Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
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/Jill Friederichs
Attorney Docket Number:	5063.02US04

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Utility application filing	1011	1	280	280
Utility Search Fee	1111	1	600	600
Utility Examination Fee	1311	1	720	720
Pages:				
Claims:				
Miscellaneous-Filing:				
Late Filing Fee for Oath or Declaration	1051	1	140	140
Petition:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**1740**

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5063.02US04

CONTINUING APPLICATION TRANSMITTAL

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

Sir:

This is a request for filing a

[X] Continuation [ ] Divisional

application, under 37 C.F.R. § 1.53(b), of pending prior Application No. 12/850,867, filed August 5, 2010 for: PATTERENED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS by: Jason K. Stowers, Alan J. Telecky, Douglas A. Keszler and Andrew Grenville. The entire disclosure of the prior application is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.

Enclosed are:

[X] Specification, Claims and Abstract - 39 pages.

[X] Drawings - 8 sheets (Figs. 1-18D).

[X] Application Data Sheet.

[ ] Declarations.

[ ] Power of Attorney.

[X] Preliminary Remarks - 3 pages.

The filing fee has been calculated as shown below:					
	No. Filed	No. Extra	Small Entity Rate	OR	Large Entity Rate
Basic Filing Fee			$70	OR	$280
Utility Search Fee			$300	OR	$600
Utility Examination Fee			$360	OR	$720
Total Claims	20 - 20	= **	x 40 = $0	OR	x 80 = $0
Independent Claims	3 - 3	= **	x 210 = $0	OR	x 420 = $0
Surcharge - Late Oath/Declaration [If applicable]			[+ $70]	OR	+ $140
Presence of Multiple Dependent Claim [If applicable]			[+ 390]	OR	[+ 780]
Utility Application Size Fee - per each additional 50 sheets that exceeds 100 sheets:			* x 200 = $	OR	* x 400 = $
		TOTAL	**$**	**TOTAL**	**$1740**
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1. [X] The Commissioner is hereby authorized to charge a credit card referenced in the electronic filing in the amount of $ 1740.00. 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.

2. [ ] Priority of *[country]* application(s) No. _____ filed _____ is claimed under 35 U.S.C. § 119. The certified copy was filed in prior Application No. _____ on _____.

3. [X] The prior application is assigned of record to Inpria Corporation recorded at Reel 025647, Frame 0344.

4. [X] An Information Disclosure Statement and Transmittal Letter are enclosed.

5. [ ] Applicant is entitled to small entity status in accordance with 37 CFR 1.27.

6. [ ] CD-ROM or CD-R in duplicate, and Compact Disc Transmittal are enclosed.

7. [ ] Request and Certification Under 35 U.S.C. 122(b)(2)(B)(i) (non-publication).

8. [X] Address all future communications to:

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Respectfully submitted,

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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.

September 18, 2015
Date

/Peter S. Dardi/
Peter S. Dardi, Ph.D.

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US04

Stowers et al. Confirmation No.: TBA

Application No.: *Continuation of 12/850,867*

Filed: Herewith

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

INFORMATION DISCLOSURE STATEMENT

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

Sir:

Pursuant to 37 C.F.R. § 1.56, the attention of the Patent and Trademark Office is hereby directed to the references listed on the attached Form PTO-SB/08a. It is respectfully requested that the information be expressly considered during the prosecution of this application, and that the references be made of record therein and appear among the "References Cited" on any patent to issue therefrom. The listing of a reference herein is not an admission that the reference is prior art or that the reference is material to patentability.

This Information Disclosure Statement is being filed with the application. No certification or fee is required.

Copies of the foreign patent references and non-patent literature references were cited by or submitted to the Office in Patent Application No. 12/850,867, filed August 5, 2010, which is

relied upon for an earlier filing date under 35 U.S.C. § 120. Thus, copies of these references are not attached. 37 C.F.R. § 1.98(d).

Copies of cited U.S. patents and U.S. published applications are not included. 37 C.F.R. 1.98(a)(2).

Applicant(s) is/are entitled to small entity status in accordance with 37 CFR 1.27.

Respectfully submitted,

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September 18, 2015
Date

/Peter S. Dardi/
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PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation of copending U.S. patent application serial number 12/850,867 to Stowers et al. filed August 5, 2010, entitled "Patterned Inorganic Layers, Radiation Based Patterning Compositions and Corresponding Methods," which claims priority to copending U.S. provisional patent application serial number 61/350,103 to Stowers et al., entitled "Photopatternable Inorganic Hardmask," both of which are 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 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

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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 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 substrate 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

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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-nm 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.

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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

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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

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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

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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.

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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.

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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 be 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 based on the

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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

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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

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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

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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 copper, 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.

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

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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 be 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

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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

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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

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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.

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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 be 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 be 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

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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

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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

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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

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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

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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

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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) light 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.

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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

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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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SCORE Placeholder Sheet for IFW Content

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REMARKS

Claims 1-20 are pending. The specification has been updated relative to the patent application to include the parent application in the cross reference to related applications. The specification has also been amended to add "copper" to a list of ions that can be included in the precursor solution. This amendment to the specification makes the specification consistent with original claim 10 and corrects this oversight in the original specification.

The specification supports the new claims as noted in the following discussion. The specification supports new claims 1 and 13, for example, at page 3, lines 9-23, page 5, lines 26-27, page 8, lines 14-17, page 21, lines 16-18 and page 23, line 16 to page 24, line 18. The specification supports claims 2, 4 and 5, for example, page 3, lines 13-15. The specification supports claims 3, 14 and 18, for example, at page 15, line 19 to page 16, line 16 and original claim 10. The specification supports claims 6 and 20, for example, at page 21, lines 16-28. The specification supports claim 7, for example, at page 9, lines 13-25 and page 13, lines 2-5. The specification supports claim 8, for example, at page 3, lines 26-30, page 21, lines 16-28 and page 23, lines 16-30. The specification supports claim 9, for example, at page 23, lines 16-30. The specification supports claim 10, for example, at page 24, lines 3-18. The specification supports claim 11, for example, at page 25, line 22 to page 26, line 1. The specification supports claim 12, for example, at page 3, lines 16-17. The specification supports claims 15-17 and 19, for example, at page 3, lines 3-30. No new matter is introduced by the claims.

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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:	23539187
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
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Warnings:					
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2	Specification	Spec.pdf	4124180 ce7428ddfc46115f3a42d1adc06b42e8621fbc7b	no	35
Warnings:					
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3	Claims	Claims.pdf	261508 ca127a6f0ddde0fc5d4175f23ac46ff6344d8a67	no	3
Warnings:					
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4	Abstract	Abstract.pdf	51844 a0bf761624161afb8fb8601fdf5b35ef4710fb2a	no	1
Warnings:					
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5	Application Data Sheet	ApplicationDataSheet_Signed.pdf	1562027 4d24267c15c368e694f4f126b52c1b0e9fa77b67	no	8
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6	Preliminary Amendment	Prelim_Remarks.pdf	59854 02b791f000a1a9c1bc1ac3586444908e1f082846	no	1
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Art Unit	TBA
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	12	20110293888		2011-12-01	Stowers et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
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	First Named Inventor	Stowers
	Art Unit	TBA
	Examiner Name	To be assigned
	Attorney Docket Number	5063.02US04

	13	20130224652		2013-08-29	Bass et al.	
	14	20120223418		2012-09-06	Stowers et al.	

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	1	H03-148659	JP	A	1991-06-25	Fujitsu Ltd	English abstract only	☐
	2	2006-284947	JP		2006-10-19	Fuji Photo Film Co Ltd	English abstract only	☐
	3	2005/043246	WO		2005-05-12	Hewlett-Packard		☐
	4	2008/082448	WO		2008-07-10	Oregon State		☐
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	6	2007-514182	JP		2008-05-31	Hewlett-Packard	abstract only, corresponds to WO 2005/043246	☐
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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).	☐
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	First Named Inventor	Stowers
	Art Unit	TBA
	Examiner Name	To be assigned
	Attorney Docket Number	5063.02US04

	10	WANG ET AL.,"TiO2 micro-devices fabricated by laser direct writing" Optics Express, August 29, 2011, 19 (18):17390-17935.	☐
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	13	Supplementary European Search Report From Corresponding European Patent Application No. 11168027.8 Dated January 6, 2012 (8 pages).	☐
	14	Office Action from copending Korean Application No. 10-2011-0052919 dated March 14, 2013.	☐
	15	Office Action from copending Japanese Application No. 2011-120402 dated June 11, 2013.	☐
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	Filing Date	2015-09-18
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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

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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.

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Name/Print	Peter S. Dardi, Ph.D.	Registration Number	39650

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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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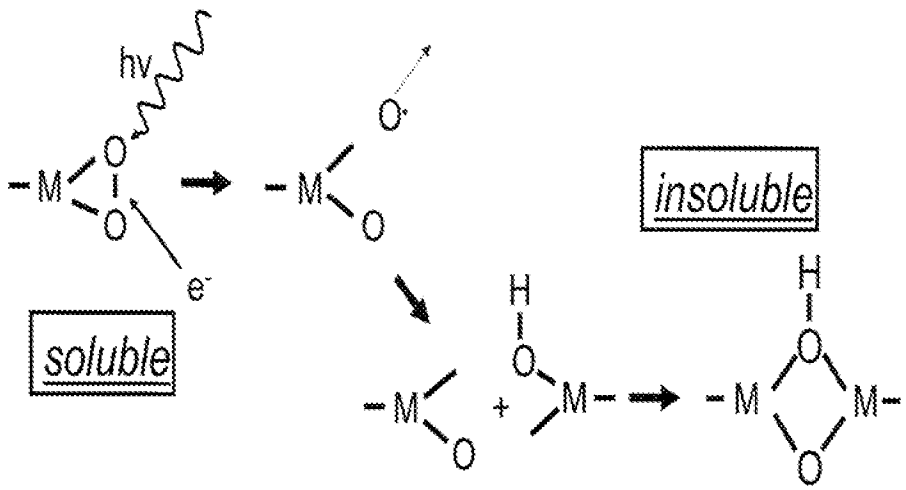

