by laser processing.

Certain embodiments concern thin oxide films or laminates comprising complex compositions with two or more metals. At least one of the metal cations has a charge greater than or equal to 3^+, and the total concentration of cations with charge greater than or equal to 3^+ exceeds 50 mol% of the metal cations in the target oxide. A non-aqueous solution comprising dissolved salts and an amount of water is prepared. The amount of water is less than 20 mol% relative to the non-aqueous solvent. The pH of the solution is increased relative to the starting solution by adding a base or by reaction of free protons via oxidation-reduction mechanisms. The final solution pH depends upon the metal cations used, but will typically be in the range of about 2-9. The increased pH results in hydrolysis of water molecules bound to the cations and condensation of these resulting hydroxo-cations. The solvent is evaporated, and the resulting solid is dissolved or dispersed in water and

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subsequently applied to a substrate as a liquid film. The liquid film is then thermally cured at a temperature between about 100 °C and 600 °C for about 5-240 minutes.

Examples of electronic devices, or components of devices, that can be made according to this invention include, without limitation, insulators, such as a gate insulator in a field effect transistor, transistors, such as a field effect transistor, and capacitors, such as a MIM capacitor. Thin films and laminates made according to this embodiment had a permittivity value within the range of from about 9 to about 12, a breakdown field from at least 3 MV cm^{-1} up to about 6 MV cm^{-1}, and a leakage current near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}. Devices made using ZircSOx:Ca had a breakdown field of about 3.6 MV cm^{-1}, and a leakage current of less than about 50 nA cm^{-2}, more typically less than about 10 nA cm^{-2}.

Field effect transistors can be made using HafSOx:La and/or ZircSOx:La as gate dielectric materials. Certain disclosed embodiments used zinc indium oxide and/or zinc tin oxide as channels. Particular field effect transistors had an on-to-off ratio of greater than 10^6, and nA cm^{-2} gate leakage currents.

Another embodiment of the present invention concerns a method for patterning a device using an inorganic photoresist. A particular embodiment of the method comprises first providing a structure to be patterned. The structure typically comprises: a substrate, such as a semiconductor material, a metal, glass, a polymeric material, or combinations thereof; a material layer for patterning, such as silica; and a resist layer. The resist layer typically includes disclosed hafnium and/or zirconium oxy hydroxy compounds. The structure is exposed to an energy source, such as an electron beam or light, with particular examples using ultraviolet light. Thereafter, material is removed to pattern the device, or it is retained as an active, patterned component of the device.

The resist may be a positive resist or a negative resist. For example, the method can include exposing the resist layer to an energy source to convert the resist layer material into a developer-soluble material. The developer-soluble material is then removed using a developer. Suitable developers may include acids, bases, and/or ultrasonic agitation, among others. Again by way of example, the method can comprise removing resist layer material exposed to the energy source. Without limiting the invention to a particular theory of operation, at least for certain

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embodiments, exposure to the energy source may cause the resist layer to polymerize, making it relatively less soluble in a developer than prior to exposure to the energy source.

One embodiment of a positive resist comprises a bilayer. A first layer of the bilayer comprises a copper formate film deposited on a hafnium oxide sulfate (HafSOx) film. The copper formate film is soluble in acid and the undoped HafSOx film is insoluble in acid. Exposing the bilayer to light through a mask or to a focused electron beam causes the two films to interdiffuse in exposed areas, thereby rendering the previously undoped HafSOx film soluble.

Another embodiment of a bilayer process for making a resist comprises depositing a first layer of a solid acid or base, where the acid or base contains one or more metal atoms, onto a substrate. A liquid suspension containing an oxide precursor, such as copper formate, is applied in a desired pattern onto the first layer. Under heated conditions, the precursor decomposes to an oxide. The oxide subsequently reacts and interdiffuses with the first layer, forming a product that can be etched to reveal a pattern. An alternate embodiment comprises depositing oxide particles onto the first layer, with or without heating, resulting in a direct reaction to form a product that can be etched. A further embodiment comprises depositing a thin layer of the oxide precursor onto the first layer. A pattern of activated precursor is then formed by light exposure through a photomask or direct writing with a focused laser or electron beam.

Another embodiment of the present invention concerns a master plate for imprint lithography. The master plate comprises a substrate, such as a flexible or glass substrate, and at least one layer of a thin film or laminate structure comprising at least one disclosed hafnium and/or zirconium oxy hydroxy compound. A particular embodiment of a master plate includes a layer of HafSOx deposited onto the substrate, and a second layer, such as a ZircSOx:Cu layer. The master plate may be patterned by exposure to an energy source, such as exposure to light or an electron beam through a mask to cause the two films to interdiffuse in exposed areas. This renders previously undoped HafSOx film soluble, which is removed to at least partially define printing features of the master plate.

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In another embodiment, masks or templates can be fabricated using the films of the present invention in a single layer process. A thin film of an inorganic precursor, such as a solid acid or base, is deposited onto a substrate in combination with a peroxide or similar anion. The film is heated to produce a structurally rigid film. It is then exposed through a photomask or via a laser or electron beam to induce condensation/crosslinking in exposed areas. The solubility of the exposed areas decreases relative to the unexposed areas. The unexposed areas can then be selectively etched, producing a negative-tone image in the film. Positive-tone images also can be formed by preheating the film to higher temperatures before exposure. In some embodiments, an $M(OH)_x/H_2O_2$ film is formed by treating a film such as HafSOx with a mixture of sodium hydroxide and hydrogen peroxide. The resulting film is then patterned by exposure to light or an electron beam.

A method for forming a device also is described, comprising providing a structure to be patterned comprising a substrate, a material layer for patterning, and a metal oxide layer comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The structure is patterned and then exposed to an energy source to form a durable material having a desired pattern produced by patterning the structure. One embodiment of a device made according to the method can include a channel array, such as a micro- or nano-channel array. For such embodiments, the method for making the device can include stamping unit features of a desired size scale into a semi-solid hafnium or zirconium compound to form a stamped layer.

An embodiment of a method for making a device having a corrosion barrier also is described. Disclosed embodiments of the method comprise providing a device, and forming at least one corrosion barrier on the device. The corrosion barrier typically comprises a metal oxide layer comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The method also can include exposing the compound to an energy source to form the corrosion barrier. Examples of such devices include metal and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal and ceramic-based systems, fibers for

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composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, and catalyst supports.

An embodiment of a method for forming fibers also is disclosed. A solution is formed comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The solution is then drawn into fibers. The fibers may be converted into solid, stable forms by any suitable process, such as hydrolysis, annealing, air pyrolysis, and combinations thereof.

Embodiments of an optical device also are described. Particular disclosed embodiments of the device comprise an optical substrate, and a substrate coating comprising disclosed hafnium and/or zirconium oxy hydroxy compounds. The layer may be an antireflective coating. The optical substrate and coating may define, for example, a dielectric mirror, an X-ray mirror, an interference filter, a diffractive grating, and/or a waveguide. The optical device also may include a layer that is transparent, such as visibly transparent or transparent to ultraviolet light. The layer may be selectively doped to provide a doped layer having luminescent ions selected from Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof. Doping the layer can be used to produce a light-emitting layer.

Embodiments of a method for making a physical ruler also are disclosed. Certain embodiments comprise forming at least one acid-soluble layer by solution deposition of disclosed hafnium and/or zirconium oxy hydroxy compounds. At least one acid-insoluble layer is formed adjacent to the acid-soluble layer, the acid-insoluble layer being formed by solution deposition of disclosed hafnium and/or zirconium oxy hydroxy compounds. Repeating these steps produces alternating layers, and the method includes accurately determining widths of alternating acid-insoluble and acid-soluble layers. Width determination can be accomplished using any suitable method, such as X-ray reflectivity. Moreover, at least one layer is etched to define a digitated secondary reference pattern for measuring objects. Certain embodiments of such a device are useful for accurately measuring dimensions using an electron microscope.

The foregoing and other objects, features, and advantages of the invention will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 provides thermogravimetric analysis (relative mass versus temperature) (TGA) for HafSOx (x = 0.70) with various pretreatments and with samples heated under flowing $N_2(g)$ at a rate of 10 °C minute^{-1}.

FIG. 2 is an XRD pattern for HafSOx powders after heating at stated temperatures in air for 1 hour, except as noted.

FIG. 3 is an XRD pattern for HafSOx:32% La powders after heating at stated temperatures for 1 hour, except as noted.

FIG. 4 is an XRD pattern for HafSOx films after heating at given temperatures in air for 5 minutes, where the very small features at 31.8° and 45.6° are attributed to the substrate.

FIG. 5 is an XRD pattern for HafSOx:24% La thin films after heating at stated temperatures in air for 5 minutes.

FIG. 6 illustrates dielectric breakdown characteristics for HafSOx film.

FIG. 7 is an SEM showing one embodiment of HafSOx deposited on tantalum (Ta) metal on a silicon dioxide substrate.

FIG. 8 is an SEM for HafSOx:24% La deposited on Ta.

FIG. 9 is an XRR pattern for HafSOx/ZircSOx multilayer thin-film comprising 14 alternating layers (7 bilayers) having a bilayer thickness of 17.6 nm.

FIG. 10 is a schematic diagram illustrating positive or negative photoresist procedures.

FIG. 11 is a schematic diagram illustrating a positive resist using a bilayer system, the illustrated embodiment comprising a Cu-doped zirconium oxide sulfate (Cu:ZircSOx) film deposited on a hafnium oxide sulfate (HafSOx) film.

FIG. 12 is a schematic diagram illustrating a bilayer process for producing a patterned oxide on a substrate.

FIG. 13 is a schematic diagram illustrating a bilayer process for producing a patterned oxide on a substrate.

FIG. 14 is a schematic diagram illustrating a single layer process for producing a patterned film on a substrate.

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FIG. 15 is a graph of thickness versus etch time for a thermally pre-treated, single-layer film.

FIG. 16 is a film patterned by an electron beam.

FIG. 17 is a schematic diagram illustrating hot embossing lithography for use with semi-solid forms of compounds disclosed herein having much higher mechanical strength, chemical stability, and unique electrical and optical properties relative to organic polymers.

FIG. 18 is a schematic diagram illustrating one method for making a physical ruler for use in standardizing measurements in applications, such as electron microscopy.

FIG. 19 is an AFM image of an unexchanged HafSOx film deposited on silica.

FIG. 20 is a TEM image of HfO_2 following ion exchange of HafSOx and thermal treatment at 850 °C.

FIG. 21 is an AFM image of a HfO_2 film deposited on silica and formed from HafSOx thermal decomposition after heating above 700 °C.

FIG. 22 is an AFM image of a HafSOx film deposited on silica, treated with 0.1M NaOH, and heated to 450 °C for 10 minutes.

FIG. 23 is an AFM image of a HfO_2 film deposited on silica, treated with 0.1M NaOH and heated to 850 °C for 10 minutes.

FIG. 24 provides XRD plots of untreated hafnia films.

FIG. 25 provides XRD plots of treated hafnia films.

FIG. 26 provides XRD plots of untreated zirconia films.

FIG. 27 provides XRD plots of treated zirconia films.

FIG. 28 is an SEM image of an indium gallium zinc oxide semiconductor film deposited on silica.

FIG. 29 is a line pattern produced via ink-jet printing and inorganic diffusion-reaction.

FIG. 30 is a pattern produced by exposing a bilayer film to UV light.

FIG. 31 is a film patterned by electron-beam writing.

FIG. 32 is a film patterned by electron-beam writing.

FIG. 33 is a film patterned photographically.

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FIG. 34 is a film patterned photographically.

FIG. 35 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

FIG. 36 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

FIG. 37 is a $HfO_{2-x}(SO_4)_x$ film patterned by an electron beam.

DETAILED DESCRIPTION

Disclosed embodiments of the present invention concern devices, including electronic devices or components of electronic devices, which can be made by solution deposition of inorganic materials. Throughout this disclosure, the singular terms "a," "an," and "the" include plural referents unless the context clearly indicates otherwise. Similarly, the word "or" is intended to include "and" unless the context clearly indicates otherwise. The term "includes" means "comprises." All percentages recited herein are atomic percentages unless indicated otherwise. All patents and publications mentioned herein are incorporated by reference in their entirety, unless otherwise indicated. In case of conflict, the present specification, including explanations of terms, will control. The materials, methods, and examples recited herein are illustrative only and are not intended to be limiting.

I. Metal Oxide Sulfate Materials Generally and U.S. Patent Publication No. 2005/0242330 A1

The present disclosure concerns embodiments of a method for solution deposition of inorganic materials, typically solution deposition of metal oxide sulfate inorganic materials that are useful for electronic applications. Embodiments of these materials are described in U.S. Patent Publication No. 2005/0242330 A1. Certain portions of that published application, from paragraph 009 through paragraph 014, are paraphrased below. References to figures in this paraphrased text refer to the figures as published with the '330 publication.

> FIG. 1 illustrates one embodiment of a process for manufacturing a dielectric precursor material. Process 10 generally comprises providing a first reactant 12, such as a metal-containing cation, providing a second reactant 14, such as a polyatomic anion, and then reacting the polyatomic anion and the metal-containing cation. The metal-containing cation and the polyatomic anion may be in solution, such as an aqueous solution, when reacted together. In one embodiment, the metal-containing cation may be provided using an aqueous solution of a hafnium oxy halide, such as hafnium

oxy chloride ($HfOCl_2$(aq)). The polyatomic anion, such as sulfate (SO_4^{2-}), may be provided using an aqueous solution of sulfuric acid (H_2SO_4(aq)). These two reactants may be mixed together using processes and relative amounts suitable for making desired materials. The mixture may be heated.

The reaction may produce a precursor solution 16. Precursor solution 16 may be immediately used as desired, such as by being applied to a substrate. Optionally, precursor solution 16 may be at least partially dehydrated and then applied. In the example given above, the precursor solution may then form hafnium oxy-hydroxy sulfate ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$). With reference to the variables in this formula, x and z may be fixed or variable, and may have any value. For example, the value of x typically is from about 0.1 to about 1.9, and a value for z is from 0.0 to about 2.0. For one embodiment the values were x=0.5 and z=0. Hydroxyl groups may be a part of the metal-containing cation, and the compound may comprise hafnium oxy-hydroxy sulfate ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$).

In other embodiments, the polyatomic anion may include one or more of sulfate (SO_4^{2-}), borate (BO_3^{3-}), phosphate (PO_4^{3-}), tungstate (WO_4^{2-}) and silicate (SiO_4^{4-}). The metal-containing cation may comprise a metal suboxide, and may include one or more of hafnium (Hf^{4+}), titanium (Ti^{4+}), zirconium (Zr^{4+}), cerium (Ce^{4+}), tin (Sn^{4+}), tantalum (Ta^{5+}), niobium (Nb^{4+}), yttrium (Y^{3+}), molybdenum (Mo^{4+}), tungsten (W^{6+}), aluminum (Al^{3+}), gallium (Ga^{3+}), zinc (Zn^{2+}), chromium (Cr^{3+}), iron (Fe^{3+}), bismuth (Bi^{3+}), lanthanides, hafnium oxy-hydroxide ($HfO_y(OH)_z^{(4-2y-z)+}$), zirconium oxy-hydroxide ($ZrO_y(OH)_z^{(4-2y-z)+}$), titanium oxy-hydroxide ($TiO_y(OH)_z^{(4-2y-z)+}$), tantalum oxy-hydroxide ($TaO_y(OH)_z^{(5-2y-z)+}$), yttrium oxy-hydroxide ($YO_y(OH)_z^{(3-2y-z)+}$), niobium oxy-hydroxide ($NbO_y(OH)z^{(4-2y-z)+}$), molybdenum oxy-hydroxide ($MoO_y(OH)_z^{(4-2y-z)+}$), tungsten oxy-hydroxide ($WO_y(OH)_z^{(6-2y-z)+}$), aluminum oxy-hydroxide ($AlO_y(OH)_z^{(3-2y-z)+}$), gallium oxy-hydroxide ($GaO_y(OH)_z^{(3-2y-z)+}$), zinc oxy-hydroxide ($ZnO_y(OH)_z^{(2-2y-z)+}$), chromium oxy-hydroxide ($CrO_y(OH)_z^{(3-2y-z)+}$), iron oxy-hydroxide ($FeO_y(OH)_z^{(3-2y-z)+}$), bismuth oxy-hydroxide ($BiO_y(OH)_z^{(3-2y-z)+}$), and oxy-hydroxides of the lanthanide series. The value of y is related to the charge on the metal cation and the amount of hydroxide and other polyatomic anion that is bound to the metal cation.

Embodiments of the method using polyatomic anions and metal-containing cations disclosed herein may result in the formation of a dielectric precursor material that does not require using organics for forming complexes, i.e., the sources of the anion and the cation do not contain organics. However, organic materials can be used, if desired or necessary for certain embodiments. For example, a non-complexing organic, such as ethanol, may be used as a partial solvent in the precursor solution. If complexing organics are not included in the precursor material, the precursor solution typically does not have to be heated or annealed at temperatures as high as 400 °C or higher, to decompose/combust any organic materials once the precursor solution is applied to a substrate. Polymerization of the

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precursor solution upon heating and/or drying results in the formation of amorphous films and not polycrystalline materials, thereby allowing solutions-based-application of the dielectric material on a substrate.

In general, disclosed embodiments of the present process may be conducted at ambient conditions, such as atmospheric pressure in air. Accordingly, vacuum processing is not required, but may be utilized if desired. The process may be conducted at a temperature above ambient, such as in a range of from about 80 °C to about 850 °C, typically in a temperature range of from about 80 °C to at most 350 °C, and often at a temperature of at most 100 °C. These low pressure and low temperature processing steps may reduce the energy requirements for disclosed processes. Due to the low temperatures useful for processing the dielectric films, the films may be processed on or applied as a solution to low-temperature substrates, such as plastic substrates. The amorphous, non-crystalline dielectric precursor solution produced allows even, conformal coverage of the precursor solution on a substrate, such as on a wafer. The solution also may be applied in a predetermined, specific pattern, such as by using inkjet printing, so that no masking or etching steps are used. Accordingly, the process of the present disclosure may eliminate or reduce the usage of hazardous or toxic materials that may be used for the formation and removal of materials during photolithography processing on substrates. Thus the present process is time efficient and environmentally "green" relative to known processes. Moreover, the hafnium oxide and sulfate materials utilized in one example embodiment of the present disclosure may not be toxic materials.

Examples of materials used in the process of the present disclosure include compounds belonging to the family of compounds including hafnium oxy hydroxy sulfates ($HfO_{2-x-z/2}(OH)_z(SO_4)_x$), hafnium oxy hydroxy tungstates ($HfO_{2-x-z/2}(OH)_z(WO_4)_x$), hafnium oxy hydroxy borates ($HfO_{2-x-z/2}(OH)_z(BO_3)_x$), hafnium oxy hydroxy phosphates ($HfO_{2-x-z/2}OH_z(PO_4)_x$), and hafnium oxy hydroxy silicates ($HfO_{2-x-z/2}OH_z(SiO_4)_x$). These materials may be polymerized at temperatures as low as 80 °C and may remain amorphous up to approximately 740 °C, and even as high as 1,200 °C. Material polymerization may be controlled by adjusting the heating rate, by using co-solvents, by other suitable methods, and by any and all combinations of such methods. Amorphous films of the present disclosure may reduce defect formation at grain boundaries and may reduce crack formation upon an amorphous-to-crystalline transition. Moreover, the dielectric films of the present disclosure may have a reasonably high dielectric constant, i.e., a dielectric constant higher than the dielectric constant of organic compounds. The ability to form high quality dielectrics by solution-based processing, such as inkjet printing applications, allows formation of low cost electronic components, such as field effect transistors or capacitors.

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FIG. 2 schematically illustrates one embodiment of a process for applying precursor solution 16 to form a dielectric material. Precursor solution 16, such as hafnium oxy sulfate, may be applied to a substrate 18, such as a wafer, by an applicator 20. In one embodiment, applicator 20 may comprise an inkjet printer having nozzles 22. The aqueous precursor solution 16 is ejected through nozzles 22 of the inkjet printer. In other embodiments, applicator 20 may comprise a spin-coater, a dip-coater, or a spray-coater such that the method of applying the precursor solution may comprise, respectively, spin-coating, dip-coating, or spray-coating. Due to the amorphous, solution-based properties of precursor solution 16, precursor solution 16 may allow good conformal coverage when applied. Once applied to the substrate surface, or to a film or films deposited on the substrate, the precursor solution may be dehydrated, such as by heating with a heater 24, or by other dehydration devices, to remove or reduce the amount of water in the precursor solution. This dehydration step may cause precipitation of an amorphous dielectric material 26, such as a hafnium oxy sulfate thin film, on wafer 18.

FIG. 3 is a graph showing possible solution concentrations for differing precursor concentrations for one embodiment of dielectric material precursor solutions 16 (see FIG. 1), in particular, for the reaction of sulfuric acid (H_2SO_4) with hafnium oxy chloride ($HfOCl_2$). More particularly, FIG. 3 shows a graph of total sulfate concentration (molarity (M)) versus total hafnium concentration (M). Region 28 represents a clear solution, i.e., a solution with no visually detectable precipitate therein, wherein region 28 is a region of excess sulfuric acid (H_2SO_4). Region 30 represents a clear solution, i.e., a solution with no visually detectable precipitate therein. Region 30 is a region of excess hafnium oxy chloride ($HfOCl_2$). Line 32 represents a stoichiometric line wherein sulfuric acid and hafnium oxy chloride are each present in a one-to-one ratio (1:1 stoichiometric ratio). Region 34 represents a precipitation area, i.e., a solution having a visually detectable precipitate therein. Region 34, or portions thereof, therefore, may represent solutions that are not best suited for forming smooth substantially defect free films by inkjet printing applications, but its use is not foreclosed. Accordingly, when precursor solution 16 (see FIG. 2) is applied through an inkjet printer application device 20 (see FIG. 2), it may be desirable that the concentration of the first and second reactants fall within either of regions 28 or 30, but not within solids region 34. Solids present in the solutions of region 34 may occlude nozzles 22, may form an unsmooth film, or may otherwise result in unfavorable precursor solution application. In other words, the solutions of regions 28 and 30 may represent possible precursor solution "inks" that may be applied through an inkjet printhead or by a dropper method.

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II. General Discussion

New thin-film dielectrics and nanolaminates have been developed using solution deposition, typically aqueous solution deposition, of smooth, dense films. Solution deposition techniques include spin coating and inkjet printing. Solution deposition may be followed by modest thermal treatment ($T < 325\ ^{\circ}C$).

A variety of analytical techniques have been used to define the chemistry of the materials made according to the present disclosure, both as powders and films. The quality and functionality of the films have been assessed by X-ray reflectivity, electronic microscopy, and performance in electronic devices. Dielectric characteristics have been determined for working embodiments, and include permittivity values covering the range of from about 9 to about 12; breakdown fields up to at least 6 MV cm^{-1}; and leakage currents near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}. The surface smoothness and pore-free nature of the films facilitate the production of unique nanolaminated structures having individual layers at least as thin as about 2 nanometers. Relatively high permittivity films can be realized using disclosed embodiments of the present invention, while also providing high-breakdown strengths and low-leakage currents in thin-film metal-insulator-metal (MIM) capacitors and thin-film transistors (TFTs). The exceptional characteristics of the insulating films also have allowed fabrication of unique nanolaminated structures.

Amorphous materials are desirable for use as thin-film dielectrics; they do not have grain boundaries, and hence are not susceptible to roughness and charge conduction associated with crystallites. Numerous oxides of hafnium and zirconium, e.g., the simple binaries, silicates, and aluminates, have been examined as candidates for high-permittivity dielectric applications. In multiple-component materials, crystallization can be inhibited to produce more robust breakdown characteristics relative to the pure binary oxides, though permittivity may be sacrificed. These dielectric films often are formed using a variety of metal-organic or metal-salt precursors and techniques such as atomic layer deposition (ALD), chemical vapor deposition (CVD), sol-gel processing, or combinations thereof. However, making useful dielectric films by solution deposition methods that are

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both dense and amorphous may require inhibiting crystallization and cracking, both during deposition and subsequent processing.

Certain disclosed embodiments of the present invention concern the development of metal oxide films. Metal oxides are exemplified herein generally by reference to hafnium and zirconium sulfate systems having representative formulas $HfO_{2-x}(SO_4)_x$ and $ZrO_{2-x}(SO_4)_x$, respectively, where $0.1 \leq x \leq 1.5$. These compounds are referred to herein by the acronyms HafSOx and ZircSOx, respectively. To define the chemistry and physical properties of these systems, HafSOx, and doped analogs thereof, such as the La-substituted derivative HafSOx:La, have been made, both as powders and thin films. Thin-film dielectric properties of HafSOx, ZircSOx, and selected derivatives have been assessed by fabricating capacitors and TFTs. These analyses revealed that very high-quality, dense films could be produced. Film thickness and fabrication of mixed HafSOx/ZircSOx nanolaminates can now be controlled by spin-coating processes.

A number of phases and crystal structures have been reported from examination of HfO_2-SO_3-H_2O and ZrO_2-SO_3-H_2O systems. Several structures are characterized as simple hydrates of formulations $Hf(SO_4)_2 \cdot nH_2O$ or $Zr(SO_4)_2 \cdot nH_2O$, exhibiting variations in the degree of hydration and in the structural dimensionality associated with the condensation of the metal atom, sulfate groups, and water. Materials rich in metal relative to sulfate are known, including $Zr_2(OH)_2(SO_4)_3 \cdot 4H_2O$; $Hf(OH)_2SO_4$, $Zr(OH)_2SO_4$, and their hydrates; $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13} \cdot 33H_2O$ and $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$; and $Zr_3O_5SO_4$ and its hydrate. All of these structures (with the possible exception of $Zr_3O_5SO_4$) are likely unstable when subjected to air at both room temperature and under moderate heating, resulting from changes in hydrogen bonding or dehydration. This allows the dehydration and condensation processes to be used to develop amorphous films.

Starting from aqueous solutions with selected fractions of sulfate relative to hafnium (variable x), HafSOx precipitates were induced by heating. FIG. 1 is a thermogravimetric analysis (TGA) of air-dried HafSOx precipitates. TGA is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature. Heating an air-dried HafSOx precipitate leads to mass loss in three domains. Similar characteristics have been observed for other

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HafSOx derivatives as well. The large mass loss below a temperature of about 200 °C is attributed to loss of incorporated water. Mass loss in the temperature range of from about 200 °C to about 700 °C is attributed mainly to elimination of more tightly bound hydroxyl species as water. The sharp mass loss that begins above about 700 °C, is attributed to sulfate decomposition according to $SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$. Assuming dehydrated HafSOx powder is converted completely to HfO_2 between 700 °C and 950 °C, the sulfate fraction can be calculated from the mass loss. Determining mass loss of samples revealed that increasing levels of sulfate in the mother solution yielded increasing levels of sulfate in precipitates. Specifically, the sulfate-to-hafnium ratio varied from about 46% to about 71% for dehydrated formulas of $HfO_{1.54}(SO_4)_{0.46}$ and $HfO_{1.29}(SO_4)_{0.71}$, respectively. The same maximum sulfate composition precipitated whether $H_2SO_4(aq)$ or $(NH_4)_2SO_4(aq)$ was used as the sulfate source; products with sulfate levels < 46% were not examined. The onset of sulfate loss occurred above 720 °C for all samples, though some variations in the thermogravimetric profiles were observed. Peak positions for the derivatives of these heating curves, as definable values, reveal decomposition between 793 °C and 817 °C for samples tested. The highest decomposition temperatures were observed for samples having maximum sulfate content with $H_2SO_4(aq)$ as the sulfate source.

Again with reference to FIG. 1, samples with maximum sulfate content also were heated prior to TGA measurements. Mass losses associated with water were reduced, and calculated sulfate contents were similar for both preheated and regular samples. This sulfate content of 70–71% mimics the compositions of the reported crystals $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$ and $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}\cdot 33H_2O$. From TGA studies, Ahmed, Fjellvåg, and Kjekshus (*Acta Chem. Scand.*, 53, 24 (1999) also found that sulfate decomposition for $Hf_{18}O_{23}(SO_4)_{13}$ and $Zr_{18}O_{23}(SO_4)_{13}$ occurs at temperatures higher than those for the Hf and Zr disulfates within their study, and higher than those for the basic sulfates $Hf(OH)_2SO_4\cdot H_2O$ and $Zr_3O_5SO_4$ reported by others. In addition to enhanced thermal stability, a sulfate-to-metal ratio of approximately 13:18 exhibits special stability within this system. As such, this composition may be suitable for purposes where solution processing and heating are required.

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The sulfate $La_2O_2SO_4$ has a decomposition temperature of greater than 1,300 °C. Lanthanum (La) was added to the mother HafSOx solution to produce additional compounds having modified physical properties, such as modified dehydration properties and thermal characteristics, one example being thermal stability. A mixed-metal system, $Hf_{1-z}La_zO_{2-x-z/2}(SO_4)_x$ (HafSOx:La), exemplifies such compounds. To produce such compounds a solution containing the precursor materials and 23% La (total metal) was heated to form precipitates. Chemical analysis indicated that only 3% La was found in the product. From TGA, a sulfate-to-metal ratio of 71% was established, and the decomposition (as derivative peak) at 820 °C was found to be consistent with maximal sulfate content. Co-precipitation was then induced by adding NH_3(aq) to a salt solution of the constituent species containing 32% La. The chemical composition of the product was analyzed, revealing the same fraction of La as that present in the mother solution. Thermal decomposition for this formula was markedly different from undoped HafSOx. Mass loss attributed to sulfate was apparent above 700 °C, though heating features were less abrupt and no constant mass was achieved with heating to 1,000 °C, even when heating at the slower rate of 2 °C $minute^{-1}$. For this heating rate, decomposition (as derivative peak) occurs at approximately 870 °C, though this value depends on heating conditions. Complete decomposition to the oxides was accomplished by heating to 1,500 °C, yielding the formula $Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$ for the dried precipitate.