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Fig. 1

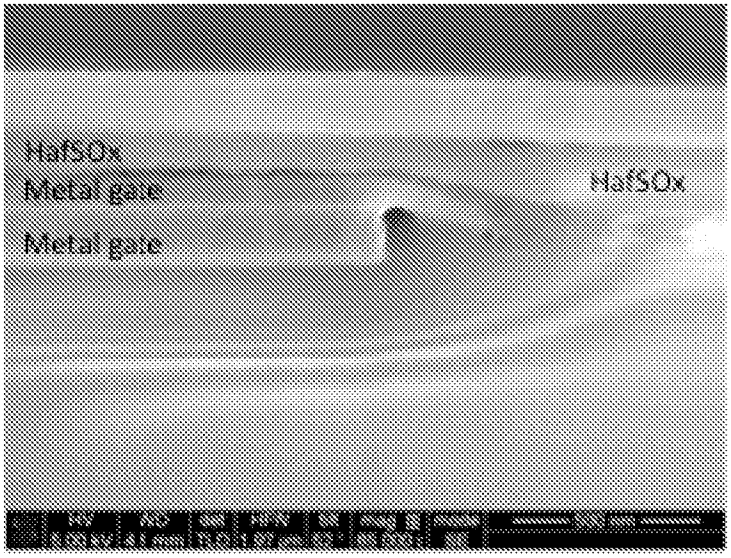

HafSOx
Metal gate
Metal gate
HafSOx

Fig. 9

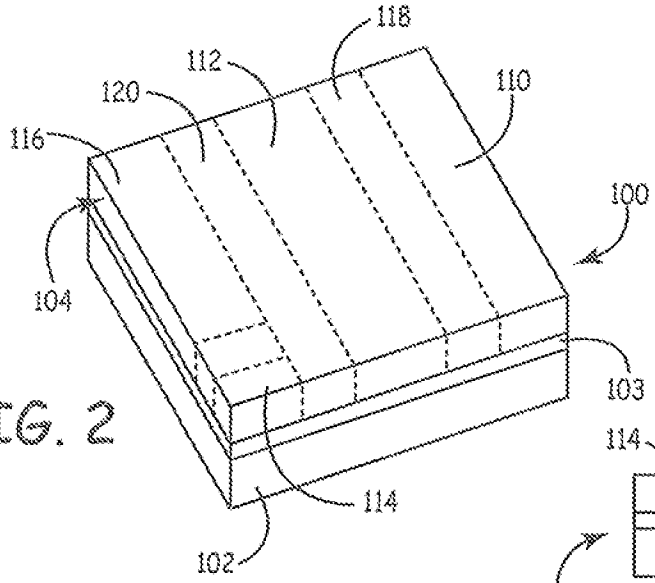


FIG. 2

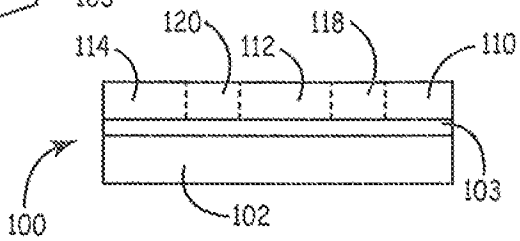


FIG. 3

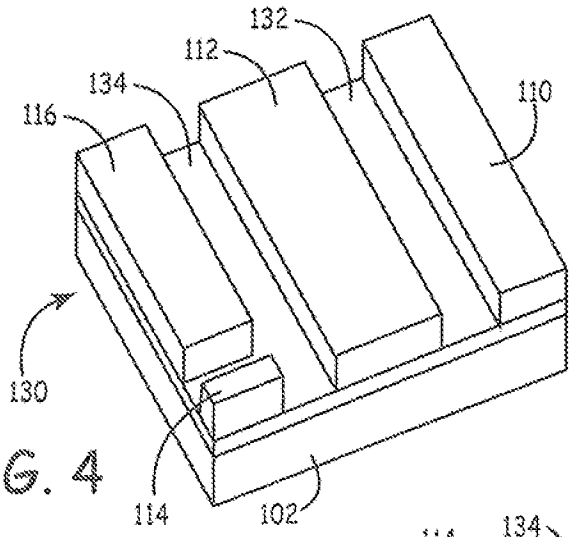


FIG. 4

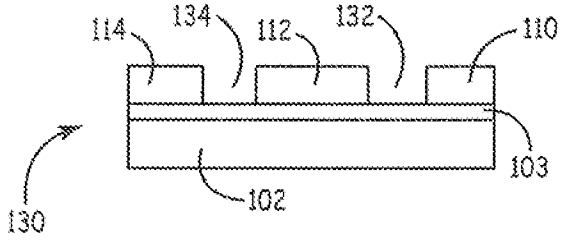


FIG. 5

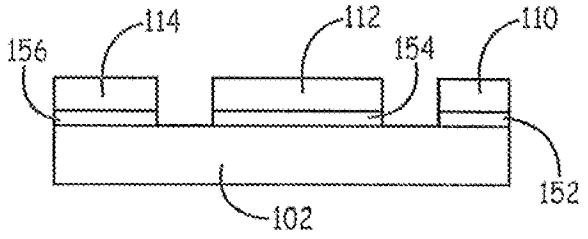


FIG. 6

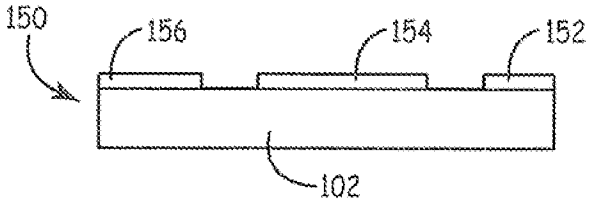


FIG. 7

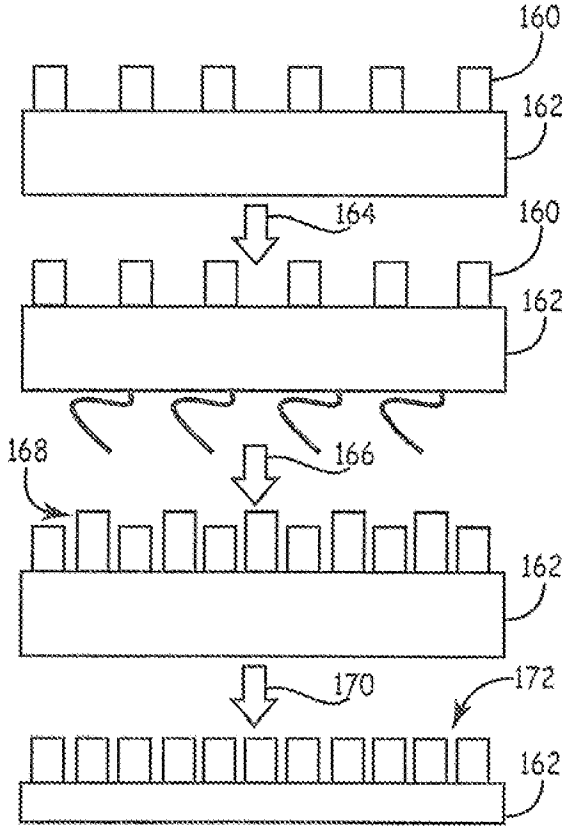


FIG. 8

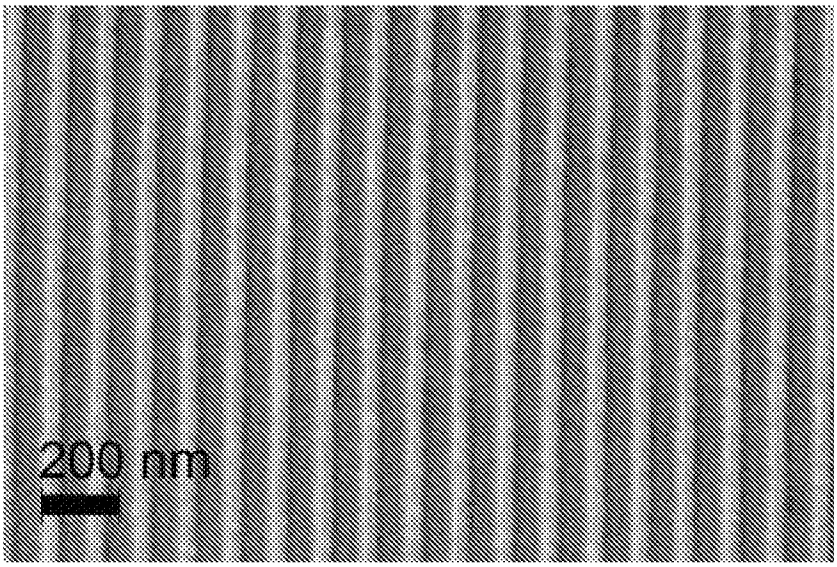


Fig. 10

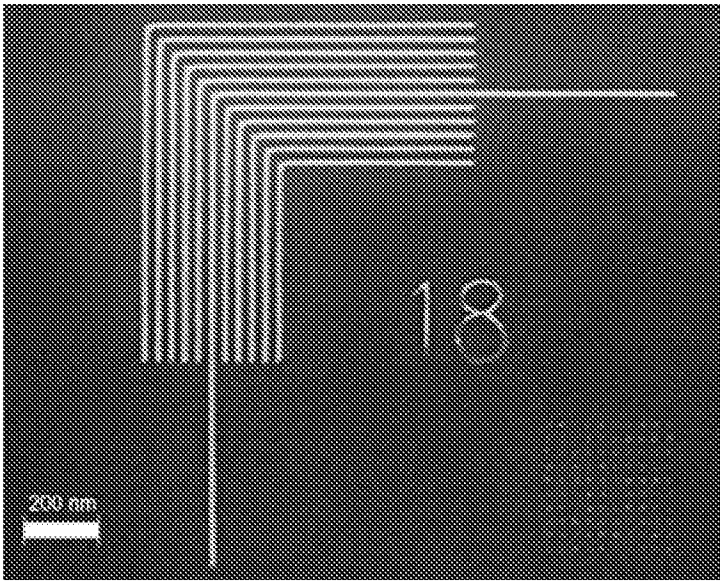


Fig. 11

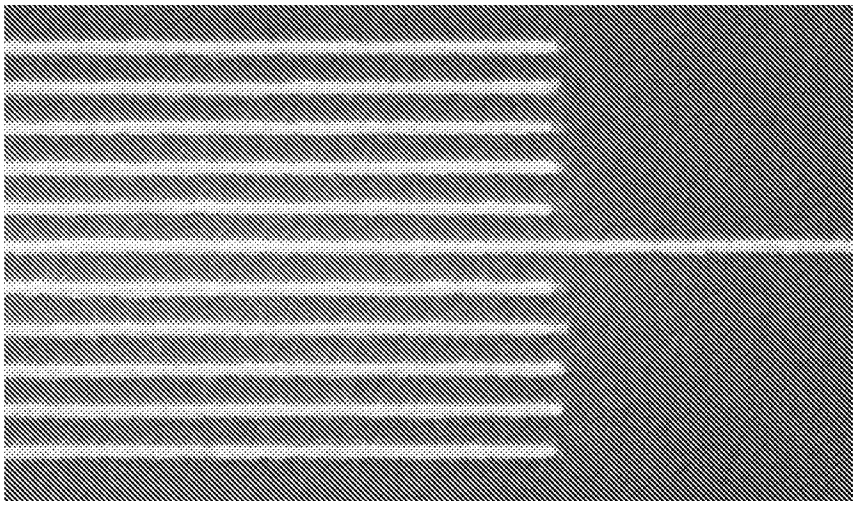


Fig. 12

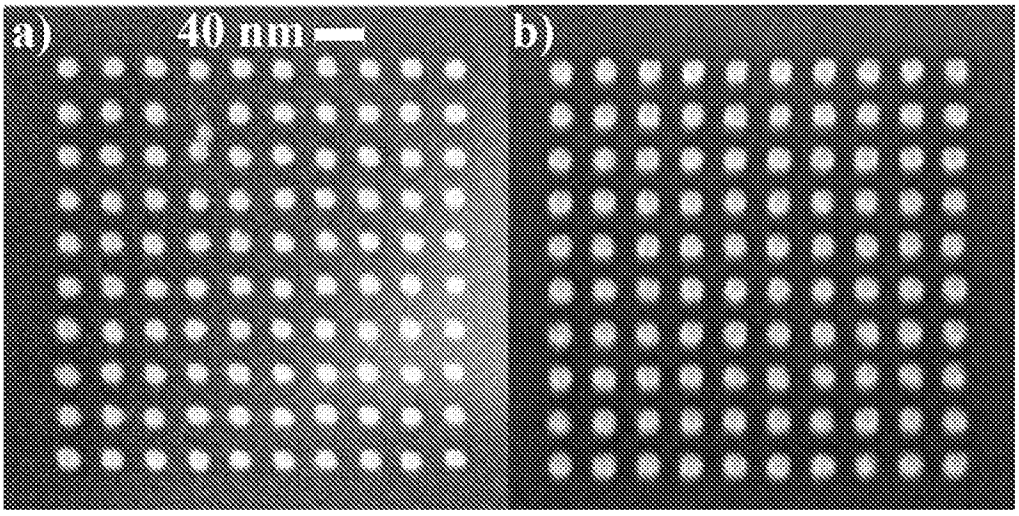


Fig. 13A

Fig. 13B

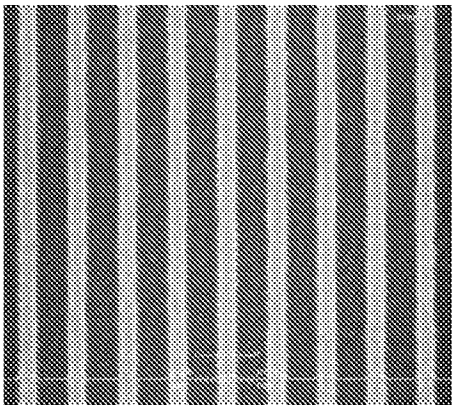


Fig. 14

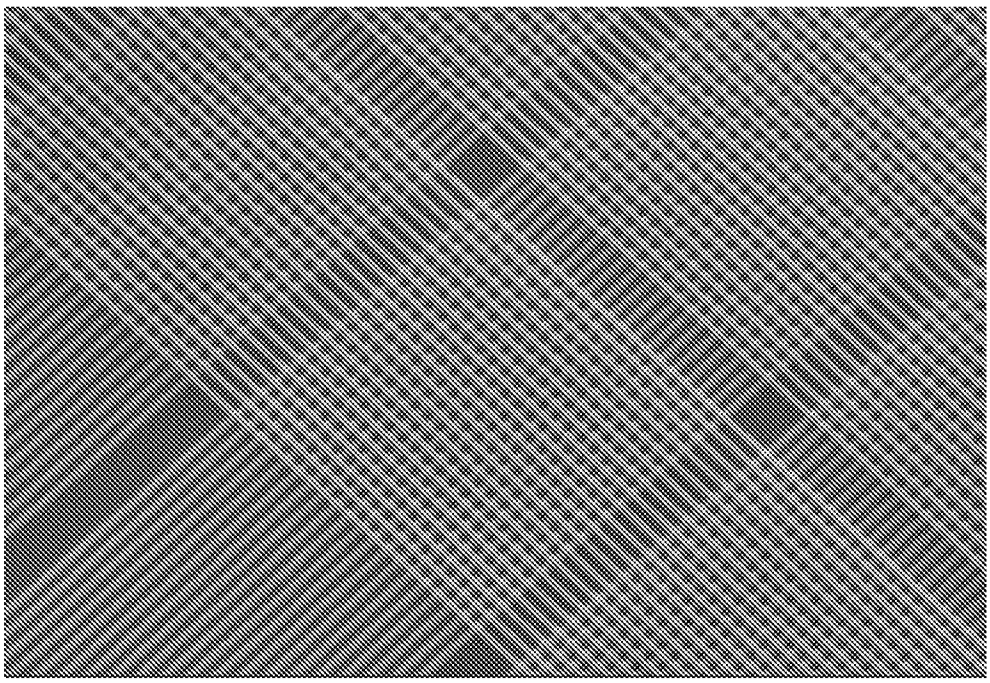


Fig. 15

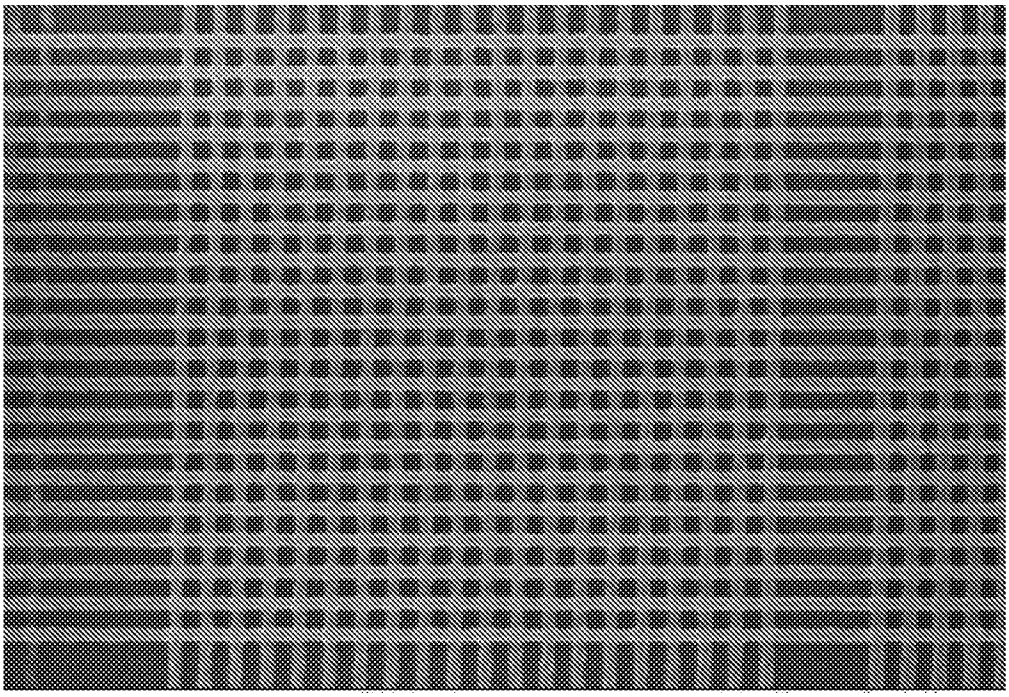


Fig. 16

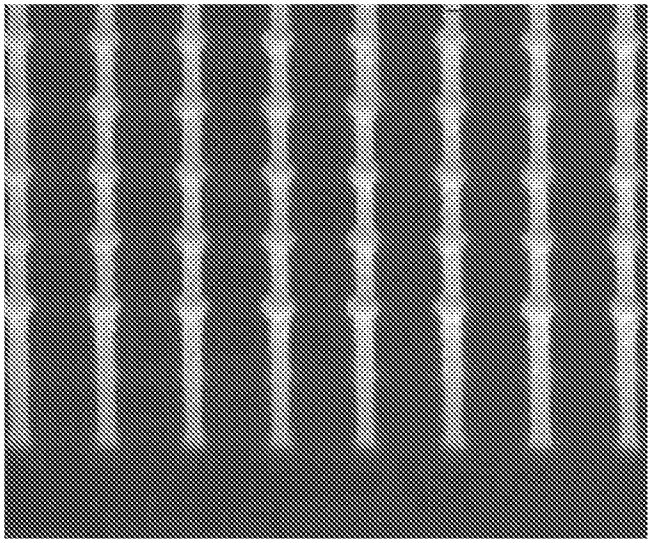


Fig. 17

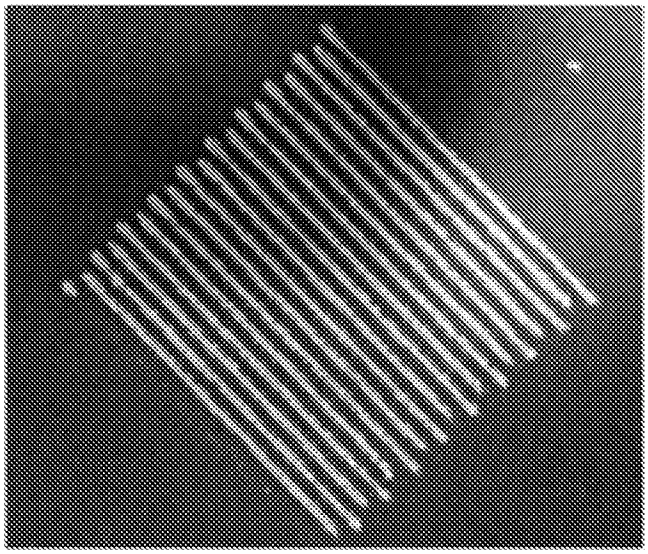


Fig. 18A

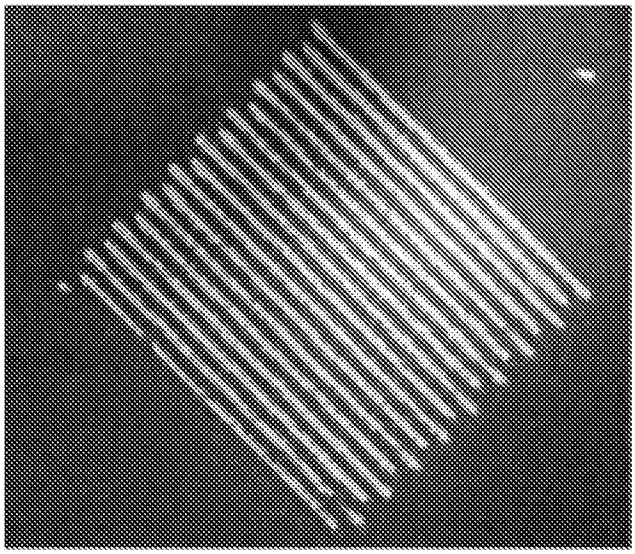


Fig. 18B

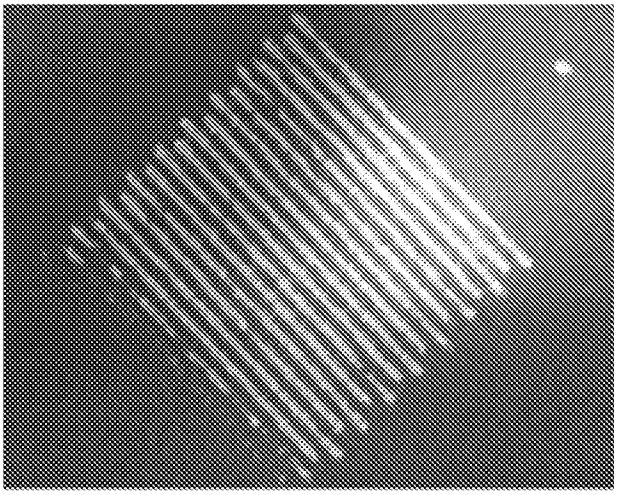


Fig. 18C

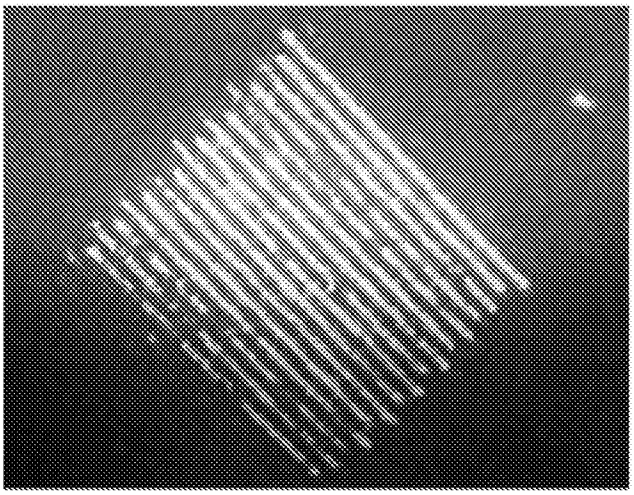


Fig. 18D

What we claim is:

1. A structure comprising a substrate and a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands and wherein the coating material has an average thickness from about 5 nm to about 30 nm, wherein exposure of the coating material to UV, EUV and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material.

2. The structure of claim 1 wherein the metal ions comprise metal suboxide ions.

3. The structure of claim 1 wherein the metal of the metal ions comprises 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.

4. The structure of claim 1 wherein the radiation sensitive ligands comprise peroxide ligands.

5. The structure of claim 1 wherein the coating material further comprises polyatomic anions.

6. The structure of claim 1 wherein the average thickness is from about 5 nm to about 25 nm.

7. The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists.

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

irradiating along a selected pattern, a layer of coating material on the surface of the substrate having an average thickness from about 5 nm to about 30 nm with UV radiation or EUV radiation at a dose of no more than about 100 mJ/cm^2, or with electron-beam radiation at a dose equivalent to no more than about 300 μC/cm^2 at 30 kV; and

contacting the irradiated layer with a developing composition to dissolve un-irradiated material to form a patterned coating material.

9. The method of claim 8 wherein the irradiation is performed with EUV at a dose of no more than about 90 mJ/cm^2.

10. The method of claim 8 wherein the irradiation is performed with e-beam radiation with a dose equivalent to no more than about 250 μC/cm^2 at 30 kV.

11. The method of claim 8 wherein the developing composition comprises tetramethyl ammonium hydroxide.

12. The method of claim 8 further comprising heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the irradiated layer with the developing composition.

13. The method of claim 8 wherein the coating material prior to irradiation comprises metal ions with radiation sensitive ligands and wherein interaction of the coating material with EUV and/or e-beam radiation alters the chemical properties of the coating material creating a structure with differential dissolution rates.

14. The method of claim 13 wherein the metal of the metal ions comprises 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, wherein the radiation sensitive ligands comprise peroxide ligands, and wherein the coating material further comprises polyatomic anions.

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15. A method for forming a patterned inorganic material on a substrate, the method comprising:

irradiating a coated substrate with a pattern of radiation wherein the coated substrate comprises a coating with a radiation patternable coating material comprising metal suboxide cations, ligands comprising a peroxide group and inorganic polyatomic anions and wherein irradiation creates a differential dissolution rate between irradiated and un-irradiated locations, wherein the coating material is formed by removing solvent from a deposited precursor solution wherein the peroxide ligand to metal ion ratio is at least about 2; and

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

16. The method of claim 15 further comprising contacting the coated substrate after heating with a developing composition to remove un-irradiated coating material to form the patterned inorganic material.

17. The method of claim 16 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.

18. The method of claim 15 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.

19. The method of claim 15 wherein the irradiating step comprises irradiation 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.

20. The method of claim 15 wherein the coating has an average thickness of about 5 nm to about 30 nm.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US04
	Application Number	
Title of Invention	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS	

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Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Alan	J.	Telecky	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Albany	State/Province	OR	Country of Residence i	US

Mailing Address of Inventor:

Address 1	2080 NW Cluster Oak Ave.		
Address 2			
City	Albany	State/Province	OR
Postal Code	97321	Country i	US

Inventor 3 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Douglas	A.	Keszler	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US04
	Application Number	
Title of Invention	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS	

City	Corvallis	State/Province	OR	Country of Residence i	US

Mailing Address of Inventor:

Address 1	8927 NW Lorri Pl		
Address 2			
City	Corvallis	State/Province	OR
Postal Code	97330	Country i	US

Inventor 4 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Andrew		Grenville	

Residence Information (Select One) (•) US Residency ( ) Non US Residency ( ) Active US Military Service

City	Eugene	State/Province	OR	Country of Residence i	US

Mailing Address of Inventor:

Address 1	1925 Fairmount Blvd		
Address 2			
City	Eugene	State/Province	OR
Postal Code	97403	Country i	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	62274		
Email Address		Add Email	Remove Email

Application Information:

Title of the Invention	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS		
Attorney Docket Number	5063.02US04	Small Entity Status Claimed	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	8	Suggested Figure for Publication (if any)	10

Filing By Reference :

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US04
	Application Number	
Title of Invention	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS	

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	◉ Customer Number	○ US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)
Customer Number	62274		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this information in the application data sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the application number blank.

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
	Continuation of	12850867	2010-08-05
Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
12850867	Claims benefit of provisional	61350103	2010-06-01

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button. Add

PTO/AIA/14 (12-13)
Approved for use through 01/31/2014. OMB 0651-0032
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US04
	Application Number	
Title of Invention	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS	

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55(d). When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX) [i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(h)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country [i]	Filing Date (YYYY-MM-DD)	Access Code [i] (if applicable)

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button. Add

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Authorization to Permit Access:

☐ Authorization to Permit Access to the Instant Application by the Participating Offices

PTO/AIA/14 (12-13)
Approved for use through 01/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US04
	Application Number	
Title of Invention	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS	

If checked, 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 instant patent application is filed access to the instant patent application. See 37 CFR 1.14(c) and (h). This box should not be checked if the applicant does not wish the EPO, JPO, KIPO, WIPO, or other intellectual property office in which a foreign application claiming priority to the instant patent application is filed to have access to the instant patent application.

In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the instant patent application with respect to: 1) the instant patent application-as-filed; 2) any foreign application to which the instant 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 instant patent application; and 3) any U.S. application-as-filed from which benefit is sought in the instant patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date of filing this Authorization.

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1 Remove

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

◉ Assignee	○ Legal Representative under 35 U.S.C. 117	○ Joint Inventor
○ Person to whom the inventor is obligated to assign.	○ Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor :

If the Applicant is an Organization check here. ☒

Organization Name	Inpria Corporation

Mailing Address Information:

Address 1	2001 NW Monroe Avenue		
Address 2	Suite 203		
City	Corvalllis	**State/Province**	OR
Country [i]	US	Postal Code	97330
Phone Number		Fax Number	

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US04
	Application Number	
Title of Invention	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS	

Email Address	

Additional Applicant Data may be generated within this form by selecting the Add button. Add

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not subsitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication . An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

Remove

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		**State/Province**	
Country i		Postal Code	
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button. Add

Signature:

Remove

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications

Signature	/Peter S. Dardi/			Date (YYYY-MM-DD)	2015-09-18
First Name	Peter	Last Name	Dardi	Registration Number	39650

Additional Signature may be generated within this form by selecting the Add button. Add

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Approved for use through 01/31/2014. 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 contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US04
	Application Number	
Title of Invention	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS	

This collection of information is required by 37 CFR 1.76. 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 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet 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.**

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 the Freedom of Information Act requires disclosure of these records.

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 inspections 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.

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.

Lam Research Ex. 1007 - Page 76 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.: 5063.02US04

Stowers et al. Confirmation No.: TBA

Application No.: *Continuation of 12/850,867*

Filed: Herewith

For: METAL NANOWIRE INKS FOR THE FORMATION OF TRANSPARENT CONDUCTIVE FILMS WITH FUSED NETWORKS

PRELIMINARY REMARKS

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

Sir:

INTRODUCTORY COMMENTS

Prior to considering the continuation application filed with this document, please consider the following remarks. This document includes the following sections.

A. 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.

September 18, 2015
Date

/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
Facsimile: (763) 571-5157

5063.02US04

CONTINUING APPLICATION TRANSMITTAL

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

Sir:

This is a request for filing a

[X] Continuation [ ] Divisional

application, under 37 C.F.R. § 1.53(b), of pending prior Application No. 12/850,867, filed August 5, 2010 for: PATTERENED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS by: Jason K. Stowers, Alan J. Telecky, Douglas A. Keszler and Andrew Grenville. The entire disclosure of the prior application is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.

Enclosed are:

[X] Specification, Claims and Abstract - 39 pages.

[X] Drawings - 8 sheets (Figs. 1-18D).

[X] Application Data Sheet.

[ ] Declarations.

[ ] Power of Attorney.

[X] Preliminary Remarks - 3 pages.

The filing fee has been calculated as shown below:					
	No. Filed	No. Extra	Small Entity Rate	OR	Large Entity Rate
Basic Filing Fee			$70	OR	$280
Utility Search Fee			$300	OR	$600
Utility Examination Fee			$360	OR	$720
Total Claims	20 - 20	= **	x 40 = $0	OR	x 80 = $0
Independent Claims	3 - 3	= **	x 210 = $0	OR	x 420 = $0
Surcharge - Late Oath/Declaration [If applicable]			[+ $70]	OR	+ $140
Presence of Multiple Dependent Claim [If applicable]			[+ 390]	OR	[+ 780]
Utility Application Size Fee - per each additional 50 sheets that exceeds 100 sheets:			* x 200 = $	OR	* x 400 = $
		TOTAL	**$**	**TOTAL**	**$1740**
**If the difference is less than zero, enter "0". Total # of sheets = (Spec and Abst pgs)+Dwg Sheets					

1. [X] The Commissioner is hereby authorized to charge a credit card referenced in the electronic filing in the amount of $ 1740.00. 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.