XRD data were collected for precipitated HafSOx powders to establish temperature ranges for crystalline phases. After air drying, a complex diffraction pattern was recorded for samples having maximum sulfate content and H_2SO_4(aq) as the sulfate source; other samples exhibited no or diffuse diffraction. XRD data for HafSOx (x = 0.70) are shown in FIG. 2. After heating air dried samples for 1 hour at temperatures between from about 100 °C to about 700 °C, the material becomes amorphous. Crystalline peaks characteristic of monoclinic HfO_2 are observed after heating at 750 °C and above for 1 hour. As the onset of sulfate loss occurs at 720 °C by TGA, crystallization is found to coincide with sulfate loss. Inclusion of 3% La generates similar diffraction profiles for temperatures up to 1,000 °C.

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XRD data for HafSOx:32% La are shown in FIG. 3. Both the precipitated material and that heated to 700 °C are X-ray amorphous. Just as with unsubstituted HafSOx, a detectable crystalline phase forms between 700 °C and 750 °C (1 hour heating), which is the temperature interval over which sulfate begins to decompose. Yet with substitution of 32% La, monoclinic HfO_2 is not the detected phase. Rather, the diffraction profile is consistent with cubic (or tetragonal) HfO_2, the phases of HfO_2 often stabilized by lanthanide atom inclusion. High-temperature heating generates $Hf_2La_2O_7$ and monoclinic HfO_2 as predicted from consideration of the appropriate phase diagrams. Intermediate temperature oxide phases are consistent with work on the system ZrO_2-La_2O_3 by Zhang, Kershaw, Dwight and Wold (*J. Solid State Chem.*, 72, 131 (1988)), who found that 10–37% lanthanum stabilizes cubic zirconia at 900 °C, with phase separation occurring at 1,050 °C.

HafSOx and HafSOx:La thin films having thicknesses of from about 200 nanometers to about 300 nanometers were fabricated for materials characterization. Compositions for the films were determined with electron-probe microanalysis (EPMA), based on relative concentrations of Hf, La, Cl, and S. Oxygen levels are less precise by this method, so dehydrated formulas are expressed. Two representative HafSOx films heated at 325 °C (5 minutes) were determined to be $HfO_{0.985}(SO_4)_{0.67}Cl_{0.69}$ and $HfO_{0.915}(SO_4)_{0.85}Cl_{0.47}$, representing 67% and 85% sulfate relative to hafnium. The 85% sulfate film was further heated to 650 °C (5 minutes) and determined to be $HfO_{1.275}(SO_4)_{0.71}Cl_{0.03}$. Also, the HafSOx:La film heated at 330 °C (5 minutes) was determined to be $Hf_{0.76}La_{0.24}O_{0.73}(SO_4)_{0.96}Cl_{0.38}$. For HafSOx heated to 650 °C, the sulfate ratio was reduced to 71%, which matches the composition for heat precipitated HafSOx powders with maximal sulfate. For HafSOx:La, the measured fraction of La (24%) agrees well with the 23% La concentration in the precursor solution.

Transmission Fourier transform infrared (FTIR) analyses for HafSOx ($x \sim 0.67$ & 0.85), and HafSOx:La films were collected after heating for 5 minutes at selected temperatures. FTIR spectra were used to detect principally two functional groups. Absorption in the range 3000–3600 cm^{-1} is attributed to hydroxyl groups; and absorption in the range 1000–1200 cm^{-1} is attributed to sulfate groups. With heating, hydroxyl absorption diminishes over the range from about 325 °C to about

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600 °C, while sulfate stretches are nearly eliminated between about 650 °C and 700 °C for HafSOx films, and between about 700 °C and 750 °C for the HafSOx:La film. (The profiles for sulfate absorption are slightly distorted since SiO_2 from the substrates absorbs at a similar energy, but spectra are qualitatively correct.)

Thin-film XRD data were collected for HafSOx (x ~ 0.67 & 0.85) and HafSOx:24% La films after heating at indicated temperatures for 5 minutes each, as shown in FIGS. 4 and 5, respectively. For both HafSOx compositions, films are X-ray amorphous from about 325 °C to about 650 °C. Monoclinic HfO_2 is detected at about 700 °C and above. HafSOx:La films are amorphous from about 330 °C to about 700 °C, while a cubic phase is detected from about 750 °C to about 1000 °C. The cubic phase is apparently unstable at 1,100 °C, as separation into monoclinic HfO_2 and $Hf_2La_2O_7$ phases commences. For HafSOx and HafSOx:La films, loss of sulfate can be directly correlated with oxide crystallization, which is consistent with powder behavior.

Films of HafSOx, ZircSOx, and derivatives thereof, were deposited by spin-coating for use as dielectrics. MIM capacitors were tested to determine the parameters of permittivity and loss tangent at 1 kHz, as well as electric-field breakdown strength. "Breakdown" is defined as the field where current density surpasses 10 $\mu A\ cm^{-2}$. Similar tests were conducted for HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, and ZircSOx:Ca. FIG. 6 illustrates dielectric breakdown characteristics for HafSOx dielectric film where the aluminum dot contacts represent an area of 0.011 cm^2. HafSOx and ZircSOx films had breakdown fields of 4–6 MV cm^{-1}. A breakdown field of 3.6 MV cm^{-1} was found for ZircSOx:Ca. At an applied field of 1 MV cm^{-1}, all six variations exhibited leakage current less than 50 nA cm^{-2}, and leakage currents less than 10 nA cm^{-2} were observed for many compositions. Permittivity values of from about 9 to about 12, and loss tangent < 1% were measured for all variations.

Field-effect transistors (FETs) were fabricated with HafSOx:La or ZircSOx:La as the gate dielectrics and zinc indium oxide or zinc tin oxide as the channels. Current modulation was achieved; drain-to-source current saturated with increasing drain-to-source voltage, providing an on-to-off ratio greater than 10^6; and gate leakage currents are in the range of pA cm^{-2}. These results clearly indicate that

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HafSOx:La and ZircSOx:La films are sufficiently robust for device integration; the requirement for a quality dielectric/channel interface is also met.

As a new class of amorphous multi-component oxide dielectric films, HafSOx, ZircSOx, and their derivatives may be compared to other mixed systems, particularly aluminates and silicates, represented as $(MO_2)_{1-x}(Al_2O_3)_x$ and $(MO_2)_{1-x}(SiO_2)_x$ where M = Hf or Zr. Various film compositions for each of these systems have been deposited by conventional vapor phase techniques. In the cases of Hf or Zr aluminates and silicates with 20–50 mol% Al_2O_3 or SiO_2 (as common compositions for dielectric applications), crystallization typically occurs at about 800 °C to about 1,000 °C, in conjunction with phase segregation. For tested HafSOx powders and films, crystallization occurs at approximately 700 °C as sulfate decomposes. As dielectrics, these aluminates and silicates exhibit permittivity values of 10–15, compared to values of 9–12 for HafSOx and ZircSOx. This new class of oxide sulfate materials can be considered amorphous, moderate temperature, medium permittivity dielectrics.

Scanning electron microscopy (SEM) and X-ray reflectivity (XRR) were used to further examine film qualities. SEM images for HafSOx and HafSOx:La films are shown in FIGS. 7 and 8. These images reveal smooth surfaces and dense, uniform cross-sections for films having thicknesses in the range of from about 150 nanometers to ahout 300 nanometers, as typically used for dielectric testing. FIG. 7 shows a SiO_2 substrate 710 upon which a 506-nm layer of Ta metal 712 and a 160-nm HafSOx film 714 have been deposited. FIG. 8 shows a SiO_2 substrate 810 upon which a 512-nm layer of Ta metal 812 and a 192-nm HafSOx/La film 814 have been deposited.

As a stringent measure of reproducibility for thinner film fabrication, multilayer structures with a HafSOx/ZircSOx repeating motif were deposited and analyzed by XRR. The interference pattern from one XRR scan is shown in FIG. 9. Positions of peak maxima, representative of standing wave harmonics, were used to find the thickness of the repeating bilayer. By systematically varying the thicknesses of HafSOx and ZircSOx independently, the thicknesses of the individual layers were determined. Within a nanolaminate stack, single layers as thin as about

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3 nanometers were measured. As high order reflections in the diffraction pattern are observed, each bilayer was deposited with a variability < 0.5, including roughness.

Shrinking device dimensions have led to the need to replace thin, high leakage-current SiO_2 as a dielectric in Si CMOS technologies. The replacement dielectrics must exhibit a high permittivity, allowing thicker layers to exhibit the same device capacitance with smaller leakage currents. HfO_2 and ZrO_2 have attracted considerable attention as replacement gate dielectrics because of their desirable dielectric properties and thermal properties. One of the challenges for HfO_2 and ZrO_2 dielectrics is making smooth, dense, pinhole-free, ultra-thin films having a thickness less than or equal to 13 nm. Previously ultra-thin films have been formed using atomic layer deposition (ALD). Despite some promising results from ALD, the processing requires using a vacuum with long deposition times (1 Å/min), which leads to high costs and low throughput. This has driven some work on the solution based deposition of HfO_2 and ZrO_2. To date these films have not reached the same uniformity and density of the ALD films.

Using an exchange reaction, ultra-thin $M(OH)_x$ and MO_x films can be fabricated that rival ALD quality and are suitable for use in DRAM (dynamic random access memory) and Si CMOS (complementary metal-oxide semiconductor) technologies. For disclosed embodiments, the films are deposited in a sulfate form via inorganic condensation using spin-coating. For example, a semi-solid film can be formed with the composition $MO_x \cdot HCl \cdot H_2SO_4$. The sulfate is removed by ion exchange using an aqueous sodium hydroxide solution:

$$MO_x \cdot HCl \cdot H_2SO_4 + OH^-(aq) \rightarrow M(OH)_{2x} + Cl^-(aq) + SO_4^{2-}(aq)$$

The resulting hydroxo and/or oxide films are smooth, dense, and pinhole free. For example, HfO_2 films with a thickness of about 2 nanometers can fabricated from HafSOx films. Exchanged films are subjected to thermal treatments up to about 800 °C for about 10 seconds to 10 minutes, resulting in a film surface roughness of about 0.1 nanometer. Such film characteristics satisfy requirements for metal-dielectric gates in CMOS and related technologies, while replacing expensive atomic layer deposition processing with low-cost spin-on or misting techniques.

The deposited semi-solid hydrated hydroxo films allow for anion exchange without disruption of the films' morphology. For example, oxoanions such as SO_4^{2-},

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WO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-}, VO_4^{3-}, AlO_4^{5-}, GaO_4^{5-}, and their protonated forms, e.g., HPO_4^{2-}, $H_2PO_4^-$, and the halides F^-, Cl^-, Br^-, and I^-, can be selectively exchanged by placing the films in a metal salt bath, e.g., Na_2SO_4(aq). This provides opportunities to optimize film performance for electronic applications and other applications, such as ion exchange chromatography and filtration.

For some embodiments of oxide films, it is difficult to produce single-source precursor liquid suspensions that can be directly applied to a substrate to provide a complex composition, e.g., two or more metal atoms. The following methods allow the production of such liquid suspensions and their use as single-source precursors for deposition of films of suitable quality for device applications.

The following describes a general method for synthesizing an aqueous precursor solution and depositing metal oxide films using the precursor. The aqueous precursor is distinctive in that it comprises polymeric or oligomeric metal-hydroxo compounds condensed via hydrolysis in a non-aqueous polar solvent and subsequently transferred to an aqueous environment for deposition. Advantageous thin-film electrical and optical properties and processing temperatures are achieved by condensing metal hydroxides to dense solid oxides without deleterious organic contaminants. Disclosed embodiments of the synthetic method follow the general procedure: 1) dissolution of metal salt in polar solvent; 2) hydrolysis and condensation; 3) solvent evaporation; 4) dissolution in H_2O; and 5) solution deposition and curing.

One or more soluble salts comprising a metal cation (M^{a+}) and one or more anions (X^{b-}) are dissolved in a non-complexing, non-aqueous polar solvent such as aliphatic alcohols or nitriles, particularly lower (10 carbon atoms or fewer) alkyl alcohols and nitriles, such as methanol, ethanol, acetonitrile, or a mixture thereof. Many solvent systems are possible. Suitable solvents for a particular application can be selected by considering boiling point (typically less than 150 °C), low toxicity, and acid-base and redox properties compatible with intended solution-phase reactions. Metal sources may include simple ionic or molecular salts ($Zn(NO_3)_2$, $SnCl_4$, etc.); oxy or hydroxy salts ($ZrO(NO_3)_2$, ZnOHCl, etc.); or potentially organic salts ($Fe(CH_3CO_2)_2$, $Cu(CHOO)_2$, etc.). At least one of the metal cations must have a formal charge greater than or equal to 3^+ and the total concentration of such ions

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(M^{a+} where $a \geq 3$) should exceed 50 mol% of the metal cations in the target oxide. Concurrently, an amount of H_2O is introduced into the solution as hydrates of the metal salts described above, as a pure liquid, or a basic solution detailed below. The amount of water is determined by the cations chosen; typical amounts of water will not exceed 20 mol% of the non-aqueous polar solvent.

The pH of the solution is then raised relative to the starting pH by adding an appropriate base or by reaction of free protons via oxidation-reduction mechanisms. The increased pH drives hydrolysis of the H_2O ligands bound by the acidic ($a \geq 3$) cations and condensation of the resulting hydroxo-cations. The final solution pH depends upon the metal cations used, but will typically be in the range of about 2-9. This may be accomplished using one of the following techniques, or any and all combinations thereof:

a) Addition of a basic aqueous solution containing NH_4OH, $(NH_4)_3PO_4$, CsOH, or similar compounds. Specific compounds (NH_4OH) may be chosen to decompose or volatilize during subsequent processing. Other cations (e.g., Cs) or polyatomic anions
(e.g., PO_4^{-3}) may be used if they are intended to comprise part of the final oxide film to achieve unique morphological, optical, or electrical properties following dehydration.

b) Addition and dissolution of a small amount of a basic oxide such as CaO or SrO, with a similar goal of inclusion in the final oxide film.

c) Addition of NH_3 or other gaseous compounds, which form a basic solution in H_2O.

d) Addition of electropositive metal reducing agents, such as Zn, Al or Fe, which may consume protons through direct reduction to H_2, or as part of other proton-consuming oxidation-reduction processes such as the reduction of NO_3^-. Resultant cationic species are thercafter incorporated into the final oxide film.

e) Addition of aqueous or gaseous oxidizing or reducing agents such as N_2H_4, H_2CO, or H_2O_2 in liquid form, or as soluble salts, with a similar purpose of consuming protons or decomposing counter ions but without inclusion in the final oxide film.

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The solution may be stirred at room temperature, heated, or exposed to solvothermal conditions to promote thermohydrolysis and condensation, depending on the final composition desired. Following a suitable reaction period the solution will contain one or more soluble oligomeric or polymeric metal-hydroxo cationic species. These species may be homo or hetero-metallic in nature. The degree of condensation is limited by the restricted molar ratio of H_2O (aquo- and hydroxo-ligands) available, while the decreased polarity and size of the non-aqueous solvent relative to H_2O may prevent additional condensation and precipitation processes through steric effects or altered charge-screening properties.

Soluble metal species are isolated by evaporating the non-aqueous solvent. Isolated metal-hydroxo compounds may form crystalline or amorphous solids or gels depending on certain processing considerations, such as solvent, counterion, and hydrolysis ratio.

Precursor solutions for oxide films are prepared by dissolving or dispersing the isolated solid in H_2O. The resulting sol or solution is homogenous, and may or may not be thermodynamically stable.

Precursor solutions are applied to a substrate using any suitable technique, including printing, spin, spray, or dip-coating to form a patterned or blanket liquid film. Liquid films are thermally cured under atmospheric conditions for about 5-240 minutes at a temperature from about 100 °C to 600 °C. Vacuum or forming gas (e.g., H_2 and flowing N_2 or Ar) anneals may be used to alter oxygen stoichiometry or cation oxidation state as appropriate for the chemical or optoelectronic properties desired.

The smoothness and high atomic density of the films described herein allow fabrication of purely inorganic nanolaminates via solution processing. These films represent a new platform for developing a wide range of applications, as discussed further below.

III. Applications

A person of ordinary skill in the art will appreciate that the HafSOx and ZircSOx compounds, and films comprising such compounds, can be used to make a number of different devices, and can be used to practice a variety of processes

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utilizing such compounds. Metal-organic precursors have been extensively employed in the solution-based deposition of inorganic oxides. The presence of the organic moiety necessitates a high-temperature burnout step, which leads to significant volume change and generally to crystallization and the phenomenon of "mud cracking." These problems are eliminated by using disclosed embodiments of the present invention and suitable inorganic compositions to form amorphous HafSOx and ZircSOx films, where simple dehydration and polymerization lead to film quality preservation. To understand phase stability, representative HafSOx and HafSOx:La powders and films were characterized at various temperatures. Thin-films based on HafSOx and ZircSOx were deposited in multiple configurations in order to examine the quality and utility of the films. Several derivatives have been used to produce capacitor dielectrics. HafSOx:La and ZircSOx:La were used to form gate dielectrics in FET devices. Nanolaminate layers of HafSOx and ZircSOx exhibited remarkable smoothness with reproducibility within a couple atomic layers. Classes of films comprising HafSOx, ZircSOx, and their derivatives are useful, amongst other things, as electrical insulators, protective barriers, optical coatings, and/or as inorganic polymers for photolithography.

A. Patterned films for Resist, Imprint Lithography, and Printing

Photolithography is commonly used to transfer geometric shapes on a mask to the surface of a silicon wafer or other semiconductor. For the past four decades, photolithographic processing has been the driving force for the improvements in resolution and dimensional control of device features in the microelectronics industry. These advances have made possible the high-performance personal computers, cell phones, CD players, and other innumerable advanced electronic products that are now considered to be essential parts of our lives. The photolithographic advances that have made these products possible have largely centered on developing short-wavelength exposure tools and an extraordinary extension in the resolution and feature-size capabilities of polymer resists. As the quest for ever smaller features and device-yield improvements continue, however, the limitations and inefficiencies of polymer-based resist technology are becoming more evident.

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The smallest feature sizes realized via lithography have been produced by electron-beam writing of inorganic materials. The beam-dose energies required to produce these features, however, have been much too high to receive more than passing interest for use in a manufacturing environment.

During the deposition and processing of the films described herein, it is possible to control the film hydration level, which provides a method for controlling the interdiffusion of stacked films and their resulting physical and chemical properties. This controlled interdiffusion with resulting induced modifications in material solubility, coupled with the high quality of the films, was used to develop a new lithographic patterning method involving amorphous and crystalline films. This methodology involves depositing and reacting two distinct films, and it is designated as bilayer diffusion. In addition, small coordinating species such as peroxide (O_2^{2-}) can be incorporated into aqueous-based inorganic liquid suspensions and films to provide an additional, new lithographic patterning method. In this technique, energy (e.g., light, electron beam, heat) can be applied to films, inducing condensation reactions that alter the solubility of the film, thereby allowing lithographic patterning.

Patterns can be formed using a positive or negative photoresist. This process is illustrated schematically in FIG. 10 with reference to a laminate structure 1010 having a silicon substrate 1012, a silica layer 1014 and a resist layer 1016. For positive resists, the resist layer 1016 is exposed to an energy source, such as UV light, wherever the underlying material is to be removed. In these resists, exposure to the UV light changes the chemical structure of the resist layer 1016 so that it becomes more soluble in the developer. The exposed resist layer 1016 is then removed by the developer solution, leaving areas of the bare underlying material. In other words, "whatever shows, goes." The mask 1018, therefore, contains an exact copy of the pattern which is to remain on the wafer.

Negative resists behave in just the opposite manner. Exposure to the UV light causes the negative resist to polymerize, and it therefore is more difficult to dissolve. As a result, the negative resist 1020 remains on the surface wherever it is exposed, and the developer solution removes only the unexposed portions. Masks

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used for negative photoresists, therefore, contain the inverse (or photographic "negative") of the pattern to be transferred.

Resist materials in current use for electronics manufacture are organic polymers. These polymers exhibit coiling, morphologies, and diffusion chemistries that limit pattern resolution. Inorganic thin films of the present invention form the basis for a new resist technology. Here, negative resists can be realized by exposing the inorganic films in semi-solid form to light or electron beams, causing them to lose solvent, particularly water during dehydration, or small coordinating ligands such as O_2^{2-}. This hardens the films, rendering them insoluble in acid.

One embodiment of a positive resist can be made using a bilayer system. A first layer of the bilayer comprises a copper formate film deposited on a hafnium oxide sulfate (HafSOx) film. The copper formate film is soluble in acid and the undoped HafSOx film is insoluble in acid. Exposing the bilayer to light through a mask or to a focused electron beam causes the two films to interdiffuse in exposed areas, thereby rendering the previously undoped HafSOx film soluble.

One embodiment of this process is illustrated schematically in FIG. 11. With reference to FIG. 11, a laminate structure 1110 is first formed, such as by spin coating or inkjet coating suitable materials, in desired orders and thicknesses as required to define a working device. More specifically, a substrate material 1112 is first selected. A person of ordinary skill in the art will appreciate that any of a number of substrate materials potentially can be used to practice this embodiment of the present invention. Solely by way of example, and without limitation, suitable substrates include semiconductor materials, metals, glass, polymeric materials, and combinations thereof. As such the resist technology can be useful for a variety of applications in semiconductor manufacture. Once a suitable substrate 1112 is selected, a first layer 1114 of HafSOx is solution deposited onto the substrate 1112. Thereafter, a second layer, such as a layer 1116 of Cu:ZircSOx, is solution deposited onto layer 1114. The laminate structure 1110 is then subjected to an energy source, such as an electron beam or light, through a mask. Upon exposure to light or an electron beam through a mask, the two films interdiffuse in the exposed areas to render the previously undoped HafSOx film soluble to produce a laminate structure 1120. The exposed structure 1120 is then developed. The previously undoped

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HafSOx film is soluble, and hence is removed as indicated in laminate structure 1130.

On a flexible or glass substrate, the pattern illustrated in structure 1130 can be considered the master plate for imprint lithography or for generalized printing processes such as gravure printing. Forming a hardened patterned material of HafSOx in this way also provides a means for developing micro- and nano-channel arrays in the fabrication of devices for fluid control and delivery. Such devices could be applied in medical diagnostics, ink delivery, and chemical synthesis.

Another embodiment of a bilayer process is shown in FIG. 12. The process produces a patterned oxide on a selected substrate 1210. The substrate can, for example, be a glass, semiconductor wafer, metal, metal alloy, plastic, or a combination thereof. The first step of the process involves depositing a thin film 1212 (from about 1 nm to about 100 nm) of a solid acid or base, e.g., hydrated sulfate, phosphate, nitrate, silicate, aluminate, borate, or mixtures thereof, containing one or more of the metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu. In addition the solid acid/base can contain one or more of NH_3, OH, F, Cl, Br, I. The solid acid/base is preferably deposited via spin coating or printing; physical and vapor deposition are additional options. As one example, the solid acid can be deposited from an aqueous solution of $HfOCl_2$ and H_2SO_4(aq) via spin coating. The solid acid is heated sufficiently to produce a structurally rigid film 1212, such as by heating at about 50 °C for about 2 minutes. In the printing mode of operation, the substrate 1210 can be placed on a heated platen (about 25 – 300 °C), and an ink containing an oxide precursor 1214, e.g., copper formate, can be applied in a desired pattern by delivery through an ink-jet head or by bringing the substrate 1210 into contact with a template containing the precursor 1214. The template comprises a portion of a microcontact, letterpress, or gravure printer. Under heated conditions (greater than about 250 °C), the precursor 1214 decomposes to an oxide, subsequently reacting and interdiffusing with the solid acid, forming a product 1216 that can readily be washed or etched to reveal a pattern 1218. The oxide precursor also may be replaced by an ink suspension or paste containing fine oxide micro- or

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nanoparticles. Application of the fine particles with or without heating results in a direct reaction to form a product that can be etched to reveal a pattern.

An alternate embodiment is shown in FIG. 13 for producing a patterned oxide on a selected substrate 1310. The initial step involves depositing a solid acid 1312 or base onto the substrate. The oxide precursor 1314 is then applied as a blanket coat via spin coating, printing, chemical vapor, or physical vapor deposition. A pattern of activated precursor 1316 is then formed by exposure to an energy source, such as light, via a photomask. Suitable light sources include an unfiltered deuterium lamp or a light source producing light at 193 nm, among others. Alternatively, a pattern of activated precursor 1316 is formed by directly writing with a focused laser or electron beam. If necessary, the activated and patterned structure 1316 can then be heated to a temperature from about 125 °C to about 350 °C to promote interdiffusion of the two layers. The exposed areas can then be etched to produce the desired pattern 1318. A procedure to improve exposure sensitivity involves using a very thin layer (about 2 nm) of oxide precursor on the solid acid. The precursor layer is then covered with a layer of an oxide that is deposited via any suitable technique, such as chemical or physical vapor deposition or by solution casting of oxide nanoparticles. The layers interdiffuse following exposure of the thin layer of precursor.

The processes described above correlate to a positive resist technology. It is also possible to select solid acids/bases and precursors that will produce insoluble products. These products can be used to produce positive images in at least two ways. In one embodiment, the two layers completely interdiffuse to form a single insoluble layer. Following printing or exposure and development, the soluble portions of the film are then washed or etched to reveal a positive pattern. In an alternative approach, interdiffusion occurs only at the interface between the precursor and the solid acid/base to produce a thin, insoluble barrier layer. This barrier layer is then used to control the etching of the film stack to produce a positive image. The barrier layer is photosensitive. Prior to light exposure, it prevents reaction between the precursor and solid acid/base layers that would otherwise readily interdiffuse on contact. Once the barrier layer is photosensitized,

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it becomes a reactive oxide. The barrier is "broken," and the top layer can then interdiffuse with the lower layer.

Next-generation patterning, whether based on photo or imprinting, uses masks or templates, typically fabricated by electron-beam lithography. Many of these templates or masks are being fabricated with the hard mask HSQ (hydrogen silsesquioxane). HSQ masks are widely used for fabricating a variety of electronic, data storage, and microelectromechanical devices. HSQ is also under development as a hard master/template for imprint lithography.

Masks or templates can be fabricated using the films described herein in a single layer process as shown in FIG. 14. The first step of the process involves depositing a thin film (from about 1 nm to about 100 nm) of an inorganic precursor 1410 onto a substrate 1412. The inorganic precursor1410 may be a solid acid or base, e.g., hydrated sulfate, phosphate, nitrate, silicate, aluminate, borate, or mixtures thereof, containing one or more of the metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu in combination with peroxide or similar coordinating anion. In addition the solid acid/base and peroxide mixture can contain one or more of NH_3, OH, F, Cl, Br, I. The solid acid/base is preferably deposited via spin coating, liquid misting, or printing; physical and vapor deposition are additional options. As one example, the solid acid can be deposited from an aqueous solution of $HfOCl_2$ H_2SO_4(aq), and H_2O_2(aq) via spin coating. The solid acid is heated sufficiently, such as to a temperature of from about 50 °C to about 125 °C, and for a period of time from about 10 seconds to about 10 minutes to produce a structurally rigid film. The film is then exposed through a photomask or via a defined laser or electron beam to induce condensation in the exposed areas. The solubility of exposed areas 1414 decreases relative to unexposed regions, so the unexposed regions can be selectively etched in acid or base. Examples of acids or bases that can be used include hydrochloric acid, sulfuric acid, hydroxgen peroxide, sodium hydroxide, and tetramethyl ammonium hydroxide, among others. Typically, the concentration of the acids or bases used is within the range of about 0.1 M to about 1 M. The film is then developed in aqueous acid or base to etch the unexposed regions following an optional thermal cure at a temperature greater than about

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100 °C. This process produces a negative-tone image in the film. For many compositions, the resulting patterned films are amorphous, providing the means to realize high-resolution, small critical-dimension patterning without the limitations generally associated with crystalline films. By preheating the applied film to higher temperatures prior to field exposures, differential etching rates can be induced to realize positive-tone images. FIG. 15 demonstrates differential etching rates for thermally pre-treated, single-layer film. The graph demonstrates that thermal treatment affects etching rates such that exposed regions etch faster than unexposed regions following an initial time.

In another embodiment, a HafSOx film is treated with a mixture of sodium hydroxide and hydrogen peroxide, resulting in anion exchange and formation of a $M(OH)_x/H_2O_2$ film. Alternatively, a previously prepared $M(OH)_x$ film may be soaked in hydrogen peroxide to form a $M(OH)_x/H_2O_2$ film. The resulting $M(OH)_x/H_2O_2$ film is then patterned by exposure to light or an electron beam. These techniques provide a means for directly patterning simple of complex MO_x films without a polymer resist. For example, HfO_2 films may be directly patterned for use as high k dielectrics in Si CMOS circuits and printed electronics applications. In another example, a patterned TiO_2 film can be produced from a $Ti(OH)_x/H_2O_2$ film formed by solution deposition of $Ti(OH)_4$ in H_2O_2.

These methods substantially eliminate diffusion used in two-layer embodiments, lower exposure doses, and improve line-edge roughness and critical dimensions. FIG. 16 is an AFM (atomic force microscope) image of a HafSOx film patterned via a single-layer, negative tone process with an electron beam at dose levels ranging from greater than 0 $\mu C/cm^2$ to at least 400 $\mu C/cm^2$. The nanometer scale to the right of the image indicates the height of the features etched into the film. As shown in FIG. 16, features have been written via electron-beam exposure at dose levels as low as 2 $\mu C/cm^2$. This dose level is comparable to the best known chemically amplified polymer resists and 1000 times lower than that previously demonstrated for an inorganic resist. Features can be produced with a resolution of less than about 20 nm. In addition, the films demonstrate structural integrity (e.g., smooth, dense, pinhole-free) to less than 3 nm, nearly an order of magnitude smaller than that demonstrated for HSQ.