2. [ ] Priority of *[country]* application(s) No. _____ filed _____ is claimed under 35 U.S.C. § 119. The certified copy was filed in prior Application No. _____ on _____.

3. [X] The prior application is assigned of record to Inpria Corporation recorded at Reel 025647, Frame 0344.

4. [X] An Information Disclosure Statement and Transmittal Letter are enclosed.

5. [ ] Applicant is entitled to small entity status in accordance with 37 CFR 1.27.

6. [ ] CD-ROM or CD-R in duplicate, and Compact Disc Transmittal are enclosed.

7. [ ] Request and Certification Under 35 U.S.C. 122(b)(2)(B)(i) (non-publication).

8. [X] Address all future communications to:

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

Respectfully submitted,

/Peter S. Dardi/

Peter S. Dardi, Ph.D.
Registration No. 39,650

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.

September 18, 2015
Date

/Peter S. Dardi/
Peter S. Dardi, Ph.D.

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATIONS USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

As a below named inventor, I hereby declare that:

This Declaration is directed to:

[ ] The attached application, or

[X] United States or PCT international application number 14/858,612 filed on September 18, 2015.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I have read and understand the contents of the above-identified application, including the claims.

I acknowledge the duty to disclose to the United States Patent Office all information known to me to be 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 acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

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

Inventor's signature

9/29/2015
Date

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATIONS USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

As a below named inventor, I hereby declare that:

This Declaration is directed to:

[ ] The attached application, or

[X] United States or PCT international application number 14/858,612 filed on September 18, 2015.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I have read and understand the contents of the above-identified application, including the claims.

I acknowledge the duty to disclose to the United States Patent Office all information known to me to be 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 acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

Alan J. Telecky
Full name of inventor (given name, family name)

Inventor's signature

9/24/2015
Date

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATIONS USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

As a below named inventor, I hereby declare that:

This Declaration is directed to:

[ ] The attached application, or

[X] United States or PCT international application number 14/858,612 filed on September 18, 2015.

The above-identified application was made or authorized to be made by me.

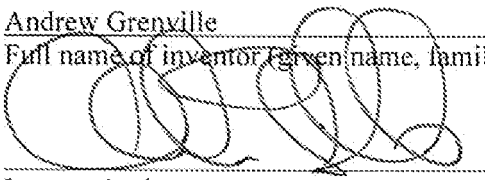
I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I have read and understand the contents of the above-identified application, including the claims.

I acknowledge the duty to disclose to the United States Patent Office all information known to me to be 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 acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

Andrew Grenville
Full name of inventor (given name, family name)



Inventor's signature

9/28/15
Date

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATIONS USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

As a below named inventor, I hereby declare that:

This Declaration is directed to:

[ ] The attached application, or

[X] United States or PCT international application number 14/858,612 filed on September 18, 2015.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I have read and understand the contents of the above-identified application, including the claims.

I acknowledge the duty to disclose to the United States Patent Office all information known to me to be 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 acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

Douglas A. Keszler
Full name of inventor (given name, family name)

Douglas A Keszler
Inventor's signature

30 September 2015
Date

Electronic Acknowledgement Receipt

EFS ID:	23660637
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
Receipt Date:	01-OCT-2015
Filing Date:	18-SEP-2015
Time Stamp:	11:47:58
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	Oath or Declaration filed	150930_signed_declarations.pdf	602487 4dc316c77065bb54838a3699cfe1b07aa6dcb0fd	no	4

Warnings:	
Information:	

Total Files Size (in bytes):	602487

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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 FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 14/858,612

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	280
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	600
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	720
TOTAL CLAIMS (37 CFR 1.16(i))	20 minus 20 =	*			OR	x 80 =	0.00
INDEPENDENT CLAIMS (37 CFR 1.16(h))	3 minus 3 =	*				x 420 =	0.00
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).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	1600

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))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		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))							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 found in the appropriate box in column 1.

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
14/858,612	09/18/2015	1722	1740	5063.02US04	20	3

CONFIRMATION NO. 1074

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

FILING RECEIPT

OC000000077822291

Date Mailed: 10/02/2015

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**

Inventor(s)

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

Applicant(s)

Inpria Corporation, Corvalllis, OR;

Assignment For Published Patent Application

Inpria Corporation

Power of Attorney: None

Domestic Priority data as claimed by applicant

This application is a CON of 12/850,867 08/05/2010
which claims benefit of 61/350,103 06/01/2010

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

If Required, Foreign Filing License Granted: 10/01/2015
The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 14/858,612**
Projected Publication Date: 01/14/2016
Non-Publication Request: No

Early Publication Request: No
Title

PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

Preliminary Class

430

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

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 (1-866-999-4258).

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.

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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).

SelectUSA

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

Lam Research Ex. 1007 - Page 89 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

REMARKS

Claims 1-20 are pending. The specification has been updated relative to the patent application to include the parent application in the cross reference to related applications. The specification has also been amended to add "copper" to a list of ions that can be included in the precursor solution. This amendment to the specification makes the specification consistent with original claim 10 and corrects this oversight in the original specification.

The specification supports the new claims as noted in the following discussion. The specification supports new claims 1 and 13, for example, at page 3, lines 9-23, page 5, lines 26-27, page 8, lines 14-17, page 21, lines 16-18 and page 23, line 16 to page 24, line 18. The specification supports claims 2, 4 and 5, for example, page 3, lines 13-15. The specification supports claims 3, 14 and 18, for example, at page 15, line 19 to page 16, line 16 and original claim 10. The specification supports claims 6 and 20, for example, at page 21, lines 16-28. The specification supports claim 7, for example, at page 9, lines 13-25 and page 13, lines 2-5. The specification supports claim 8, for example, at page 3, lines 26-30, page 21, lines 16-28 and page 23, lines 16-30. The specification supports claim 9, for example, at page 23, lines 16-30. The specification supports claim 10, for example, at page 24, lines 3-18. The specification supports claim 11, for example, at page 25, line 22 to page 26, line 1. The specification supports claim 12, for example, at page 3, lines 16-17. The specification supports claims 15-17 and 19, for example, at page 3, lines 3-30. No new matter is introduced by the claims.

Lam Research Ex. 1007 - Page 90 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

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 No. 39,650

Customer No. 62274
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1250 East Moore Lake Drive
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Telephone: (404) 949-5730

Lam Research Ex. 1007 - Page 91 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Acknowledgement Receipt

EFS ID:	23721639
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
Receipt Date:	07-OCT-2015
Filing Date:	18-SEP-2015
Time Stamp:	17:44:23
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	Preliminary Amendment	Corr_Prelim_Remarks.pdf	70873 0d00253ca9ae9adcaf90b5af8e259fe70a373df7	no	1

Warnings:	
Information:	

2	Applicant Arguments/Remarks Made in an Amendment	Remarks.pdf	125351 9ad9a55869ccedeae5bb94c45e23d3336f214991	no	2

Warnings:	
Information:	
Total Files Size (in bytes):	196224

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

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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US04

Stowers et al. Confirmation No.: 1074

Application No.: 14/858,612

Filed: September 18, 2015

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

CORRECTED PRELIMINARY REMARKS

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

Sir:

INTRODUCTORY COMMENTS

Prior to considering the continuation application filed on September 18, 2015, please consider the following remarks. The Remarks section of this Preliminary Remarks document is identical with the Preliminary Remarks filed with the Application, and this document is filed to correct the title that was inadvertently incorrect in the original document. This document includes the following sections.

A. 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.

October 7, 2015
Date

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

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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P.O. Box 1450
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www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
14/858,612	09/18/2015	Jason K. Stowers	5063.02US04

CONFIRMATION NO. 1074

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

PUBLICATION NOTICE

OC000000079919892

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

Publication No.US-2016-0011505-A1
Publication Date:01/14/2016

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

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US04

Stowers et al. Confirmation No.: 1074

Application No.: 14/858,612

Filed: September 18, 2015

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

POWER OF ATTORNEY BY APPLICANT

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

Sir:

I hereby appoint the Practitioners associated with **Customer Number 62274** as my/our attorneys or agents and 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.

Please recognize or change the correspondence address for this application to:

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

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

The undersigned (whose title is supplied below) is authorized to act on behalf of the Applicant (e.g., where the Applicant is a juristic entity).

Inpria Corporation, Applicant

Date: 3/19/16

Signature

Andrew Grenville

Name Printed or Typed

CEO

Title

Electronic Acknowledgement Receipt

EFS ID:	25362880
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
Receipt Date:	31-MAR-2016
Filing Date:	18-SEP-2015
Time Stamp:	16:09:41
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	Power of Attorney	Signed_POA.pdf	226777 7413da5ea4939e187cf381dcceeae621070a16ac	no	1

Warnings:	
Information:	

Total Files Size (in bytes):	226777

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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

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New International Application Filed with the USPTO as a Receiving Office

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Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
14/858,612	09/18/2015	Jason K. Stowers	5063.02US04

CONFIRMATION NO. 1074

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

POA ACCEPTANCE LETTER

OC000000082155387

Date Mailed: 04/13/2016

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 03/31/2016.

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.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/zmoguss/

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14858612	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	04/20/2016								
	1	÷								
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/858,612	09/18/2015	Jason K. Stowers	5063.02US04	1074

62274 7590 04/25/2016

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
04/25/2016	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. 14/858,612	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 2 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 _____.

☐ 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) *1-20* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☐ Claim(s) _____ is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☒ Claim(s) *1-20* 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.

Election/Restrictions

2. Restriction to one of the following inventions is required under 35 U.S.C. 121:

I. Claims 1-7, drawn to a structure, classified in G03F 7/0043.

II. Claims 8-20, drawn to a method, classified in B41C 2210/04.

3. Inventions I 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, Invention I, claims 1-7, that the product as claimed can be made by another and materially different process, either by process by instant claims 8-14 or process by instant claims 15-20.

4. 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/or examination burden if restriction were not required because one or more of the following reasons apply:

The search and consideration of two independent and distinct invention should be conducted in a variety of classes and subclasses, and it is a burden for the examination.

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 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 or pre-AIA 35 U.S.C. 103(a) of the other invention.

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

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 14/858,612	Filing Date 09/18/2015	☐ To be Mailed

ENTITY: ☒ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

	(Column 1)	(Column 2)		
FOR	NUMBER FILED	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

		(Column 1)		(Column 2)	(Column 3)		
	06/14/2016	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
AMENDMENT	Total (37 CFR 1.16(i))	* 20	Minus	** 20	= 0	X $80 =	0
	Independent (37 CFR 1.16(h))	* 3	Minus	***3	= 0	X $420 =	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**

		(Column 1)		(Column 2)	(Column 3)		
		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
AMENDMENT	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
/SHEILA D. CHAPMAN/

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.

REMARKS

Claims 1-20 are pending. The Examiner imposed a restriction requirement between two claim groups. Applicant elects Group I, claims 1-7 without traverse.

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/

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Lam Research Ex. 1007 - Page 107 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Acknowledgement Receipt

EFS ID:	26060608
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
Receipt Date:	14-JUN-2016
Filing Date:	18-SEP-2015
Time Stamp:	15:16:32
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_RR.pdf	399039 19388164b4db7644e4596e7af372fdf34892deb2	yes	6

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Response to Election / Restriction Filed	1	1
	Claims	2	5
	Applicant Arguments/Remarks Made in an Amendment	6	6
Warnings:			
Information:			
	Total Files Size (in bytes):	399039	

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.: 5063.02US04
Stowers et al.	Confirmation No.: 1074
Application No.: 14/858,612	Examiner: Chanceity N. Robinson
Filed: September 18, 2015	Group Art Unit: 1722

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

RESPONSE TO RESTRICTION REQUIREMENT

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

Dear Sir:

In response to the Restriction Requirement dated April 25, 2016, Applicants submit the following, which comprises the following sections:

A. Listing of 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 14, 2016
Date

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

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.

1. (Original) A structure comprising a substrate and a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands and wherein the coating material has an average thickness from about 5 nm to about 30 nm, wherein exposure of the coating material to UV, EUV and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material.

2. (Original) The structure of claim 1 wherein the metal ions comprise metal suboxide ions.

3. (Original) The structure of claim 1 wherein the metal of the metal ions comprises 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.

4. (Original) The structure of claim 1 wherein the radiation sensitive ligands comprise peroxide ligands.

5. (Original) The structure of claim 1 wherein the coating material further comprises polyatomic anions.

6. (Original) The structure of claim 1 wherein the average thickness is from about 5 nm to about 25 nm.

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7. (Original) The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists.

8. (Original) A method for forming a patterned structure comprising a substrate and a patterned coating material on a surface of the substrate, the method comprising:

irradiating along a selected pattern, a layer of coating material on the surface of the substrate having an average thickness from about 5 nm to about 30 nm with UV radiation or EUV radiation at a dose of no more than about 100 mJ/cm^2, or with electron-beam radiation 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 coating material.

9. (Original) The method of claim 8 wherein the irradiation is performed with EUV at a dose of no more than about 90 mJ/cm^2.

10. (Original) The method of claim 8 wherein the irradiation is performed with e-beam radiation with a dose equivalent to no more than about 250 $\mu C/cm^2$ at 30 kV.

11. (Original) The method of claim 8 wherein the developing composition comprises tetramethyl ammonium hydroxide.

12. (Original) The method of claim 8 further comprising heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the irradiated layer with the developing composition.

13. (Original) The method of claim 8 wherein the coating material prior to irradiation comprises metal ions with radiation sensitive ligands and wherein interaction of the coating material with EUV and/or e-beam radiation alters the chemical properties of the coating material creating a structure with differential dissolution rates.

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14. (Original) The method of claim 13 wherein the metal of the metal ions comprises 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, wherein the radiation sensitive ligands comprise peroxide ligands, and wherein the coating material further comprises polyatomic anions.

15. (Original) A method for forming a patterned inorganic material on a substrate, the method comprising:

irradiating a coated substrate with a pattern of radiation wherein the coated substrate comprises a coating with a radiation patternable coating material comprising metal suboxide cations, ligands comprising a peroxide group and inorganic polyatomic anions and wherein irradiation creates a differential dissolution rate between irradiated and un-irradiated locations, wherein the coating material is formed by removing solvent from a deposited precursor solution wherein the peroxide ligand to metal ion ratio is at least about 2; and

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

16. (Original) The method of claim 15 further comprising contacting the coated substrate after heating with a developing composition to remove un-irradiated coating material to form the patterned inorganic material.

17. (Original) The method of claim 16 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.

18. (Original) The method of claim 15 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.

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19. (Original) The method of claim 15 wherein the irradiating step comprises irradiation 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.

20. (Original) The method of claim 15 wherein the coating has an average thickness of about 5 nm to about 30 nm.

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EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	3	((14/858612) or (12/850867)).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 13:58
L2	5	((14/858612) or (12/850867) or (13/284531)).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 14:05
L3	123950	substrate and (metal adj ion)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
L4	19	radiation adj sensitive adj ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
L5	14	3 and 4	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
L6	13	5 and (UV or EUV or electron-beam or ultraviolet)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
L7	6	6 and differential	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:19
L8	4	7 and peroxide	US-PGPUB;	OR	ON	2016/06/27

			USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			14:19
L9	1	(14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 14:21
L10	1	9 and about	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:22
L11	1	10 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/327).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:23
S1	1	(14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/16 13:02
S2	66252	(metal adj ions) and (ligands)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:02
S3	29121	(UV or ultraviolet or electron-beam or EUV) and S2	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:03
S4	6581	S3 and ((alter$1 or change$1) with chemical)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S5	5760	S4 and substrate	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT;	OR	ON	2016/06/16 13:04

			IBM_TDB			
S6	1990	S5 and peroxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S7	85	S5 and (peroxide with ligand)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S8	65	S7 and anion	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S9	14	S8 and polyatomic and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S10	14	S9 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/327 OR G03F7/0002 OR G03F7/11 OR G03F7/09 OR G03F7/2002 OR G03F7/2037 OR G03F7/30 OR G03F7/2004 OR G03F7/32 OR H01L29/7869 OR H01L27/1225 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 B32B2457/14 OR B32B9/005 OR B82Y10/00 OR B82Y40/00 OR C01G1/10 OR C01G25/006 OR C01G25/06 OR C01G27/006 OR C01G27/06).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:07

EAST Search History (Interference)

<This search history is empty>

6/27/2016 2:23:30 PM
C:\Users\crobinson4\Documents\EAST\Workspaces\14858612.wsp

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14858612	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

CPC- SEARCHED		
Symbol	Date	Examiner
G03F 7/20	06/27/2016	CR

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

SEARCH NOTES		
Search Notes	Date	Examiner
East, Assignee and Inventorship Search	06/27/2016	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
	14858612	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	06/27/2016								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
	8	N								
	9	N								
	10	N								
	11	N								
	12	N								
	13	N								
	14	N								
	15	N								
	16	N								
	17	N								
	18	N								
	19	N								
	20	N								

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www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/858,612	09/18/2015	Jason K. Stowers	5063.02US04	1074

62274 7590 06/30/2016

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Moore Lake Plaza, Suite 205
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Fridley, MN 55432

EXAMINER	
ROBINSON, CHANCEITY N	

ART UNIT	PAPER NUMBER
1722	

MAIL DATE	DELIVERY MODE
06/30/2016	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. 14/858,612	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 *06/14/2016*.

☐ 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) *1-20* is/are pending in the application.

5a) Of the above claim(s) *8-20* is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-7* 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 *09/18/2015* 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 *09/18/2015*.

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

Election/Restrictions

2. Claims 8-20 are withdrawn from further consideration pursuant to 37 CFR 1.142(b) as being drawn to a nonelected method, there being no allowable generic or linking claim. Election was made **without** traverse in the reply filed on 06/14/2016.

3. Applicant's election without traverse of Group I, claims 1-7 in the reply filed on 06/14/2017 is acknowledged.

Double Patenting

4. 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. See MPEP § 717.02 for applications subject to examination under the first inventor to file provisions of the AIA as explained in MPEP § 2159. See MPEP §§ 706.02(l)(1) - 706.02(l)(3) for applications not subject to examination under the first inventor to file provisions of the AIA. A terminal disclaimer must be signed in compliance with 37 CFR 1.321(b).

The USPTO Internet website contains terminal disclaimer forms which may be used. Please visit www.uspto.gov/forms/. The filing date of the application in which the form is filed determines what form (e.g., PTO/SB/25, PTO/SB/26, PTO/AIA/25, or PTO/AIA/26) 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.

5. Claims 1-7 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-17 of U.S. Patent No. 8,415,000 B2. Although the claims at issue are not identical, they are not patentably distinct from each other because both the instant claims and patent ‘000 have claims drawn to a structure comprising a substrate a coating material on a surface of the substrate, wherein the coating material

comprises metal ions with radiation sensitive ligands (patterned inorganic material). Both the instant claims and patent ‘000 recite open claim language; therefore, other components may be comprised in their respective invention.

6. Claims 1-7 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-19 of U.S. Patent No. 9,281,207 B2. Although the claims at issue are not identical, they are not patentably distinct from each other because both the instant claims and patent ‘207 have claims drawn to a structure comprising a substrate a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands . Both the instant claims and patent ‘207recite open claim language; therefore, other components may be comprised in their respective invention.

Claim Rejections - 35 USC § 112

7. 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.

8. Claims 1-7 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. Instant claims 1-7 recite the term, “about”. The term "about" in claims 1 and is a relative term which renders the claim indefinite. The term "about" is not defined by the claim, the specification does not provide a

standard for ascertaining the requisite degree, and one of ordinary skill in the art would not be reasonably apprised of the scope of the invention. Appropriate correction is required.

Claim Rejections - 35 USC § 103

9. In the event the determination of the status of the application as subject to AIA 35 U.S.C. 102 and 103 (or as subject to pre-AIA 35 U.S.C. 102 and 103) is incorrect, any correction of the statutory basis for the rejection will not be considered a new ground of rejection if the prior art relied upon, and the rationale supporting the rejection, would be the same under either status.

10. 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.

11. 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.

12. Claims 1-7 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.

Regarding claims 1-7, Stowers et al. disclose a structure comprising a substrate and a coating material an aqueous precursor solutions 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 the coating material has an average thickness from about 5 nm to about 30 nm (approx. 2 nm, which encompasses the instant claimed range of about 5 nm), wherein exposure of the coating material to UV , EUV, and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and unexposed regions of the coating material (see introduction section).

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).

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

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BIB DATA SHEET

CONFIRMATION NO. 1074

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
14/858,612	09/18/2015	430	1722	5063.02US04

APPLICANTS

Inpria Corporation, Corvalllis, OR;

INVENTORS

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

**** CONTINUING DATA ***************************

This application is a CON of 12/850,867 08/05/2010 PAT 9176377
which claims benefit of 61/350,103 06/01/2010

**** FOREIGN APPLICATIONS ***************************

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED ****

10/01/2015

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	20	3

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

FILING FEE RECEIVED		
1740	FEES: Authority has been given in Paper No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other _____ ☐ Credit

BIB (Rev. 05/07).

Notice of References Cited	Application/Control No. 14/858,612	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	CPC Classification	US Classification
	A	US-				
	B	US-				
	C	US-				
	D	US-				
	E	US-				
	F	US-				
	G	US-				
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	I	US-				
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	N					
	O					
	P					
	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.