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The film application, heating, and etching steps associated with a polymer resist, as well as the vacuum and high-temperature processing steps of the inorganic material, have been eliminated in the patterning process. The resulting patterned film could be a functional component of an electronic device, a hard mask for subsequent patterning of the underlying substrate, or a template for imprinting. Except for the electron-beam exposure, all processing is conducted in a normal environment in air. Considering the elimination of several processing steps, the disclosed technique provides a new method to improve device production yields and lower fabrication costs. Relying on the exclusive use of aqueous chemistries, the process is also environmentally green, and washed products can be completely recovered and recycled. The technique has applications to many advancing technologies. Its use is not restricted only to the systems described herein.

B. Imprint Lithography

Hot embossing and photo-initiated imprint lithography are additional methods for producing patterns in HafSOx, ZircSOx and related materials. The hot-embossing process, illustrated schematically in FIG. 17, most commonly has been applied to creating patterns with organic polymers. The semi-solid form of HafSOx and related compositions provides an opportunity to pattern inorganic materials having much higher mechanical strength, chemical stability, and unique electrical and optical properties relative to organic polymers.

With reference to FIG. 17, HafSOx or related inorganic material, instead of an organic polymer, is solution deposited, such as by spin coating or inkjet printing, on a suitable substrate 1712 to form HafSOx layer 1714. Substrate 1712 and HafSOx layer 1714 define laminate structure 1710. A stamp 1716 with unit features of desired size scale, such as nanometer, micrometer or millimeter size scale, is pressed into the semi-solid HafSOx or related film layer 1714 to form stamped layer 1718. Stamped layer 1718 and substrate 1712 are then heated to harden the HafSOx. The stamp is then removed to define a patterned HafSOx material in patterned laminate structure 1720.

Alternatively, peroxide or related small, weakly coordinating ligand can be added to HafSOx, ZircSOx, and related materials. Subsequently, during the

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stamping step, the film can be exposed to short wavelength light, promoting chemical condensation and hardening of the patterned film. The stamp is then removed to define a pattern film. This technique represents a new innovation in step-and-flash imprint lithograpy (SFIL) that is commonly used to imprint polymer materials.

C. Measuring Device

The chemistry developed for the bilayer positive resist technology noted above also can be used to fabricate a physical ruler, as illustrated in FIG. 18, for use in standardizing measurements in suitable fields, such as electron microscopy. In this application, a nanolaminate 1810 of alternating acid-soluble layers 1812 and acid-insoluble layers 1814 is deposited. The acid soluble layers are formed by solution deposition of a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8. Typically this layer is doped with copper. The acid-insoluble layers are formed by solution deposition of a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to 3.8.

The widths of the layers 1812 and 1814 are accurately determined, such as by using X-ray reflectivity. The acid-soluble layers 1812 are then etched to reveal a

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finger-type pattern 1820 that can be used as a secondary reference in accurately measuring objects in an electron microscope.

D. Corrosion Barriers

The precursor liquid can be coated onto a suitable substrate, such as a metal or alloy or ceramic, to form a corrosion barrier. In addition, the liquid can be drawn into fibers, placed in a mold, or used alone. The liquid is converted into solid, stable form by any suitable process, including hydrolysis, annealing, or pyrolysis in air. Typically, this requires heating to temperatures, and for a period of time, effective to achieve the desired results, such as a temperature normally above 100 °C for at least a few seconds, more typically at least a few minutes.

Because of the atomically dense nature of the films, potential applications include, but are not limited to, thermal, corrosion and oxidation protection for metals and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal and ceramic-based systems, fibers for composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, catalyst supports, as well as many others. The ability to laminate the films provides an opportunity to randomize the location of defects in one layer relative to another, providing enhanced corrosion protection.

E. Optical Coatings

The precursor liquids can be coated as individual layers and in multilayer formats onto suitable optical substrates to produce antireflection coatings, dielectric mirrors, X-ray mirrors, interference filters, waveguides, planar coatings, and scratch-resistant surfaces. Multilayer periodicity is achieved by alternately depositing at least two material compositions. Single layer periodicity can be achieved by etching, as described for photolithography processes. The amorphous nature, sharp interfaces between layers, and abilities to control dielectric constants provides a process for realizing performance near theoretical limits.

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In multilayer or single layer configurations, which have been selectively deposited or etched, the periodic structure is appropriate for diffracting applications. Combinations of single or multiple materials and/or voids may define the structures. The use of void space allows for great contrast of physical properties within given structures. Functional characteristics may be enhanced or realized by the use of void space. Optical gratings may be similarly defined.

Because substantially smooth surface films can be deposited according to embodiments of the method disclosed herein, films may be used to planarize substrate layers such as metal, ceramics, and plastics that exhibit greater degrees of roughness.

F. Luminescent Films

A material may absorb energy and emit photons in a number of luminescent processes. The luminescent events may involve only the predominant phase (or host), or also may include added elements. A single material may serve as host for numerous luminescent additives. Many of the disclosed film compositions are visibly transparent with transparency potentially extending into the ultraviolet portion of the spectrum. These materials potentially function well as luminescent host materials. These materials can be selectively doped with common luminescent ions, including by way of example, and without limitation, Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof, to yield light-emitting films of interest for lighting and display applications.

G. Printed Electronics

Manufacturers are seeking new, efficient fabrication methods that eliminate the limitations of conventional vapor deposition and lithographic processing. Printing and related maskless techniques are widely regarded as paths forward for realizing advancement in manufacturing efficiencies for back-plane electronics.

The disclosed solution-processed thin films exhibit morphological and device-functional characteristics similar to those achieved by the most advanced vapor-phase processing methods. Solutions of the disclosed compositions can be imprinted, such as with microcontact, gravure, an inkjet printer or other suitable

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means. The resulting imprinted solutions can be used to fabricate stable inorganic transistor arrays exhibiting device mobilities of about 10 cm^2/Vs with dielectric leakage current densities less than about 20 nA/cm^2. Dielectric and semiconductor inks also can be printed onto glass substrates to produce transistor arrays having mobility of about 5 cm^2/Vs and dielectric leakage currents less than about 100 nA/cm^2. MIM capacitor arrays can be fabricated with relative dielectric constants greater than about 5 and leakage current densities less than about 50 nA/cm^2.

IV. EXAMPLES

The following examples are provided to exemplify particular features of working and/or hypothetical embodiments of the present invention. A person of ordinary skill in the art will appreciate that the scope of the present invention is not limited to the particular features stated in such examples.

Example 1

This example describes a general method that has been used to prepare solutions as sources for bulk precipitates or for use as thin film precursors. The following reagents were used: $HfOCl_2 \cdot 8H_2O$ (Alfa Aesar, 99+% excluding 1.5%Zr); $ZrOCl_2 \cdot 8H_2O$ (Wah Chang spectrographic grade); $La_2(SO_4)_3$ (Alfa Aesar, 99.9%); $La(NO_3)_3 \cdot 6H_2O$ (Johnson Matthey, 99.9%); $Ce_2(SO_4)_3 \cdot 8H_2O$ (Strem, 99%); CaO (Alfa Aesar, 99.95%); $(NH_4)_2SO_4$ (Mallinkrodt AR); H_2SO_4(aq) (EM Science, GR ACS, 95-98%); and NH_3(aq) (EM Science, GR ACS, 28-30%). All solutions were prepared by combining $HfOCl_2$ or $ZrOCl_2$ with $La_2(SO_4)_3$, $Ce_2(SO_4)_3$, or CaO as necessary for a total metal concentration of about 0.8 M, followed by addition of sulfate solution, for a total metal concentration of about 0.5 M. These solutions were directly used for heat-induced precipitation and spin-coating dielectric films. Additional modifications were made as necessary to serve as precursors for hydroxide precipitation reactions or nanolaminate depositions.

Example 2

This example describes a general method that has been used for bulk precipitation from solutions made according to Example 1. Precipitation was

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induced by immersing tubes of solution in a boiling water bath for 40 minutes. For hydroxide-induced precipitation, $HfOCl_2$ and $La_2(SO_4)_3$ were mixed as 23% La (metal percent), followed by addition of solutions of $La(NO_3)_3$ and $(NH_4)_2SO_4$ to provide a hafnium concentration ([Hf]) of about 0.39 M, a lanthanum concentration ([La]) of about 0.18 M, and a sulfate ([SO_4]) concentration of about 0.42 M. 1.9 mole equivalents (relative to total metals) of saturated NH_3(aq) were then added quickly and the resulting mixture stirred for 1 minute. All precipitates were separated from the supernatant by paper filtration with suction, including several rinses with de-ionized water. The filtrates were dried at room temperature for 1 day. Samples were subsequently heated in alumina crucibles in ambient air at temperatures from about 100 °C to about 1,500 °C for about 1 to about 4 hours. XRD data was collected with a Siemens D5000 diffractometer, utilizing Cu Kα radiation. Thermogravimetric data were collected with a Shimadzu TGA-50 by heating samples (10–20 mg) in a Pt crucible under flowing N_2(g), typically at a rate of 10 °C $minute^{-1}$, and holding for 15 minutes at the highest temperature. Inductively coupled plasma atomic emission spectroscopy (ICPAES) was conducted with a Jobin Yvon JY2000 analysis setup. Samples were dissolved in digestion bombs at 200 °C for a few hours and diluted to measurable levels.

Example 3

This example describes a general method that has been used for deposition of thin films using solutions made according to Example 1. Thin-films of HafSOx, ZircSOx, and derivatives with added La, Ce, or Ca, were deposited on Si substrates by spin-coating at 3,000 rpm for 30 seconds, followed by immediate hotplate polymerization at 135° C for 1.5–2 minutes (additional heating on a 325 °C oven surface for 15 seconds to about 2 minutes may be required for certain derivatives). This process was repeated until desired deposited film thicknesses were obtained. A final oven anneal at 325 °C for 5–10 minutes was used.

Precursors for nanolaminate films were prepared by adding H_2SO_4 to $HfOCl_2$ or $ZrOCl_2$ as 46% sulfate relative to metal. Solutions were diluted to a metal concentration of 0.03–0.13 M. Alternating layers of HafSOx and ZircSOx were deposited in the same fashion as described for dielectric films.

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The silicon substrates had a surface of SiO_2 or Ta metal. A 500-nanometer Ta surface was used for dielectric testing. A 200-nanometer SiO_2 surface was used for all other purposes. The surfaces were prepared for deposition by ultrasonic cleaning in (Decon Labs, Contrad 70) solution at 45 °C for 45 minutes, then rinsing the surfaces thoroughly with Millipore water before deposition.

XRD data were collected with a Rigaku RAPID diffractometer, employing Cu Kα radiation generated from a rotating anode at 50 kV and 270 mA. The incident beam angle was 7.6°, while the diffracted beam was collected with an image plate. XRR data were collected with Cu Kα radiation. Low angle reflections up to 10° (2θ) were collected at 0.005° steps. Transmission FTIR data were collected with a Nicolet 5PC spectrometer, with an uncoated substrate as reference. EPMA was collected.

MIM capacitor structures were completed by thermally evaporating circular contacts of Al (1.2 mm diameter) on deposited dielectrics. Parameters of dielectric constant and loss tangent were obtained. Bottom-gate transistor structures also were fabricated by sputtering inorganic channel materials without active heating. ZTO-channel devices were subsequently heated to 325 °C for 1 hour. Aluminum source and drain contacts were thermally evaporated. Transistor characterization was performed.

Example 4

This example describes a general method for producing smooth, dense, and pinhole-free ultra-thin nanolaminate films as thin as about 2 nm. Precursor solutions containing $HfOCl_2 \cdot 8H_2O$ or $ZrOCl_2 \cdot 8H_2O$, H_2O_2 (30%) and H_2SO_4(aq) were prepared as described in U.S. Patent Publication No. 2005/0242330 A1. The precursor solutions contained a metal ion concentration of about 0.05 M to 0.4 M with 70% H_2O_2 and 50% sulfate relative to metal. The difference in metal ion concentrations allowed for thickness per coat variation from 3 nm to 25 nm. Thin films were deposited on silica substrates with thermally grown SiO_2. Substrates were cleaned by using an ultrasonic bath with Contrad-70 solution at 45 °C for 60 minutes followed by a rinse with deionized water. Films were deposited by using a spin coater with a spin rate of 3000 rpm for 30 seconds followed by hotplate

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polymerization at 125 °C for 1-2 minutes. Spin-coating and polymerization steps were repeated until the desired thickness was reached. After the desired thickness had been reached, some films were heated to crystallization temperature. Other films were first treated in a 0.1 M-0.5 M NaOH bath for 1-2 minutes, then rinsed in a deionized water bath for 1-2 minutes before the thermal treatment.

Thin-film characterization using X-ray diffraction (XRD) analysis was performed on a Rigaku R-AXIS RAPID with Cu Kα radiation. Atomic force microscopy (AFM) measurements were performed using a Digital Instruments Nanoscope III Mulitmode AFM operated in contact mode with a Veeco NP-20 SiN probe and a scan frequency of 1.15 Hz. X-ray reflectivity (XRR) measurements were performed using a Bruker Discover D8 and used to determine surface and interfacial roughness of the films. Compositional analyses were acquired on a Cameca SX-50 electron microprobe equipped with 4 tunable wavelength dispersive spectrometers. Accelerating voltages of 12, 16 and 22 kV were used and averaged over 5 points to monitor O, Cl, Na, S, and Si Kα intensities and Zr and Hf Lα intensities. Standards used for analysis were MgO, Hf, Zr, FeS_2 (pyrite), $Ca_5(PO_4)_3Cl$ (apatite), Si, and Si_3AlNaO_8 (albite). Corrections to the raw intensity were made by using Probe for Windows automation and analysis package. The StrataGEM compositional analysis software package was used for thin film geometry corrections by comparing experimental K-ratios to simulated values.

Amorphous, atomically flat, dense, pinhole-free thin films were deposited via spin coating for the as-deposited and exchanged films. FIG. 19 is an AFM image of an unexchanged HafSOx film with a roughness of about 0.1 nm. FIG. 20 is a TEM image of an HfO_2 film following ion exchange of HafSOx and thermal treatment at 850 °C. Unexchanged films remained smooth and amorphous up to 600 °C for Zr and 650 °C for Hf. However, after heating above these temperatures, films crystallized and became rough, forming volcano-like features at the surface. FIG. 21 is an AFM image of a HfO_2 film deposited on silica. The HfO_2 film was formed by thermal decomposition of $HafSO_x$. The resulting film had a roughness of about 5 nm, resulting in volcano-like peaks. These features were most likely caused by the loss of SO_3. This was supported by thermal gravimetric analysis of Hf sulfate

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powder, where sulfate decomposition
(SO_3 (g) → SO_2 (g) and ½ O_2 (g)) occurs above 700 °C.

To eliminate the volcano effects, films were treated in a 0.1-0.5 M NaOH(aq) bath for 1-2 minutes to remove the SO_4^{2-} and Cl^- anions from the film before heating. NaOH previously has been shown to effectively exchange hydroxy anions for other anions in zirconium salts. The NaOH treatment caused a thickness reduction of 40-45% (giving layer thickness of 2-15 nm), but the treatment had little effect on the smoothness (~1Å) or amorphous nature of the films when heated below 500 °C or 550 °C for zirconia and hafnia, respectively.

FIG. 22 is an AFM image of a HafSOx film deposited on silica, subsequently treated with 0.1 M NaOH and heated to 450 °C for 10 minutes. The resulting film had a roughness of approximately 0.1 nm. Films heated above these temperatures crystallized, yet remained smooth at temperatures up to 850 °C.

FIG. 23 shows a HfO_2 film deposited on silica, subsequently treated with 0.1 M NaOH and heated to 850 °C for 10 minutes. The resulting crystallized film remained smooth with a roughness of about 0.2 nm.

A drop in crystallization temperature was seen in the X-ray diffraction plots (FIGS. 24-27). In FIGS. 24-27, the substrate peaks have been removed with software. The *'s represent the major tetragonal phase peaks. FIG. 24 is an XRD plot of the untreated HfO_2 film crystallized as a mixture of tetragonal and monoclinic phases at 700 °C. The HfO_2 plot is a reference plot for the monoclinic phase. In contrast, FIG. 25 is an XRD plot of the 0.1 M NaOH-treated hafnia film crystallized only in the monoclinic phase at 550 °C. The HfO_2 plot is a reference plot for the monoclinic phase. FIG. 26 is an XRD plot of untreated zirconia films crystallized in a mixed monoclinic and tetragonal phase at 650 °C. The ZrO_2 plot is a reference plot for the monoclinic phase. As seen in FIG. 27, the 0.13 M NaOH-treated zirconia films crystallized only in the tetragonal phase at 500 °C. Upon further heating, films developed both monoclinic and tetragonal phases. The tetragonal phases of HfO_2 and ZrO_2 have been observed in previous thin film studies. The lower crystallization temperature, crystallization and loss of thickness indicated that the NaOH treatment removed anions (SO_4^{2-} and Cl^-) from the thin films.

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Electron probe microanalysis (EPMA) of a film deposited from the 0.4 M Hf solution and heated to 350 °C for 5 minutes gave a film with composition $HfO_{1.32}(SO_4)_{0.61}Cl_{0.15}$. The chlorine in the film was a result of kinetic trapping as a consequence of the rapid thermal dehydration. Films that were treated in the NaOH(aq) bath did not have measurable sulfur levels (less than 0.01 atomic percent), and less than 0.3 atomic percent Cl was observed. This confirmed that the sulfur and chlorine were both removed from the films in the NaOH(aq) bath. EPMA also verified that the residual sodium left in the film after the treatment was less than 0.3 atomic percent.

Example 5

In a specific embodiment of the approach described above, hydrated indium and gallium nitrate salts ($In(NO_3)_3 \cdot 0.5H_2O$ and $Ga(NO_3)_3 \cdot 9.5H_2O$) were dissolved in methanol (CH_3OH). Final concentrations were [In] = 0.288 M, [Ga] = 0.170 M. Zinc powder was then added to the solution, and the flask sealed. The final concentration of zinc was 0.2 M. Reacting over a period of 1-7 days, the powder was slowly oxidized and dissolved to bring the total metal ion concentration to 0.658 M. The methanolic solution was exposed to air, and the methanol was allowed to evaporate at room temperature. The solid residue remaining in the solution was then dissolved in H_2O to a total metal concentration of 0.395 M. This precursor solution was spin-coated on a SiO_2 substrate with a conductive back contact and annealed to 450 °C for 1-4 hours. Following annealing, a transparent, amorphous $InGa_{0.6}Zn_{0.7}O_{3.15}$ semiconductor film was obtained as shown in the SEM image of FIG. 28. Aluminum source and drain contacts were thermally evaporated onto the oxide semiconductor film through a shadow mask to produce a thin film transistor (TFT). Field effect mobility for these TFTs was shown to exceed 8 $cm^2 V^{-1} s^{-1}$.

Example 6

This example describes two general methods of bilayer inorganic lithographic processing. In one working embodiment, a HafSOx film with a thickness from about 30 nm to about 60 nm was solution deposited onto a SiO_2/Si substrate. The substrate was placed directly onto a hot-plate set at about 50 °C and

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heated to impart structural integrity to the film. The resulting film was acid insoluble. The substrate was then placed on a heated platen (about 50 °C to 200 °C) of an ink-jet printer, where copper formate lines were printed onto the substrate via a thermal ink-jet head. Copper formate decomposed and diffused into the HafSOx film on heating, rendering the film soluble. Following a rinse in water, additional heating to about 300 °C, and development in dilute acid, the drawn lines were clearly evident as shown in FIG. 29.

In another working embodiment, patterns also were produced via photolithography. Exposure of a $HfO_{2-x}(SO_4)_x$ bilayer film with deep UV light using an unfiltered deuterium lamp promoted copper formate decomposition for subsequent interdiffusion and development of the pattern shown in FIG. 30. Feature sizes were reduced to about 22 nm with electron beam writing. The interdiffusion process can be spatially controlled via electron-beam energies to draw patterns and objects on the nanoscale. Highly resolved patterns were produced at charge dose levels near 150 $\mu C/cm^2$, representing a sensitivity similar to that of many polymer resists. FIGS. 31 and 32 are two patterns produced by electron-beam writing at a dose of level of about 200 $\mu C/cm^2$. In FIG. 31, the line spacing is 500 nm as measured by an electron microscope.

Example 7

This example describes general methods for patterning a single-layer inorganic film. A single inorganic film containing peroxide or related coordinating species is spin-cast, liquid misted, or ink-jet printed onto an appropriate substrate. The film is heated at modest temperatures of less than 100°C to provide structural integrity to the film. The film is then exposed through a photomask to high-energy light, a maskless pattern via spatial light modulation, a defined laser beam, or electron beam to define a pattern or other preferred film features. Two examples of photographically patterned films are shown in FIGS. 33 and 34. FIG. 33 is a patterned $ZrO_{2-x}(SO_4)_x$ film. FIG. 34 is a patterned TiO_2 film. The TiO_2 film was about 15-50 nm thick. It was patterned using an unfiltered deuterium lamp, followed by etching with 0.1-0.2 M HCl for less than 60 seconds. FIGS. 35-37 are $HfO_{2-x}(SO_4)_x$ films patterned by an electron beam. The films were about 30-60 nm

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thick. They were patterned using an electron beam at a dose level of 200 $\mu C/cm^2$, followed by etching with 5-12 M HCl for about 1-4 minutes.

In view of the many possible embodiments to which the principles of the disclosed invention may be applied, it should be recognized that the illustrated embodiments are only preferred examples of the invention and should not be taken as limiting the scope of the invention. Rather, the scope of the invention is defined by the following claims. We therefore claim as our invention all that comes within the scope and spirit of these claims.

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We claim:

1. A device comprising a thin film or laminate structure comprising at least one hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to about 3.8.

2. The device according to claim 1 wherein the thin film or laminate has a permittivity value within the range of from about 9 to about 12, a breakdown field up to at least 6 MV cm^{-1}, and a leakage current near 1 nA cm^{-2} at field strengths of 1 MV cm^{-1}.

3. The device according to claim 1 where the compound further comprises lanthanum, and has a formula $M_{1-z}La_zO_{2-x-z/2}(SO_4)_x$ (MSOx:La), where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to about 3.8.

4. The device according to claim 1 where the compound is HafSOx, HafSOx/La, ZircSOx, ZircSOx:La, HafSOx:Ce, or ZircSOx:Ca, the device having leakage current less than 50 nA cm^{-2} and permittivity values of from about 9 to about 12.

5. The device according to claim 1 where the device is a field effect transistor comprising HafSOx:La and/or ZircSOx:La as a gate dielectric and zinc indium oxide and/or zinc tin oxide as channels, the transistor having an on-to-off ratio of greater than 10^6, and gate leakage currents are in the range of pA cm^{-2}.

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6. The device according to claim 1, further comprising an optical substrate where the thin film or laminate structure forms a coating on the optical substrate.

7. The device according to claim 6 where the coating is an antireflective coating and/or the coating is transparent to visible or ultraviolet light.

8. The device according to claim 6 where the optical substrate and coating define a dielectric mirror, an X-ray mirror, an interference filter, a diffractive grating, and/or a waveguide.

9. The optical device according to claim 7 where the coating is selectively doped to provide a doped light-emitting layer having luminescent ions selected from Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, and combinations thereof.

10. The device according to claim 1 where the device is a master plate for imprint lithography and the thin film or laminate structure is deposited onto a flexible or glass substrate, the thin film or laminate structure comprises a first layer of HafSOx deposited onto the substrate and a second layer comprising ZircSOx:Cu, and where the laminate structure comprising the first and second layers is patterned by exposure to an energy source.

11. The master plate according to claim 10 where exposure to light or an electron beam through a mask causes the two layers to interdiffuse in exposed areas, thereby rendering previously undoped HafSOx layer soluble, the soluble HafSOx layer being removed to define at least partial printing features of the master plate.

12. A method for making a device, comprising:

providing a thin film or laminate structure, the structure comprising a substrate and one or more layers deposited onto the substrate;

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at least one of the one or more layers comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to about 3.8; and

exposing the structure to an energy source.

13. The method according to claim 12 where the thin film or laminate structure comprises a substrate, a first layer for patterning, and a second layer comprising the hafnium and/or zirconium oxy hydroxy compound, where the second layer is a positive resist layer, exposure to an energy source converts the resist layer material into a developer-soluble material, and the method further comprises removing resist layer material exposed to the energy source by treating the resist layer with a developer solution to pattern the structure.

14. The method according to claim 12 where the thin film or laminate structure comprises a substrate, a first layer for patterning and a second layer comprising the hafnium and/or zirconium oxy hydroxy compound, where the second layer is a negative resist layer, exposure to an energy source causes the resist layer to polymerize, and the method further comprises patterning the structure by treating the structure with a developer to remove material not exposed to the energy source.

15. The method according to claim 13 where the positive resist comprises a bilayer, where a second layer of the bilayer comprises an acid-soluble Cu-doped zirconium oxide sulfate (ZircSOx:Cu) film deposited on an insoluble hafnium oxide sulfate (HafSOx) film, and where exposure to an energy source comprising light or an electron beam through a mask causes the ZircSOx:Cu film and the HafSOx film to interdiffuse in exposed areas, thereby rendering the HafSOx film soluble.

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16. The method according to claim 12 where the hafnium and/or zirconium oxy hydroxy compound comprises sulfate, and where the sulfate is subsequently removed by ion exchange with an aqueous basic solution, the basic solution comprising a Group I metal hydroxide, soluble Group II metal hydroxide, soluble Group III metal hydroxide, soluble lanthanide hydroxide, ammonium hydroxide, and/or aqueous tertiary amine, or a combination thereof.

17. The method according to claim 12 comprising:

providing a suitable substrate comprising a semiconductor material, a metal, glass, silica, a polymeric material, or combinations thereof;

solution depositing a first HafSOx film onto the substrate;

solution depositing a second ZircSOx:Cu film onto the first film to form a laminate structure;

exposing the laminate structure to an energy source to cause the HafSOx film and the ZircSOx:Cu film to interdiffuse in exposed areas, thereby rendering previously undoped HafSOx film soluble; and

developing the exposed structure to remove HafSOx film.

18. The method according to claim 12 where the thin film or laminate structure comprises a substrate, a first layer of insoluble hafnium oxide sulfate (HafSOx) deposited onto the substrate, and a second layer comprising copper formate deposited onto the first layer, and where the laminate structure comprising the first and second layers is heated to a temperature from about 50 °C to about 200 °C to cause the copper formate to decompose and interdiffuse with the HafSOx layer, thereby producing a soluble product, the soluble product being removed.

19. The method according to claim 12 where the thin film or laminate structure comprises a substrate and a first layer comprising a solid inorganic acid or base, the solid inorganic acid or base comprising a metal having an atomic number in the range of 21-78, the first layer further comprising a peroxide or other coordinating anion, where the first layer is soluble in acid or base, the first layer is

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heated to a temperature from about 50 °C to about 125 °C to produce a structurally rigid film, and exposure to a laser, an electron beam, and/or light through a mask causes exposed areas of the film to become less soluble than unexposed areas, the unexposed areas being removed to define a pattern in the amorphous or crystalline film.

20. The method according to claim 19 where the film is exposed to an electron beam at a dose level of from greater than 0 $\mu C/cm^2$ to at least 400 $\mu C/cm^2$, more typically from about 2 $\mu C/cm^2$ to about 400 $\mu C/cm^2$, to define a pattern in the film with linewidths extending below 5 nm.

21. The method according to claim 19 where the patterned film is amorphous or crystalline, demonstrating structural integrity to less than about 3 nm.

22. The method according to claim 12, where the device includes a micro- or nano-channel array, and where the structure comprises a substrate, a first layer and a second layer, the second layer being a metal oxide layer, the method further comprising:

patterning the structure; and

exposing the structure to an energy source to form a durable material having a desired pattern produced by patterning the structure.

23. The method according to claim 12 further comprising stamping unit features of a desired size scale into a semi-solid hafnium or zirconium compound and related organic-free semi-solids to form a stamped layer that is thermally or photo hardened.

24. A device made according to the method of claim 12, the device selected from metal and metal/ceramic-based thermal protection systems, organic-based displays and electronics, solar cells, high emissivity coatings, interface coatings for oxide-based ceramic matrix systems, protective coatings on phosphors, environmental barrier coatings for metal- and ceramic-based systems, fibers for

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composites and fiber lasers, corrosion protection in molten metal processing, monolithic materials for thermal insulation, and catalyst supports.

25. A method for making a device having a corrosion barrier, comprising:

providing a device;

forming at least one corrosion barrier on the device comprising a metal oxide layer comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to about 3.8; and

exposing the compound to an energy source to form the corrosion barrier.

26. A method for forming fibers, comprising:

providing a composition comprising a hafnium and/or zirconium oxy hydroxy sulfate ($MO_{2-x-z/2}(OH)_z(SO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy tungstate ($MO_{2-x-z/2}(OH)_z(WO_4)_x$) compound, hafnium and/or zirconium oxy hydroxy borate ($MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$) compound, a hafnium and/or zirconium oxy hydroxy phosphate ($MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$) compound, and/or hafnium and/or zirconium oxy hydroxy silicate ($MO_{2-2x-z/2}(OH)_z(SiO_4)_x$) compound, where M is hafnium or zirconium, x and z may be fixed or variable, and have any value for x in a range of from about 0.1 to about 3.5/(polyatomic ion charge), and any value for z in a range of from 0.0 to about 3.8;

forming a solution comprising the compound;

drawing the solution into fibers; and

converting the fibers into solid, stable fibers.

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27. A method for making a metal oxide film where the film comprises at least two metals, the method comprising:

making a solution comprising dissolving one or more soluble salts consisting essentially of a metal cation and one or more anions in a non-complexing, non-aqueous polar solvent, where at least one of the metal cations has a formal charge greater than or equal to 3^+ and the concentration of metal cations with a formal charge greater than or equal to 3^+ exceeds 50 mol% of the metal cations in the metal oxide film, and where the solvent has a boiling point less than about 150 °C;

raising the pH of the solution, where raising the pH comprises adding a basic aqueous solution, adding a small amount of a soluble basic oxide, adding a gaseous compound capable of forming a basic aqueous solution, adding an electropositive metal which may consume protons and is incorporated into the film, adding an aqueous or gaseous oxidizing agent which consumes protons or decomposes counter ions but is not incorporated into the film, or any combination thereof;

producing a solid by evaporating the non-aqueous solvent;

dissolving the solid in water;

depositing the dissolved solid onto a substrate to form a patterned or blanket liquid film; and

thermally curing the film.

28. A method for making a metal oxide film, comprising:

providing a thin film or laminate structure, the structure comprising a substrate and one or more layers deposited onto the substrate, at least one of the one or more layers comprising a metal-acid film, the metal-acid film comprising a metal cation and an acid anion;

removing the acid anion by ion exchange with an aqueous basic solution, the basic solution comprising a Group I metal hydroxide, soluble Group II metal hydroxide, soluble Group III metal hydroxide, soluble lanthanide hydroxide, ammonium hydroxide, and/or aqueous tertiary amine, or any combination thereof; and

exposing the structure to an energy source, the energy source comprising a thermal energy source, a microwave energy source, a light source, or a laser.

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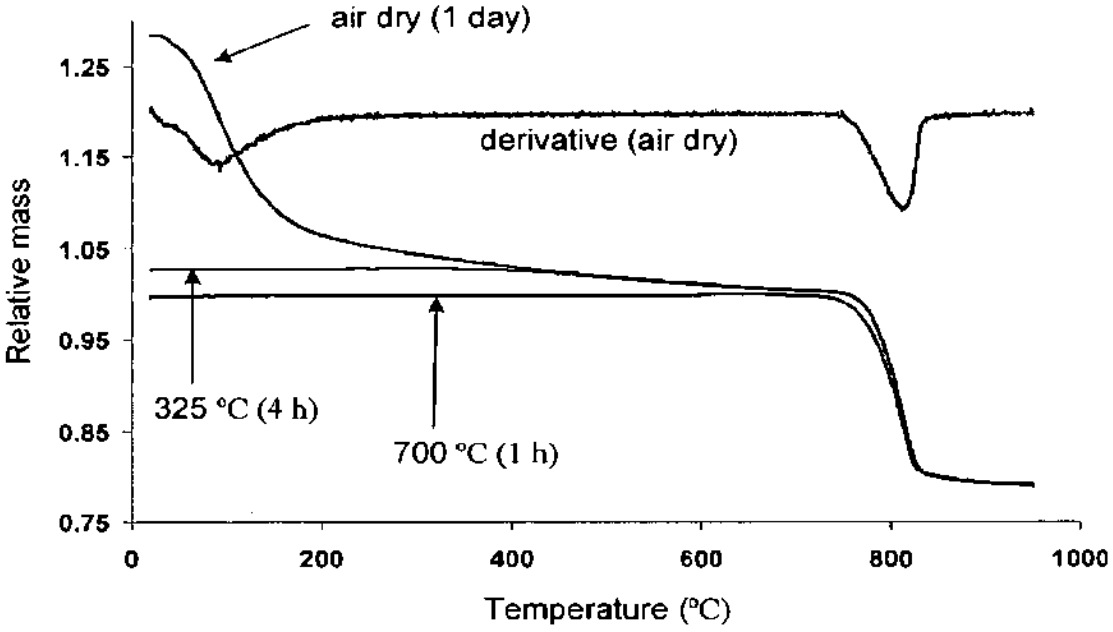

air dry (1 day)
derivative (air dry)
325 °C (4 h)
700 °C (1 h)
Relative mass
1.25
1.15
1.05
0.95
0.85
0.75
0
200
400
600
800
1000
Temperature (°C)

FIG. 1

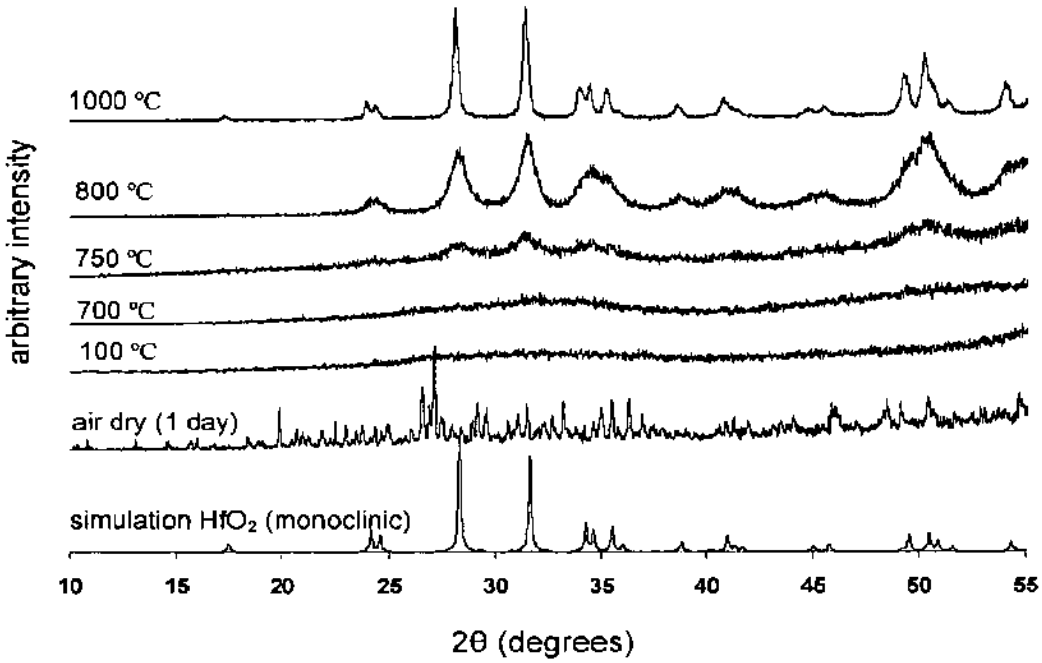

1000 °C
800 °C
750 °C
700 °C
100 °C
air dry (1 day)
simulation HfO2 (monoclinic)
arbitrary intensity
10
15
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 2

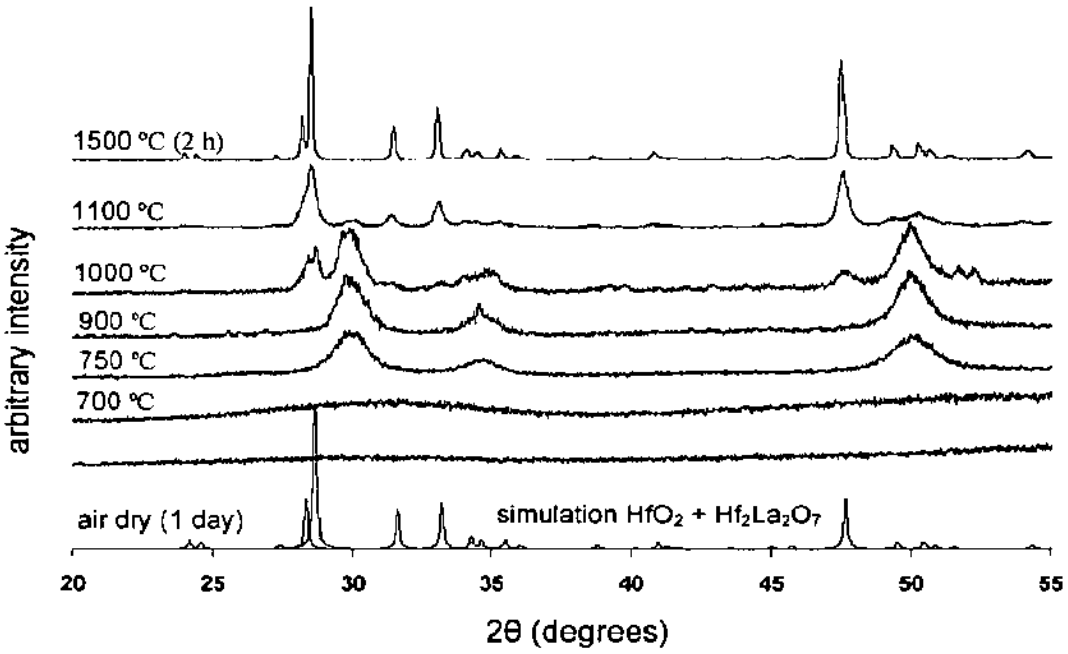

1500 °C (2 h)
1100 °C
1000 °C
900 °C
750 °C
700 °C
air dry (1 day)
simulation HfO_2 + $Hf_2La_2O_7$
arbitrary intensity
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 3

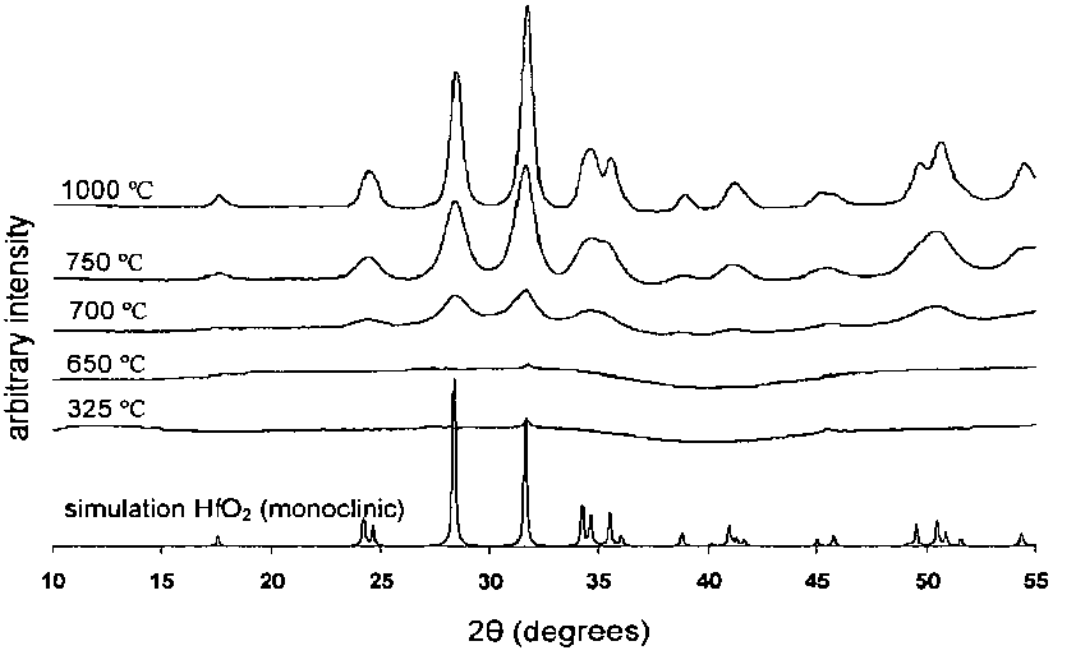

1000 °C
750 °C
700 °C
650 °C
325 °C
simulation HfO_2 (monoclinic)
arbitrary intensity
10
15
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 4

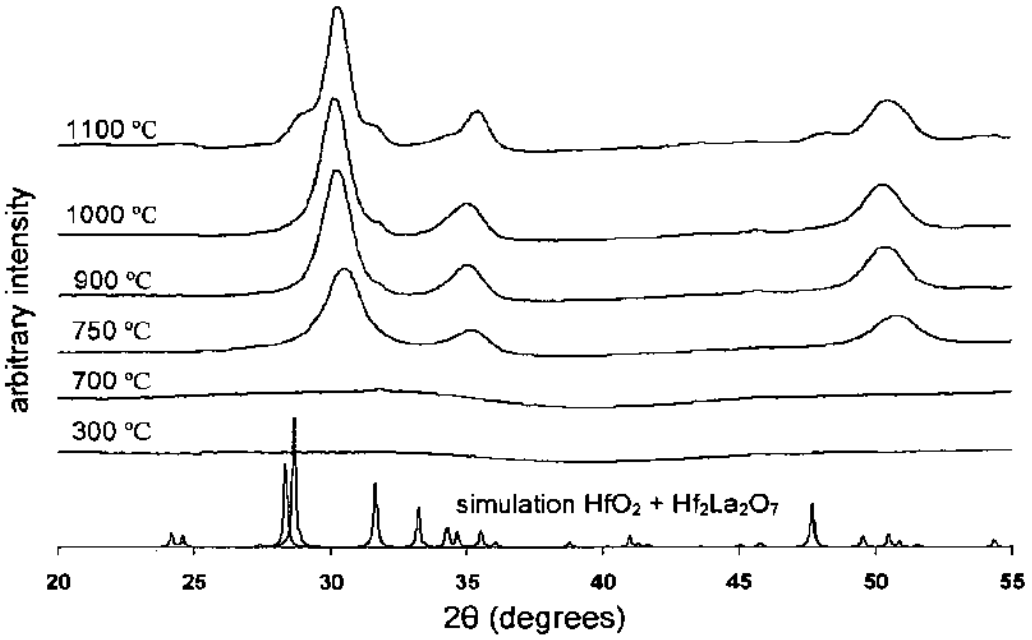

1100 °C
1000 °C
900 °C
750 °C
700 °C
300 °C
simulation HfO_2 + $Hf_2La_2O_7$
arbitrary intensity
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 5

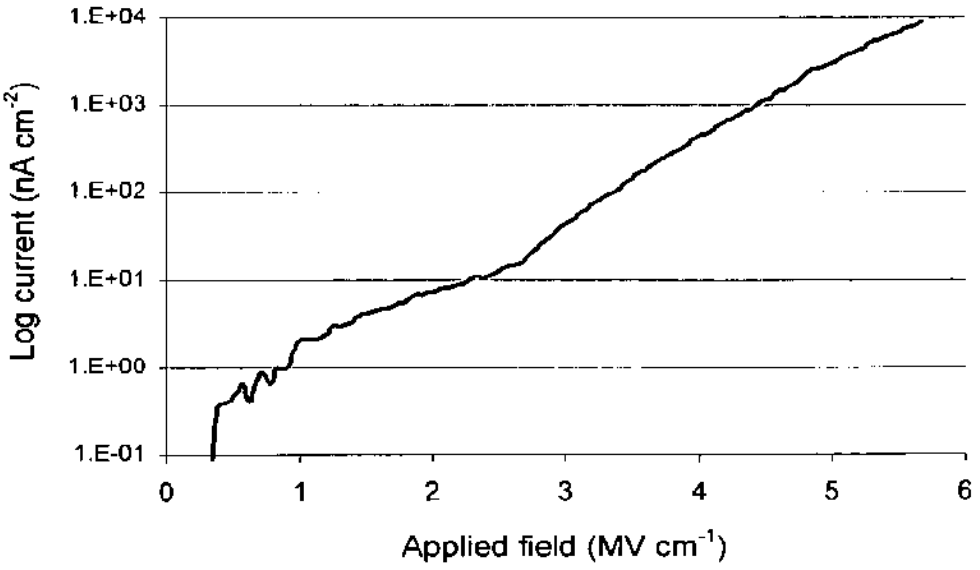

1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
Log current (nA cm^{-2})
0
1
2
3
4
5
6
Applied field (MV cm^{-1})