PTO/SB/08a (01-10)
Approved for use through 07/31/2012. OMB 0651-0031
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	
Filing Date	2015-09-18
First Named Inventor	Stowers
Art Unit	TBA
Examiner Name	To be assigned
Attorney Docket Number	5063.02US04

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		0968-05-28	Hamling	
	2	4102683		1978-07-25	DiPiazza	
	3	4370405		1983-01-25	O'Toole et al.	
	4	4732841		1988-03-22	Radigan	
	5	4891303		1990-01-02	Garza et al.	
	6	4910122		1990-03-20	Arnold et al.	
	7	5025094		1991-06-18	King	
	8	5672243		1997-09-30	Hsia et al.	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./

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	9	6020269		2000-02-01	Wang et al.	
	10	6060380		2000-05-09	Subramanian et al.	
		ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./				
	11	6183716		2001-02-06	Sleight et al.	
	12	6194323		2001-02-27	Downey et al.	
	13	6197896		2001-03-06	Aviram et al.	
	14	6268457		2001-07-21	Kennedy et al.	
	15	6287951		2001-09-11	Lucas et al.	
	16	6420088		2002-07-16	Angelopoulos et al.	
		ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./				
	17	6583071		2003-06-24	Weidman et al.	
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14858612 - GAU: 1722

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Attorney Docket Number	5063.02US04

	20	6927108		2005-08-09	Weng et al.	
	21	6946677		2005-09-20	Ostergard	
	22	7001821		2006-02-21	Aggarwal et al.	
	23	7208341		2007-04-24	Lee et al.	
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	25	8053370		2011-08-11	Yang et al.	
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	27	8415000		2013-04-09	Stowers et al.	corresponds to US20110293888

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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.	

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	2	20040067444		2004-04-08	Wakabayahsi et al.	
	3	20050242330		2005-11-03	Herman et al.	
		ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./				
	4	20060088962		2006-04-27	Herman et al.	
	5	20060234138		2006-10-19	Fehlhaber et al.	
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	13	20130224652		2013-08-29	Bass et al.		
	14	20120223418		2012-09-06	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	H03-148659	JP	A	1991-06-25	Fujitsu Ltd	English abstract only	☐
	2	2006-284947	JP		2006-10-19	Fuji Photo Film Co Ltd	English abstract only	☐
	3	2005/043246	WO		2005-05-12	Hewlett-Packard		☐
	4	2008/082448	WO		2008-07-10	Oregon State		☐
	5	2009/120169	WO		2009-10-01	Oregon State		☐
	6	2007-514182	JP		2008-05-31	Hewlett-Packard	abstract only, corresponds to WO 2005/043246	☐
	7	10-2008-0090383	KR		2008-10-08	Oregon State	abstract only, corresponds to WO 2008/082448	☐

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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	AHMED ET AL., "Synthesis and Characterization of Zirconium and Hafnium Sulfates, Hydroxide Sulfates and Oxide Sulfates", Acta Chemica Scandinavica, 53:24-33 (1999).	☐
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	3	MEYERS ET AL., "Solution-Processed Aluminum Oxide Phosphate Thin-Film Dielectrics" Chem. Mater., 2007, 19, 4023-4029. Abstract Only.	☐
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	6	OWEN ET AL., "1/8 μm optical lithography," J. Vac. Sci. Technol. B 10, 3032 (1992). Abstract Only.	☐
	7	STOWERS, "Direct Patterning of Solution Deposited Metal Oxides", A Dissertation to Oregon State University, August 14, 2008 (149 pages).	☐
	8	STOWERS ET AL., "High resolution, high sensitivity inorganic resists", Microelectronic Engineering, 86:730-733 (2009).	☐
	9	STOWERS ET AL., "Directly patterned inorganic hardmask for EUV lothography," Proc. SPIE 7969, 796915 (2011); http://dx.doi.org/10.1117/12.879542	☐

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./

14858612 - GAU: 1722	Application Number Receipt date: 09/18/2015
INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**	Filing Date: 2015-09-18
	First Named Inventor: Stowers
	Art Unit: TBA
	Examiner Name: To be assigned
	Attorney Docket Number: 5063.02US04

	10	WANG ET AL.,"TiO2 micro-devices fabricated by laser direct writing" Optics Express, August 29, 2011, 19 (18):17390-17935.	☐
	11	ZHANG ET AL., "Stabilization of Cubic ZrO2 with Rh(III) and/or La(III), Journal of Solid State Chemistry, 72:131-136 (1988).	☐
	12	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.	☐
	13	Supplementary European Search Report From Corresponding European Patent Application No. 11168027.8 Dated January 6, 2012 (8 pages).	☐
	14	Office Action from copending Korean Application No. 10-2011-0052919 dated March 14, 2013.	☐
	15	Office Action from copending Japanese Application No. 2011-120402 dated June 11, 2013.	☐
	16	Office Action from copending Taiwan Application No. 100116897 dated July 29, 2013 (14 pages with translation). ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./	☒

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EXAMINER SIGNATURE

Examiner Signature	/Chanceity Robinson/	Date Considered	06/16/2016

*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.

PTO/SB/06 (09-11)
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 14/858,612	Filing Date 09/18/2015	☐ 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	09/30/2016	(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))	* 12	Minus	** 20	= 0	X $80 =	0
	Independent (37 CFR 1.16(h))	* 1	Minus	***3	= 0	X $420 =	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
BRENDA HARRISON

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Dardi & Herbert, PLLC
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1250 East Moore Lake Drive
Fridley, MN 55432
Telephone: (763) 412-3827
Facsimile: (763) 571-5157

Attorney Docket No. 5063.02US04

AMENDMENT TRANSMITTAL

In re the application of:

Stowers et al.

Confirmation No.: 1074

Application No.: 14/858,612

Examiner: Robinson, Chanceity N.

Filed: September 18, 2015

Group Art Unit: 1722

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

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

Sir:

Transmitted herewith is an Amendment in the above-identified application.

Enclosed are:

[X] Amendment (8 pages).

[ ] Petition for Extension of Period for Response.

[X] Information Disclosure Statement.

The filing fee has been calculated as shown below:

	Claims Remaining After Amendment	Highest No. Previously Paid For	Present Extra (Equals)	Small Entity Rate	Add'l Fee	OR	Large Entity Rate	Add'l Fee
Total	12	- 20	= 0	x 40	$ 0		x 80	$
Indep.	1	- 3	= 0	x 210	$ 0		x 420	$
Mult. Dep.			=	+ 390	$		+ 780	$
				TOTAL	$ 0	OR	TOTAL	$

[ ] First Presentation of Multiple Dependent Claim [MDC]

* 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, write "20" in this space.
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, write "3" in this space.
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found from the equivalent box in Column 1 of a prior Amendment or the number of claims originally filed.

[ ] 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 referenced in the electronic filing in the amount of $_____. 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.

Respectfully submitted,

/Kayla J. Fossen/

Kayla J. Fossen
Registration No. 69,343

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.

September 30, 2016	/Kayla J. Fossen/
Date	Kayla J. Fossen, Reg, # 69,343

Lam Research Ex. 1007 - Page 140 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

REMARKS

Claims 1-7 and 21-25 are pending. By this Amendment no claims are amended, claims 8-20 are cancelled for possible further prosecution, new claims 21-25 are added. Support for new claim 21 can be found, for example, at page 2, line 30. Support for new claim 22 can be found, for example, at page 22, lines 15-18. Support for new claim 23 can be found, for example, at page 25, line 22-23. Support for new claim 24 can be found, for example, at page 20, lines 10-11. Support for new claim 25 can be found, for example, at page 23, lines 26-30. No new matter is added.

Non-Statutory Double Patenting

Claims 1-7 are rejected on the ground of non-statutory obviousness type double patenting as unpatentable over claims 1-17 of U.S. Pat. No. 8,415,000 ('000). As stated by the MPEP the claims at issue must be patentably distinct from the first patent. MPEP 1504.06. The claims must be viewed on the whole. With all due respect, as discussed further below, there is a difference between thickness and other dimensions. Claims 1-17 of '000 does not teach or discuss thickness of the coating. Therefore, claims 1-17 of '000 do not render the present invention patentably indistinct. Withdrawal of the non-statutory obviousness type double patenting rejection is respectfully requested.

Claims 1-7 are rejected on the ground of non-statutory obviousness type double patenting as unpatentable over claims 1-19 of U.S. Pat. No. 9,281,207 ('207). With all due respect, claims 1-19 of '207 are directed toward a system of a hardmask and a resist layer. The presently claimed invention is not directed toward a similar system. Therefore, claims 1-19 of '207 do not render the present invention patentably indistinct. Withdrawal of the non-statutory obviousness type double patenting rejection is respectfully requested.

Lam Research Ex. 1007 - Page 141 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

35 U.S.C. § 112

Claims 1-7 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. In particular, the Examiner raised specific issues with respect to the term "about".

It is very respectfully submitted that the term "about" is a well-settled term of approximation. Well-established case law shows that a suitable construction is to identify if a particular reference or accused device falls within the claimed range with the upper limit of the range being the stated value as modified by the term "about". "Such broadening usages as "about" must be given reasonable scope; they must be viewed by the decision maker as they would be understood by persons experienced in the field of the invention. Andrew Corp. v. Gabriel Electronics, Inc., 847 F.2d 819, 821-22, 6 USPQ2d 2010, 2013 (Fed. Cir.), cert. denied, 488 U.S. 927, 109 S.Ct. 312, 102 L.Ed.2d 330 (1988)." Modine Mfg. Co. v. U.S. Int'l Trade Comm'n, 75 F.3d 1545, 1554 (Fed. Cir. 1996) abrogated on other grounds by Festo Corp. v. Shoketsu Kinzoku Kogyo Kabushiki Co., Ltd., 234 F.3d 558 (Fed. Cir. 2000.

"The district court held the Knop patent claims invalid, stating that terms in the claims such as "approach each other", "close to", "substantially equal", and "closely approximate", with reference to the E-plane and H-plane RPEs, were too vague to satisfy the requirement of definiteness stated in 35 U.S.C. § 112. The criticized words are ubiquitous in patent claims. Such usages, when serving reasonably to describe the claimed subject matter to those of skill in the field of the invention, and to distinguish the claimed subject matter from the prior art, have been accepted in patent examination and upheld by the courts." Andrew Corp. v. Gabriel Electronics, Inc., 847 F.2d 819, 821 (Fed. Cir. 1988).). "The district court, though discussing enablement, spoke also of indefiniteness of 'stretch rate,' a matter having to do with § 112, second paragraph, and relevant in assessment of infringement. The use of stretching … at a rate exceeding **about**

10% per second' in the claims is not indefinite. Infringement is clearly assessable through use of a stop watch." *W. L. Gore & Associates, Inc. v. Garlock, Inc.*, 721 F.2d 1540, 1557 (Fed. Cir. 1983) (emphasis added). In contrast, when "the meaning of claims is in doubt, especially when ... there is close prior art, they are properly declared invalid." *Amgen Inc. v. Chugai Pharmaceutical Co. Ltd.*, 18 USPQ2d 1016, 1031 (Fed. Cir. 1991). "In arriving at this conclusion, we caution that our holding that the term "about" renders indefinite claims 4 and 6 should not be understood as ruling out any and all uses of this term in patent claims." *Id.* "The meaning of the word 'about' is dependent on the facts of a case, the nature of the invention, and the knowledge imparted by the totality of the earlier disclosure to those skilled in the art." *Eiselstein v. Frank*, 34 USPQ2d 1467, 1471 (Fed. Cir. 1995).

In view of the above comments, Applicant believes that the claims are presently clear. Applicant respectfully requests withdrawal of the rejection of claims 1-7 under 35 U.S.C. § 112, second paragraph as being indefinite.

35 U.S.C. § 103

The Examiner rejected claims 1-7 under 35 U.S.C. 103(a) as obvious over Jason Stowers, Douglas A. Keszler, “High resolution, high sensitivity inorganic resists”, (2009) (Stowers). Claims 2-7 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 claim 1, respectfully, Stowers does not teach or suggest each and every aspect of the claimed invention. Stowers teaches a line with a line-width-roughness of 2 nm. Stowers, abstract. A person of skill in the art would understand a line-width-roughness to describe the sharpness of a developed line. The thickness of the film in Stowers is 35nm. Stowers, bridging paragraph between page 730 and 731. Line-width-roughness and thickness are two different measurements. Claim 1 discusses the average thickness of the coating material. In claim 1 this thickness is about 5 nm to about 30 nm. Stowers does not teach or suggest each and every element of claim 1. 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 1-7 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.

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
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Lam Research Ex. 1007 - Page 145 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Acknowledgement Receipt

EFS ID:	27086421
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
Receipt Date:	30-SEP-2016
Filing Date:	18-SEP-2015
Time Stamp:	14:32:41
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 Letter	Amendment_Transmittal.pdf	28769 d04d2a0327b6f67068a5c66900f72a0553ee0f74	no	2

Warnings:

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2		Amendment.pdf	48303 66466f9c14284f29d301ea35c260711195ae96bb	yes	8
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	Document Description		**Start**	**End**	
	Amendment/Req. Reconsideration-After Non-Final Reject		1	1	
	Claims		2	3	
	Applicant Arguments/Remarks Made in an Amendment		4	8	
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3	Information Disclosure Statement (IDS) Form (SB08)	Supplemental_IDS_US_IDS_Form_SB_08a.pdf	1035271 9e8c8f1ed6f53e45b990199b4a6db176fa63b8c2	no	4
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5	Foreign Reference	JP_2010508560.pdf	6262450 d30b78e0e4810a678690e15b482d2fd2e2015d78	no	49
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7	Foreign Reference	WO2008082448A1.pdf	3633730 a6f06d5009ae165c0cfa95ddb833c11afc9de032	no	74
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14858612
Filing Date	2015-09-18
First Named Inventor	Stowers
Art Unit	1722
Examiner Name	Robinson, Chanceity N.
Attorney Docket Number	5063.02US04

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	1	2001154366	JP	A	2001-06-08	Fujitsu Ltd	English Abstract	
	2	2010508560	JP	A	2010-03-18	Oregon State University	Corresponds to WO 2008082448A1	
	3	2011524627	JP	A	2011-09-01	Oregon State University	Corresponds to WO 2009120169A1	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14858612
	Filing Date	2015-09-18
	First Named Inventor	Stowers
	Art Unit	1722
	Examiner Name	Robinson, Chanceity N.
	Attorney Docket Number	5063.02US04

	4	2008082448	WO	A1	2008-07-10	Oregon State University	Corresponds to JP 2010508560A	
	5	2009120169	WO	A1	2009-10-01	Oregon State University	Corresponds to JP 2011524627A	

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	1	Office Action from copending Japanese Application No. 2015-207978 dated August 23, 2016 (6 pages).	X

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	14858612
	Filing Date	2015-09-18
	First Named Inventor	Stowers
	Art Unit	1722
	Examiner Name	Robinson, Chanceity N.
	Attorney Docket Number	5063.02US04

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

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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.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

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)	2016-09-30
Name/Print	Kayla J. Fossen	Registration Number	69,343

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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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 inspections 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.

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PATTERN FORMING METHOD USING RESIST COMPOSITION CONTAINING SILICON-CONTAINING POLYMER

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Classification: **- international:** ***C08L83/04; G03F7/075; H01L21/027;*** (IPC1-7): G03F7/075; H01L21/027

- cooperative:

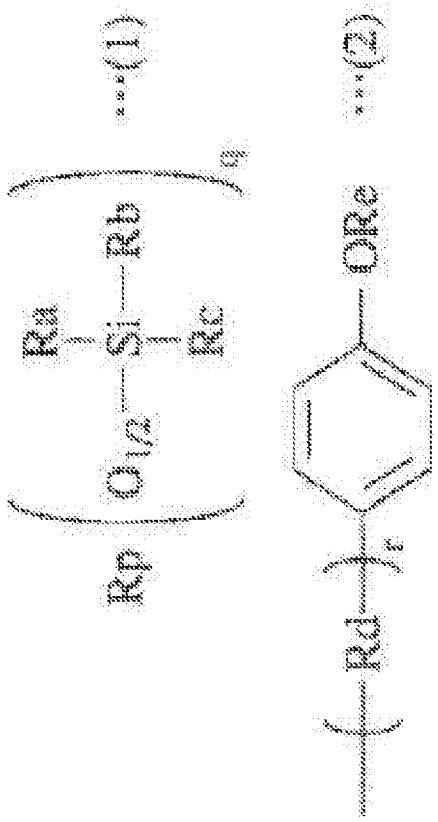
Application number: JP19990341638 19991201

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Abstract of JP2001154366 (A)

PROBLEM TO BE SOLVED: To form a minute pattern excellent in 02-RIE resistance by development with an alkali developing solution in a pattern forming method using a resist composition containing a silicon-containing polymer. SOLUTION: A lower resist layer is formed with a 1st resist material and an upper resist layer is formed on the lower resist layer with a 2nd resist material containing a silicon-containing polymer of formula 1 (where R is the skeleton of the silicon-containing polymer; Ra, Rb and Rc are each alkyl, alkenyl, aryl or a group of formula 2 (where Rd is a divalent organic group); Re is -H, a monovalent organic group or organosilyl; Ra to Re are each one or a plurality of functional groups; (p) and (q) are each an integer of >=1; and (r) is 0 or 1)).; The upper resist layer is patterned by exposure, post-exposure baking and development and the lower resist layer is etched through the remaining upper resist layer after the patterning as a mask.


...(1)
...(2)
Rb
Ra
Si
Rc
O 1/2
Rp
q
ORe
Rd
r

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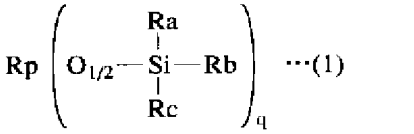
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(54)【発明の名称】　ケイ素含有ポリマを含むレジスト組成物を用いるパターン形成方法

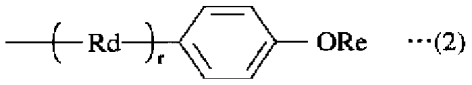
(57)【要約】
【課題】　ケイ素含有ポリマを含むレジスト組成物を用いるパターン形成方法に関し、O_2－ＲＩＥ耐性に優れ、また、アルカリ現像液に依る現像で微細なパターンが形成できるようにする。
【解決手段】　第１レジスト材料で下層レジスト層を形成し、その上に、一般式（１）（式中、Ｒ：ケイ素含有ポリマの骨格、Ｒａ，Ｒｂ，Ｒｃ：それぞれ独立にアルキル基、アルケニル基、アリール基又は一般式（２）（式中、Ｒｄ：二価の有機基、Ｒｅ：－Ｈ、一価の有機基又はオルガノシリル基、Ｒａ～Ｒｅ：それぞれ一種類又は複数種類の官能基、ｐ，ｑ：１以上の整数、ｒ：０または１）で表されるケイ素含有ポリマを含む第２レジスト材料で上層レジスト層を形成し、上層レジスト層を露光、露光後ベーク、現像を行なってパターニングし、パターニングに依って残った上層レジスト層をマスクに下層レジスト層をエッチングする。

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【特許請求の範囲】
【請求項１】被加工基板上に、第１のレジスト材料を用いて下層レジスト層を形成する工程と、
前記下層レジスト層上に、一般式（１）、即ち、
【化１】



式中で、
Ｒ：ケイ素含有ポリマの骨格
Ｒａ，Ｒｂ，Ｒｃ：それぞれ独立にアルキル基、アルケニル基、アリール基または一般式（２）で表される物質の何れかである
【化２】