FIG. 6

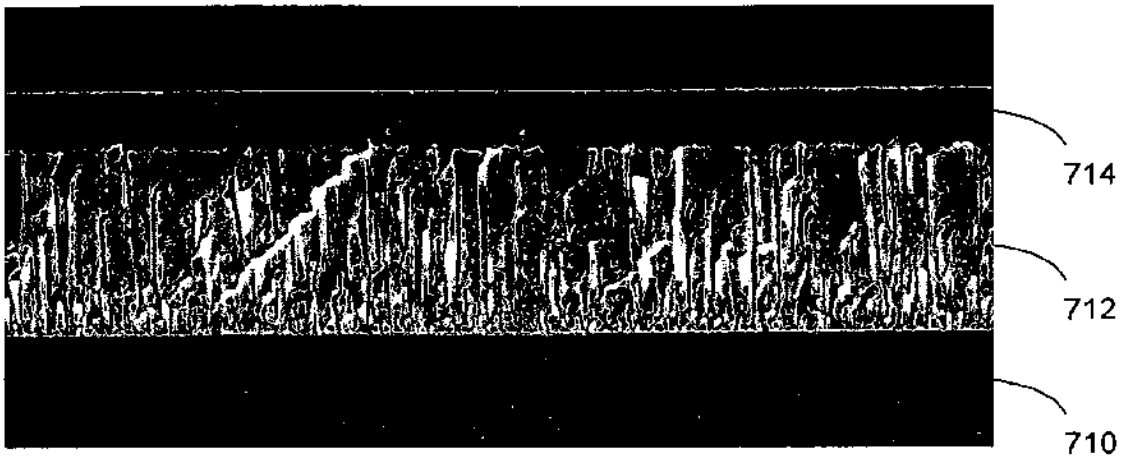


FIG. 7

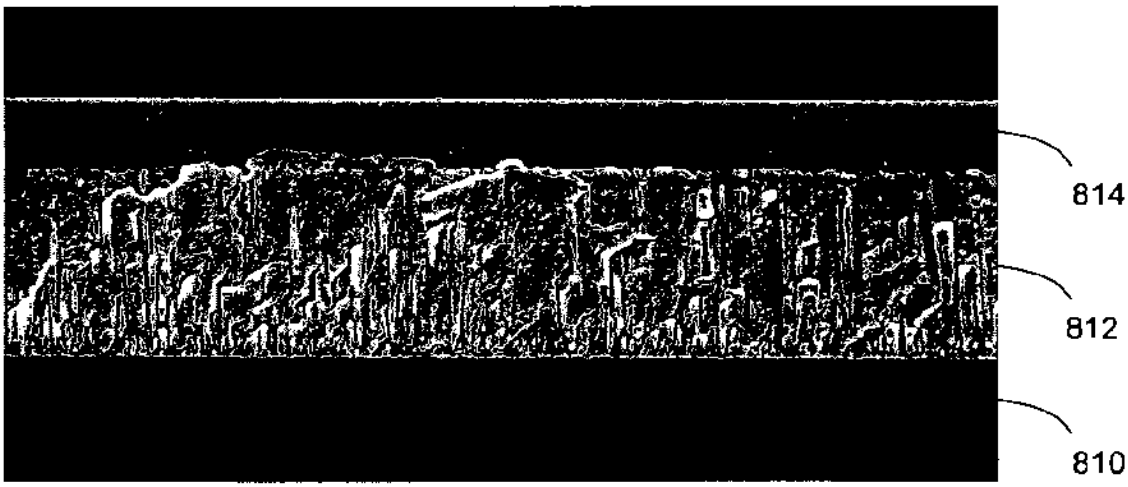


FIG. 8

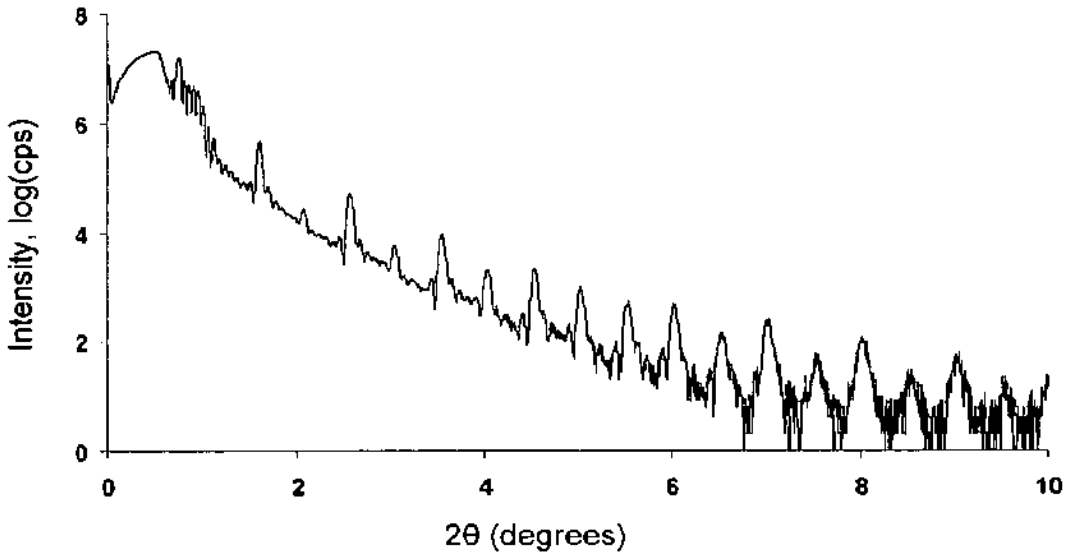


FIG. 9

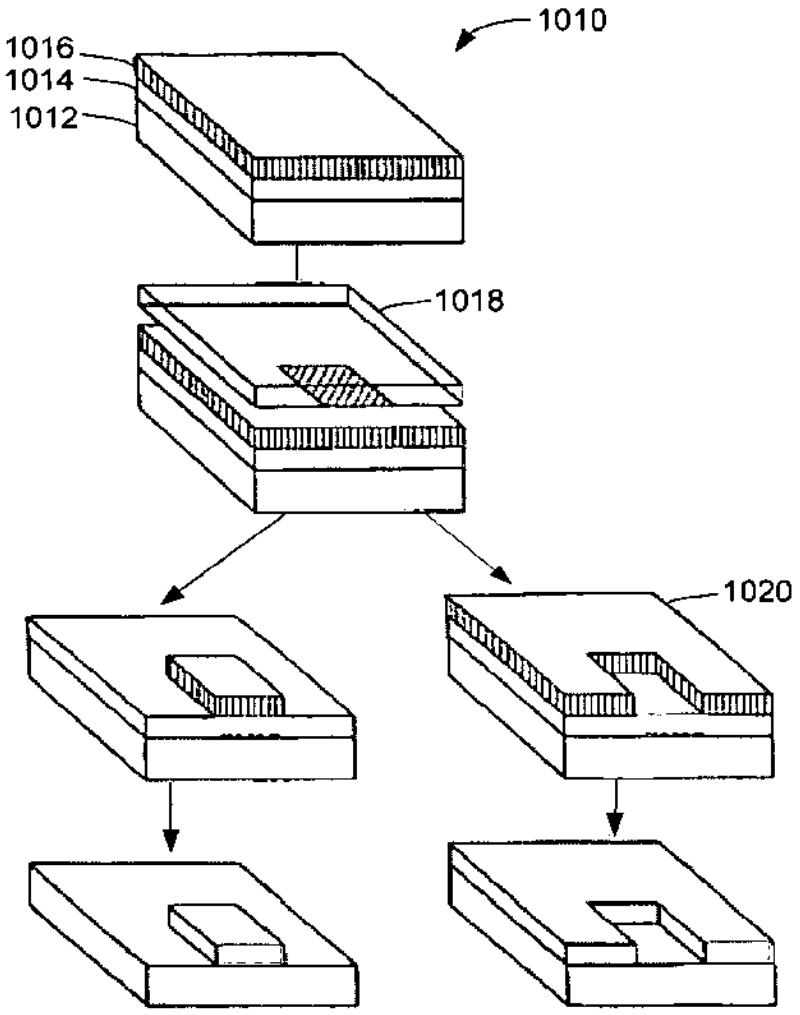


FIG. 10

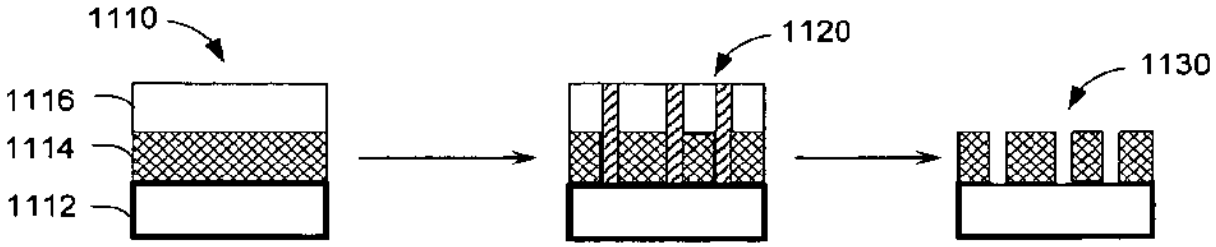


FIG. 11

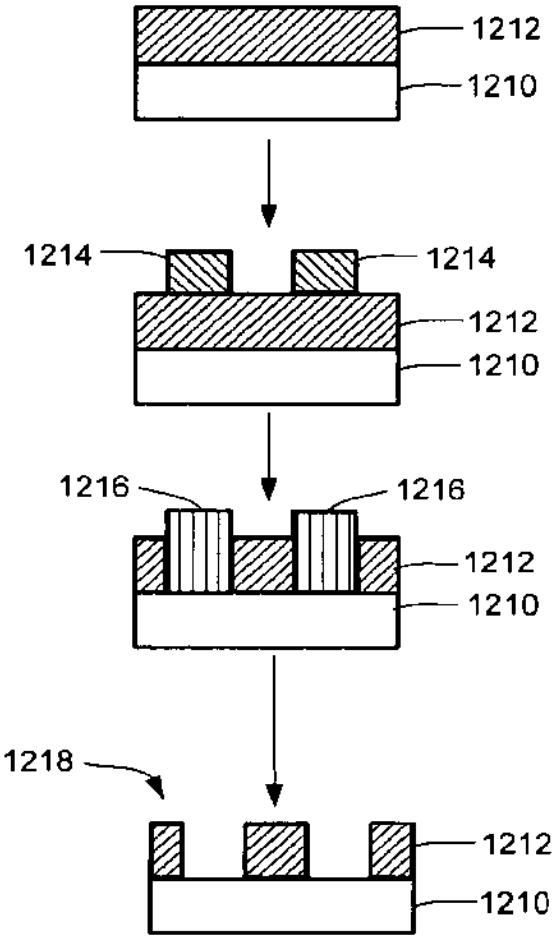

1212
1210
1214
1214
1212
1210
1216
1216
1212
1210
1218
1212
1210

FIG. 12

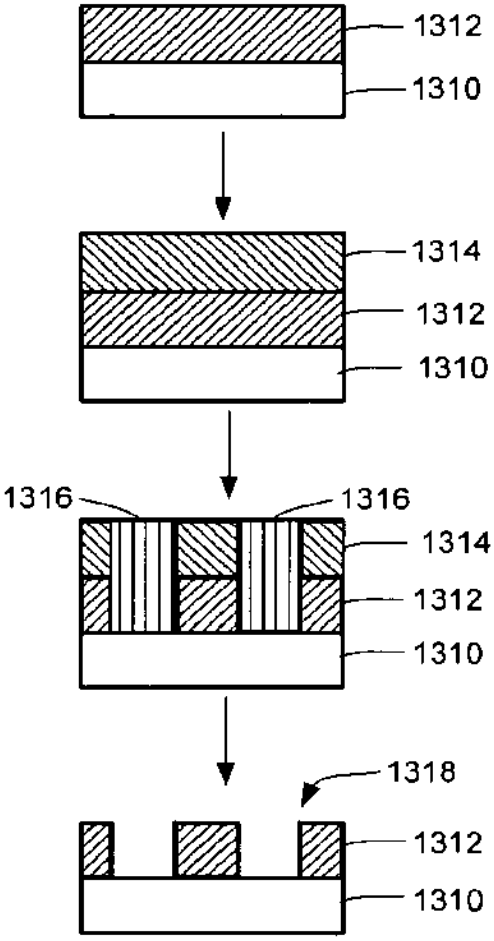

1312
1310
1314
1312
1310
1316
1316
1314
1312
1310
1318
1312
1310

FIG. 13

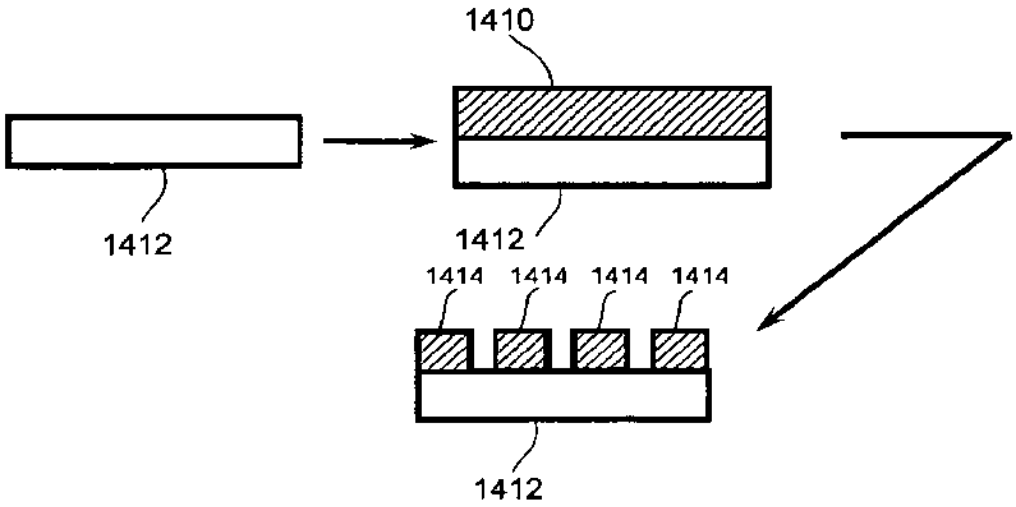

1410
1412
1412
1414
1414
1414
1414
1412

FIG. 14

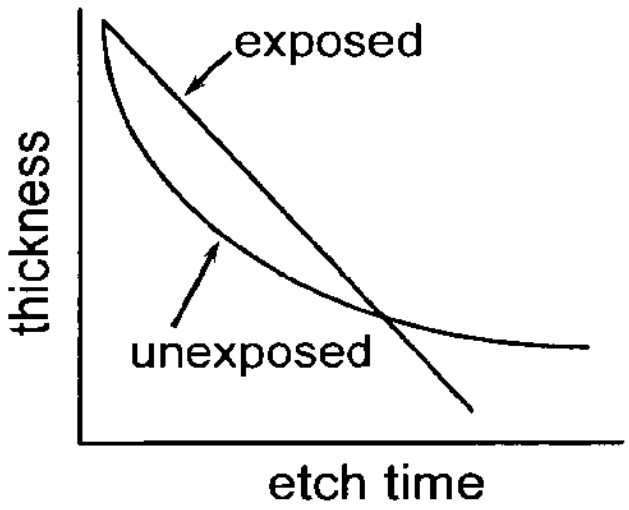

exposed
thickness
unexposed
etch time

FIG. 15

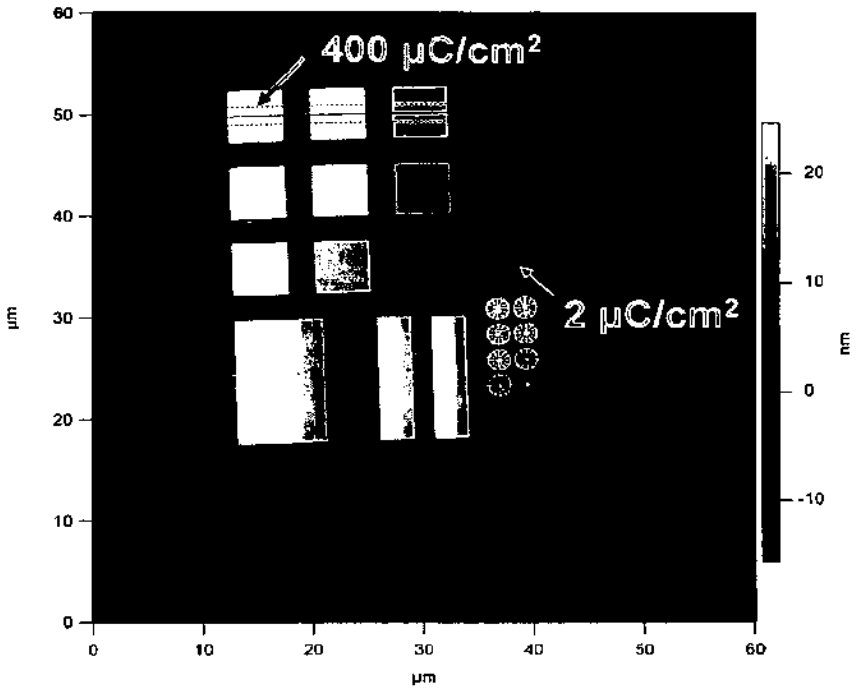

400 μC/cm²
2 μC/cm²
μm
μm
nm
60
50
40
30
20
10
0
0
10
20
30
40
50
60
20
10
0
-10

FIG. 16

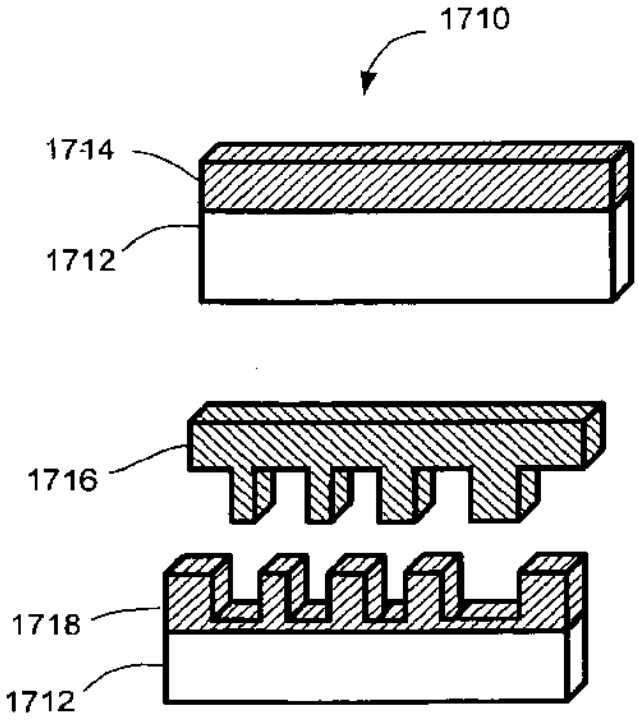

1710
1714
1712
1716
1718
1712

FIG. 17

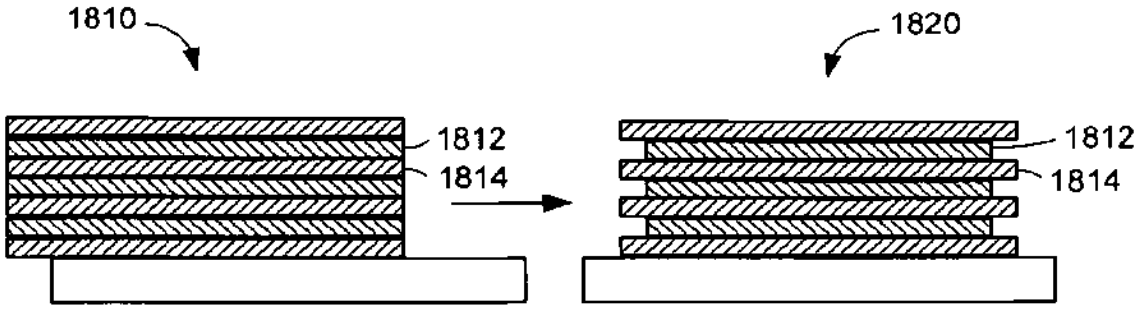


FIG. 18

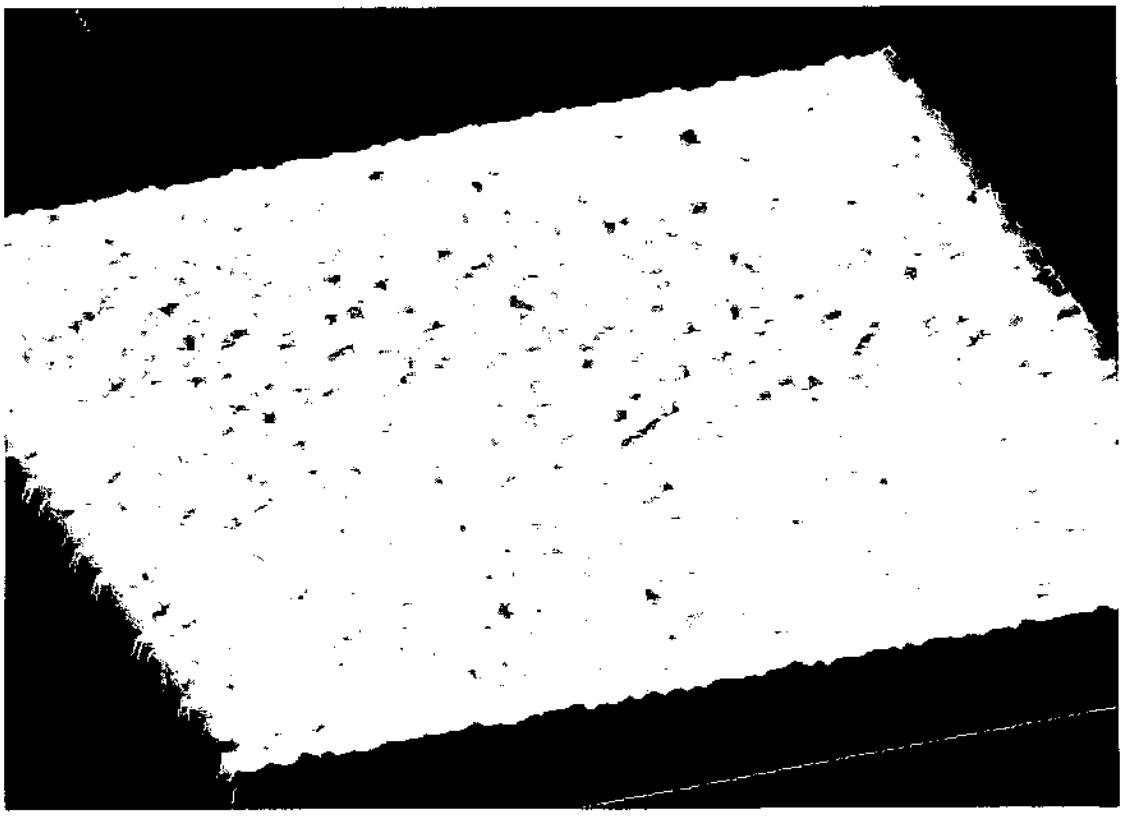


FIG. 19

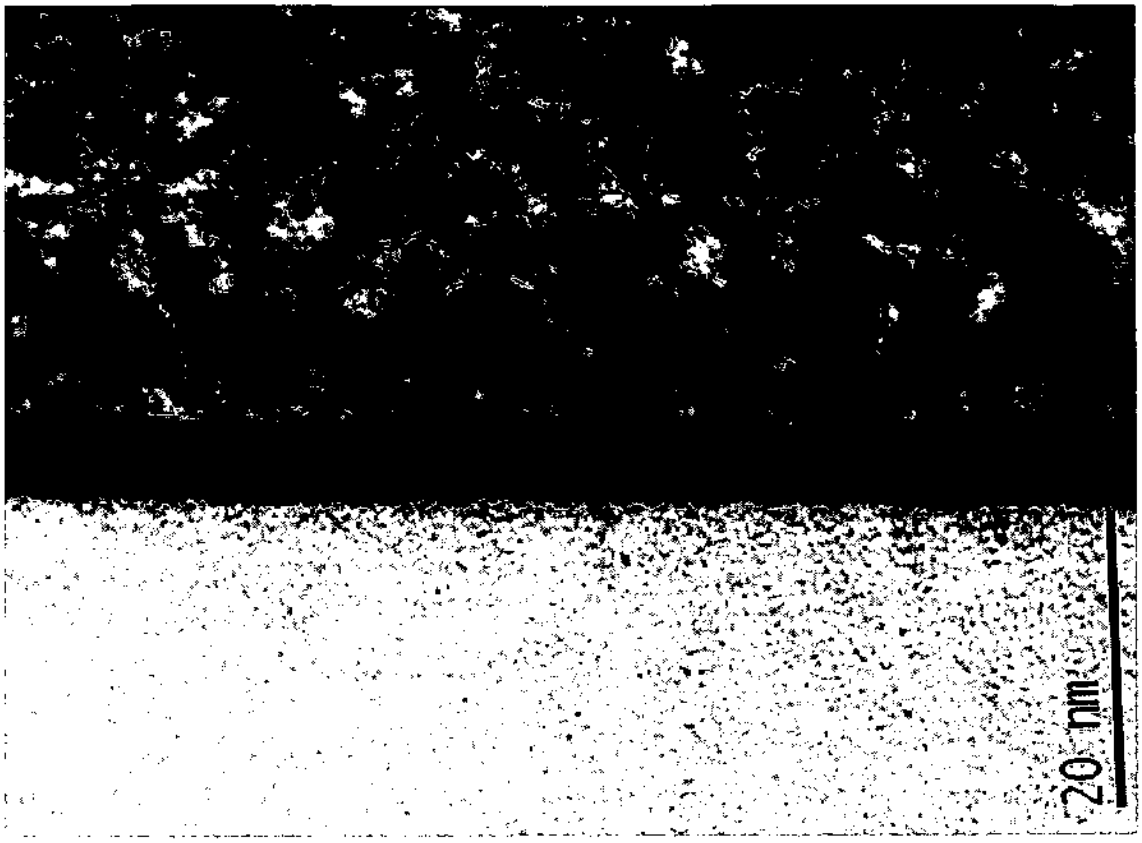


FIG. 20

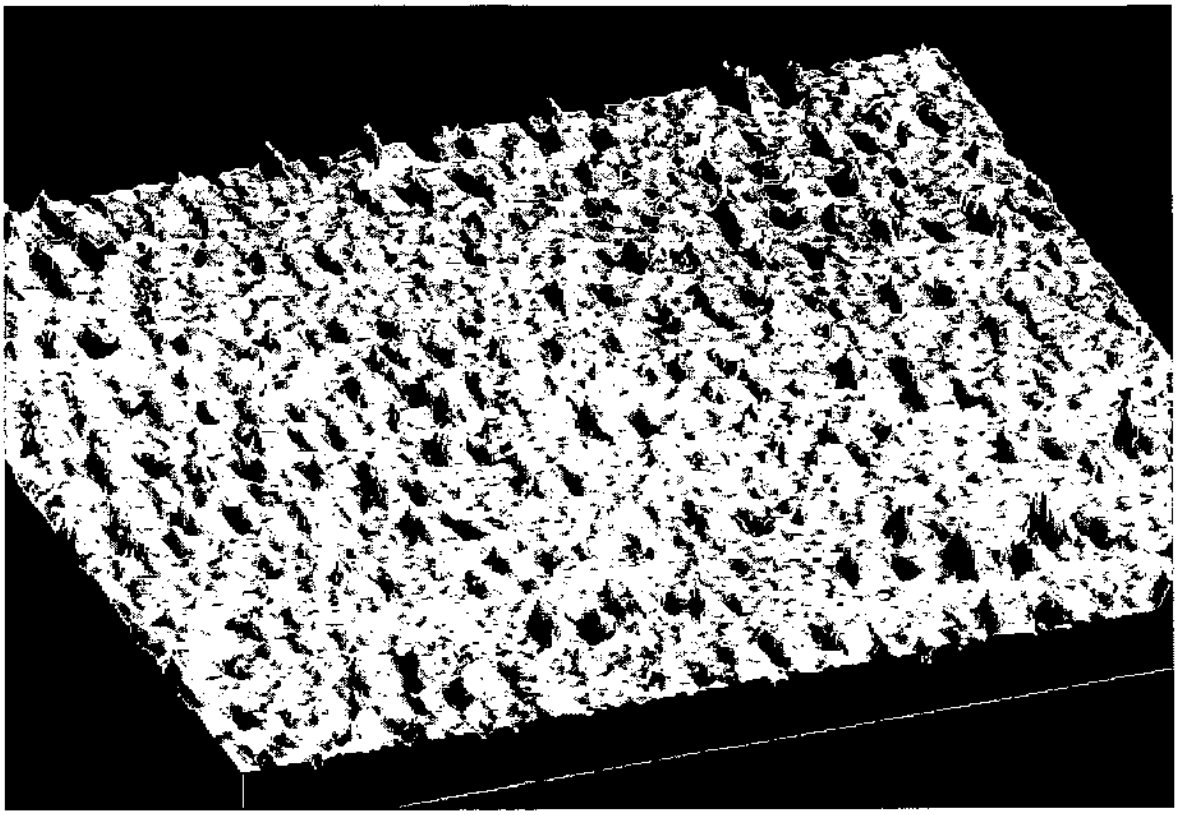


FIG. 21

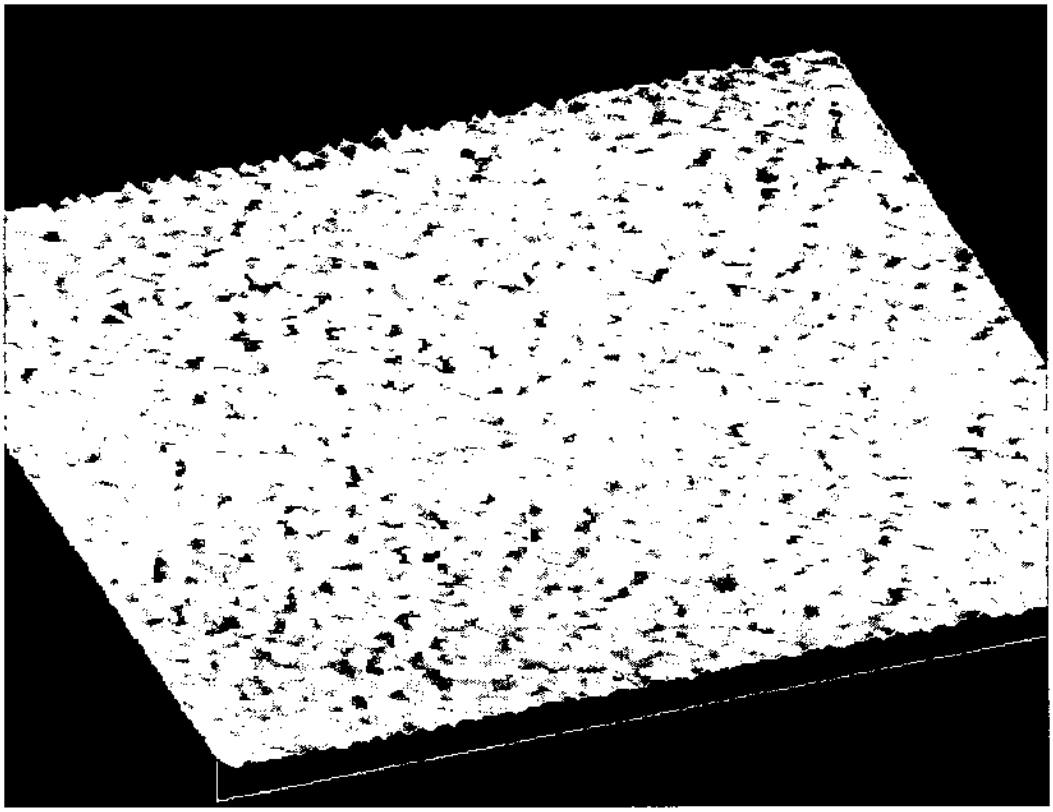


FIG. 22

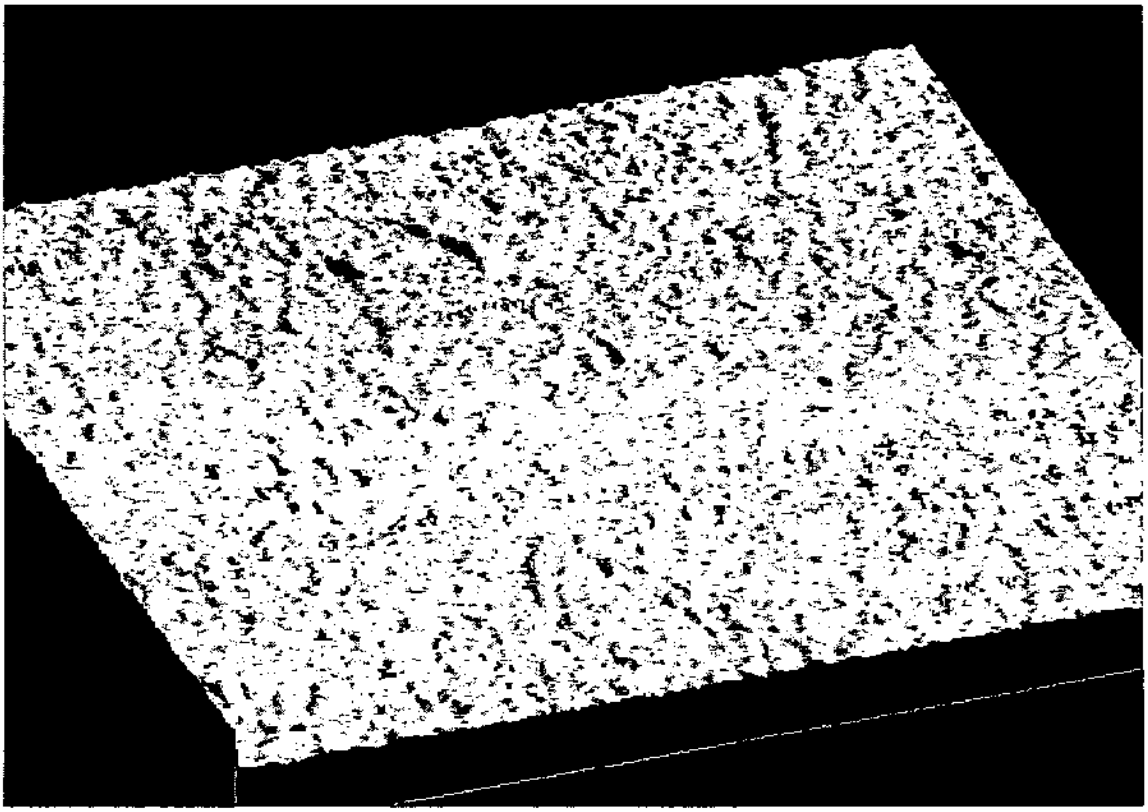


FIG. 23

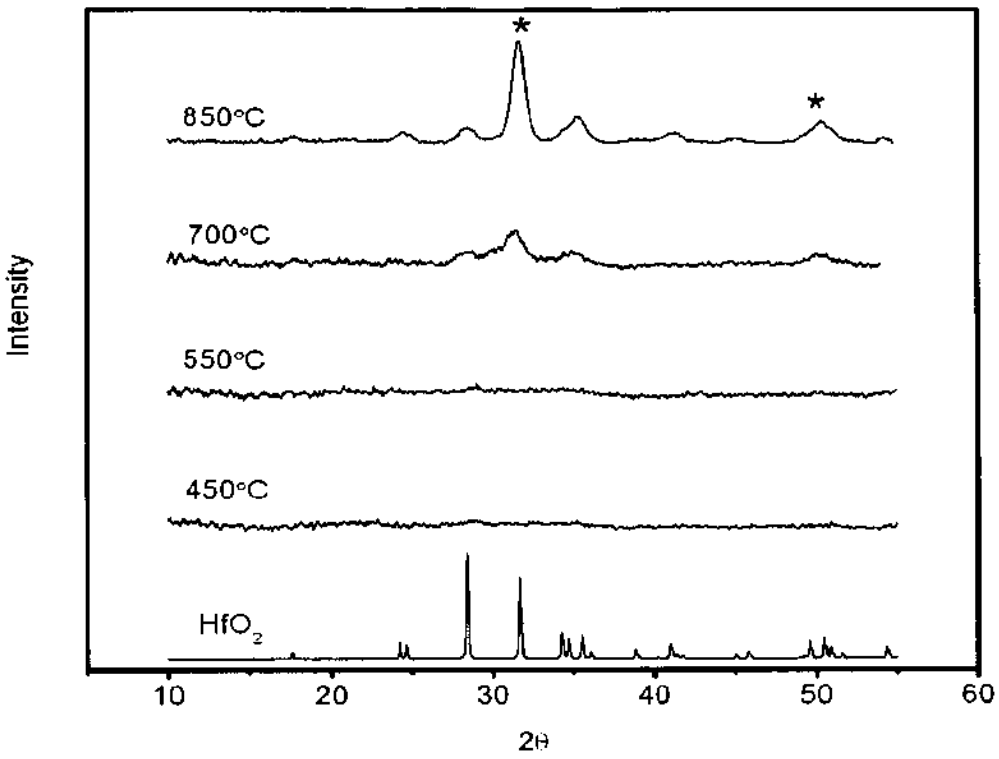


FIG. 24

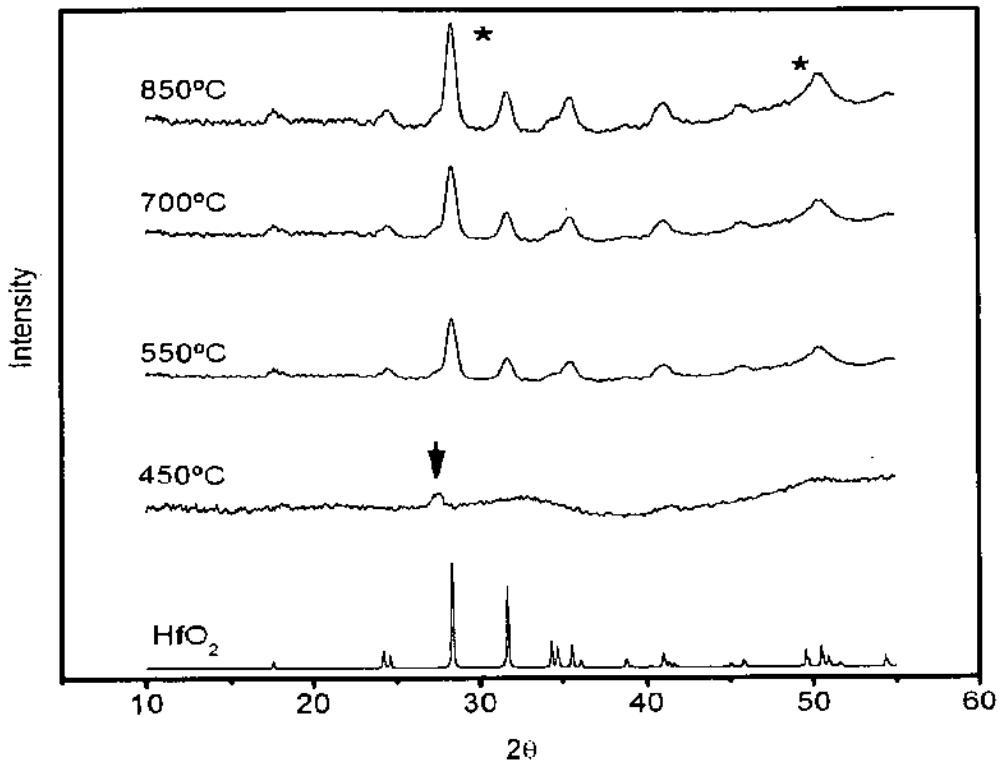


FIG. 25

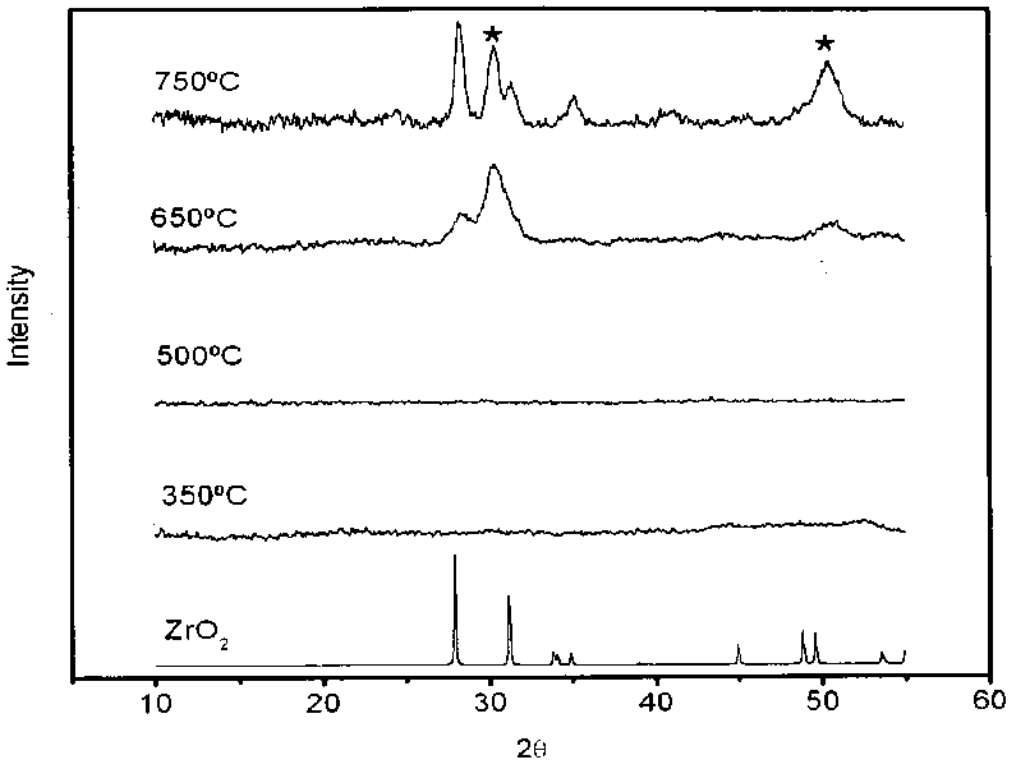


FIG. 26

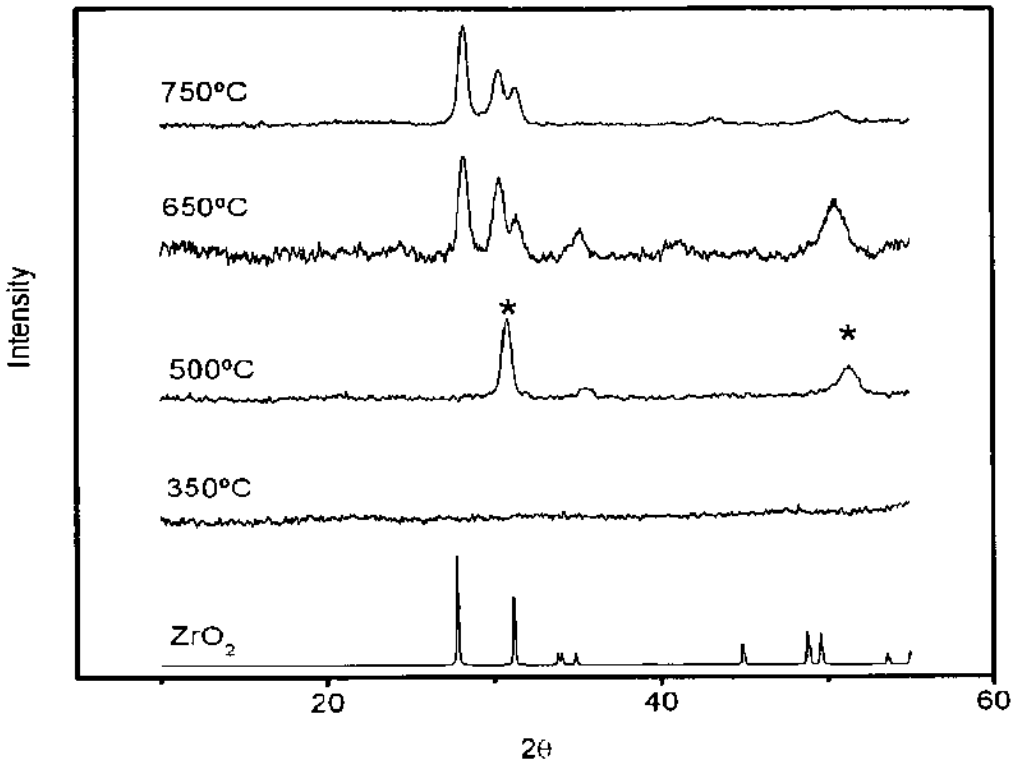


FIG. 27

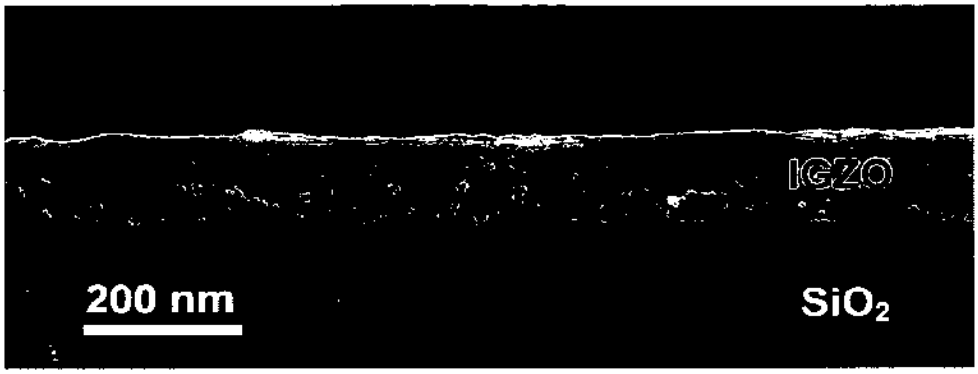


FIG. 28

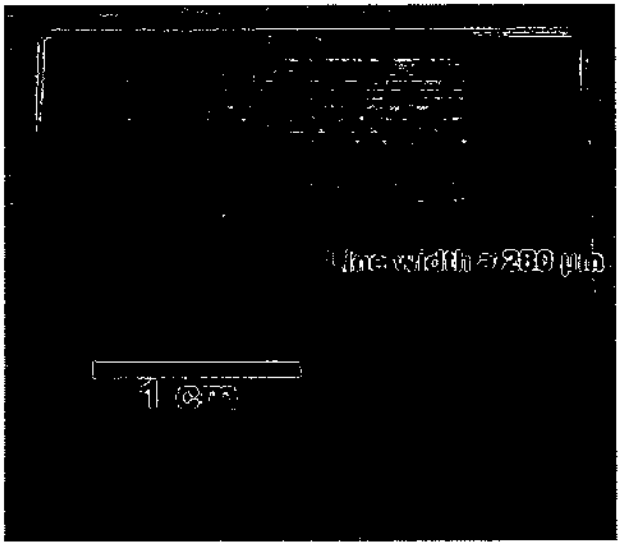


FIG. 29



FIG. 30



FIG. 31

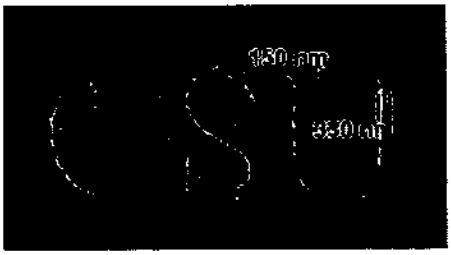


FIG. 32

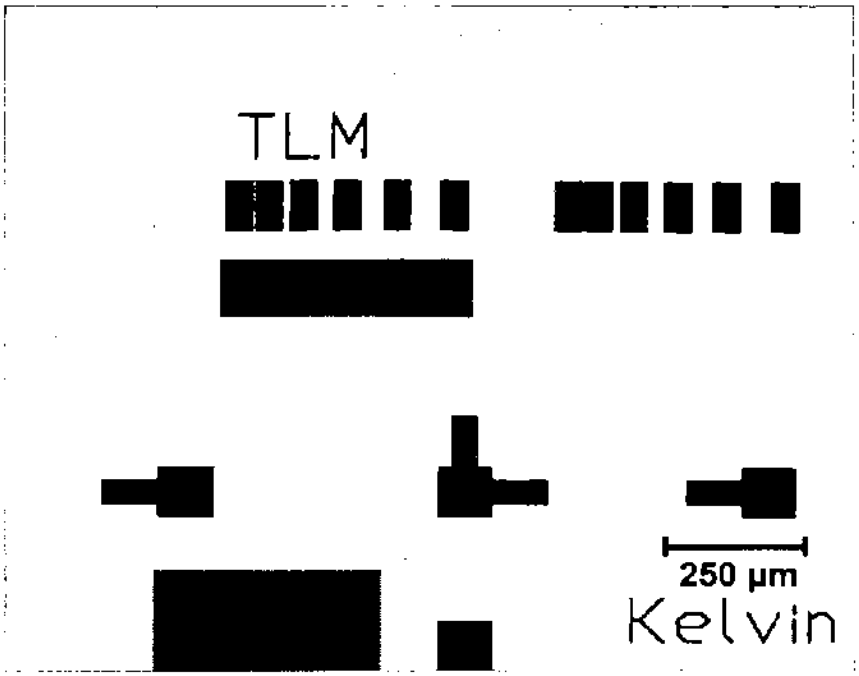


FIG. 33

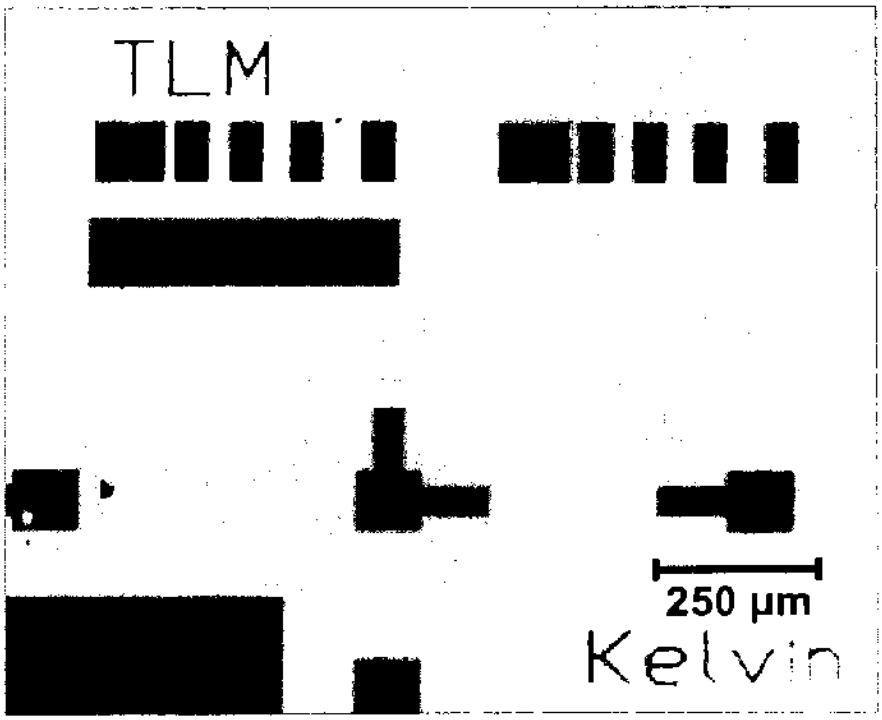


FIG. 34

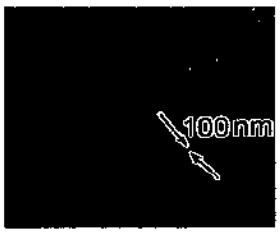


FIG. 35

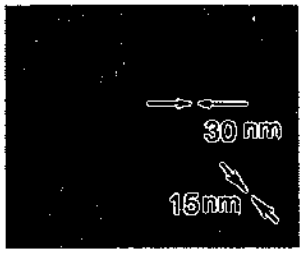


FIG. 36

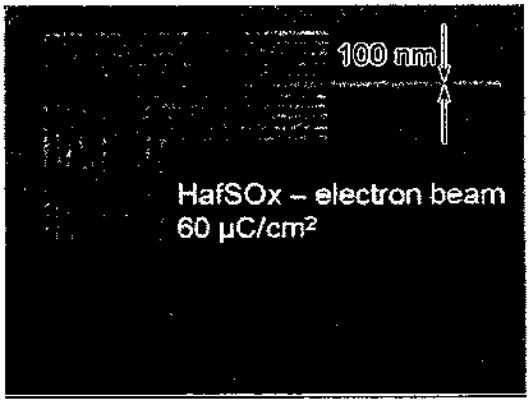


FIG. 37

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 08/04096

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - H01L 21/00 (2008.04)
USPC - 438/151; 257/E21.01
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC: 438/151; 257/E21.01
IPC(8): H01L 21/00 (2008.04)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 438/151; 257/E21.01; IPC(8): H01L 21/00 (2008.04) (text delimited)
Chemical Engineering and Biotech Research

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST: US Patents full-text; US PGPubs full-text; EPO Abstracts; and JPO Abstracts; Google
Terms: zirconium oxy hydroxy sulfate; hafnium oxy hydroxy sulfate; electronic device; photoresist; tungstate; lanthanum; photolithograph; optical and glass substrate; photo and resist, fibers, metal oxide, and dielectric.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2005/0242330 A1 (Herman et al.) 03 Nov. 2005 (03.11.2005), para [0009] - [0012], [0018]-[0029]; Figures	1, 2-4, 12, 16, 25, 28 --- 5-11, 13-15, 17-24, 26-27
Y	US 2006/0088962 A1 (Herman et al.) 27 Apr. 2006 (27.04.2006), para [0006]-[0023]; Figures	5-11, 13-15, 17-24, 27
Y	US 6,197,896 B1 (Aviram et al.) 06 March 2001 (06.03.2001), abstract; col 3, ln 50-56; col 5, ln 50-53)	10-11, 13-15, 17-24, 27
Y	US 3,385,915 A (Hamling) 28 May 1968 (28.05.1968), col 1, ln 40-45; col 2, ln 18-26	26

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 June 2008 (11.06.2008)	26 JUN 2008
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (April 2007)

Electronic Patent Application Fee Transmittal

Application Number:	12850867
Filing Date:	05-Aug-2010
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Kayla Jo Fossen/Jill Friederichs
Attorney Docket Number:	5063.02US02

Filed as Small Entity

Utility under 35 USC 111(a) Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Extension - 1 month with $0 paid	2251	1	100	100

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
		Total in USD ($)		**100**

Electronic Acknowledgement Receipt

EFS ID:	20579720
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Kayla Jo Fossen
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	31-OCT-2014
Filing Date:	05-AUG-2010
Time Stamp:	17:09:04
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$100
RAM confirmation Number	4017
Deposit Account	503863
Authorized User	FOSSEN, KAYLA J.

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Extension of Time	Ext.pdf	79150 f6f7fc170904b2405eefb2323013dde2173ece01	no	1
Warnings:					
Information:					
2	Appeal Brief Filed	AppealBrief.pdf	2505322 c168f2fb154862478e487cfb964a35405abaa469	no	28
Warnings:					
Information:					
3	Foreign Reference	JP2006-284947_Nakamura.pdf	5068497 27ee1b5b2cdc0072f4fca00aeb27b2b171ba6214	no	104
Warnings:					
Information:					
4	Foreign Reference	KR2008-0090383_Keszler.pdf	6822306 1016e472654df474e319f417e8e777d2e2b558f9	no	118
Warnings:					
Information:					
5	Foreign Reference	WO2009120169A1.pdf	3314824 b87148a4a77b639cc4c6a140c8912020df8131b2	no	74
Warnings:					
Information:					
6	Non Patent Literature	STOWERS_ET_AL_2009.pdf	397551 a894facc3bc516b39b54118ab5e15fbcc474b768	no	4
Warnings:					
Information:					
7	Fee Worksheet (SB06)	fee-info.pdf	30526 427aa887fc4511a5a34a3615c85833cb221ff78c	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	18218176		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US02
Jason K. Stowers et al.	Confirmation No.: 1662
Application No.: 12/850,867	Examiner: Chanceity N. Robinson
Filed: August 5, 2010	Group Art Unit: 1722

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

PETITION FOR EXTENSION OF PERIOD FOR RESPONSE
UNDER 37 C.F.R. § 1.136(a)

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Pursuant to 37 C.F.R. § 1.136(a), an extension of time of one (1) month (from September 30, 2014 to October 31, 2014) within which to file the Appeal Brief for which a Notice of Appeal was filed July 31, 2014 is requested. The Commissioner is authorized to charge to a credit card in the amount of $100.00 for the extension fee for a small entity. The Commissioner is authorized to charge Deposit Account No. 50-3863 for any underpayments, overpayments or additionally required fees.

Respectfully submitted,

/Kayla J. Fossen/

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Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

October 31, 2014
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. # 69,343

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02	1662

62274 7590 02/24/2015

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Fridley, MN 55432

EXAMINER
ROBINSON, CHANCEITY N

ART UNIT	PAPER NUMBER
1722	

MAIL DATE	DELIVERY MODE
02/24/2015	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No. 12/850,867	Applicant(s) STOWERS ET AL.	
	Examiner CHANCEITY ROBINSON	Art Unit 1722	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *3* MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *10/31/2014*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5)☒ Claim(s) *1-30* is/are pending in the application.

5a) Of the above claim(s) *14-30* is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-13* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☐ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

1. The present application is being examined under the pre-AIA first to invent provisions.

DETAILED ACTION

2. In view of the Appeal Brief filed on 10/31/2014, PROSECUTION IS HEREBY REOPENED. New grounds of rejection are set forth below.

To avoid abandonment of the application, appellant must exercise one of the following two options:

(1) file a reply under 37 CFR 1.111 (if this Office action is non-final) or a reply under 37 CFR 1.113 (if this Office action is final); or,

(2) initiate a new appeal by filing a notice of appeal under 37 CFR 41.31 followed by an appeal brief under 37 CFR 41.37. The previously paid notice of appeal fee and appeal brief fee can be applied to the new appeal. If, however, the appeal fees set forth in 37 CFR 41.20 have been increased since they were previously paid, then appellant must pay the difference between the increased fees and the amount previously paid.

A Supervisory Patent Examiner (SPE) has approved of reopening prosecution by signing below:

/CYNTHIA H. KELLY/

Supervisory Patent Examiner, Art Unit 1722

Double Patenting

3. The nonstatutory double patenting rejection is based on a judicially created doctrine grounded in public policy (a policy reflected in the statute) so as to prevent the

unjustified or improper timewise extension of the "right to exclude" granted by a patent and to prevent possible harassment by multiple assignees. A nonstatutory double patenting rejection is appropriate where the claims at issue are not identical, but at least one examined application claim is not patentably distinct from the reference claim(s) because the examined application claim is either anticipated by, or would have been obvious over, the reference claim(s). See, e.g., *In re Berg*, 140 F.3d 1428, 46 USPQ2d 1226 (Fed. Cir. 1998); *In re Goodman*, 11 F.3d 1046, 29 USPQ2d 2010 (Fed. Cir. 1993); *In re Longi*, 759 F.2d 887, 225 USPQ 645 (Fed. Cir. 1985); *In re Van Ornum*, 686 F.2d 937, 214 USPQ 761 (CCPA 1982); *In re Vogel*, 422 F.2d 438, 164 USPQ 619 (CCPA 1970); and *In re Thorington*, 418 F.2d 528, 163 USPQ 644 (CCPA 1969).

A timely filed terminal disclaimer in compliance with 37 CFR 1.321(c) or 1.321(d) may be used to overcome an actual or provisional rejection based on a nonstatutory double patenting ground provided the reference application or patent either is shown to be commonly owned with this application, or claims an invention made as a result of activities undertaken within the scope of a joint research agreement. A terminal disclaimer must be signed in compliance with 37 CFR 1.321(b).

The USPTO internet Web site contains terminal disclaimer forms which may be used. Please visit http://www.uspto.gov/forms/. The filing date of the application will determine what form should be used. A web-based eTerminal Disclaimer may be filled out completely online using web-screens. An eTerminal Disclaimer that meets all requirements is auto-processed and approved immediately upon submission. For more

information about eTerminal Disclaimers, refer to

http://www.uspto.gov/patents/process/file/efs/guidance/eTD-info-I.jsp.

4. Claims 1-13 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-23 of U.S. Patent No. 8,206,892 in view of Keszler et al. (WO 2009/120169 A1). Although the claims at issue are not identical, they are not patentably distinct from each other because both the US Patent '892 and the instant claims recite an aqueous inorganic patterning precursor solution comprising mixture of water, metal suboxide cations, polyatomic inorganic anions and radiation sensitive ligands comprising peroxide groups (a coordinating species comprising a peroxide group ‘892). Both the US Patent ‘892 and the instant claims recite open claim language, “comprising”, therefore, other elements and steps may be added to their respective inventions.

Although US Patent ‘892 does not explicitly disclose the solution has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours without additional mixing as instantly claimed. The examiner has added Keszler et al. to teach a laminate structure comprising a precursor solution comprising solid inorganic acid or base and peroxide (abstract, claims and [0018-0019. 0065-0068 & 0155]). Keszler et al. teach in lines 28-29 on page 16 disclosed that excellent stability is exhibited when the ratio of the sulfate radical to the metal ions is 13:18.

Keszler et al. teach that the precursor solution contained a metal ion concentration (metal suboxide cation) of about 0.05 M to 0.4 with 70% H2O2 (radiation sensitive

ligands comprising peroxide group) and 50% sulfate (polyatomic anion) relative to each metal. The difference in metal ion concentration allowed for thickness per coat (film) variation from 3 nm to 25 nm (Example 4, para. [0155]). Therefore the molar concentration affects the thickness and is therefore optimizable. The molar concentration of ligands to metal suboxide cations could have been easily selected by one of ordinary skill in the art to adjust the properties of the precursor solution.

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide cations to yield desired molar concentration ratio in view of film thickness. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Further it is noted that limitation of "wherein the precursor solution is stable with respect to phase separation for at least about 2 hours without additional mixing" is intended use language of the precursor. *In re Leshin*, 125 USPQ 416, 417-418; 277 F2d 197 (CCPA 1960).

The precursor solution of U.S. Patent No. 8,206,892 in view of Keszler et al. (WO 2009/120169 A1) will also be stable.

Claim Rejections - 35 USC § 103

5. The following is a quotation of pre-AIA 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained through the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the

art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

6. The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under pre-AIA 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.

2. Ascertaining the differences between the prior art and the claims at issue.

3. Resolving the level of ordinary skill in the pertinent art.

4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

7. Claims 1-13 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Herman et al. (US 2005/0242330 A1) in view of Keszler et al. (KR2008/0090383; citations from corresponding US PGPUB 2011/0045406 A1).

Regarding claims 1 and 7-9, Herman et al. disclose an aqueous inorganic patterning precursor solution (dielectric material) comprising a metal containing cation a polyatomic anion, wherein the metal containing cation includes one or more HfO^{2+}, ZrO^{2+}, etc. and the polyatomic anion includes one or more of sulfate, borate and tungstate, and etc. (figures, claims and [0009-0010 and 0014-0016]).

Herman et al. do not explicitly disclose the precursor solution comprises radiation sensitive ligands comprising peroxide groups as instantly recited. Also, Herman et al. do not explicitly disclose the molar concentration ratio of ligands to metal suboxide cations is at least about 2 or least about 5 or at least about 7 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours or 24 hours without

additional mixing as instantly recited. It is noted that the term “about" is relative terminology. The molar concentration ratio is optimizable. The examiner has added Keszler et al. to teach a laminate structure comprising a precursor solution comprising solid inorganic acid or base and peroxide (abstract, claims and [0018-0019. 0065-0068 & 0155]). Keszler et al. teach that the precursor solution contained a metal ion concentration (metal suboxide cation) of about 0.05 M to 0.4 with 70% H2O2 (radiation sensitive ligands comprising peroxide group) and 50% sulfate (polyatomic anion) relative to each metal. The difference in metal ion concentration allowed for thickness per coat (film) variation from 3 nm to 25 nm (Example 4, para. [0155]). The molar concentration affects the film thickness. As such, the molar concentration is optimizable. The molar concentration of ligands to metal suboxide cations could have been easily selected by one of ordinary skill in the art to adjust the properties of the precursor solution. It would have been obvious to one of ordinary skill in the art at the time of the invention to include a ligand comprising peroxide group to the precursor solution of Herman et al. in view of aiding in bonding and oxidation.

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide cations to yield desired molar concentration ratio in view of the film thickness. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Further it is noted that limitation of “wherein the precursor is solution is stable with respect to phase separation for at least about 2 hours without additional mixing” is

intended use language of the precursor. *In re Leshin*, 125 USPQ 416, 417-418; 277 F2d 197 (CCPA 1960).

The precursor solution of Herman et al. (US 2005/0242330 A1) in view of Keszler et al. (KR2008/0090383; citations from corresponding US PGPUB 2011/0045406 A1) will also be stable.

Further regarding claims 2 and 3, Herman et al. do not explicitly disclose the metal suboxide cation concentration from about 0.01 M to about 1.4M as instantly recited or polyatomic anion concentration about 0.75 to about 1.5 times the metal suboxide cation concentration as instantly recited. It is noted that the term “about" is relative terminology. The concentration is optimizable.

The examiner has added Keszler et al. to teach a laminate structure comprising a precursor solution comprising solid inorganic acid or base and peroxide (abstract, claims and [0018-0019. 0065-0068 & 0155]). Keszler et al. disclose in order to enhance thermal stability there should be sulfate content of 70-71% and sulfate to metal ratio of approximately 13:18 exhibit stability within the solution [0079-0080]. Keszler et al. teach that the precursor solution contained a metal ion concentration (metal suboxide cation) of about 0.05 M to 0.4 with 70% H2O2 (radiation sensitive ligands comprising peroxide group) and 50% sulfate (polyatomic anion) relative to each metal. The difference in metal ion concentration allowed for thickness per coat (film) variation from 3 nm to 25 nm (Example 4, para. [0155]). The molar concentration affects the thickness. As such, it is optimizable. The molar concentration of ligands to metal suboxide cations could have been easily selected by one of ordinary skill in the art to adjust the properties of

the precursor solution. It would have been obvious to one of ordinary skill in the art at the time of the invention to include a ligand comprising peroxide group to the precursor solution of Herman et al. in view of aiding in bonding and oxidation.

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide cations to yield desired molar concentration ratio in view of the film thickness. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Further regards to claims 4, 5 and 6, Herman et al. teach HfO^{2+} and ZrO^{2+} as metal containing cations and sulfate, borate and tungstate as polyatomic inorganic anions (figures, claims and [0009-0010 and 0014-0016]).

Further regards to claim 10, Herman et al. teach metal such as HF and Zr (claims).

Regarding claims 11-13, Herman et al. do not explicitly disclose a method of formation of a radiation sensitive inorganic coating precursor solution as instantly recited. However, Keszler et al. teach a method for formation of an inorganic precursor composition combining a first aqueous solution comprising metal suboxide cations and a complexing solution comprising a ligand having peroxide group ([0064 and 0097] and, claims and figures examples).The first aqueous solution is mixed with the complexing solution to form a ligand-cation mixture prior to introduction of the inorganic anions ([0064 and 0097] and, claims and figures examples). The ligand-cation mixture solution

is aged at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion ([0064 and 0097] and, claims and figures examples).

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to easily conceive the teaching of Keszler et al. to the method of patterning a dielectric material in Herman et al.

8. Claims 1-13 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Keszler et al. (WO 2009/120169 A1).

Regarding claims 1-3, Keszler et al. teach an aqueous inorganic patterning precursor solution (line 20 on page 25 to line 12 on page 32) comprising water, HfOCl2 (metal suboxide cations), H2O2 and H2SO4 (polyatomic inorganic anions). Keszler et al. teach in example 4 that the metal suboxide cations have a concentration of 0.05M - 0.4 M. Keszler et al. teach in example 4 that the sulfate has a concentration of 50% of the total concentration of the metal cations.

Keszler et al. do not teach the precursor solution has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the precursor solution is stable with respect to phase separation for at least about 2 hours without additional mixing as instantly recited. Although the concentration is lower than the range claimed in claim 3, Keszler et al. teach in lines 28-29 on page 16 that excellent stability is exhibited when the ratio of the sulfate radical to the metal ions is 13:18.

Keszler et al. recognize in Example 4 on page 38 that the precursor solution containing a metal ion concentration of (metal suboxide cation) of about 0.05 M to 0.4 with 70% H2O2 (radiation sensitive ligands comprising peroxide group) and 50% sulfate

(polyatomic anion) relative to each metal. The difference in metal ion concentration allowed for thickness per coat (film) variation from 3 nm to 25 nm (Example 4, para. [0155]).

Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify/optimize the contents of the ligands and metal suboxide cations to yield desired molar concentration ratio in view of the film thickness. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Further it is noted that limitation of "wherein the precursor is solution is stable with respect to phase separation for at least about 2 hours without additional mixing" is intended use language and adds no patentable weight to the claim. *In re Leshin*, 125 USPQ 416, 417-418; 277 F2d 197 (CCPA 1960). The precursor solution of Keszler et al. will also be stable.

Regarding claim 4, Keszler et al. teach on lines 3-14 on page 15 discloses that the metal oxide is HfO2.x(SO4)×, ZrO2.x(SO4)x, wherein 0.1≤X≤ 1.5.

Regarding claims 5 and 6, Keszler et al. teach on line 31 on page 21 to line 5 on page 22 disclose that in the precursor solution, the polyatomic inorganic anions WO_4^{2-}, PO43-, AsO43-, SiO_4^{4-}, GaO_4^{5-} and SO_4^{2-}.

Regarding claims 7-9, it is known to persons having ordinary skill in the art that an increase in the ratio of ligands can improve the stability of the metal suboxide cations. Therefore, the stability of the solution can be formed by persons having ordinary skill in the art by simply adjusting or optimizing the concentration. Discovery of

optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Regarding claim 10 , Keszler et al. teach on lines 12-17 on page 30 that the metal can be Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nd, Pm, Sin, Eu, Gd, Tb, Dy, Ho, Er, Tin, Yb and Lu.

Regarding claim 11, Keszler et al. teach a method for forming a radiation sensitive inorganic coating precursor solution. Keszler et al. teach on line 20 on page 25 to line 12 on page 32 a method for formation of an inorganic pattern precursor solution comprising using an aqueous solution of HfOC12 (corresponding to the metal suboxide cations), H_2O_2 and H_2SO_4 (corresponding to the polyatomic inorganic anions) as a precursor solution. However, the mixing method of dissolving HfOCl2 in water followed by mixing it with H_2O_2 and H_2SO_4 can be easily derived by persons skilled in the art. Therefore, the invention of claim 1 can be achieved by any person skilled in the art by adjusting or optimizing the amounts of compounds. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215.

Regarding claims 12 and 13, Keszler et al. teach on line 5 on page 26 to line 9 on page 27 that O_2 of hydrogen peroxide can provide ligands (i.e. forming a ligand-cation mixture solution). Furthermore, aging the ligand-cation mixture solution at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion can be easily adjusted or optimized and changed by a person skilled in the art through routine experimentation.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CHANCEITY ROBINSON whose telephone number is (571)270-3786. The examiner can normally be reached on Monday to Friday (with every other Friday off): 9:00 -6:00 pm eastern time.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Cynthia Kelly can be reached on (571)272-1526. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CHANCEITY ROBINSON/
Primary Examiner, Art Unit 1722

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

CPC- SEARCHED		
Symbol	Date	Examiner
G03F7/0042	05/04/2014	CR

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner
430	270.1, 302, 322, 325, 326, 942	09/09/2013	CR

SEARCH NOTES		
Search Notes	Date	Examiner
East, Assignee, IDS asnd Inventorship Search	09/09/2013	CR
East and IDS Search	05/04/2014	CR
Consulted Cynthia Kelly and QAS Tierney	02/19/2015	CR

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner

	/CHANCEITY ROBINSON/ Primary Examiner.Art Unit 1722

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	**Art Unit**
	CHANCEITY ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	02/19/2015								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
	8	✓								
	9	✓								
	10	✓								
	11	✓								
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	28	N								
	29	N								
	30	N								
	31	-								
	32	-								
	33	-								
	34	-								
	35	-								
	36	-								

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	**Art Unit**
	CHANCEITY ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	02/19/2015								
	37	-								
	38	-								

PTO/SB/08a (01-10)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02-US-02

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20020076495		2002-06-20	Maloney et al.	
	2	20040067444		2004-04-08	Wakabayahsi et al.	
	3	20130224652		2013-08-29	Bass et al.	

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	1							☐

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	12850867
	Filing Date	2010-08-05
	First Named Inventor	Jason K. Stowers
	Art Unit	1722
	Examiner Name	Chanceity N. Robinson
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	1		☐

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EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02-US-02

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☒ Fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☐ None

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Kayla J. Fossen/	Date (YYYY-MM-DD)	2015-05-06
Name/Print	Kayla J. Fossen	Registration Number	69343

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

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4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Patent Application Fee Transmittal

Application Number:	12850867
Filing Date:	05-Aug-2010
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Kayla Jo Fossen/Jill Friederichs
Attorney Docket Number:	5063.02US02

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
Submission- Information Disclosure Stmt	2806	1	90	90
		Total in USD ($)		**90**

Electronic Acknowledgement Receipt

EFS ID:	22266364
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Kayla Jo Fossen
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	06-MAY-2015
Filing Date:	05-AUG-2010
Time Stamp:	10:32:59
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$90
RAM confirmation Number	7199
Deposit Account	503863
Authorized User	FOSSEN, KAYLA J.