Ｒｄ：二価の有機基
Ｒｅ：－Ｈ、一価の有機基またはオルガノシリル基
Ｒａ～Ｒｅ：それぞれ一種類或いは複数種類の官能基
ｐ及びｑ：１以上の整数
ｒ：０または１
で表されるケイ素含有ポリマを含んでなる第２のレジスト材料を用いて上層レジスト層を形成する工程と、
前記上層レジスト層を露光、露光後のベーク、現像を行なってパターニングする工程と、
前記パターニングに依って残った前記上層レジスト層をマスクとして前記下層レジスト層をエッチングする工程とを順に実施することを特徴とするケイ素含有ポリマを含むレジスト組成物を用いるパターン形成方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、O_2 プラズマ・エッチングに対する耐性が高く、また、アルカリ現像液で現像して微細なパターンが得られるレジストの主剤として有用なケイ素含有ポリマを含むレジスト組成物を用いるパターン形成方法に関する。
【０００２】
【従来の技術】現在、半導体装置が高集積化されるに伴い、配線の微細化及び多層化が進行しつつあり、従って、リソグラフィ工程で用いられるレジストについても様々な要求がなされ、例えば、解像性向上の他、パターン寸法精度の維持などが重視されている。
【０００３】また、今後、露光光源の短波長化が進行すれば、レジストに於ける光透過率の維持は難しくなる為、レジスト膜厚の薄膜化は必須であり、従って、エッチング耐性の向上は不可避である。
【０００４】更にまた、配線の微細化に対応する高精度のフォト・マスクを製造する場合、或いは、近年、急速に高記録密度化が進んでいる磁気抵抗効果ヘッドの製造する場合などに於いても、半導体製造分野に於けるリソグラフィ技術と同様なリソグラフィ技術が適用されるので、レジストに対する要求は共通したものとなっている。
【０００５】前記した問題を解消する技術としてサーフェスイメージングが提案され、なかでもケイ素含有ポリマからなるレジスト組成物を用いた二層レジスト法が有効であるとされている。
【０００６】二層レジスト法は、有機樹脂を０．５〔μｍ〕の膜厚となるように塗布して下層レジスト膜を形成し、その上に膜厚０．１〔μｍ〕程度の上層レジスト膜を形成し、先ず、上層レジスト膜の露光及び現像を行なってパターンを形成し、その上層レジスト・パターンをマスクとして下層レジスト膜のエッチングを行なうことで、高アスペクト比のレジスト・パターンを得る技法である。
【０００７】この二層レジスト法に用いられるレジスト材料に要求される性能としては、酸素・反応性イオン・エッチング（O_2 ｒｅａｃｔｉｖｅ ｉｏｎ ｅｔｃｈｉｎｇ：O_2 －ＲＩＥ）に対する耐性の他、感度、解像性、保存安定性などが要求され、しかも、近年では、単層レジストで一般的に使用されているアルカリ現像を適用可能であることも要求されている。
【０００８】現在、アルカリ可溶性のケイ素含有ポリマは公知であるが（要すれば「特許第２６１９３５８号」、「特許第２５７３９９６号」などを参照）、従来の技術に依るケイ素含有ポリマの合成は複雑であって、しかも、その感度及び解像性は不十分である。
【０００９】
【発明が解決しようとする課題】本発明では、O_2 －ＲＩＥ耐性に優れ、また、アルカリ現像液に依る現像で微細なパターンが得られるレジストの主剤であるケイ素含有ポリマを含むレジスト組成物を用いてパターンを形成する方法を提供しようとする。
【００１０】
【課題を解決するための手段】本発明のパターン形成方法を実施するのに用いるレジスト組成物に含まれるケイ素含有ポリマは、ポリマ骨格の末端にアルカリ可溶性基としてフェノールを有するか、或いは、露光または酸触媒などの添加剤の働きに依ってアルカリ可溶性を示すフェノール誘導体の何れかを有することが基本になっていて、そのケイ素含有ポリマを主剤とする化学増幅型レジスト組成物は大変優れた性能を発揮することができ、しかも、このケイ素含有ポリマは、ポリマ末端のシラノール基をフェノール誘導体を含むトリオルガノシリル基でシリル化することで簡単に合成することができるものであり、本発明は、前記レジスト組成物を用いてパターンを形成するのに極めて有効な方法である。

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【００１１】前記したところから、本発明に依るケイ素含有ポリマを含むレジスト組成物を用いるパターン形成方法に於いては、被加工基板上に、第１のレジスト材料を用いて下層レジスト層を形成する工程と、前記下層レジスト層上に、一般式（１）で表されるケイ素含有ポリマを含んでなる第２のレジスト材料を用いて上層レジスト層を形成する工程と、前記上層レジスト層を露光、露光後のベーク、現像を行なってパターニングする工程と、前記パターニングに依って残った前記上層レジスト層をマスクとして前記下層レジスト層をエッチングする工程とを順に実施することを特徴とする。

【００１２】前記手段を採ることに依り、O_2 －ＲＩＥ耐性に優れ、また、アルカリ現像液に依る現像で微細パターンが得られる優れた性能のケイ素含有ポリマを主剤とする化学増幅型レジスト組成物を用い、微細且つ精密なパターンを形成する方法が実現され、半導体装置の高集積化、或いは、磁気抵抗効果ヘッドの高記録密度化などに寄与することができる。

【００１３】

【発明の実施の形態】本発明で用いるケイ素含有ポリマは前記一般式（１）で表され、Ｒａ、Ｒｂ、Ｒｃの少なくとも一つは前記一般式（２）であり、そして、前記一般式（２）以外の二つは、それぞれ独立にアルキル基、アルケニル基、アリール基であって、好ましくは炭素数１～３のアルキル基である。

【００１４】一般式（２）に於けるＲｄは、二価の有機基であれば特に限定されないが、炭素数１～１０の鎖状アルキレン基または環状アルキレン基、又は、これ等を組み合わせたものが好ましいのであるが、なかでも、炭素数１～３の鎖状アルキレン基が望ましく、又、Ｒｄは複数種存在しても良く、一般式（２）中のｒは０又は１である。つまり、ｒ＝０では、二価の有機基Ｒｄを含まない。

【００１５】一般式（２）に於けるＲｅは、－Ｈ、一価の有機基またはオルガノシリル基を表していて、このＲｅの少なくとも一部が、露光により酸発生剤から生じた酸の作用によって脱離する官能基である場合には、本発明に依るレジスト組成物は、同じく本発明に依るケイ素含有ポリマ及び光酸発生剤を必ず含んで化学増幅型レジストとなる。

【００１６】また、この場合のＲｅとしては、例えばトリオルガノシリル基、ｔ－ブトキシカルボニル基、テトラヒドロピラニル基、２－アルキルアダマンチル基などの四級炭素の官能基を挙げることができる。

【００１７】ここで、酸の作用で脱離するＲｅ基は、全Ｒｅ基のうちのゼロより大きい任意の割合を占めることができ、その割合は当該ポリマを含むレジスト組成物に求められる特性に応じて決定される。

【００１８】また、酸の作用で脱離しないＲｅは、－Ｈ、一価の有機基またはオルガノシリル基であり、一価の有機基としては炭素数１～３のアルキル基とし、そして、オルガノシリル基を炭素数１～３のアルキル基を有するシリル基とすることが好ましい。尚、Ｒｅは複数種が存在して良い。

【００１９】更にまた、Ｒｅの少なくとも一部が－Ｈである場合には、本発明に依るレジスト組成物は、同じく本発明に依るケイ素含有ポリマ及び光酸発生剤及び架橋剤を必ず含んで化学増幅型レジストとなる。

【００２０】－Ｈは、全Ｒｅ基のうちのゼロより大きい任意の割合を占めることができ、その割合は、当該ポリマを含むレジスト組成物に求められる特性に応じて決定される。

【００２１】このとき、－Ｈ以外のＲｅは、一価の有機基又はオルガノシリル基であり、一価の有機基は特に限定されることはないが、オルガノシリル基としては炭素数１～３のアルキル基を有するシリル基が好ましい。
尚、Ｒｅは複数種が存在して良い。

【００２２】一般式（１）のケイ素含有ポリマは、これを主剤とし、酸発生剤を添加して化学増幅型ポジ型レジスト組成物、更には、架橋剤を添加すると化学増幅型ネガ型レジストとなる。

【００２３】酸発生剤としては、ジフェニルヨードニウム塩、トリフェニルスルホニウム塩などのオニウム塩、或いは、ベンジルトシレート、ベンジルスルホネートなどのスルホン酸エステル、ジブロモビスフェノールＡ、トリスジブロモプロピルイソシアヌレートなどのハロゲン化有機化合物が好ましいが、使用可能な酸発生剤はこれ等に限られない。

【００２４】酸発生剤の添加量は、本発明に依るケイ素含有ポリマの１００重量部に対して０．１～２０重量部の範囲が好ましく、これより添加量が少ない場合には、化学増幅型ポジ型レジストとしての感度が充分に得られず、また、多い場合には、成膜性や解像度の低下を招来する。

【００２５】架橋剤としては、アルキル化メチロールメラミンやそのオリゴマ、又は、ビスヒドロキシメチルフェノールやエポキシ化合物を用いることが好ましく、その添加量は、本発明に依るケイ素含有ポリマの１００重量部に対して１～４０重量部の範囲が好ましく、これより添加量が少ない場合には、化学増幅型ネガ型レジストとしての感度が充分に得られず、また、多い場合には、成膜性や解像度の低下を招来する。

【００２６】一般式（１）で表される本発明に依るケイ素含有ポリマに於いて、ポリマ骨格部分Ｒとしては、
① 一般式（３）で表されるＲｆが－Ｈ、一価の有機基、トリオルガノシリル基の何れかであって、ｍ＞１、ｎ≧０である四官能シロキサンポリマ骨格であるか、

【化３】

$$\left(SiO_{4/2}\right)_p \left(O_{1/2}Rf\right)_q \qquad \cdots(3)$$

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或いは、

【００２７】②　一般式（４）で表されるＲｆが－Ｈ、一価の有機基、トリオルガノシリル基の何れかであって、Ｒｇが一価の有機基であり、更に、ｍ＞１、ｎ≧０である三官能シロキサンポリマ骨格であるか、

【化４】

$$\left(\mathrm{Rg\ SiO_{2/3}}\right)_p\left(\mathrm{O_{1/2}Rf}\right)_q \quad \cdots(4)$$

或いは、

【００２８】③　一般式（５）で表されるＲｆが－Ｈ、一価の有機基またはトリオルガノシリル基のいずれかであって、Ｒｈ、Ｒｈ′が同一でも相異なっても良い一価の有機基であり、更に、ｍ＞１、ｎ≧０である二官能シロキサンポリマ骨格であるか、

【化５】

$$\left(\mathrm{Rh\ Rh'SiO_{2/2}}\right)_p\left(\mathrm{O_{1/2}Rf}\right)_q \cdots(5)$$

或いは、

【００２９】④　一般式（６）で表されるＲｆが－Ｈ、一価の有機基またはトリオルガノシリル基のいずれかであって、Ｒｉが二価の有機基であり、更に、ｍ＞１、ｎ≧０であるシロキサンポリマ骨格である。

【化６】

$$\left(\mathrm{O_{3/2}\,Si\,Ri\,SiO_{3/2}}\right)_p\left(\mathrm{O_{1/2}\,Rf}\right)_q \quad \cdots(6)$$

【００３０】尚、本発明に依るケイ素含有ポリマは、そのポリマ骨格Ｒとして、上掲の一種か二種以上を有することができる。

【００３１】Ｒｆ、Ｒｇ、Ｒｈ、Ｒｈ′の一価の有機基としては、炭素数１～１０のアルキル基並びにそれ等の置換基を用いることが好ましく、また、Ｒｉの二価の有機基としては、炭素数１～３のアルキレン基を用いることが好ましい。

【００３２】本発明で用いるケイ素含有ポリマの重量平均分子量は、ポリスチレン換算で、１５００～１０００００が好ましく、これより低分子量では耐熱性が低下し、また、高分子量であればレジストとして解像性が悪くなる。

【００３３】本発明で用いるケイ素含有ポリマを用いてレジスト材料を作成し、そのレジスト材料を用いてレジスト・パターンを形成するには、被加工基板上に本レジスト層を直接形成する手段を採るか、或いは、被加工基板上に第一のレジスト（下層レジスト）層を形成し、引き続き、本発明によるレジスト材料を用いて第二のレジスト（上層レジスト）層を形成し、この上層レジスト層を露光及び現像してパターンを形成し、得られた上層レジスト・パターンをマスクとして下層レジスト膜のエッチングを行なってレジスト・パターンを形成すれば良い。

【００３４】下層レジスト層の材料としては、有機材料、例えば、ノボラック樹脂、ビニルフェノール樹脂からなる市販のレジスト材料、ポリアニリン系やポリチオフェン系の導電性材料を用いることができ、また、その厚さは０．１〔μｍ〕～１０．０〔μｍ〕の範囲で選択するが、０．２〔μｍ〕～１．０〔μｍ〕の範囲にすると好結果が得られる。

【００３５】また、上層レジスト層を形成する為に本発明に依るレジスト材料を塗布する場合、必要に応じて溶剤を用いて良く、その溶剤としては、有機溶剤、例えば、プロピレングリコールモノメチルエーテルアセテート、ｎ－ブチルエーテル、メチルイソブチルケトンなどを使用することができる。

【００３６】本発明で用いるレジスト材料を塗布する方法は、通常のレジスト材料を塗布する方法と何ら変わるところはなく、例えばスピン・コート法などを適用することができ、そのレジスト材料の塗布厚さは０．０３〔μｍ〕～１．０〔μｍ〕の範囲で選択すれば良く、これよりも薄いとエッチング時の寸法変動が大きくなり、厚いと解像性が低下することになり、好ましくは、塗布厚さを０．０５〔μｍ〕～０．２〔μｍ〕の範囲とする。

【００３７】露光を行なう場合の放射線源としては、可視光、紫外線、ＫｒＦエキシマ・レーザ、ＡｒＦエキシマ・レーザ、F_2 エキシマ・レーザなど、ＶＵＶ、ＥＵＶ、電子線、イオン・ビームなどを用いて良い。

【００３８】本発明で用いるレジスト材料を現像するには、アルカリ現像液としてテトラメチルアンモニウムハイドロオキサイド（ＴＭＡＨ）水溶液、水酸化カリウム水溶液などが使用可能である。

【００３９】また、下層レジスト層をエッチングする場合、酸素を含むガスのプラズマ・エッチングを適用することができ、特に、酸素と二酸化硫黄の混合ガスに依るエッチングが好ましく、また、プラズマ・エッチング装置としては高密度プラズマ・エッチング装置を用いると良い。

【００４０】以下、本発明で用いるレジスト材料の具体例を挙げて説明するが、本発明で用いるレジスト材料は、これ等の具体例に限定されるものではない。

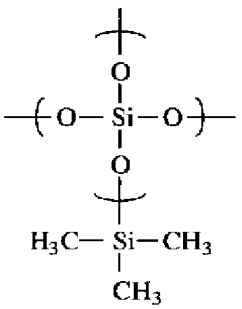
【００４１】例１（ケイ素含有ポリマに関する例）

ケイ素含有ポリマを合成する場合について説明する。

【００４２】還流管及び温度計を取り付け、且つ、窒素フローした四つ口フラスコを準備し、一般式（７）で表されるシロキサンポリマ５〔ｇ〕（分子量５０００）をメチルイソブチルケトン（ＭＩＢＫ）１００〔ｍｌ〕に溶解し、攪拌し、油浴で７０〔℃〕に加熱した。

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【化７】



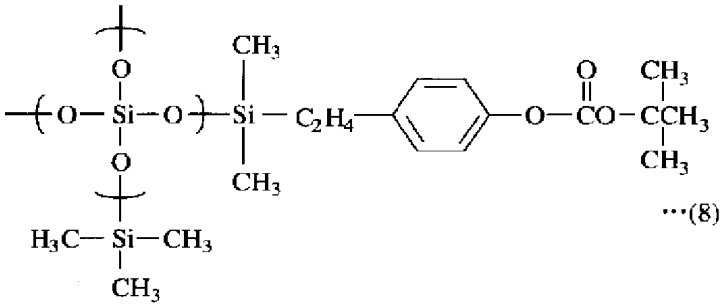
…(7)

【００４３】滴下ロートからターシャリブトキシカルボニルオキシフェニルエチルジメチルクロロシランを３．５〔ｇ〕と、これと等モルのピリジンを３０〔分〕とを３０〔分〕で滴下し、４〔時間〕反応を行なった。

【００４４】室温まで放冷した後、分液ロートに移して水層が中性になるまで水洗してから、有機層を液層分離濾紙で濾過して前記四つ口フラスコに移し、共沸に依り水抜きして目的とするポリマのＭＩＢＫ溶液を得た。

【００４５】前記ＭＩＢＫ溶液を濃縮した後、アセトニトリルで低分子量成分を除去し、一般式（８）のポリマを得た。このポリマに於ける分子量は１００００、分散度は２．４であった。

【化８】



…(8)

【００４６】このポリマのＭＩＢＫ溶液をＳｉウエハに回転塗布し、ホット・プレート上で９０〔℃〕／６０〔秒〕のベーキングを行なって試料を作成し、これを２．３８〔%〕テトラメチルアンモニウムハイドロオキサイド（ＴＭＡＨ）水溶液に浸漬しても溶解しないことを確認した。

【００４７】例２（ケイ素含有ポリマに関する例）

ケイ素含有ポリマを合成する場合について説明する。

【００４８】還流管及び温度計を取り付け、且つ、窒素フローした四つ口フラスコを準備し、一般式（７）で表されるシロキサンポリマ５〔ｇ〕（分子量５０００）をメチルイソブチルケトン（ＭＩＢＫ）１００〔ｍｌ〕に溶解し、攪拌し、油浴で７０〔℃〕に加熱した。

【００４９】滴下ロートからターシャリブトキシカルボニルオキシフェニルエチルジメチルクロロシランを３．５〔ｇ〕と、これと等モルのピリジンを３０〔分〕とを３０〔分〕で滴下し、４〔時間〕反応を行なった。

【００５０】室温まで放冷した後、分液ロートに移して水層が中性になるまで水洗してから、有機層を液層分離濾紙で濾過して前記四つ口フラスコに移し、共沸に依り水抜きして目的とするポリマのＭＩＢＫ溶液を得た。

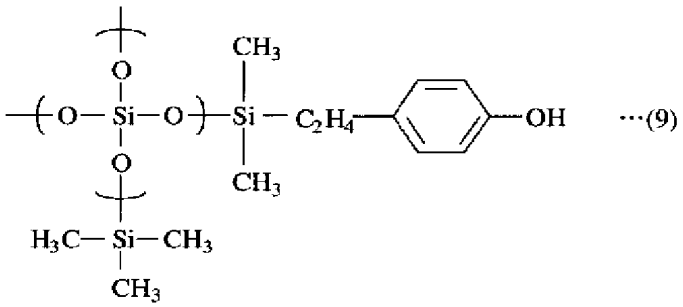
【００５１】前記ＭＩＢＫ溶液を濃縮した後、アセトニトリルで低分子量成分を除去し、このポリマを再度１００〔ｍｌ〕のＭＩＢＫに溶解し、油浴で７０〔℃〕に加熱した。

【００５２】ピペットで塩酸２．０〔ｇ〕を滴下し、３〔時間〕反応を行なった。

【００５３】室温まで放冷した後、分液ロートに移して水層が中性になるまで水洗してから、有機層を液層分離濾紙で濾過して前記四つ口フラスコに移し、共沸に依り水抜きして目的とするポリマのＭＩＢＫ溶液を得た。

【００５４】前記ＭＩＢＫ溶液を濃縮した後、ヘキサンで低分子量成分を除去し、一般式（９）のポリマを得た。このポリマの分子量は１００００、分散度は２．４であった。

【化９】



…(9)

【００５５】このポリマのＭＩＢＫ溶液をＳｉウエハに回転塗布し、ホット・プレート上で９０〔℃〕／６０〔秒〕のベーキングを行なって試料を作成し、これを２．３８〔%〕テトラメチルアンモニウムハイドロオキ

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サイド（ＴＭＡＨ）水溶液に浸漬したところ迅速に溶解した。

【００５６】例３（レジスト組成物に関する例）
レジスト組成物を作成する場合について説明する。

【００５７】例１で得た分子量１００００でｔ－ブトキシカルボニル基を有するケイ素含有ポリマ１００重量部と、酸発生剤として５重量部のトリフェニルスルフォニウムトリフレートをＭＩＢＫに溶解してレジスト溶液を調製した。

【００５８】Ｓｉウエハ上にノボラック樹脂ベースの溶液を回転塗布し、窒素フローしたオーブン中で２８０〔℃〕、３０〔時間〕のベーキングを行ない、０．４〔μｍ〕の下層レジスト層を形成した。

【００５９】再び、前記調製したレジスト溶液を下層レジスト層上に回転塗布し、１１０〔℃〕、６０〔秒〕のプリ・ベーキングを行なって０．１〔μｍ〕の上層レジスト層を形成した。

【００６０】電子線露光後、直ちに１００〔℃〕／６０〔秒〕のポストエクスポージャベーキングを行ない、２．３８〔％〕ＴＭＡＨ水溶液で現像を行なったところ、現像液への溶解速度は、露光部で３００〔Å／ｓ〕以上、未露光部で５〔Å／ｓ〕以下であって、この溶解速度の差から０．３〔μｍ〕のパターンを解像した。

【００６１】また、平行平板型のＲＩＥ（ｒｅａｃｔｉｖｅ　ｉｏｎ　ｅｔｃｈｉｎｇ）装置を用い、ＲＦパワー：０．１６〔Ｗ／ｃｍ^2〕、酸素流量：１０〔ｓｃｃｍ〕、ガス圧１０〔ｍＴｏｒｒ〕でエッチング・レートを測定したところ、下層のノボラック系レジストに比較して約１００倍高いO_2 －ＲＩＥ耐性を示した。

【００６２】例４（レジスト組成物に関する例）
レジスト組成物を作成する場合について説明する。

【００６３】例２で得た分子量８５００でフェノール基を有するケイ素含有ポリマ１００重量部と、架橋剤として２０重量部のメトキシメテルメラミンと、酸発生剤として３重量部のトリフェニルスルフォニウムトリフレートをＭＩＢＫに溶解してレジスト溶液を調製した。

【００６４】例３と同様にして形成した層厚０．４〔μｍ〕の下層レジスト層上に前記調製したレジスト溶液を回転塗布し、１１０〔℃〕、６０〔秒〕のプリ・ベーキングを行なって０．１〔μｍ〕の上層レジスト層を形成した。

【００６５】電子線露光後、直ちに１１０〔℃〕／１２０〔秒〕のポストエクスポージャベーキングを行なった後、２．３８〔％〕ＴＭＡＨ水溶液で現像したところ、現像液への溶解速度は、露光部で１〔Å／ｓ〕以下、未露光部で１０００〔Å／ｓ〕以上であって、この溶解速度の差から０．３５〔μｍ〕のパターンを解像した。