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	US_IDS_Form__SB_08a_signed.pdf	612021 0b6c60a4de140fd259079f084f86aee0a1720c88	no	4
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30887 4fc3d6d1e21e0a048a318eda59d08e5bcd581020	no	2
Warnings:					
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		Total Files Size (in bytes):	642908		

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New Applications Under 35 U.S.C. 111
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National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US02
Jason K. Stowers et al.	Confirmation No.: 1662
Application No.: 12/850,867	Examiner: Chanceity N. Robinson
Filed: August 5, 2010	Group Art Unit: 1722

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

AMENDMENT

Mail Stop AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

In response to the Office Action dated February 24, 2015, please enter the following amendments and consider the following remarks. The present response comprises the following sections:

A. Amendments of the Claims

B. Remarks

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

May 26, 2015
Date

/Peter S. Dardi/
Peter S. Dardi, Reg. # 39,650

AMENDMENTS OF THE CLAIMS

A detailed listing of all claims that are, or were, in the present application, irrespective of whether the claim(s) remains under examination in the application are presented below. The claims are presented in ascending order and each includes one status identifier. Those claims not cancelled or withdrawn but amended by the current amendment utilize the following notations for amendment: 1. deleted matter is shown by strikethrough for six or more characters and double brackets for five or less characters; and 2. added matter is shown by underlining.

1. (Currently Amended) An aqueous inorganic patterning precursor solution comprising a mixture of water, metal suboxide cations, polyatomic inorganic anions and radiation sensitive ligands comprising peroxide groups, wherein the solution has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the precursor solution is stable with respect to phase separation for at least about 24 hours without additional mixing, wherein the precursor solution has a metal suboxide cation concentration from about 0.01 M to about 1.4 M and a polyatomic anion concentration from 0.75 to 1.5 times the metal suboxide cation concentration.

2. (Currently Amended) The aqueous inorganic patterning precursor solution of claim 1 having a metal suboxide cation concentration from about [[0.01]] 0.1 M to about [[1.4]] 1.0 M.

3. (Cancelled)

4. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof.

5. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the polyatomic anions comprise sulfate.

Lam Research Ex. 1004 - Page 998 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

6. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the polyatomic anions comprise borate, phosphate, tungstate, silicate or combinations thereof.

7. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

8. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 7.

9. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 having a stability of at least 24 hours without additional mixing.

10. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the metal suboxide cations comprise Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or a combination thereof.

11. (Currently Amended) A method for formation of a radiation sensitive inorganic coating precursor solution, the method comprising:

combining a first aqueous solution comprising metal suboxide cations, a complexing solution comprising a ligand having a peroxide group and a composition comprising a polyatomic inorganic anion to form the coating precursor solution, wherein the molar concentration ratio of ligands to metal suboxide cations is at least abont 2, wherein the first aqueous solution is mixed with the complexing solution to form a ligand-cation mixture solution prior to introduction of the inorganic anions, and wherein the ligand-cation mixture solution is aged at least about 5 minutes prior to the addition of a solution comprisimg the polyatomic anion.

12. (Cancelled)

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13. (Currently Amended) The method of claim 12 wherein the ligand-cation mixture solution is aged at least about 15 minutes prior to the addition of a solution comprising the polyatomic anion.

14. (Withdrawn) The method of claim 11 further comprising:

forming a layer of a radiation patternable coating material comprising the coating precursor solution to form a coated substrate;

heating the coated substrate to remove at least a portion of the solvent;

irradiating the coated substrate with a pattern of radiation to condense a coating at the irradiated locations; and

heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the coating with a developer.

15. (Withdrawn) The method of claim 14 wherein the radiation is ultraviolet light.

16. (Withdrawn) The method of claim 14 wherein the radiation is light having a wavelength of about 193 nm.

17. (Withdrawn) The method of claim 14 wherein the radiation is extreme ultraviolet light.

18. (Withdrawn) The method of claim 14 wherein the radiation comprises an electron beam.

19. (Withdrawn) The method of claim 14 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof and wherein the polyatomic anions comprise sulfate anions.

20. (Withdrawn) The method of claim 14 wherein the coating material comprises a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

Lam Research Ex. 1004 - Page 1000 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

21. (Withdrawn) The method of claim 14 wherein the formation of the coated substrate is performed using spin coating, spray coating, dip coating or knife edge coating.

22. (Withdrawn) The method of claim 14 wherein the layer of coating material has an average thickness from about 1 nm to about 40 nm.

23. (Withdrawn) The method of claim 14 wherein the radiation is directed through a mask to expose selected portions of the coated substrate.

24. (Withdrawn) The method of claim 14 wherein a laser beam or an electron beam is scanned over the coated substrate to expose selected portions of the coated substrate.

25. (Withdrawn) The method of claim 14 further comprising exposing the coated substrate with a developing composition to at least partially remove the coating composition at unexposed locations.

26. (Withdrawn) The method of claim 25 wherein the developing composition is contacted with the coated substrate for no more than about 75 seconds.

27. (Withdrawn) The method of claim 25 wherein the developing composition comprises tetramethyl ammonium hydroxide.

28. (Withdrawn) The method of claim 27 wherein the developing composition has a concentration of tetramethyl ammonium hydroxide of about 2.38 weight percent.

29. (Withdrawn) The method of claim 14 wherein the substrate is treated along a surface with a hydrophilic surface treatment prior to the forming of the radiation patternable coating material.

Lam Research Ex. 1004 - Page 1001 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

30. (Withdrawn) The method of claim 14 wherein the forming of the radiation patternable coating material comprises a plurality of coating steps to form a coating material of a selected thickness.

31.-38. (Cancelled)

Lam Research Ex. 1004 - Page 1002 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

REMARKS

Claims 1, 2, 4-11 and 13-30 are pending. Claims 14-30 are withdrawn pending rejoinder. By this Amendment, claims 3 and 12 are cancelled without prejudice in view of the amendment of claim 1. Claims 1 and 11 are amended to more particularly point out the claimed invention. Specifically, amended claim 1 includes the features of original claims 2 and 3 as well as to amend the range of stability times. Claim 11 is amended to introduce features of claims 12 and 13. Claims 2 and 13 are amended in view of the amendments of claims 1 and 11. The specification supports the stability time in claim 1, for example, at page 19, lines 12-17. The specification supports the amendment of claim 2, for example, at page 15, lines 7-11, and claim 13, for example, at page 15, lines 7-11. No new matter is introduced by the amendments.

Double Patenting

The Examiner rejected claims 1-13 on the ground of nonstatutory double patenting as being unpatentable over claims 1-23 of US Pat. No. 8,206,892 (hereinafter the '892 patent) in view of PCT application WO 2009/120169 A1 to Keszler et al. (hereinafter Keszler 2009). This rejection has been modified with the addition of Keszler 2009 relative to the form of the rejection in the previous Office Action. Applicant notes that Keszler 2009 has been cited by itself for rendering the claimed invention obvious as addressed below. With all due respect, the '892 patent is prior art to the present application by way of its priority documents so that the double patent rejection is inappropriate. On the other hand, the '892 patent is essentially identical to Keszler 2009. The rejection over Keszler 2009 is addressed in detail below. Therefore, it is believed that the present double patenting rejection is moot. Since the double patenting rejection is inappropriate based on the priority date of the reference, Applicant respectfully requests withdrawal of the rejection of claims 1-13 on the ground of nonstatutory double patenting as being unpatentable over claims 1-23 of the'892 patent in view of Keszler 2009.

Lam Research Ex. 1004 - Page 1003 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Rejections over Herman and Keszler 2008

The Examiner rejected claims 1-13 under 35 U.S.C. § 103(a) as obvious over US Pub. No. 2005/0242330 to Herman et al. (Herman) in view of KR2008/0090383 to Keszler et al. (Keszler 2008) (citations from corresponding US Pub. No. 2011/0045406). Claims 2-10 directly or indirectly depend on claim 1. Claims 12 and 13 are directly or indirectly dependent on claim 11. To advance prosecution, Applicant has amended claims 1 and 11 to more particularly point out Applicant's claimed invention, even though Applicant maintains that the previous claims were patentable. In view of the amendments, it is particularly clear that the combination of Herman and Keszler 2008 does not disclose all the features of claim 1 or claim 11 and do not raise a reasonable expectation of success, and that the combination does not render Applicant's presently claimed invention *prima facie* obvious. Furthermore, Applicant bas presented unexpected results that clearly rebut any showing of *prima facie* obviousness. Applicant respectfully requests reconsideration of the rejection based on the following comments.

"In rejecting claims under 35 U.S.C. §103, the examiner bears the initial burden of presenting a *prima facie* case of obviousness." *In re Rijckaert*, 28 USPQ2d 1955, 1956 (Fed. Cir. 1993). *Prima facie* obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. *In re Ochiai*, 37 USPQ 1127, 1131 (Fed. Cir. 1995). "The test for obviousness *vel non* is statutory. It requires that one compare the claim's 'subject matter as a whole' with the prior art 'to which said subject matter pertains.'".

Claim 1 and Dependent Claims

Claim 1 has been amended to insert a range of metal cation concentrations and ratio of polyatomic anions to metal cation concentrations. Referring to Fig. 3 of Herman, Herman explicitly indicates that such solutions under amended claim 1 would be unstable, i.e., result in precipitation. As stated in paragraph [0015] of Herman, the precipitation is visually detected in

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several hours. Claim 1 has also been amended to indicate that the claimed stability lasts for at least 24 hours. Thus, Herman emphatically indicates that Applicant's presently claimed invention exhibits features not found in the Herman materials. Nothing in Keszler 2008 overcomes this issue from Herman since Keszler 2008 does not describe precursor solution stability. Thus, respectfully, the amended claim 1 is clearly not *prima facie* obvious over the combined teachings of Herman and Keszler 2008.

Claim 11 and Dependent Claims

Claim 11 has been amended to specify the mixing order and timing of the mixing with the ligands to form a ligand-metal ion mixture that is aged prior to the addition of the polyatomic anions. Herman of course does not teach such peroxide based ligands, so Herman clearly does not teach the order of combing reactants that are not present at all. Keszler does not teach these features either. The Office Action cites to paragraphs [0064] and [0097] as well as the claims and "figures examples" for teaching that the a ligand cation mixture is formed and aged for at least about 5 minutes prior to the introduction of the inorganic anions. With all due respect, these paragraphs do not describe peroxide ligands. Referring to the Examples, Example 4 described the inclusion of peroxides in relatively low concentrations in the precursor solutions. Example 4 does not describe any particular process for mixing the constituents. Certainly, Example 4 does not suggest at all aging of an initial mixture. Similarly, the claims do not mention a mixing order or aging of a ligand-metal ion mixture prior to the addition of the polyatomic anions. Applicant has discovered significant advantages from the claimed process. With all due respect, the combined teachings of Herman and Keszler 2008 clearly does not render the amended method claims *prima facie* obvious.

Peroxide Ligand Concentrations

With regard to independent claims 1 and 11, as stated by the Examiner, Herman does not teach radiation sensitive ligands comprising peroxide groups. Office Action, page 6. Keszler

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2008 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two. Office Action, page 8. Keszler 2008, therefore, does not make up for the deficiencies of Herman.

The Examiner asserted that "[t]he molar concentration is optimizable." "Discovery of optimum value of result effective variable in known process is ordinarily within skill of the art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ 215." Office Action page 15. Respectfully, the Examiner has made significant errors of law and fact. "The Board affirmed the examiner's rejection 'because one of ordinary skill in the art would have recognized after reading the prior art that the dimension recited in the claims are result-effective variables, **and because the prior art further discloses values including those in the claims.**'" *In re Applied Materials, Inc.*, 692 F.3d 1289, 1295 (Fed. Cir. 2012)(emphasis added). "First, the Board's conclusion that the prior art discloses dimensional values **overlapping the ranges** claimed in Applied's Patent is supported by substantial evidence." *Id.* (emphasis added.).

"We are aware that precedent of our reviewing court holds that it is not inventive to discover the optimum or workable ranges of a result-effective variable by routine experimentation, where the general conditions of a claim are disclosed in the prior art. *In re Applied Materials, Inc.*, 692 F.3d 1289, 1297 (Fed. Cir. 2012). Yet the *Applied Materials* court held that the general conditions of the claim were met because the prior art disclosed values overlapping the claimed ranges. *Id.* Thus, the situation we consider here is more like that before the court in *Sebek*, rather than that in *Applied Materials*, because the prior art disclosed values are all substantially outside the claimed range." *Ex parte Shimamura*, 2013 WL 6907688 (Patent Tr. & App. Bd. 2013). "While it may ordinarily be the case that determination of optimum values for parameters of prior art process would be at least prima facie obvious, that conclusion depends upon what prior art discloses with respect to those parameters and, if prior art disclosure suggests the outer limits of the range of suitable variables, and that the optimum resides within that range, and if there are indicates elsewhere that in fact that

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optimum should be sought within that range, determination of optimum values outside that range may not be obvious." *In re Sebek*, 465 F.2d 904, 907 (CCPA 1972).

With all due respect, the cited references do not cite overlapping values of the parameters of the claimed invention. Similarly, the cited references teach no basis whatsoever to optimize the parameters or to modify the values to meet the present claims. The references provide no teachings that would make the claimed parameters even obvious to try under any criteria under the law. Thus, under the law, *prima facie* obviousness has not been established just in the context of the peroxide ligand concentrations alone. Respectfully, the Examiner has not pointed to any additional teachings of the art that would suggest obviousness.

No Reasonable Expectation of Success and Unexpected Results

With respect to claim 1, Herman provides evidence that there would be no reasonable expectation of forming a precursor solution with the claimed stability. With all due respect, the only basis that the Examiner has on the stability can be expected is based on Applicant's own result. As described below, the stability described in Keszler 2008 as well as Keszler 2009 relates to **stability of the solid material** formed by precursor solution and not to the precursor solution. Respectfully, the teachings of the cited references do not provide a reasonable expectation of forming a precursor solution with the claimed stability without stirring.

Furthermore, with respect to all of the claims, a person of ordinary skill in the art would not have expected unbound ligand in the precursor solution to result in improved patterning properties. While Applicant respectfully maintains that *prima facie* obviousness has not been established, even if it were established, this has also been soundly rebutted on the current facts. "It is well settled that a prima facie case of obviousness may be rebutted 'where the results of optimizing a variable, which was known to be result effective, (are) unexpectedly good.'" *In re Boesch*, 617 F.2d 272, 276 (C.C.P.A. 1980) (citing *In re Antonie*, 559 F.2d 618, 620, (C.C.P.A. 1977)). "It is also well settled that proof of unexpected properties may be in the form of direct or

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indirect comparative testing of the claimed compounds ... and the closest prior art." *In re Boesch*, 617 F.2d at 276 (citing *In re Payne*, 606 F.2d 303, 316, (C.C.P.A. 1979)).

Applicant has presented clear unexpected results, which are the subject of US 8,415,000, which is a child application related to the present case. In particular, the ability to obtain a previously unachievable patterning with photolithography is clearly an unexpected result as evidenced by the issuance of the '000 patent. The **USPTO** has clearly substantiated the unexpectedness, i.e., non-obviousness, of the patterning results associated with the presently claimed invention. With all due respect, on the record as a whole, the Examiner has failed to establish obviousness by a preponderance of the evidence.

Summary

Since the combined teachings of Herman and Keszler 2008 do not teach or suggest all of the features of Applicant's claimed invention and do not provide a reasonable expectation of success, and since Applicant has presented unexpected results, Herman and Keszler 2008 clearly do not render Applicant's claimed invention obvious by a preponderance of the evidence. Applicant respectfully requests withdrawal of the rejection of claims 1-13 under 35 U.S.C. § 103(a) as obvious over Herman and Keszler 2008. While Applicant does not acquiesce in the assertions regarding the dependent claims, these issues are not discussed further in view of the discussions of claims 1 and 11 that make the issue of dependent claims presently moot.

Rejections over Keszler 2009

The Examiner rejected claims 1-13 under 35 U.S.C. 103(a) as obvious over Keszler 2009. Claims 2-10 directly or indirectly depend on claim 1. Claims 12 and 13 directly or indirectly depend on claim 11. Applicant notes that Keszler 2009 is essentially identical to Keszler 2008. Therefore, relevant portions of the analysis in the above section are summarized in the current

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section, although additional arguments are also presented. Since Keszler 2009 does not disclose all the features of claim 1 or claim 11 and does not provide a reasonable expectation of success and since unexpected results are presented Keszler 2009 does not render Applicant's presently claimed invention obvious by a preponderance of the evidence. Applicant respectfully requests reconsideration of the rejection based on the following comments.

Claim 1

With regard to claim 1, as stated by the Examiner, Keszler 2009 does not teach or suggest a molar concentration ratio of ligands to metal suboxide cations of at least about two. Office Action, page 9. In addition, Keszler 2009 does not teach or suggest the claimed ratio of polyatomic anions to the metal cations. On page 10 of the Office Action, the Examiner notes that the Examples in Keszler 2009 teach a ratio of sulfate anions to metal cations of 50% and asserts that "Keszler et al teach in lines 28-29 on page 16-that excellent stability is exhibited when the ratio of the sulfate radical [sic-anion] to the metal ions is 13:18." With all due respect, values of 0.5 and 13:18 are outside of the presently claimed range of anion to metal ratios of 0.75 to 1.5. On page 15, lines 4-6, Keszler 2009 teach a range of 0.1 to 1.5 for the ratio of anions to metal atoms, but only examined the properties from about 46% to about 71%, as noted at page 16, lines 9-11. One can surmise that knowledge of the results in Herman would have guided the inventors of Keszler 2009 to select anion ratios believed to be more stable, which would have excluded the presently claimed ranges. Also, Keszler 2009 seems to refer to "special stability" associated with anion to metal ion ratio values of 13:18 during post deposition processing and not in the solution phase. Keszler does not describe solution stability and certainly does not teach or suggest the ability to have a stable precursor solution that can be stable for 24 hours without stirring for the claims concentration ranges.

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Claim 11

Keszler 2009 does not teach the initial formation of a mixture of ligands and metal cations prior to the addition of polyatomic anions. Keszler certainly does not teach or suggest a period of aging for the ligand-cation mixture solution. These processing features are completely absent from the teachings of Keszler 2009. Applicant has found unexpected improvement resulting from the claimed processing procedures. Thus, claim 11 is clearly not *prima facie* obvious over Keszler 2009.

Peroxide Ligand Ratio

For solution processing, Keszler teaches 70% peroxide ligands relative to metal atoms. Keszler does not teach or suggest Applicant's claimed range of peroxide ligands. Similarly, Keszler does not teach any concentration dependence associated with peroxide ligand amounts.

A *prima facie* case of obviousness exists if the claimed ranges "overlap or lie inside ranges disclosed by prior art." *In re Wertheim*, 541 F.2d 257, 191 USPQ 90 (CCPA 1976); *In re Woodruff*, 919 F.2d 1575, 16 USPQ2d 1934 (Fed. Cir. 1990); *In re Geisler*, 116 F.3d 1465, 1469-71, 43 USPQ2d 1362, 1365-66 (Fed. Cir. 1997). If the claimed ranges do not overlap with the prior art ranges, a *prima facie* case of obviousness exists if they are so close that one skilled in the art would have expected them to have the same properties. "[A] prior art reference that discloses a range encompassing a somewhat narrower claimed range is sufficient to establish a *prima facie* case of obviousness." *In re Peterson*, 315 F.3d 1325, 1330, 65 USPQ2d 1379, 1382-83 (Fed. Cir. 2003). See also *In re Harris*, 409 F.3d 1339, 74 USPQ2d 1951 (Fed. Cir. 2005). Based on a fact intensive inquiry, a range may be disclosed in multiple prior art references instead of a single prior art reference. *Iron Grip Barbell Co., Inc. v. USA Sports, Inc.*, 392 F.3d 1317, 1322, 73 USPQ2d 1225, 1228 (Fed. Cir. 2004).

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"*KSR* did not create a presumption that all experimentation in fields where it is already a background of useful knowledge is 'obvious to try,' without considering the nature of the science or technology." *Leo Pharmaceutical Products, Ltd. v. Stanek*, 726 F.3d 1346, 1356 (Fed. Cir. 2013)(*inter partes reexamination*), quoting *Abbott Labs. v. Sandoz, Inc.*, 544 F.3d 1341, 1352 (Fed. Cir. 2008). "The problem was not known, the possible solutions to solving the problem were not known or finite, and the solution was not predictable. Therefore, the claimed invention would not have been obvious to try to one of ordinary skill in the art. Indeed ordinary artisans would not have thought to try all because they would not have recognized the problem." *Leo Pharmaceutical Products, Ltd.*, 726 F.3d at 1356-1357. "As an initial matter, an invention can often be the recognition of a problem itself." *Id.* at 1353. "Without a reasonable expectation of success or clues pointing to the most promising combinations, an artisan could have spent years experimenting without success." *Id.*

With all due respect, the teaching in Keszler 2009 do not teach overlapping ratios of peroxide ligands and do not point to the claimed ranges in the present application and does not identify any problem to be solved with adjustment of the peroxide ligand amounts. Applicant has demonstrated unexpected results with respect to both stability and to patterning resolution. Based on the claimed peroxide ligand range alone, a preponderance of the evidence does not established obviousness of Applicant's claimed invention. Furthermore, Applicant has amended their claims to provided additional bases which on their own also establish patentability.

No Reasonable Expectation of Success and Unexpected Results

With respect to claim 1, with all due respect, the only basis that the Examiner has on the stability can be expected is based on Applicant's own result. The stability described in Keszler 2009 relates to **stability of the solid material** formed by precursor solution and not to the precursor solution. Furthermore, Keszler 2009 does not explain what stability is implied by their

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qualitative assertion of stability. Respectfully, the teachings of Keszler 2009 do not provide a reasonable expectation of forming a precursor solution with the claimed stability without stirring.

Furthermore, with respect to all of the claims, a person of ordinary skill in the art would not have expected unbound ligand in the precursor solution to result in improved patterning properties. While Applicant respectfully maintains that *prima facie* obviousness has not been established, even if it were established, this has also been soundly rebutted on the current facts. "It is well settled that a prima facie case of obviousness may be rebutted 'where the results of optimizing a variable, which was known to be result effective, (are) unexpectedly good.'" *In re Boesch*, 617 F.2d 272, 276 (C.C.P.A. 1980) (citing *In re Antonie*, 559 F.2d 618, 620, (C.C.P.A. 1977)). "It is also well settled that proof of unexpected properties may be in the form of direct or indirect comparative testing of the claimed compounds ... and the closest prior art." *In re Boesch*, 617 F.2d at 276 (citing *In re Payne*, 606 F.2d 303, 316, (C.C.P.A. 1979)).

Applicant has presented clear unexpected results, which are the subject of US 8,415,000, which is a child application related to the present case. In particular, the ability to obtain a previously unachievable patterning with photolithography is clearly an unexpected result as evidenced by the issuance of the '000 patent. The **USPTO** has clearly substantiated the unexpectedness, i.e., non-obviousness, of the patterning results associated with the presently claimed invention.. With all due respect, on the record as a whole, the Examiner has failed to establish obviousness by a preponderance of the evidence.

Summary

Since the teachings of Keszler 2009 do not teach or suggest all of the features of Applicant's claimed invention and do not provide a reasonable expectation of success, and since Applicant has presented unexpected results, Keszler 2009 clearly does not render Applicant's claimed invention obvious by a preponderance of the evidence. Applicant respectfully requests withdrawal of the rejection of claims 1-13 under 35 U.S.C. § 103(a) as obvious over Keszler

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2009. While Applicant does not acquiesce in the assertions regarding the dependent claims, these issues are not discussed further in view of the discussions of claims 1 and 11 that make the issue of dependent claims presently moot.

CONCLUSION

In view of the foregoing, it is submitted that this application is in condition for allowance. Favorable consideration and prompt allowance of the application are respectfully requested.

The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,

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Electronic Acknowledgement Receipt

EFS ID:	22437611
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	26-MAY-2015
Filing Date:	05-AUG-2010
Time Stamp:	11:27:47
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Amendment/Req. Reconsideration-After Non-Final Reject	Amdt.pdf	65262 471cb2cab93f2830ab2b5218867689469ffe5bec	no	1

Warnings:	
Information:	

2	Claims	Claims.pdf	365899 74b303e197d665308987c953d232700d257add04	no	5
Warnings:					
Information:					
3	Applicant Arguments/Remarks Made in an Amendment	Remarks.pdf	1096114 cbf6859b3312721196cd45b14433ce6541cf2dbb	no	11
Warnings:					
Information:					
			Total Files Size (in bytes):	1527275	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (09-11)
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 12/850,867	Filing Date 08/05/2010	☐ To be Mailed

ENTITY: ☐ LARGE ☒ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT **05/26/2015**

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	* 28	Minus	** 38	= 0	X $40 =	0
Independent (37 CFR 1.16(h))	* 2	Minus	***5	= 0	X $210 =	0
☐ Application Size Fee (37 CFR 1.16(s))						
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
					TOTAL ADD'L FEE	0

AMENDMENT

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
☐ Application Size Fee (37 CFR 1.16(s))						
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
					TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

LIE
/PATRICIA WARNER/

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02	1662

62274 7590 06/04/2015

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EXAMINER	
ROBINSON, CHANCEITY N	

ART UNIT	PAPER NUMBER
1722	

MAIL DATE	DELIVERY MODE
06/04/2015	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No. 12/850,867	Applicant(s) STOWERS ET AL.	
	Examiner CHANCEITY ROBINSON	Art Unit 1722	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *3* MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *05/26/2015*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☒ This action is **FINAL**. 2b)☐ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5)☒ Claim(s) *1,2,4-11 and 13-30* is/are pending in the application.

5a) Of the above claim(s) *14-30* is/are withdrawn from consideration.

6)☒ Claim(s) *1,2,4-8,10 and 11* is/are allowed.

7)☒ Claim(s) *9 and 13* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☒ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date *05/06/2015*.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

1. The present application is being examined under the pre-AIA first to invent provisions.

DETAILED ACTION

2. The Applicant's request for reconsideration filed on May 26, 2015 received. Claims 1, 11 and 13 have been amended. Claims 3, 12, 31-38 have been canceled. Claims 14-30 have been withdrawn.

3. The text of those sections of Title 35, U.S.C. code not included in this action can be found in the prior Office Action issued on February 24, 2015.

Claim Rejections - 35 USC § 112

4. The following is a quotation of 35 U.S.C. 112(b):
> (b) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.

> The following is a quotation of 35 U.S.C. 112 (pre-AIA), second paragraph: The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

5. Claim 13 is rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention. Claim 13 depends on cancel claim 12. Therefore, the claim as written is indefinite. Appropriate correction is required.

6. The following is a quotation of 35 U.S.C. 112(d):

> (d) REFERENCE IN DEPENDENT FORMS.—Subject to subsection (e), a claim in dependent form shall contain a reference to a claim previously set

> forth and then specify a further limitation of the subject matter claimed. A claim in dependent form shall be construed to incorporate by reference all the limitations of the claim to which it refers.
>
> The following is a quotation of 35 U.S.C. 112 (pre-AIA), fourth paragraph:
>
> Subject to the [fifth paragraph of 35 U.S.C. 112 (pre-AIA)], a claim in dependent form shall contain a reference to a claim previously set forth and then specify a further limitation of the subject matter claimed. A claim in dependent form shall be construed to incorporate by reference all the limitations of the claim to which it refers.

7. Claim 9 is rejected under 35 U.S.C. 112(d) or pre-AIA 35 U.S.C. 112, 4th paragraph, as being of improper dependent form for failing to further limit the subject matter of the claim upon which it depends, or for failing to include all the limitations of the claim upon which it depends. Claim 9 recites the limitation of "precursor solution of claim 1 having a stability of at least 24 hours without additional mixing. However, claim 9 does not further limit claim 1, because claim 1 recites precursor solution is stable for at least 24 hours without additional mixing. Applicant may cancel the claim(s), amend the claim(s) to place the claim(s) in proper dependent form, rewrite the claim(s) in independent form, or present a sufficient showing that the dependent claim(s) complies with the statutory requirements.

Response to Arguments

8. Applicant's arguments with respect to claims 1, 2, 4-11 and 13 have been considered but are moot because the arguments do not apply to any of the references being used in the current rejection.

Response to Withdrawn Claims

9. Applicants acknowledge that the Examiner stated that a provisional election was made with traverse in January 2012 to prosecute the invention of Group I, claims 1-13. Applicant affirmed the election of Group I claims 1-13 without traverse in Applicant Arguments/Remarks mailed on 01/13/2014. For purposes to move the present application closer to a notice allowance, it is suggested that Applicants cancel claims 14-30.

Allowable Subject Matter

10. Claims 1, 2, 4-8, 10 and 11 are allowed. No other prior art teaches an aqueous inorganic coating precursor solution or a method for formation of a radiation sensitive inorganic coating precursor solution as instantly recited.