【００６６】また、前記と同様、平行平板型のＲＩＥ装置を用い、ＲＦパワー：０．１６〔Ｗ／ｃｍ^2〕、酸素流量：１０〔ｓｃｃｍ〕、ガス圧１０〔ｍＴｏｒｒ〕でエッチング・レートを測定したところ、下層のノボラック系レジストに比較して約１００倍高いO_2 －ＲＩＥ耐性を示した。

【００６７】本発明の構成要件は、特許請求の範囲に記載した通りであるが、それを逸脱しない範囲で、多くの改変を実現することができるので、以下に挙げる。尚、ここでは、請求項１に記載された本発明の構成要件を記号（ａ）で代表させる。

【００６８】（ｂ）（ａ）に於けるＲｅが酸触媒及び加熱に依って離脱する官能基であることを特徴とするケイ素含有ポリマを用いること。

【００６９】（ｃ）（ａ）又は（ｂ）に於いて、ケイ素含有ポリマの骨格部分が一般式（３）で表される四官能シロキサンポリマ骨格部分であるケイ素含有ポリマを用いること。尚、一般式（３）中に於けるＲｆは－Ｈ、一価の有機基、トリオガノシリル基の何れかを表し、ｍ＞１、ｎ≧０である。

【００７０】（ｄ）（ａ）又は（ｂ）に於いて、ケイ素含有ポリマの骨格部分が一般式（４）で表される三官能シロキサンポリマ骨格部分であるケイ素含有ポリマを用いること。尚、一般式（４）中でＲｆは－Ｈ、一価の有機基またはトリオルガノシリル基のいずれか、Ｒｇは一価の有機基を表し、ｍ＞１、ｎ≧０である。

【００７１】（ｅ）（ａ）又は（ｂ）に於いて、ケイ素含有ポリマの骨格部分が一般式（５）で表される二官能シロキサンポリマ骨格部分であるケイ素含有ポリマを用いること。尚、一般式（５）中でＲｆは－Ｈ、一価の有機基またはトリオルガノシリル基のいずれか、Ｒｈ、Ｒｈ′は同一でも異なっても良く、それぞれ一価の有機基を表し、ｍ＞１、ｎ≧０である。

【００７２】（ｆ）（ａ）又は（ｂ）に於いて、ケイ素含有ポリマの骨格部分が一般式（６）で表されるシロキサンポリマ骨格部分であるケイ素含有ポリマを用いること。尚、一般式（６）中でＲｆは－Ｈ、一価の有機基またはトリオルガノシリル基のいずれか、Ｒｉは二価の有機基を表し、ｍ＞１、ｎ≧０である。

【００７３】（ｇ）（ａ）乃至（ｆ）に示したケイ素含有ポリマを単独、又は、複数同時に含むレジスト組成物を用いること。

【００７４】（ｈ）光酸発生剤を含む（ｇ）のレジスト組成物を用いること。

【００７５】（ｉ）架橋剤、溶解抑止剤を含む（ｈ）のレジスト組成物を用いること。

【００７６】（ｊ）（ｇ）、（ｈ）、（ｉ）に示したレジスト組成物を用い、被加工基板上にレジスト層を形成し、このレジスト層の露光、必要に応じて実施する露光後ベーク、現像を行なってレジスト・パターンを形成すること。

【００７７】前記改変例は、何れも電子デバイスの製造は勿論のこと、磁気ヘッドの製造、フォト・マスクの製

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造などに適用して有効である。

【００７８】

【発明の効果】本発明に依るケイ素含有ポリマを含むレジスト組成物を用いるパターン形成方法に於いては、被加工基板上に、第１のレジスト材料を用いて下層レジスト層を形成し、下層レジスト層上に、一般式（１）で表されるケイ素含有ポリマを含んでなる第２のレジスト材料を用いて上層レジスト層を形成し、上層レジスト層を露光、露光後のベーク、現像を行なってパターニングし、パターニングに依って残った上層レジスト層をマスクとして下層レジスト層をエッチングする。

【００７９】前記構成を採ることに依り、O_2 －ＲＩＥ耐性に優れ、また、アルカリ現像液に依る現像で微細パターンが得られる優れた性能のケイ素含有ポリマを主剤とする化学増幅型レジスト組成物を用い、微細且つ精密なパターンを形成する方法が実現され、半導体装置の高集積化、或いは、磁気抵抗効果ヘッドの高記録密度化などに寄与することができる。

フロントページの続き

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

Inventor(s):

Applicant(s):

Classification: **- international:** ***B05D7/24; B32B9/00; G02B1/11***
- cooperative: **C01G1/10**; **C01G25/006**; **C01G25/06**; **C01G27/006**; **C01G27/06**; **C23C18/06**; **C23C18/1216**; **C23C18/1225**; **C23C18/1295**; **G02B1/10**; **H01L21/02181**; **H01L21/02189**; **H01L21/02192**; **H01L21/02194**; **H01L21/02282**; **H01L21/0337**; **H01L21/28194**; **H01L29/4908**; **H01L29/7869**; C01P2002/02; C01P2002/72; C01P2002/88; C01P2004/03; C01P2004/04; C01P2006/40; Y10S430/114; Y10S430/143

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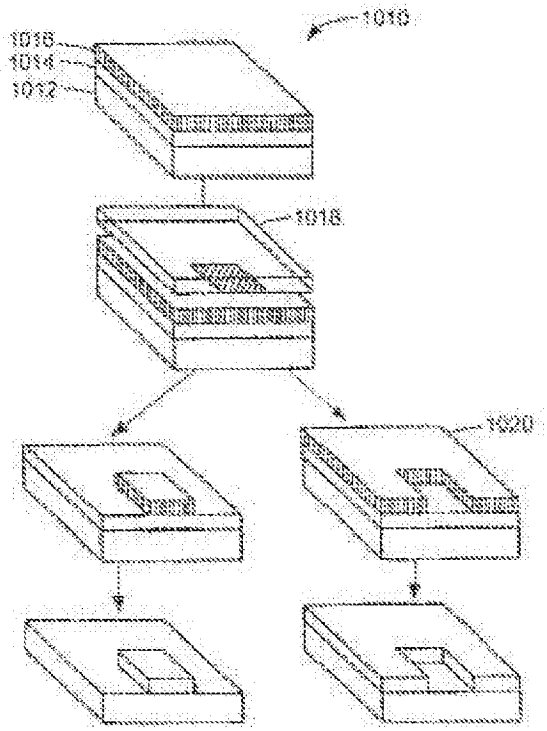
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Devices having a thin film or laminate structure comprising hafnium and/or zirconium oxy hydroxy compounds, and methods for making such devices, are disclosed. The hafnium and zirconium compounds can be doped, typically with other metals, such as lanthanum. 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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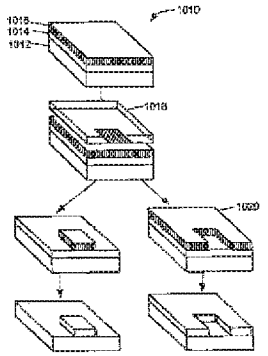
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(54)【発明の名称】溶液処理薄膜および積層体、薄膜および積層体を備えた装置、その使用および製造方法

(57)【要約】
ハフニウムおよび／もしくはジルコニウムオキシヒドロキシ化合物を備える薄膜または積層構造体を有する装置およびかかる装置の製造方法を開示する。ハフニウムおよびジルコニウム化合物は、通常ランタンのような他の金属でドープすることができる。電子装置またはそれを作成し得る構成材の例には、限定することなく、絶縁体、トランジスタおよびコンデンサがある。ポジ型もしくはネガ型レジストを用いて装置をパターン化する方法も開示する。例えば、インプリントリソグラフィー用のマスタープレートを作成することができる。腐食バリアを有する装置の製造方法の実施形態も開示する。光学基板およびコーティングを備える光学的装置の実施形態も開示する。電子顕微鏡を用いて寸法を正確に測定する物理的ルーラーの実施形態も開示する。



【特許請求の範囲】
【請求項１】
少なくとも一つのハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物で、Ｍｔがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変で、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、ｚが０．０～３．８の範囲のいずれかの値を取る化合物を含む薄膜または積層構造体を備えた装置。
【請求項２】
前記薄膜または積層体が、約９～１２の誘電率値、少なくとも６ＭＶｃｍ$^{-1}$までの破壊電界強度、電界強度１ＭＶｃｍ$^{-1}$でｌｎＡｃｍ$^{-2}$近くの漏洩電流を有する請求項１に記載の装置。
【請求項３】
前記化合物がさらにランタンを含み、式$M_{1-z}La_zO_{2-x-z/2}(SO_4)_x$（ＭＳＯｘ：Ｌａ）を有し、Ｍがハフニウムまたはジルコニウムであり、ｘおよびｚが固定または可変で、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲におけるいずれかの値を取り、ｚが０．０～約３．８の範囲におけるいずれかの値を取る請求項１に記載の装置。
【請求項４】
前記化合物がＨａｆＳＯｘ，ＨａｆＳＯｘ／Ｌａ，ＺｉｒｃＳＯｘ，ＺｉｒｃＳＯｘ：Ｌａ，ＨａｆＳＯｘ：Ｃｅ，またはＺｉｒｃＳＯｘ：Ｃａであり、前記装置が５０ｎＡｃｍ$^{-2}$未満の漏洩電流と、約９～約１２の誘電率値を有する請求項１に記載の装置。
【請求項５】
前記装置がＨａｆＳＯｘ：Ｌａおよび／またはＺｉｒｃＳｏｘ：Ｌａをゲート誘電体として、また酸化亜鉛インジウムおよび／または酸化亜鉛スズをチャネルとして備える電界効果トランジスタであり、該トランジスタが10^6を超えるオン／オフ比と、ｐＡｃｍ$^{-2}$の範囲のゲート漏洩電流を有する請求項１に記載の装置。
【請求項６】
光学基板を更に備え、前記薄膜または積層構造体が前記光学基板上のコーティングを形成する請求項１に記載の装置。
【請求項７】
前記コーティングが反射防止コーティングであり、および／または前記コーティングが可視光または紫外光を通す請求項６に記載の装置。
【請求項８】
前記光学基板およびコーティングが誘電体ミラー、Ｘ線ミラー、干渉フィルター、回折格子および／または導波管を画成する請求項６に記載の装置。
【請求項９】
前記コーティングを選択的にドーピングして、Mn^{2+}，Sb^{3+}，Sn^{2+}，Bi^{3+}，Eu^{3+}，Tb^{3+}，Eu^{2+}，Gd^{3+}，Tm^{2+}およびその組み合わせから選択した発光イオンを有するドーピングした発光層を付与する請求項７に記載の光学的装置。
【請求項１０】
前記装置がインプリントリソグラフィー用のマスタープレートで、前記薄膜または積層構造体をフレキシブルもしくはガラス基板上に堆積し、該薄膜または積層構造体が基板上に堆積したＨａｆＳＯｘの第１層と、ＺｉｒｃＳＯｘ：Ｃｕからなる第２層トを備え、前記第１層および第２層を備える積層構造体をエネルギー源への露出によってパターン化す

る請求項１に記載の装置。
【請求項１１】
マスクを介して光または電子ビームへの露出で、２つの層を露出領域で相互拡散させて、予め未ドープのＨａｆＳＯｘ層を可溶性にし、該可溶性のＨａｆＳＯｘ層を除去してマスタープレートの少なくとも部分的印刷形態を画成する請求項１０に記載のマスタープレート。
【請求項１２】
薄膜または積層構造体を設け、該構造体が基板と該基板上に堆積した１個またはそれ以上の層とを備え、
前記１個またはそれ以上の層の少なくとも一つがハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物からなり、Ｍがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変であり、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、ｚが０．０～３．８の範囲のいずれかの値を取り、
前記構造体をエネルギー源に露出することを備えることを特徴とする装置の製造方法。
【請求項１３】
前記薄膜または積層構造体が、基板と、パターン化用の第１層と、ハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物からなる第２層とを備え、前記第２層がポジ型レジスト層で、エネルギー源への露出により該レジスト層の材料を現像液に可溶な材料に変換し、前記方法がさらに、前記レジストを現像液で処理することにより前記エネルギー源に露出したレジスト層の材料を除去して前記構造体をパターン化することを備える請求項１２に記載の方法。
【請求項１４】
前記薄膜または積層構造体が、基板と、パターン化用の第１層と、ハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物からなる第２層とを備え、前記第２層がネガ型レジスト層で、エネルギー源への露出により該レジスト層を重合化し、前記方法がさらに、前記構造体を現像液で処理してエネルギー源に未露出の材料を除去することによって前記構造体をパターン化することを備える請求項１２に記載の方法。
【請求項１５】
前記ポジ型レジストが二重層からなり、該二重層の第２層が不溶性酸化ハフニウム硫酸塩（ＨａｆＳＯｘ）膜上に堆積した酸可溶のＣｕドープ酸化ジルコニウム硫酸塩（ＺｉｒｃＳＯｘ：Ｃｕ）膜を備え、光または電子ビームからなるエネルギー源へのマスクを介した露出によりＺｉｒｃＳＯｘ：Ｃｕ膜およびＨａｆＳＯｘ膜を露出領域で相互拡散させて、前記ＨａｆＳＯｘ膜を可溶性にする請求項１３に記載の方法。
【請求項１６】
前記ハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物が硫酸塩からなり、該硫酸塩をその後塩基水溶液でのイオン交換によって除去し、前記塩基水溶液がＩ族金属の水酸化物、可溶性のII族金属の水酸化物、可溶性のIII族金属の水酸化物、可溶性のランタニド水酸化物、水酸化アンモニウムおよび／または水性第３アミン、またはその組合せからなる請求項１２に記載の方法。
【請求項１７】
半導体材料、金属、ガラス、シリカ、高分子材料またはその組合せからなる適当な基板を用意し、
前記基板に第１のＨａｆＳＯｘ膜を溶液堆積し、

第２のＺｉｒｃＳＯｘ：Ｃｕ膜を前記第１膜上に溶液堆積して積層構造体を形成し、
前記積層構造体をエネルギー源に露出して、前記ＨａｆＳＯｘ膜および前記ＺｉｒｃＳＯｘ：Ｃｕ膜を露出領域で相互拡散させ、これにより予め未ドープのＨａｆＳＯｘ膜を可溶性にし、
前記露出した構造体を現像してＨａｆＳＯｘ膜を除去することを備える請求項１２に記載の方法。
【請求項１８】
前記薄膜または積層構造体が基板と、該基板上に堆積した不溶性の酸化ハフニウム硫酸塩（ＨａｆＳＯｘ）の第１層と、前記第１層上に堆積したギ酸銅からなる第２層とを備え、前記第１層および第２層を備える積層構造体を約５０℃～約２００℃の温度に加熱してギ酸銅を分解し、ＨａｆＳＯｘ層と相互拡散させて可溶性のな生成物を生成し、該可溶性の生成物を除去する請求項１２に記載の方法。
【請求項１９】
前記薄膜または積層構造体が、基板と、固体無機酸もしくは塩基を含む第１層とを備え、前記固体無機酸もしくは塩基が原子番号２１～７８を有する金属を含み、前記第１層がさらにペルオキシドまたは他の配位アニオンを含み、前記第１層が酸または塩基に可溶で、該第１層を約５０℃～約１２５℃まで加熱して構造的に硬い膜を生成し、マスクを介してレーザー、電子ビームおよび／または光に露出して膜の露出領域を未露出領域より低い可溶性とし、前記未露出領域を除去してパターンを膜に画成する請求項１２に記載の方法。
【請求項２０】
前記膜に電子ビームを０μＣ／ｃｍ^{2}より大きく少なくとも４００μＣ／ｃｍ^2、より一般的には約２μＣ／ｃｍ^{2}から約４００μＣ／ｃｍ^{2}の線量レベルで露出させてパターンを膜に画成する請求項１９に記載の方法。
【請求項２１】
前記パターン化膜の構造的完全性が約３ｎｍ未満である請求項１９に記載の方法。
【請求項２２】
前記装置がマイクロまたはナノチャンネルアレイを含み、前記構造体が基板と、第１層と、金属酸化物層である第２層とからなり、前記方法がさらに、前記構造体をパターン化し、
前記構造体をエネルギー源に露出して、前記構造体のパターン化によっ生成した所望のパターンを有する耐久性の材料を形成することを備える請求項１２に記載の方法。
【請求項２３】
さらに所定サイズ単位容貌を半固体ハフニウムまたはジルコニウム化合物にスタンプしてスタンプ層を形成することを備える請求項２２に記載の方法。
【請求項２４】
請求項２２の方法にしたがって作成し、金属および金属／セラミック系熱保護システム、有機系のディスプレイおよび電子機器、太陽電池、高放射率コーティング、酸化物系セラミックマトリックスシステム用の界面コーティング、りん光体上の保護コーティング、金属系およびセラミック系システム用の環境障壁コーティングと、複合体およびファイバーレーザー用ファイバー、溶融金属処理における腐食保護、断熱材用モノリシック材料および触媒担体から選択した装置。
【請求項２５】
装置を用意し、
金属酸化物層を備える前記装置上にハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z($

PO_4）$_x$）化合物および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}$（OH）$_z$（SiO_4）$_x$）化合物で、Mがハフニウムまたはジルコニウム、xおよびzが固定もしくは可変であり、xが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、zが０．０～３．８の範囲のいずれかの値を取る化合物からなる少なくとも一つの腐食バリアを形成し、

前記化合物をエネルギー源に露出して前記腐食バリアを形成することを備えることを特徴とする腐食バリアを有する装置の製造方法。

【請求項２６】

ハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}$（OH）$_z$（SO_4）$_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}$（OH）$_z$（WO_4）$_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}$（OH）$_z$（BO_3）$_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}$（OH）$_z$（PO_4）$_x$）化合物および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}$（OH）$_z$（SiO_4）$_x$）化合物で、Mがハフニウムまたはジルコニウム、xおよびzが固定もしくは可変であり、xが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、zが０．０～３．８の範囲のいずれかの値を取る化合物からなる組成物を用意し、

前記化合物を有する溶液を形成し、

前記溶液をファイバーにし、

前記ファイバーを固体の安定したファイバーに変換することを備えることを特徴とするファイバーの製造方法。

【請求項２７】

少なくとも２個の金属を備える金属酸化物膜を製造するに当たり、

金属カチオンおよび１個またはそれ以上のアニオンから主としてなる１個またはそれ以上の可溶塩を非錯化で、非水性の極性溶媒に溶解して溶液を作成し、前記金属カチオンの少なくとも１個が3^+より大きい形式電荷を有し、3^+より大きい形式電荷を有する金属カチオンの濃度が前記金属酸化物膜にける金属カチオンの５０モル％を越え、また前記溶媒が約１５０℃未満の沸点を有し、

前記溶液のｐＨを上げ、該ｐＨの上昇が、塩基水溶液の添加、少量の可溶性塩基酸化物の添加、塩基水溶液を形成し得るガス状化合物の添加、プロトンを消費し膜内に添合し得る電気的陽性の金属の添加、プロトンを消費するか、もしくは対イオンを分解するが膜に添合しない液状またはガス状の酸化剤の添加、またはその組合せからなり、

非水溶性の溶媒を揮発することによって固体を生成し、

前記固体を水に溶解し、

前記溶解した固体を基板上に堆積してパターン化又はブランケット液体膜を形成し、

前記膜を熱で硬化することを備えることを特徴とする金属酸化物膜の製造方法。

【発明の詳細な説明】

【技術分野】

【０００１】

関連出願の参照

本願は、２００６年１１月１日に出願された米国特許仮出願第６０／８５６０７０号の優先権を主張し、参照することにより完全に本願に組み込まれる。

【０００２】

技術分野

本発明は、電子および光学用途を含む目的用の空間的に定義された構造体を構築するのに有用な無機金属酸化物材料を備えた作品および装置の実施形態と、その製造および使用方法の実施形態とに関するものである。

【０００３】

政府支援の承認

本発明の実施形態は、ＤＡＲＰＡ認可番号ＨＲ００１１－０６－０００４５で連邦政府の補助金を用いて開発した。米国政府は、本発明における特定の権利を有する。

【背景技術】

【０００４】

電子装置は、材料の逐次的な堆積およびエッチングのような反復プロセス工程を用いて現在形成されている。無機材料を有する装置に関して、金属－有機前駆体が無機酸化物の溶液系堆積用に広く用いられてきた。有機部分の存在は、有機材料を除去するための高温焼却工程を必要とする。この工程は、大きな体積変化、結晶化および「泥割れ」現象を生起する場合がある。それに関連した欠陥が、かかる材料のコーティングとしての装置内での機能を阻害する。

【０００５】

電子装置用途に対する材料を溶液処理する方法が特許された。例えば、「有機薄膜トランジスタ構造体および回路用の予備パターン化基板およびその製造方法」の名称の特許文献１には、基板の表面に所望の回路構造を形成して、有機薄膜タランジスタ（ＯＴＦＴ）構造の形成および導電性通路の相互連結に有用な材料を受け取る領域を予備パターン化することが開示されている。特許文献１によると、ＯＴＦＴ材料が、インクジェット印刷のような印刷技術を用いて予備パターン化領域に堆積される。

【０００６】

特許文献２には、薄膜材料を溶液処理してトランジスタを製造することが開示されている。特許文献２は、導電性の溶液処理した薄膜材料接点と、半導体の溶液処理した薄膜材料活性領域と、誘電体の溶液処理した薄膜材料アイソレーションを順次配置して形成し、トランジスタ操作が可能な溶液処理した薄膜構造を形成することを開示する。