Conclusion

11. Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any

extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CHANCEITY ROBINSON whose telephone number is (571)270-3786. The examiner can normally be reached on Monday to Friday (with every other Friday off): 9:00 -6:00 pm eastern time.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Cynthia Kelly can be reached on (571)272-1526. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CHANCEITY ROBINSON/
Primary Examiner, Art Unit 1722

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

CPC- SEARCHED		
Symbol	Date	Examiner
G03F7/0042	05/04/2014	CR

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner
430	270.1, 302, 322, 325, 326, 942	09/09/2013	CR

SEARCH NOTES		
Search Notes	Date	Examiner
East, Assignee, IDS asnd Inventorship Search	09/09/2013	CR
East and IDS Search	05/04/2014	CR
Consulted Cynthia Kelly and QAS Tierney	02/19/2015	CR
East and IDS Search	06/01/2015	CR

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner

	/CHANCEITY ROBINSON/ Primary Examiner.Art Unit 1722

PTO/SB/08a (01-10)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02-US-02

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20020076495		2002-06-20	Maloney et al.	
	2	20040067444		2004-04-08	Wakabayahsi et al.	
	3	20130224652		2013-08-29	Bass et al.	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							☐

Receipt date: 05/06/2015	Application Number	12850867 12850867 - GAU: 1722
INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99**)	Filing Date	2010-08-05
	First Named Inventor	Jason K. Stowers
	Art Unit	1722
	Examiner Name	Chanceity N. Robinson
	Attorney Docket Number	5063.02-US-02

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1		☐

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/Chanceity Robinson/	Date Considered	06/01/2015

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	3	(("20020076495") or ("20040067444") or ("20130224652")).PN.	US-PGPUB; USPAT	OR	OFF	2015/06/01 08:15
L2	3891065	HfO or ZrO or (metal adj suboxide or (oxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 08:57
L3	3	1 and 2	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 08:58
L4	2	3 and inorganic	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 08:58
L5	0	4 and polyatomic	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 08:58
L6	1	4 and anion	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 08:58
L7	9	ligand-cation	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 09:02
L8	4	2 and 7	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT;	OR	ON	2015/06/01 09:02

			IBM_TDB			
S2	1	("20050242330").PN.	US-PGPUB; USPAT	OR	OFF	2013/09/09 11:09
S3	0	("102008009009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:14
S4	0	("2008009009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:15
S5	6	("2008009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:15
S6	2	("20110045406").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:18
S7	0	S6 and age	US-PGPUB; USPAT	OR	ON	2013/09/09 11:51
S8	63710	complexing	US-PGPUB; USPAT	OR	ON	2013/09/09 11:51
S9	1	S6 and S8	US-PGPUB; USPAT	OR	ON	2013/09/09 11:51
S10	1	S6 and (suboxide)	US-PGPUB; USPAT	OR	ON	2013/09/09 11:52
S11	17460	(430/270.1,302,322,325,325,946).CCLS.	US-PGPUB; USPAT	OR	OFF	2013/09/09 12:18
S12	10	S11 and (ligand with peroxide)	US-PGPUB; USPAT	OR	ON	2013/09/09 12:19
S13	5	(water and suboxide and polyatomic) with ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2014/05/04 19:46
S14	5	S13 AND ((G03F7/0042).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2014/05/04 19:46
S15	1	("7820361").PN.	US-PGPUB; USPAT	OR	OFF	2014/05/04 22:07

S16	1	("20090246690").PN.	US-PGPUB; USPAT	OR	OFF	2014/05/04 22:10
S17	1	("8206892").PN.	US-PGPUB; USPAT	OR	OFF	2014/12/17 14:00
S18	13	(("2006284947") or ("2009120169") or ("20080090383") or ("2009120169") or ("20050242330")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 14:02
S19	3	("8415000").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 14:16
S20	3	("20110045406").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 14:46
S21	2	S20 and peroxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 14:53
S22	6	("2009120169").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 15:02
S23	0	S22 and ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 15:02
S24	2	("6548126").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/18 10:33
S25	1	("8206892").PN.	US-PGPUB; USPAT	OR	OFF	2015/02/19 10:30
S26	2	(("8206892") or ("20110045406")).PN.	US-PGPUB; USPAT	OR	OFF	2015/02/19 11:50
S27	2	(("8206892") or ("20110045406") or ("2009120169")).PN.	US-PGPUB; USPAT	OR	OFF	2015/02/19 12:04

S28	16	(("8206892") or ("20110045406") or ("2009120169")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2015/02/19 12:04
S29	1	("20050242330").PN.	US-PGPUB; USPAT	OR	OFF	2015/02/19 14:45
S30	1	S29 and thermal	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2015/02/19 14:45
S31	3	("20110045406").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2015/02/19 14:46
S32	1	S31 and thermal	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2015/02/19 14:46

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L9	1766653	HfO or ZrO or (metal adj suboxide or (oxide))	US-PGPUB; USPAT; UPAD	OR	ON	2015/06/01 09:03
L10	8	ligand-cation	US-PGPUB; USPAT; UPAD	OR	ON	2015/06/01 09:03

6/1/2015 9:04:24 AM
C:\Users\crobinson4\Documents\EAST\Workspaces\12850867.wsp

Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564
Ex. 1004 - Page 1029

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	06/01/2015								
	1	✓								
	2	✓								
	3	-								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
	8	✓								
	9	✓								
	10	✓								
	11	✓								
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	28	N								
	29	N								
	30	N								
	31	-								
	32	-								
	33	-								
	34	-								
	35	-								
	36	-								

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	**Art Unit**
	CHANCEITY ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	06/01/2015								
	37	-								
	38	-								

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US02
Stowers et al.	Confirmation No.: 1662
Application No.: 12/850,867	Examiner: Chanceity N. Robinson
Filed: August 5, 2010	Group Art Unit: 1722

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

AMENDMENT AFTER FINAL

Mail Stop AF
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

In response to the Office Action dated June 4, 2015, please enter the following amendments and consider the following remarks. The present response comprises the following sections:

A. Amendments of the Claims

B. Remarks

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

June 22, 2015
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. # 69,343

AMENDMENTS OF THE CLAIMS

A detailed listing of all claims that are, or were, in the present application, irrespective of whether the claim(s) remains under examination in the application are presented below. The claims are presented in ascending order and each includes one status identifier. Those claims not cancelled or withdrawn but amended by the current amendment utilize the following notations for amendment: 1. deleted matter is shown by strikethrough for six or more characters and double brackets for five or less characters; and 2. added matter is shown by underlining.

1. (Previously Presented) An aqueous inorganic patterning precursor solution comprising a mixture of water, metal suboxide cations, polyatomic inorganic anions and radiation sensitive ligands comprising peroxide groups, wherein the solution has a molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the precursor solution is stable with respect to phase separation for at least about 24 hours without additional mixing, wherein the precursor solution has a metal suboxide cation concentration from about 0.01 M to about 1.4 M and a polyatomic anion concentration from 0.75 to 1.5 times the metal suboxide cation concentration.

2. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 having a metal suboxide cation concentration from about 0.1 M to about 1.0 M.

3. (Cancelled)

4. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof.

5. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the polyatomic anions comprise sulfate.

6. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the polyatomic anions comprise borate, phosphate, tungstate, silicate or combinations thereof.

7. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

8. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 having a molar concentration ratio of ligands to metal suboxide cations of at least about 7.

9. (Cancelled)

10. (Previously Presented) The aqueous inorganic patterning precursor solution of claim 1 wherein the metal suboxide cations comprise Cu, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Y, Zr, Nb, Mo, In, Sn, Sb, Hf, Ta, W, Ir, Pt, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or a combination thereof.

11. (Previously Presented) A method for formation of a radiation sensitive inorganic coating precursor solution, the method comprising:

combining a first aqueous solution comprising metal suboxide cations, a complexing solution comprising a ligand having a peroxide group and a composition comprising a polyatomic inorganic anion to form the coating precursor solution, wherein the molar concentration ratio of ligands to metal suboxide cations is at least about 2, wherein the first aqueous solution is mixed with the complexing solution to form a ligand-cation mixture solution prior to introduction of the inorganic anions, and wherein the ligand-cation mixture solution is aged at least about 5 minutes prior to the addition of a solution comprising the polyatomic anion.

12. (Cancelled)

Lam Research Ex. 1004 - Page 1034 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

13. (Currently Amended) The method of claim [[12]]11 wherein the ligand-cation mixture solution is aged at least about 15 minutes prior to the addition of a solution comprising the polyatomic anion.

14. (Withdrawn) The method of claim 11 further comprising:

forming a layer of a radiation patternable coating material comprising the coating precursor solution to form a coated substrate;

heating the coated substrate to remove at least a portion of the solvent;

irradiating the coated substrate with a pattern of radiation to condense a coating at the irradiated locations; and

heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the coating with a developer.

15. (Withdrawn) The method of claim 14 wherein the radiation is ultraviolet light.

16. (Withdrawn) The method of claim 14 wherein the radiation is light having a wavelength of about 193 nm.

17. (Withdrawn) The method of claim 14 wherein the radiation is extreme ultraviolet light.

18. (Withdrawn) The method of claim 14 wherein the radiation comprises an electron beam.

19. (Withdrawn) The method of claim 14 wherein the metal suboxide cations comprise HfO^{+2}, ZrO^{+2} or combinations thereof and wherein the polyatomic anions comprise sulfate anions.

20. (Withdrawn) The method of claim 14 wherein the coating material comprises a molar concentration ratio of ligands to metal suboxide cations of at least about 5.

Lam Research Ex. 1004 - Page 1035 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

21. (Withdrawn) The method of claim 14 wherein the formation of the coated substrate is performed using spin coating, spray coating, dip coating or knife edge coating.

22. (Withdrawn) The method of claim 14 wherein the layer of coating material has an average thickness from about 1 nm to about 40 nm.

23. (Withdrawn) The method of claim 14 wherein the radiation is directed through a mask to expose selected portions of the coated substrate.

24. (Withdrawn) The method of claim 14 wherein a laser beam or an electron beam is scanned over the coated substrate to expose selected portions of the coated substrate.

25. (Withdrawn) The method of claim 14 further comprising exposing the coated substrate with a developing composition to at least partially remove the coating composition at unexposed locations.

26. (Withdrawn) The method of claim 25 wherein the developing composition is contacted with the coated substrate for no more than about 75 seconds.

27. (Withdrawn) The method of claim 25 wherein the developing composition comprises tetramethyl ammonium hydroxide.

28. (Withdrawn) The method of claim 27 wherein the developing composition has a concentration of tetramethyl ammonium hydroxide of about 2.38 weight percent.

29. (Withdrawn) The method of claim 14 wherein the substrate is treated along a surface with a hydrophilic surface treatment prior to the forming of the radiation patternable coating material.

Lam Research Ex. 1004 - Page 1036 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

30. (Withdrawn) The method of claim 14 wherein the forming of the radiation patternable coating material comprises a plurality of coating steps to form a coating material of a selected thickness.

31.-38. (Cancelled)

Lam Research Ex. 1004 - Page 1037 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

REMARKS

Claims 1, 2, 4-8, 10, 11, and 13-30 are pending. By this Amendment, claim 9 is cancelled and claim 13 is amended. Claims 14-30 were previously withdrawn pending rejoinder, which is respectfully currently requested.

Claim Rejections under 35 U.S.C. § 112

Claim 13 was rejected under 35 U.S.C. §112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention. In particular, the Examiner has indicated that claim 13 depends on cancelled claim 12. Claim 13 has been amended to be properly dependent on claim 11, obviating the rejection.

Claim 9 was rejected under 35 U.S.C. § 112 (pre-AIA), fourth paragraph, as being of improper dependent form for failing to further limit the subject matter of the claim upon which it depends, or for failing to include all the limitations of the claim upon which it depends. Claim 9 has been cancelled, obviating the rejection.

Rejoinder under MPEP 809 and 821.04

The Examiner indicated that to move the present application closer to a notice of allowance, the Applicant should cancel previously withdrawn claims 14-30. Respectfully, because the previously withdrawn claims are directly or indirectly dependent on allowed claim 11, claims 14-30 should be rejoined and allowed. Claim 11 is a linking claim.

"In order to be eligible for rejoinder, a claim to a nonelected invention must depend from or otherwise require all the limitations of an allowable claim. A withdrawn claim that does not require all the limitations of an allowable claim will not be rejoined. Furthermore, where restriction was required between a product and a process of making and/or using the product, and

the product invention was elected and subsequently found allowable, all claims to a nonelected process invention must depend from or otherwise require all the limitations of an allowable claim for the claims directed to that process invention to be eligible for rejoinder." See MPEP § 821.04(b).

"The linking claims must be examined with, and thus are considered part of, the invention elected. When all claims directed to the elected invention are allowable, should any linking claim be allowable, the restriction requirement between the linked inventions must be withdrawn." See MPEP 809.

Claims 14-30 are directly or indirectly dependent on allowed claim 11. The claims, therefore, are eligible for rejoinder and must be rejoined since a linking claim has been allowed. Rejoinder and allowance of claims 14-30 is respectfully requested.

CONCLUSION

In view of the foregoing, it is submitted that this application is in condition for allowance. Favorable consideration and prompt allowance of the application are respectfully requested.

The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,

/Kayla J. Fossen/

Kayla J. Fossen
Registration No. 69,343

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Lam Research Ex. 1004 - Page 1039 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Acknowledgement Receipt

EFS ID:	22698628
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Kayla Jo Fossen
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	22-JUN-2015
Filing Date:	05-AUG-2010
Time Stamp:	15:28:23
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Response After Final Action	AmdtAF.pdf	64678 d6a0d83cb185b2860ee9d4449138408d220cbcdd	no	1

Warnings:	
Information:	

2	Claims	Claims.pdf	357387 d72b92dfde3ffdb2c6c52ae84bbf95cd08f7db0e	no	5
Warnings:					
Information:					
3	Applicant Arguments/Remarks Made in an Amendment	Remarks.pdf	170654 bc04310cf8bd0d51ce2c805689e20a7c7bc9d7de	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	592719	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 12/850,867	Filing Date 08/05/2010	☐ To be Mailed

ENTITY: ☐ LARGE ☒ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

AMENDMENT **06/22/2015**

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	* 27	Minus	** 38	= 0	X $40 =	0
Independent (37 CFR 1.16(h))	* 2	Minus	***5	= 0	X $210 =	0
☐ Application Size Fee (37 CFR 1.16(s))						
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
					TOTAL ADD'L FEE	0

AMENDMENT

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
☐ Application Size Fee (37 CFR 1.16(s))						
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
					TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

LIE
/SHAREILL COLES/

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**
If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

62274 7590 06/25/2015

DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

EXAMINER
ROBINSON, CHANCEITY N

ART UNIT	PAPER NUMBER
1722	

DATE MAILED: 06/25/2015

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02	1662

TITLE OF INVENTION: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$480	$0	$0	$480	09/25/2015

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

62274 7590 06/25/2015
DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission
I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02	1662

TITLE OF INVENTION: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$480	$0	$0	$480	09/25/2015

EXAMINER	ART UNIT	CLASS-SUBCLASS
ROBINSON, CHANCEITY N	1722	430-270100

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).
- ❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
- ❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.
1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. The following fee(s) are submitted:
- ❑ Issue Fee
- ❑ Publication Fee (No small entity discount permitted)
- ❑ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**
- ❑ A check is enclosed.
- ❑ Payment by credit card. Form PTO-2038 is attached.
- ❑ The director is hereby authorized to charge the required fee(s), any deficiency, or credits any overpayment, to Deposit Account Number _____ (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)
- ❑ Applicant certifying micro entity status. See 37 CFR 1.29 — NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
- ❑ Applicant asserting small entity status. See 37 CFR 1.27 — NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
- ❑ Applicant changing to regular undiscounted fee status. — NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

Lam Research Ex. 1004 - Page 1044 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02	1662

62274 7590 06/25/2015

DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

EXAMINER	
ROBINSON, CHANCEITY N	

ART UNIT	PAPER NUMBER
1722	

DATE MAILED: 06/25/2015

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 12/850,867	Applicant(s) STOWERS ET AL.	
	Examiner CHANCEITY ROBINSON	Art Unit 1722	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to *06/22/2015*.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on_____.
2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.
3. ☒ The allowed claim(s) is/are *1, 2, 4-8, 10, 11 and 13-30* . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov .
4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:
   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).
6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____ .
5. ☐ Examiner's Amendment/Comment
6. ☒ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/CHANCEITY ROBINSON/
Primary Examiner, Art Unit 1722

1. The present application is being examined under the pre-AIA first to invent provisions.

DETAILED ACTION

Election/Restrictions

2. Claims 1, 2, 4-8, 10, 11 and 13 are allowable. The restriction requirement between Group I (claims 1-13), Group II (claims 14-30) & Group III, (claims 31-38) , as set forth in the Office action mailed on 09/16/2013 , has been reconsidered in view of the allowability of claims to the elected invention pursuant to MPEP § 821.04(a). **The restriction requirement is hereby withdrawn as to any claim that requires all the limitations of an allowable claim.** Specifically, the restriction requirement of 09/16/2013 is partially withdrawn. Claims 14-30, directed to method no longer withdrawn from consideration because the claim(s) requires all the limitations of an allowable claim. However, claims 31-38, directed to structure withdrawn and canceled from consideration because they do not all require all the limitations of an allowable claim.

In view of the above noted withdrawal of the restriction requirement, applicant is advised that if any claim presented in a continuation or divisional application is anticipated by, or includes all the limitations of, a claim that is allowable in the present application, such claim may be subject to provisional statutory and/or nonstatutory double patenting rejections over the claims of the instant application.

Once a restriction requirement is withdrawn, the provisions of 35 U.S.C. 121 are no longer applicable. See In re Ziegler, 443 F.2d 1211, 1215, 170 USPQ 129, 131-32 (CCPA 1971). See also MPEP § 804.01.

3. The following is an examiner's statement of reasons for allowance: Claims 1, 2, 4-8, 10, 11 and 13-30 are allowed. No other prior art teaches an aqueous inorganic patterning precursor solution as instantly claimed. No other prior art teaches a method for formation of a radiation sensitive inorganic precursor solution as instantly claimed.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CHANCEITY ROBINSON whose telephone number is (571)270-3786. The examiner can normally be reached on Monday to Friday (with every other Friday off): 9:00 -6:00 pm eastern time.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Cynthia Kelly can be reached on (571)272-1526. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CHANCEITY ROBINSON/
Primary Examiner, Art Unit 1722

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

CPC- SEARCHED		
Symbol	Date	Examiner
G03F7/0042	05/04/2014	CR

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner
430	270.1, 302, 322, 325, 326, 942	09/09/2013	CR

SEARCH NOTES		
Search Notes	Date	Examiner
East, Assignee, IDS asnd Inventorship Search	09/09/2013	CR
East and IDS Search	05/04/2014	CR
Consulted Cynthia Kelly and QAS Tierney	02/19/2015	CR
East and IDS Search	06/01/2015	CR
East Search Updated	06/24/2015	CR

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner
430	270.1	06/24/2015	CR

	/CHANCEITY ROBINSON/ Primary Examiner.Art Unit 1722

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	**Art Unit**
	CHANCEITY ROBINSON	1722

CPC						
Symbol					**Type**	**Version**
G03F		7	/	0042	F	2013-01-01
Y10T		428	/	24355	A	2015-01-15
			/			
			/			
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			/			
			/			

CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
			/					
			/					

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	27	
/CHANCEITY ROBINSON/ Primary Examiner.Art Unit 1722	06/24/2015	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	**Art Unit**
	CHANCEITY ROBINSON	1722

US ORIGINAL CLASSIFICATION		INTERNATIONAL CLASSIFICATION										
CLASS	SUBCLASS	CLAIMED					NON-CLAIMED					
430	270.1	G	0	3	F	7 / 00 (2006.01.01)						
CROSS REFERENCE(S)												
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)											

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	27	
/CHANCEITY ROBINSON/ Primary Examiner.Art Unit 1722	06/24/2015	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	**Art Unit**
	CHANCEITY ROBINSON	1722

☒ **Claims renumbered in the same order as presented by applicant** ☐ **CPA** ☐ **T.D.** ☐ **R.1.47**

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1	14	17		33										
2	2	15	18		34										
	3	16	19		35										
3	4	17	20		36										
4	5	18	21		37										
5	6	19	22		38										
6	7	20	23												
7	8	21	24												
	9	22	25												
8	10	23	26												
9	11	24	27												
	12	25	28												
10	13	26	29												
11	14	27	30												
12	15		31												
13	16		32												

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 27	
/CHANCEITY ROBINSON/ Primary Examiner.Art Unit 1722 (Primary Examiner)	06/24/2015 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure 1

U.S. Patent and Trademark Office

Part of Paper No. 20150624

OK TO ENTER: /C.R./

06/24/2015

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US02
Stowers et al.	Confirmation No.: 1662
Application No.: 12/850,867	Examiner: Chanceity N. Robinson
Filed: August 5, 2010	Group Art Unit: 1722

For: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

AMENDMENT AFTER FINAL

Mail Stop AF
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

In response to the Office Action dated June 4, 2015, please enter the following amendments and consider the following remarks. The present response comprises the following sections:

A. Amendments of the Claims

B. Remarks

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.

CERTIFICATE OF ELECTRONIC TRANSMISSION

I hereby certify that this paper is being transmitted electronically to the U.S. Patent and Trademark Office on the date shown below.

June 22, 2015
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. # 69,343

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S2	1	("20050242330").PN.	US-PGPUB; USPAT	OR	OFF	2013/09/09 11:09
S3	0	("102008009009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:14
S4	0	("2008009009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:15
S5	6	("2008009083").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:15
S6	2	("20110045406").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2013/09/09 11:18
S7	0	S6 and age	US-PGPUB; USPAT	OR	ON	2013/09/09 11:51
S8	63710	complexing	US-PGPUB; USPAT	OR	ON	2013/09/09 11:51
S9	1	S6 and S8	US-PGPUB; USPAT	OR	ON	2013/09/09 11:51
S10	1	S6 and (suboxide)	US-PGPUB; USPAT	OR	ON	2013/09/09 11:52
S11	17460	(430/270.1,302,322,325,325,946).CCLS.	US-PGPUB; USPAT	OR	OFF	2013/09/09 12:18
S12	10	S11 and (ligand with peroxide)	US-PGPUB; USPAT	OR	ON	2013/09/09 12:19
S13	5	(water and suboxide and polyatomic) with ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2014/05/04 19:46

S14	5	S13 AND ((G03F7/0042).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2014/05/04 19:46
S15	1	("7820361").PN.	US-PGPUB; USPAT	OR	OFF	2014/05/04 22:07
S16	1	("20090246690").PN.	US-PGPUB; USPAT	OR	OFF	2014/05/04 22:10
S17	1	("8206892").PN.	US-PGPUB; USPAT	OR	OFF	2014/12/17 14:00
S18	13	(("2006284947") or ("2009120169") or ("20080090383") or ("2009120169") or ("20050242330")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 14:02
S19	3	("8415000").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 14:16
S20	3	("20110045406").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 14:46
S21	2	S20 and peroxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 14:53
S22	6	("2009120169").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 15:02
S23	0	S22 and ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2014/12/17 15:02
S24	2	("6548126").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	OFF	2014/12/18 10:33

Lam Research Ex. 1004 - Page 1057 - Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

			DERWENT; IBM_TDB			
S25	1	("8206892").PN.	US-PGPUB; USPAT	OR	OFF	2015/02/19 10:30
S26	2	(("8206892") or ("20110045406")).PN.	US-PGPUB; USPAT	OR	OFF	2015/02/19 11:50
S27	2	(("8206892") or ("20110045406") or ("2009120169")).PN.	US-PGPUB; USPAT	OR	OFF	2015/02/19 12:04
S28	16	(("8206892") or ("20110045406") or ("2009120169")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2015/02/19 12:04
S29	1	("20050242330").PN.	US-PGPUB; USPAT	OR	OFF	2015/02/19 14:45
S30	1	S29 and thermal	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2015/02/19 14:45
S31	3	("20110045406").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2015/02/19 14:46
S32	1	S31 and thermal	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2015/02/19 14:46
S33	3	(("20020076495") or ("20040067444") or ("20130224652")).PN.	US-PGPUB; USPAT	OR	OFF	2015/06/01 08:15
S34	3891065	HfO or ZrO or (metal adj suboxide or (oxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 08:57
S35	3	S33 and S34	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 08:58
S36	2	S35 and inorganic	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT;	OR	ON	2015/06/01 08:58

			IBM_TDB			
S37	0	S36 and polyatomic	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 08:58
S38	1	S36 and anion	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 08:58
S39	9	ligand-cation	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 09:02
S40	4	S34 and S39	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2015/06/01 09:02

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	872681	inorganic	US-PGPUB; USPAT; UPAD	OR	ON	2015/06/24 10:20
L2	24457	inorganic with anion	US-PGPUB; USPAT; UPAD	OR	ON	2015/06/24 10:21
L3	2821919	2 adn water	US-PGPUB; USPAT; UPAD	OR	ON	2015/06/24 10:21
L4	23297	2 and water	US-PGPUB; USPAT; UPAD	OR	ON	2015/06/24 10:21
L5	19787	4 and (metal)	US-PGPUB; USPAT; UPAD	OR	ON	2015/06/24 10:21
L6	6	(metal adj suboxide adj cation)	US-PGPUB; USPAT; UPAD	OR	ON	2015/06/24 10:21
L7	5	5 and 6	US-PGPUB;	OR	ON	2015/06/24 10:21

			USPAT; UPAD			
L8	5	7 AND ((G03F7/0042 OR Y10T428/24355 OR C01F17/00 OR C01G1/10 OR C01G27/006 OR C01G27/06 OR C01P2002/02 OR C01P2002/72 OR C01P2002/88 OR C01P2004/03 OR C01P2004/04 OR C01P2006/40 OR C23C18/06 OR C23C18/1216 OR C23C18/1225 OR C23C18/1295 OR G02B1/10 OR H01L21/02181 OR H01L21/02189 OR H01L21/02192 OR H01L21/02194 OR H01L21/02282 OR H01L21/0337 OR H01L21/28194 OR H01L29/4908 OR H01L29/7869 OR Y10S430/114 OR Y10S430/143).CPC.)	US-PGPUB; USPAT; UPAD	OR	ON	2015/06/24 10:22
S41	1766653	HfO or ZrO or (metal adj suboxide or (oxide))	US-PGPUB; USPAT; UPAD	OR	ON	2015/06/01 09:03
S42	8	ligand-cation	US-PGPUB; USPAT; UPAD	OR	ON	2015/06/01 09:03

6/ 24/ 2015 10:23:14 AM
C:\ Users\ crobinson4\ Documents\ EAST\ Workspaces\ 12850867.wsp

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	06/17/2015								
1	1	=								
2	2	=								
	3	-								
3	4	=								
4	5	=								
5	6	=								
6	7	=								
7	8	=								
	9	-								
8	10	=								
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26	29	=								
27	30	=								
	31	-								
	32	-								
	33	-								
	34	-								
	35	-								
	36	-								

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	12850867	STOWERS ET AL.
	Examiner	**Art Unit**
	CHANCEITY ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☒ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	06/17/2015								
	37	-								
	38	-								

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

62274 7590 06/25/2015
DARDI & HERBERT, PLLC
Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Electronic
Certificate of ~~Mailing or~~ Transmission by EFS

I hereby certify that this Fee(s) Transmittal is being deposited ~~with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885~~, on the date indicated below.

Kayla J. Fossen	(Depositor's name)
Kayla J. Fossen	(Signature)
9/18/15	(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/850,867	08/05/2010	Jason K. Stowers	5063.02US02	1662

TITLE OF INVENTION: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	~~SMALL~~ Undiscounted	~~$480~~ $960	$0	$0	~~$480~~ $960	09/25/2015

EXAMINER	ART UNIT	CLASS-SUBCLASS
ROBINSON, CHANCEITY N	1722	430-270100

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).
- ☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
- ☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 Dardi & Herbert, PLLC
2 Peter S. Dardi, Ph.D.
3 Kayla J. Fossen

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: Inpria Corporation

(B) RESIDENCE: (CITY and STATE OR COUNTRY): Corvallis, Oregon

Please check the appropriate assignee category or categories (will not be printed on the patent): ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. The following fee(s) are submitted:
- ☒ Issue Fee
- ☒ Publication Fee (No small entity discount permitted)
- ☐ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**
- ☐ A check is enclosed.
- ☒ Payment by credit card. ~~Form PTO-2038 is attached.~~
- ☒ The director is hereby authorized to charge the required fee(s), any deficiency, or credits any overpayment, to Deposit Account Number 50-3863 ~~(enclose an extra copy of this form).~~

5. **Change in Entity Status** (from status indicated above)
- ☐ Applicant certifying micro entity status. See 37 CFR 1.29
- ☐ Applicant asserting small entity status. See 37 CFR 1.27
- ☒ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature Kayla J. Fossen Date 09/18/15

Typed or printed name Kayla J. Fossen Registration No. 69,343

PTOL-85 Part B (10-13) Approved for use through 10/31/2013 OMB 0651-0033 U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

Lam Research Ex. 1004 - Page 1063 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Patent Application Fee Transmittal

Application Number:	12850867
Filing Date:	05-Aug-2010
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Kayla Jo Fossen/Jill Friederichs
Attorney Docket Number:	5063.02US02

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Utility Appl Issue Fee	1501	1	960	960
Publ. Fee- Early, Voluntary, or Normal	1504	1	0	0
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**960**

Electronic Acknowledgement Receipt

EFS ID:	23541762
Application Number:	12850867
International Application Number:	
Confirmation Number:	1662
Title of Invention:	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Kayla Jo Fossen
Filer Authorized By:	
Attorney Docket Number:	5063.02US02
Receipt Date:	18-SEP-2015
Filing Date:	05-AUG-2010
Time Stamp:	17:28:41
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$960
RAM confirmation Number	4300
Deposit Account	503863
Authorized User	FOSSEN, KAYLA J.

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Issue Fee Payment (PTO-85B)	FeeTransmittal_Signed.pdf	152534 52aca4bc9ed33bc274bd747da83f342d693cec18	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	32708 0b4b597259af582ff4365f34455b04799c2da36d	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	185242		

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New Applications Under 35 U.S.C. 111
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Receipt date: 08/28/2012	Application Number	12850867	12850867 - GAU: 1722
INFORMATION DISCLOSURE STATEMENT BY APPLICANT	Filing Date	2010-08-05	
(Not for submission under 37 CFR 1.99)	First Named Inventor	Stower et al.	
	Art Unit	1783	
	Examiner Name	Gugliotta, Nicole T	
	Attorney Docket Number	5063.02US02	

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ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./

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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	12850867
Filing Date	2010-08-05
First Named Inventor	Jason K. Stowers
Art Unit	1783
Examiner Name	Gugliotta, Nicole T.
Attorney Docket Number	5063.02US02

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/850,867	11/03/2015	9176377	5063.02US02	1662

62274 7590 10/14/2015

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ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 1463 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

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