【０００７】

特許文献３は、本願明細書に参照して援用するもので、電子用途に有用なハフニウムおよびジルコニウム化合物に関する。特許文献３は、Ｄｏｕｇｌａｓ　Ｋｅｓｚｌｅｒ博士が発明者であり、本明細書で開示する実施形態の発明者でもある。

【先行技術文献】

【特許文献】

【０００８】

【特許文献１】米国特許第６９４６６７７号明細書

【特許文献２】米国特許第６９２７１０８号明細書

【特許文献３】米国特許出願公開第２００５／０２４２３３０号明細書

【発明の概要】

【０００９】

特許文献３は、先行技術の欠陥を解決するような化合物および無機化合物の溶液堆積を開示する。例えば、本発明に係る溶液堆積は、金属－無機堆積技術に必要な有機材料を用いることを回避し、従って有機物焼却および焼却に伴うクラッキングの問題も回避する。

【００１０】

本発明の一つの実施形態は、電子装置のような装置に関するもので、少なくとも１つのハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物及び／又はハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物で、Ｍがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変である化合物を備える薄膜または積層構造体を有する。ｘは約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を有することができる。例えば、ｘ

はオキシヒドロキシ硫酸塩化合物のような２価の電荷を有する多原子イオンに対して約０．１～約１．７５の範囲のいずれかの値を取ることができる。ｚは０．０～約３．８の範囲のいずれかの値を取ることができる。

【００１１】

特定の実施形態は、式（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）を有するハフニウムもしくはジルコニウムオキシヒドロキシ硫酸塩化合物を備える薄膜または積層体に関するもので、Ｍはハフニウムもしくはジルコニウム、ｘおよびｚは固定もしくは可変で、ｘが約０．１～約１．７５の範囲、ｚが０．０～約３．８の範囲の任意の値を取るものとする。かかる化合物はまた、ＨａｆＳＯｘおよびＺｉｒｃＳＯｘとも呼ぶ。また、ハフニウムおよびジルコニウム化合物を通常カルシウム、セリウム、ランタンまたはそれらの組合せのような他の金属でドーピングすることができる。ある実施形態では、ランタンをドーパントとして用いて式$M_{1-x}La_yO_{2-x-z/2-y/2}(OH)_z(SO_4)_x$（ＭＳＯｘ：Ｌａ）で、その組成および化学量論は上述の通りである化合物を生成する。ランタンをドーピングした化合物の特定例は、$Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$である。他の例としては、ＨａｆＳＯｘ：Ｌａ，ＺｉｒｃＳＯｘ：Ｌａ，ＨａｆＳＯｘ：ＣｅまたはＺｉｒｃＳＯｘ：Ｃａがある。ある実施形態においては、硫酸塩をその後水性塩基でのイオン交換を介して除去して、$M(OH)_x$またはMO_x膜をもたらす。適当な水性塩基には、Ｉ族金属の水酸化物、II族金属の水酸化物、III族金属の水酸化物、ランタノイドの水酸化物、水酸化アンモニウムおよび／または特に水性第３アミンがある。

【００１２】

ある実施形態は、２個またはそれ以上の金属との錯体組成物を備える酸化物の薄膜または積層体に関するものである。金属カチオンの少なくとも一つは3^+より大きい電荷を有し、3^+より大きい電荷を有するカチオンの全濃度が対象酸化物における金属カチオンの５０モル％を越える。溶解塩およびある量の水を含む非水溶液を調製する。水の量は、非水溶媒に対し２０モル％未満である。かかる溶液のｐＨは、塩基を加えることによるか、または酸化還元機構を介した遊離プロトンの反応によって、最初の溶液に対し増大させる。最終溶液のｐＨは、用いた金属カチオンに依存するが、一般に約２～９の範囲となる。増大したｐＨは、カチオンに結合した水分子の加水分解および生成したヒドロキソカチオンの濃縮をもたらす。溶媒を蒸発し、生成した固体を水に溶解または分散し、その後基板に液膜として塗布する。次いで、液膜を約１００～６００℃の温度で約５～２４０分間熱硬化する。

【００１３】

本発明に従って作成し得る電子装置、または該装置の構成材の例としては、限定することはないが、電界効果トランジスタにおけるゲート絶縁体のような絶縁体、電界効果トランジスタのようなトランジスタ、ＭＩＭコンデンサのようなコンデンサがある。本実施形態に従って作成した薄膜および積層体は、約９～約１２の範囲の誘電率と、少なくとも３$MVcm^{-1}$から約６$MVcm^{-1}$までの破壊電界と、１$MVcm^{-1}$の電界強度で１$nAcm^{-2}$近くの漏洩電流とを有する。ＺｉｒｃＳＯｘ：Ｃａを用いて作成した装置は、約３．６$MVcm^{-1}$の破壊電界と、約５０$nAcm^{-2}$未満、より一般的には約１０$nAcm^{-2}$未満の漏洩電流とを有する。

【００１４】

電界効果トランジスタは、ＨａｆＳＯｘ：Ｌａおよび／またはＺｉｒｃＳＯｘ：Ｌａをゲート絶縁体材料として用いて作成することができる。ある開示された実施形態では、酸化亜鉛インジウムおよび／または酸化亜鉛スズをチャネルとして用いる。特定の電界効果トランジスタは、10^6を超えるオンオフ比および$nAcm^{-2}$のゲート漏洩電流を有する。

【００１５】

本発明の他の実施形態は、フォトレジストを用いる装置のパターン化方法に関する。この方法の特定の実施形態は、パターン化すべき構造体をまず用意することを備える。この

構造体は、通常半導体材料、金属、ガラス、ポリマー材料またはこれらの組合せのような基板と、シリカのようなパターン化用材料層と、レジスト層とを備える。このレジスト層は、通常ここに開示したハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物を含む。前記構造体を、電子ビームまたは光のようなエネルギー源、特定例では紫外光線に曝す。その後、材料を除去して装置をパターン化するか、または装置の活性なパターン化構成材として保有する。

【００１６】

レジストは、ポジレジストでもネガレジストでもよい。例えば、前記方法は、レジスト層をエネルギー源に曝して、レジスト層ｘ材料を現像液に可溶な材料に変換することを備えることができる。次いで、現像液に可溶な材料を、現像剤を用いて除去する。適切な現像剤には、酸、塩基および／または特に超音波攪拌がある。再度一例として、本方法は、エネルギー源に曝したレジスト層材料を除去することを備えることができる。本発明を特定の動作理論に限定することなく、少なくともある実施形態に関しては、エネルギー源へ露出してレジスト層を重合し、エネルギー源への露出前よりも現像液に溶解しにくくすることができる。

【００１７】

ポジレジストの一つの実施形態は、二重層からなる。二重層の第１層は、ハフニウム酸化物硫酸塩（ＨａｆＳＯｘ）膜上に堆積した蟻酸銅膜を備える。この蟻酸銅膜は酸に溶解し、非ドープのＨａｆＳＯｘ膜は酸に溶解しない。二重層をマスクを介して光に露出するか、または集束電子ビームに露出して二つの膜を露出領域で相互拡散し、これにより予め非ドープのＨａｆＳｏｘ膜を可溶性にする。

【００１８】

レジストを作成するための二重層法の他の実施形態は、1個またはそれ以上の金属原子を含有する固形の酸または塩基から成る第１層を基板に堆積することを備える。蟻酸銅のような酸化物前駆体を含む液体懸濁液を前記第１層上に所望のパターンで塗布する。加熱条件下で、前駆体が酸化物に分解する。その後、酸化物が第１層と反応し、相互拡散して、パターンを示すのにエッチングし得る生成物を形成する。代案の実施形態は、加熱または加熱することなく酸化物粒子を第1層上に堆積し、直接反応してエッチングし得る生成物を形成することを備える。さらなる実施形態は、酸化物前駆体の薄層を第１層上に堆積することを備える。次いで、その後、フォトマスクを介した露光、または集束レーザーもしくは電子ビームでの直接書刻によって活性化前駆体のパターンを形成する。

【００１９】

本発明の他の実施形態は、インプリントリソグラフィー用のマスタープレートに関する。該マスタープレートは、フレキシブル基板またはガラス基板のような基板と、少なくとも1個のここに開示したハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物を有する薄膜または積層体の少なくとも一つの層とを備える。マスタープレートの特定実施形態は、基板上に堆積したＨａｆＳＯｘ層と、ＺｉｒｃＳＯｘ：Ｃｕ層のような第２層とを有する。このマスタープレートを、マスクを介した光または電子ビームへの露出のようなエネルギー源への露出によってパターン化して、２つの膜を露出領域で相互拡散させることができる。これは、予め非ドープのＨａｆＳＯｘ膜を可溶性にし、これを除去してマスタープレートの印刷特性を少なくとも部分的に画成する。

【００２０】

他の実施形態においては、本発明の膜を単一層法に用いてマスクまたはテンプレートを製造することができる。固体酸または塩基のような無機前駆体の薄膜を過酸化物または類似のアニオンと組み合わせて基板上に堆積する。この膜を加熱して構造的に硬い膜を生成する。次いで、フォトマスクを通して、またはレーザーもしくは電子ビームを介して暴露して露出領域に濃縮／架橋結合を誘導する。露出領域の溶解性は、非露出領域に対して減少する。次いで、非露出領域を選択的にエッチングし、膜内にネガティブトーン画像を形成する。また、ポジティブトーン画像は、露出前に膜を高温に予熱することによって形成することができる。いくつかの実施形態において、ＨａｆＳＯｘのような膜を水酸化ナト

リウムおよび過酸化水素の混合物で処理することによって$M(OH)_x/H_2O_2$膜を形成する。次いで、生成した膜を光または電子ビームに露出することによってパターン化する。

【００２１】

また、装置の製造方法を開示し、これは基板、パターン化用材料層、ここに開示したハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物を含む金属酸化物層を備えるパターン化すべき構造体を用意することを備える。この構造体をパターン化し、その後エネルギー源に露出して、構造体のパターン化によって生成した所望のパターンを有する耐久材料を形成する。この方法に従って作成した装置の一実施形態は、マイクロまたはナノチャンネルアレイのようなチャンネルアレイを含むことができる。かかる実施形態に関する装置の製造方法は、所定寸法規模の単位構成を半固体のハフニウムまたはジルコニウム化合物に刻印してスタンプ層を形成することを備えることができる。

【００２２】

腐食バリアを有する装置の製造方法の実施形態も開示する。この方法の開示した実施形態は、装置を用意し、少なくとも1個の腐食バリアを該装置上に形成することを備える。腐食バリアは、通常ここに開示したハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物を含む金属酸化物層からなる。この方法はまた、前記化合物をエネルギー源に露出して腐食バリアを形成することを備えることができる。かかる装置を例示すると、金属および金属／セラミック系の熱保護システム、有機系のディスプレイおよび電子機器、太陽電池、高放射率コーティング、酸化物系セラミックマトリックスシステム用の界面コーティング、りん光体上の保護コーティング、金属およびセラミック系システム用の環境障壁コーティング、複合体およびファイバーレーザ用の繊維、溶融金属処理における腐食保護、熱絶縁用のモノリシック材料及び触媒担体がある。

【００２３】

繊維の製造方法の実施形態も開示する。ここに開示したハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物を有する溶液を形成する。次いで、該溶液を繊維にする。該繊維を、加水分解、アニーリング、大気中での熱分解およびその組み合わせのような任意適当な方法によって固形の安定した形に転換することができる。

【００２４】

光学装置の実施形態も開示する。この装置の特定の開示した実施形態は、光学基板と、ここに開示したハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物を有する基板コーティングとを備える。層は反射防止コーティングとすることができる。光学基板およびコーティングは、例えば、誘電体反射鏡、Ｘ線反射鏡、干渉フィルター、回折格子および／または導波管を画成することができる。光学装置はまた、視覚的に透明又は紫外光に透明であるような透明な層を含むことができる。かかる層を選択的にドーピングして、Mn^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Eu^{3+}, Tb^{3+}, Eu^{2+}, Gd^{3+}, Tm^{3+}, およびその組合せから選択した発光イオンを有するドーピング層を付与することができる。この層のドーピングを用いて発光層を形成する。

【００２５】

物理的ルーラーの製造方法の実施形態も開示する。ある実施形態は、ここに開示したハフニウムおよび／ジルコニウムオキシヒドロキシ化合物の溶液堆積によって、少なくとも一つの酸可溶性層を形成することを備える。少なくとも一つの酸不溶性層を前記酸可溶性層に隣接して形成し、該酸不溶性層をここに開示したハフニウムおよび／ジルコニウムオキシヒドロキシ化合物の溶液堆積によって形成する。これらステップを繰り返して交代層を形成し、前記方法は、交代酸不溶および酸可溶性層の幅を正確に決定することを含む。幅の決定は、Ｘ線反射率のような任意適当な方法を用いて達成することができる。さらに、少なくとも一つの層をエッチングして、対象物を測定するための指状の二次基準パターンを画成する。かかる装置のある実施形態は、電子顕微鏡を用いて寸法を正確に測定するのに有効である。

【００２６】

本発明の前述した、および他の物、特徴および利点は、添付図面を参照して、以下の詳細な説明からより明らかである。

【図面の簡単な説明】

【００２７】

【図１】様々な予備処理およびN_2（気体）を１０℃／分の速度で流しながら加熱したサンプルによるＨａｆＳＯｘ（ｘ＝０．７０）に関する熱重量分析（相対湿度対温度）（ＴＧＡ）を示す。

【図２】上述した以外空気中所定温度で１時間加熱後のＨａｆＳＯｘ粉末に対するＸＲＤパターンを示す。

【図３】上述した以外所定温度で1時間加熱後のＨａｆＳＯｘ：３２％Ｌａの粉末に対するＸＲＤパターンを示す

【図４】３１．８°および４５．６°での非常に小さい構成が基板に起因する空気中所定温度で５分間加熱後のＨａｆＳＯｘ膜に対するＸＲＤパターンを示す。

【図５】空気中所定温度で５分間加熱後のＨａｆＳＯｘ：２４％Ｌａ薄膜に対するＸＲＤパターンを示す。

【図６】ＨａｆＳＯｘ膜に対する絶縁破壊特性を示す。

【図７】二酸化ケイ素基板上のタンタル（Ｔａ）金属上に堆積したＨａｆＳＯｘの一実施形態を示すＳＥＭである。

【図８】Ｔａ上に堆積したＨａｆＳＯｘ：２４％Ｌａに対するＳＥＭである。

【図９】１７．６ｎｍの二重層厚を有する１４個の交代層（７個の二重層）を備えるＨａｆＳＯｘ／ＺｉｒｃＳＯｘ多層薄膜に対するＸＲＲパターンを示す。

【図１０】ポジ型またはネガ型フォトレジスト処理を示す概略図である。

【図１１】二重層システムを用いたポジ型レジストを示す概略図で、図示形態は硫酸酸化ハフニウム（ＨａｆＳＯｘ）膜上に堆積したＣｕドープ硫酸酸化ジルコニウム（Ｃｕ：ＺｉｒｃＳＯｘ）膜を備える。

【図１２】基板上にパターン化酸化物を生成するための二重層処理を示す概略図である。

【図１３】基板上にパターン化酸化物を生成するための二重層処理を示す概略図である。

【図１４】基板上にパターン化膜を生成するための単一層処理を示す概略図である。

【図１５】熱的前処理した単一層膜に対する厚さ対エッチング時間のグラフである。

【図１６】電子ビームによってパターン化膜を示す。

【図１７】有機ポリマーに対しより高い機械的強度と、化学的安定性と、独特の電気および光学特性を有する本明細書で開示した半固体形態の化合物を用いるための熱エンボス加工リソグラフィーを示す概略図である。

【図１８】電子顕微鏡のような用途で測定を規格化するのに用いるための物理的ルーラーを作成する一つの方法を示す概略図である。

【図１９】シリカ上に堆積した未交換のＨａｆＳＯｘ膜のＡＦＭ画像である。

【図２０】ＨａｆＳＯｘのイオン交換および８５０℃の熱処理が続くHfO_2のＴＥＭ画像である。

【図２１】シリカ上に堆積し、７００℃以上で加熱後にＨａｆＳＯｘ熱分解デ形成したHfO_2膜のＡＦＭ画像である。

【図２２】シリカ上に堆積し、０．１ＭＮａＯＨで処理し、４５０℃に１０分間加熱したＨａｆＳＯｘ膜のＡＦＭ画像である。

【図２３】シリカ上に堆積し、０．１ＭＮａＯＨで処理し、８５０℃に１０分間加熱したHfO_2のＡＦＭ画像である。

【図２４】未処理の酸化ハフニウム膜のＸＲＤプロットである。

【図２５】処理した酸化ハフニウム膜のＸＲＤプロットである。

【図２６】未処理のジルコニア膜のＸＲＤプロットである。

【図２７】処理したジルコニア膜のＸＲＤプロットである。

【図２８】シリカ上に堆積した酸化インジウムガリウム亜鉛半導体のＳＥＭ画像である。

【図２９】インクジェット印刷および無機拡散反応を介して生成した線パターンを示す。

【図３０】二重層膜をＵＶ光に露出することによって生成したパターンを示す。
【図３１】電子ビーム書刻によってパターン化した膜を示す。
【図３２】電子ビーム書刻によってパターン化した膜を示す。
【図３３】写真的にパターン化した膜を示す。
【図３４】写真的にパターン化した膜を示す。
【図３５】電子ビームによってパターン化した$HfO_{2-x}(SO_4)_x$膜を示す。
【図３６】電子ビームによってパターン化した$HfO_{2-x}(SO_4)_x$膜を示す。
【図３７】電子ビームによってパターン化した$HfO_{2-x}(SO_4)_x$膜を示す。
【発明を実施するための形態】
【００２８】
本発明で開示した実施形態は、電子装置または電子装置の構成材を含む装置に関するもので、無機材料の溶液堆積によって作成することができる。本明細書中での単数用語の不定冠詞及び定冠詞は、特記しない限り複数形も含む。同様に、用語“ｏｒ”は特記しない限り“ａｎｄ”を含むことを意図する。用語「含む」は、「備える」を意味する。本明細書に列挙した百分率は、明示しない限り、原子パーセントである。本明細書において挙げた特許文献および先行技術文献は、特記しない限り、その全てをここに参照して援用する。不一致の場合、用語の説明を有する本発明の明細書は、制御するものとする。本明細書において列挙した材料、方法、および実施例は、実例のためのみであり、限定するものではない。
【００２９】
Ｉ．一般的および特許文献３に記載の金属酸化物硫酸塩材料
本発明の開示は、無機材料の溶液堆積、通常電子用途に有用な金属酸化物硫酸塩無機材料の溶液堆積の方法の実施形態に関するものである。これらの材料の実施形態は、特許文献３に開示されている。この特許文献３の段落００９から段落０１４を以下に言い換える。この言い換えた文書における図の参照は、特許文献３と共に発行された図を参照する。
「図１は、誘電性前駆体材料の製造プロセスの一実施形態を示す。プロセス１０は、一般に金属含有カチオンのような第１の反応体１２を用意し、多原子アニオンのような第２の反応体１４を用意し、次いで多原子アニオンおよび金属含有カチオンを反応させることを備える。金属含有カチオンおよび多原子アニオンは、一緒に反応させる際、水溶液のような溶液内にあるものとする。一実施形態においては、ハフニウムオキシ塩化物（$HfOCl_2$（ａｑ））のようなハフニウムオキシハロゲン化物の水溶液を用いて金属含有カチオンを付与することができる。硫酸（H_2SO_4（ａｑ））水溶液を用いて硫酸塩（SO_4^{2-}）のような多原子アニオンを付与することができる。所定材料を作成するのに適した方法及び相対量を用いてこれら２個の反応体を一緒に混合することができる。混合物を加熱してもよい。
反応は、前駆体溶液１６を生成することができる。前駆体溶液１６は、基板に塗布することによるように、所望に応じてすぐに使用することができる。随意的には、前駆体溶液１６を少なくとも部分脱水し、次いで塗布する場合がある。上述した例において、前駆体溶液１６はその後ハフニウムオキシヒドロキシ硫酸塩（$HfO_{2-x-2/z}(OH)_2(SO_4)_x$）を形成することができる。この式における変数に関して、ｘおよびｚは固定または可変であり、いかなる値も取ることができる。例えば、ｘの値は通常約０．１～約１．９であり、ｚの値は０．０～約２．０である。一つの実施形態に対する値は、ｘ＝０．５およびｚ＝０であった。水酸基が金属含有カチオンの一部であり、前記化合物がハフニウムオキシヒドロキシ硫酸塩（$HfO_{2-x-2/z}(OH)_2(SO_4)_x$）からなる場合がある。
他の実施形態において、多原子アニオンは、１個またはそれ以上の硫酸塩（SO_4^{2-}）、ホウ酸塩（BO_3^{3-}）、リン酸塩（PO_4^{3-}）、タングステン酸塩（WO_4^{2-}）およびケイ酸塩（SiO_4^{4-}）を含むことができる。金属含有カチオンは、金属亜酸化物からなる場合があり、１個またはそれ以上のハフニウム（Hf^{4+}）、チタニウム（Ti^{4+}）、ジルコニウム（Zr^{4+}）、セリウム（Ce^{4+}）、スズ（Sn^{4+}）、タ

ンタル（Ta^{5+}）、ニオブ（Nb^{4+}）、イットリウム（Y^{3+}）、モリブデン（Mo^{4+}）、タングステン（W^{6+}）、アルミニウム（Al^{3+}）、ガリウム（Ga^{3+}）、亜鉛（Zn^{2+}）、クロム（Cr^{3+}）、鉄（Fe^{3+}）、ビスマス（Bi^{3+}）、ランタニド類、ハフニウムオキシ水酸化物（$HfO_y(OH)_z^{(4-2y-z)+}$）、ジルコニウムオキシ水酸化物（$ZrO_y(OH)_z^{(4-2y-z)+}$）、チタニウムオキシ水酸化物（$TiO_y(OH)_z^{(4-2y-z)+}$）、タンタルオキシ水酸化物（$TaO_y(OH)_z^{(5-2y-z)+}$）、イットリウムオキシ水酸化物（$YO_y(OH)_z^{(3-2y-z)+}$）、ニオブオキシ水酸化物（$NbO_y(OH)_z^{(4-2y-z)+}$）、モリブデンオキシ水酸化物（$MoO_y(OH)_z^{(4-2y-z)+}$）、タングステンオキシ水酸化物（$WO_y(OH)_z^{(6-2y-z)+}$）、アルミニウムオキシ水酸化物（$AlO_y(OH)_z^{(3-2y-z)+}$）、ガリウムオキシ水酸化物（$GaO_y(OH)_z^{(3-2y-z)+}$）、亜鉛オキシ水酸化物（$ZnO_y(OH)_z^{(2-2y-z)+}$）、クロムオキシ水酸化物（$CrO_y(OH)_z^{(3-2y-z)+}$）、鉄オキシ水酸化物（$FeO_y(OH)_z^{(3-2y-z)+}$）、ビスマスオキシ水酸化物（$BiO_y(OH)_z^{(3-2y-z)+}$）、およびランタニド系列のオキシ水酸化物を含むことができる。yの値は、金属カチオンの電荷と、金属カチオンに結合する水酸化物および他の多原子アニオンの量に関係する。

ここに開示した多原子アニオンおよび金属含有カチオンを用いた方法の実施形態は、錯体を形成するための有機物を用いるのを必要としない誘電性前駆体材料、すなわち有機物を含有しないアニオンおよびカチオンの源を形成することになる場合がある。しかし、ある実施形態に対しては所望又は所要に応じて有機材料を用いることができる。例えば、エタノールのような非錯化有機物を前駆体溶液における部分溶媒として用いることができる。錯化有機物が前駆体材料に含まれない場合、該前駆体溶液を基板に塗布したら、前駆体溶液は通常４００℃またはそれ以上の高温度で加熱またはアニーリングしてあらゆる有機材料を分解／燃焼する必要がない。加熱および／または乾燥による前駆体溶液の重合は、多結晶材料でなくアモルファス膜の形成をもたらし、これにより基板上への誘電体材料の溶液を基にした塗布が可能になる。

一般に、本明細書記載の方法の実施形態は、空気中大気圧のような周囲条件で行うことができる。したがって、真空処理は必要ないが、所要に応じて利用し得る。この方法は、約８０℃～約８５０℃のような大気以上の温度、通常約８０℃から最高３５０℃、しばしば最高１００℃で行うことができる。これら低圧低温処理は、開示した方法用のエネルギー必要条件を低減することができる。誘電体膜を処理するのに有用な低温により、膜をプラスチック基板のような低温基板上で処理するか、または溶液として塗布する。生成したアモルファスの非晶質誘電性前駆体溶液は、ウエハのような基板上への前駆体溶液の等角被覆を可能にする。該溶液はまた、インクジェット印刷を用いるなどして所定の特別なパターンで塗布することができるので、マスキングまたはエッチング工程を用いることはない。したがって、本明細書の方法は、基板上のフォトリソグラフィー処理の間材料の形成および除去に用いる危険もしくは有害な材料の利用を撤廃または減少することができる。すなわち、本方法は、既知の方法に対し時間効率が良く環境に優しい。さらに、本明細書の一実施形態に用いるハフニウム酸化物および硫酸塩材料は、有毒材料ではない。

本明細書の方法に用いる材料の実施例には、ハフニウムオキシヒドロキシ硫酸塩（$HfO_{2-x-z/2}(OH)_z(SO_4)_x$）、ハフニウムオキシヒドロキシタングステン酸塩（$HfO_{2-x-z/2}(OH)_z(WO_4)_x$）、ハフニウムオキシヒドロキシホウ酸塩（$HfO_{2-x-z/2}(OH)_z(BO_3)_x$）、ハフニウムオキシヒドロキシリン酸塩（$HfO_{2-x-z/2}(OH)_z(PO_4)_x$）およびハフニウムオキシヒドロキシケイ酸塩（$HfO_{2-x-z/2}(OH)_z(SiO_4)_x$）を含む一群の化合物がある。これら材料は、８０℃程の低温で重合し、約７４０℃まで、さらには１２００℃までアモルファスを保持することができる。材料の重合は、加熱速度の調整、共溶媒の使用、他の適切な方法、およびこれらの方法のすべての組み合わせにより制御することができる。本明細書のアモルファス膜は、粒界での欠陥形成を減少することができ、またアモ

ルファス－結晶転移によりクラック形成を減少することができる。さらに、本明細書の誘電体膜は、適度に高い誘電定数、すなわち有機化合物の誘電定数よりも高い誘電定数を有する。インクジェット印刷の適用のような溶液系処理による高品質の誘電体を形成する能力は、電界効果トランジスタまたはコンデンサのような低コスト電子部品を形成することができる。

図２は、前駆体溶液１６を塗布して誘電体材料を形成する方法の一実施形態を概略的に示す。ハフニウムオキシ硫酸塩のような前駆体溶液１６を塗布器２０によってウエハのような基板１８に塗布する。一実施形態において、塗布器２０はノズル２２を有するインクジェットプリンタとすることができる。前駆体水溶液１６をインクジェットプリンタのノズル２２を通して噴出する。他の実施形態において、塗布器２０は、前駆体溶液の塗布方法がそれぞれスピンコーティング、ディップコーティングまたはスプレーコーティングからなるようにスピン塗装機、ディップ塗装機またはスプレー塗装機とすることができる。前駆体溶液１６のアモルファスな溶液特性により、前駆体溶液１６を塗布した際に、良好な等角被覆を可能にする。基板表面または基板上に堆積した一枚もしくは複数枚の膜上に一度塗布したら、ヒータ２４での加熱によって、もしくは他の脱水デバイスによって前駆体溶液を脱水して、前駆体溶液中の水分を除去または減少させることができる。この脱水工程は、ハフニウムオキシ硫酸塩薄膜のようなアモルファス誘電体材料のウエハ１８上への沈殿をもたらすことができる。

図３は、誘電体材料前駆体溶液１６の一実施態様（図１参照）、特に硫酸（H_2SO_4）とオキシ塩化ハフニウム（$HfOCl_2$）との反応に対して前駆体濃度を異ならせるために可能な溶液濃度を示すグラフである。特に、図３は、全硫酸塩濃度（モル濃度（Ｍ））対全ハフニウム濃度（Ｍ）のグラフを示す。領域２８は、透明な溶液、すなわち、目で見える沈殿物がない溶液を示し、この場合領域２８は過剰な硫酸（H_2SO_4）の領域である。領域３０は、透明な溶液、すなわち、目で見える沈殿物がない溶液を示す。領域３０は、過剰なオキシ塩化ハフニウム（$HfOCl_2$）の領域である。ライン３２は、硫酸およびオキシ塩化ハフニウムがそれぞれ１対１の比（１：１の化学量論的比）である化学量論ラインである。領域３４は、沈殿領域、すなわち目で見える沈殿物を有する溶液を示す。したがって、領域３４またはその一部は、インクジェット印刷の適用によって滑らかで実質的に欠陥のない膜を形成するのに最適でないが、その用途を除外しない溶液を示す場合がある。したがって、前駆体溶液１６（図２参照）をインクジェットプリンタ適用装置２０（図２参照）により塗布する場合、第１および第２反応体の濃度が領域２８または３０の内に入るが、固体領域３４に入らないことが望ましいばあいがある。領域３４の溶液に存在する固体は、ノズル２２をふさぐか、又は滑らかでない膜を形成するか、さもなければ好ましくない前駆体溶液の塗布をもたらす場合がある。換言すれば、領域２８および３０の溶液は、インクジェットプリントヘッドを通して、または滴下方法によって塗布し得る可能な前駆体溶液「インク」を示す。」

【００３０】

II．一般的考察

新しい薄膜誘電体およびナノ積層体が、溶液堆積、通常滑らかで高密度な膜の水溶液堆積を用いて開発されてきた。溶液堆積技術には、スピンコーティングおよびインクジェット印刷がある。溶液堆積に続いて適度な熱処理（Ｔ＜３２５℃）を行うことができる。

【００３１】

さまざまな分析技術を用いて、本発明に従って作成した材料の化学特性を粉末および膜の両方として定義した。膜の品質および機能は、Ｘ線反射率、電子顕微鏡検査法および電子装置における性能によって分析されてきた。誘電特性は、実施形態に関して決定され、約９～約１２の範囲をカバーする誘電率値と、少なくとも６$MVcm^{-1}$までの破壊電界と、電界強度１$MVcm^{-1}$で１$nAcm^{-2}$近くの漏洩電流とを含む。膜の表面滑らかさおよび間隙のない性質は、少なくとも約２ナノメーター程度の薄い個々の層を有する独特なナノ積層構造体の製造を容易にする。比較的高い誘電率の膜は、本発明の開示した実施形態を用いて実現できるが、薄膜の金属－絶縁体－金属（ＭＩＭ）コンデンサおよび薄

膜トランジスタ（ＴＦＴ）に高い破壊強度および低い漏洩電流を付与することもできる。絶縁膜の例外的な特性も、独特なナノ積層構造体の形成を可能にする。

【００３２】

アモルファス材料は、薄膜誘電体としての使用に望ましく、粒界を有さず、したがって、微結晶に伴なう粗度および電荷伝導に影響されにくい。ハフニウムおよびジルコニウムの多くの酸化物、例えば簡単な二成分、ケイ酸塩およびアルミン酸塩を、高い誘電率の誘電体用途の候補として検討した。多成分材料においては、誘電率を犠牲にし得るが、結晶化を抑制して純な２成分酸化物に対しより頑丈な破壊特性を生成することができる。これら誘電膜は、しばしば、様々な金属―有機物または金属―塩の前駆体と、原子層堆積（ＡＬＤ）、化学気相堆積（ＣＶＤ）、ゾル－ゲル処理、またはその組み合わせのような技術とを用いて形成される。しかし、溶液堆積法によって高密度でアモルファスである有用な誘電体膜を形成するには、堆積およびその後の処理中に結晶化およびクラッキングを抑制する必要がある。

【００３３】

本発明に開示したある実施形態は、金属酸化物膜の開発に関するものである。金属酸化物は、それぞれ式$HfO_{2-x}(SO_4)_x$および$ZrO_{2-x}(SO_4)_x$を有し、それぞれ０．１≦ｘ≦１．５であるハフニウムおよびジルコニウム硫酸塩系を参照することによって通常例示される。これら化合物は、ここにそれぞれ頭文字$HafSO_x$および$ZircSO_x$で表さす。これら系の化学的および物理的特性を定義するため、$HafSO_x$およびそのＬａ置換誘導体$HafSO_x$：Ｌａのようなドーピングされた類似物を、粉末および薄膜として両方作成する。$HafSO_x$、$ZircSO_x$およびその選択した誘導体の薄膜誘電特性は、コンデンサおよびＴＦＴを組み立てることにより評価される。これら分析によって、高品質で高密度の膜が生成し得ることが示された。混合$HafSO_x$／$ZircSO_x$ナノ積層体の膜厚および製作は、現在スピンコーティング法によって制御し得る。

【００３４】

多くの相および結晶構造体が、$HfO_2-SO_3-H_2O$および$ZrO_2-SO_3-H_2O$系の検討から報告されている。いくつかの構造体は、水和度並びに金属原子、硫酸塩基および水の凝縮に伴った構造的次元の変動を示す式$Hf(SO_4)_2\cdot nH_2O$または$Zr(SO_4)_2\cdot nH_2O$の簡単な水和物として特徴付けられる。硫酸塩に対し金属が豊富な既知の材料としては、$Zr_2(OH)_2(SO_4)_3\cdot 4H_2O$と；$Hf(OH)_xSO_4$およびその水和物と；$Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}\cdot 33H_2O$および$Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$と；$Zr_3O_5(SO_4)_{13}$およびその水和物とがある。これら構造体の全て（可能であれば$Zr_3O_5SO_4$は除く）は、室温および水素の結合又は脱水の変化をもたらす温和な加熱下の両方で大気に施した際に不安定になりがちである。これによって、脱水及び凝縮処理を用いてアモルファス膜を開発するのが可能になる。

【００３５】

ハフニウムに対する硫酸塩の選択した画分（変数ｘ）を有する水溶液から出発して、ＨａｆＳＯｘ沈殿物を加熱によって生起する。図１は、風乾したＨａｆＳＯｘ沈殿物の熱重量分析（ＴＧＡ）である。ＴＧＡは、サンプルの重量（質量）の変化を温度の関数として測定するのに用いる温度分析技術である。風乾したＨａｆＳＯｘ沈殿物を加熱すると、３つの領域に質量損失を生じる。同様の特徴が、他のＨａｆＳＯｘ誘導体においても観察される。約２００℃の温度以下での大きな質量損失は、結合した水の損失に起因する。約２００℃～約７００℃の温度範囲における質量損失は、主に水としてより強固に結合したヒドロキシル基の排除に起因する。約７００℃以上で開始する急な質量損失は、$SO_3(g)\rightarrow SO_2+1/2O_2(g)$に従う硫酸塩分解に起因する。脱水ＨａｆＳＯｘ粉末が７００℃から９５０℃の間でHfO_2に完全に転換すると仮定すると、硫酸塩画分は、質量損失から計算できる。サンプルの質量損失を決定することにより、母溶液における硫酸塩の増大レベルが、沈殿物における硫酸塩の増大レベルわもたらすことがわかった。とくに

、硫酸塩対ハフニウムの比が、それぞれ$HfO_{1.54}(SO_4)_{0.46}$および$HfO_{1.29}(SO_4)_{0.71}$の脱水式に対し約４６％～約７１％まで変化した。H_2SO_4（ａｑ）または$(NH_4)_xSO_4$（ａｑ）を硫酸塩源として使用していても、同じ最大量の硫酸塩組成物が沈殿したが、４６％未満の硫酸塩レベルを有する生成物は検討しなかった。熱重量プロファイルにおいていくらかばらつきが観察されたが、硫酸塩損失の開始は、すべてのサンプルで７２０℃以上で起こった。誘導体に対するこれら加熱曲線の定義し得る値としてのピーク位置は、試験したサンプルでは７９３℃から８１７℃間での分解を示した。最高分解温度は、硫酸塩源としてH_2SO_4（ａｑ）を用いて最大硫酸塩含有量を有するサンプルで観察された。

【００３６】

再び図１を参照するに、最大硫酸塩含有量のサンプルもＴＧＡ測定の前に加熱した。水と関連した質量損失を減じ、予熱したサンプルおよび規格のサンプルの両方で算出した硫酸塩含有量は類似していた。この７０～７１％硫酸塩含有量は、報告した結晶$Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}33H_2O$および；$Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}S\cdot 33H_2O$の組成を再現する。ＴＧＡ研究より、Ａｈｍｅｄ，Ｆｊｅｌｌｖａｇ，およびＫｊｅｋｈｕｓもまた、$Hf_{18}O_{23}(SO_4)_{13}$および$Zr_{18}O_{23}(SO_4)_{13}$に対する硫酸塩分解が、この研究内においてＨｆおよびＺｒ二硫酸塩に対するものよりも高く、また他者により報告された基本の硫酸塩$Hf(OH)_2(SO_4)\cdot H_2O$および$Zr_3O_5SO_4$に対するものよりも高い温度で起こることを見い出した。増大した熱安定性に加えて、約１３：１８の硫酸塩対金属の比が、この系内で特別な安定性を示す。また、この組成が溶液処理および加熱を要求する目的に関して適切な場合がある。

【００３７】

硫酸塩$La_2O_2SO_4$は、１３００℃を超える分解温度を有する。ランタン（Ｌａ）をＨａｆＳＯｘ母溶液に加えて、修正した脱水特性および、一例として熱安定性である熱的特性のような修飾した物理的性質を有する付加的な化合物を生成する。混合金属システム、すなわち$Hf_{1-z}La_zO_{2-x-z/2}(SO_4)_x$（ＨａｆＳＯｘ：Ｌａ）は、かかる化合物を例示する。かかる化合物を生成するためには、前駆体材料および２３％Ｌａ（全金属）を含む溶液を加熱して沈殿物を形成する。化学分析は、わずか３％のＬａが生成物に見い出されることを示された。ＴＧＡから、７１％の硫酸塩対金属の比が認められ、８２０℃での分解（誘導体ピークとして）が、最大硫酸塩含有量と一致することを見い出した。次いで、NH_3（ａｑ）を、３２％Ｌａ含有構成種の塩溶液に加えることによって共沈澱を誘導した。生成物の化学組成を分析して、母溶液に存在するものと同じＬａ画分を示した。この式に対する熱分解は、未ドーピングのＨａｆＳＯｘと著しく異なった。毎分２℃／分の緩徐な速度で加熱する場合でも、加熱特性は急変せず、一定質量が１０００℃までの加熱で達成されないが、硫酸塩に起因した質量欠損が７００℃以上で明白である。この加熱速度に関して、分解（誘導体ピークとして）が約８７０℃で起こるが、この値は加熱条件による。酸化物への完全分解は、１５００℃まで加熱して、乾燥沈殿物用の式$Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$を得ることにより達成される。

【００３８】

ＸＲＤデータを沈殿したＨａｆＳＯｘ粉末に対して収集して、結晶質相に対する温度範囲を確立する。風乾後、複雑な回折パターンを最大硫酸塩含有量および硫酸塩源としてのH_2SO_4（ａｑ）を有するサンプルに対して記録し、他のサンプルは該パターンを示さないか、または拡散回折を示した。ＨａｆＳＯｘ（ｘ＝０．７０）に対するＸＲＤデータを図２に示す。サンプルを約１００℃～約７００℃で１時間加熱風乾後、該物質はアモルファスとなった。単斜晶HfO_2の結晶ピーク特性が、７５０℃およびそれ以上で１時間加熱後に観察される。硫酸塩損失の開始がＴＧＡによって７２０℃で起こるので、結晶化が硫酸塩損失と一致することがわかった。３％Ｌａの含有は、１０００℃までの温度に対して類似の回折プロファイルを発生する。

【００３９】
ＨａｆＳＯｘ：３２％Ｌａに対するＸＲＤデータを図３に示す。沈澱物および７００℃まで加熱した沈殿物は共にＸ線アモルファスである。未置換のＨａｆＳＯｘと同様に、検出可能な結晶質相が７００℃～７５０℃（１時間加熱）で形成され、これは硫酸塩が分解し始める温度間隔である。３２％Ｌａで置換しても、単斜晶HfO_2は検出される相ではない。むしろ、回折プロファイルは立方晶（または正方晶）HfO_2と一致し、HfO_2の相がランタニド原子包含によってしばしば安定化される。高温加熱は、適切な状態図の考察から予想した通り、$Hf_2La_2O_7$および単斜晶HfO_2を生成する。中間温度酸化物相は、１０～３７％のランタンが９００℃で立方晶ジルコニアを安定化し、１０５０℃で相分離が起こることを発見したＺｈａｎｇ，Ｋｅｒｓｈａｗ，およびＤｗｉｇｈｔによる$ZrO_2-La_2O_3$系での研究と一致した。

【００４０】
約２００ナノメートル～約３００ナノメートルの厚さを有するＨａｆＳＯｘおよびＨａｆＳＯｘ：Ｌａ薄膜を、材料特性のために作成した。かかる膜に関する組成を、Ｈｆ，Ｌａ，ＣｌおよびＳの相対濃度に基づくＥＭＰＡで画定した。酸素レベルは、この方法では正確ではないので、脱水した式で表した。３２５℃で加熱（５分間）した２個の代表的なＨａｆＳＯｘ膜は、ハフニウムに対し６７％および８５％の硫酸塩を示す$HfO_{0.985}(SO_4)_{0.67}Cl_{0.69}$および$HfO_{0.915}(SO_4)_{0.85}Cl_{0.47}$と画定した。８５％硫酸塩膜をさらに６５０℃に加熱（５分間）し、$HfO_{1.275}(SO_4)_{0.71}Cl_{0.03}$と画定した。また、３３０℃で加熱（５分間）したＨａｆＳＯｘ：Ｌａ膜は、$Hf_{0.76}La_{0.24}O_{0.73}(SO_4)_{0.96}Cl_{0.38}$と画定した。６５０℃に加熱したＨａｆＳＯｘに関して、硫酸塩比を７１％まで減ずると、最大硫酸塩を有する加熱沈殿したＨａｆＳＯｘ粉体の組成と一致する。ＨａｆＳＯｘ：Ｌａに関して、Ｌａ（２４％）の測定画分は、前駆体溶液における２３％Ｌａ濃度とよく一致する。

【００４１】
ＨａｆＳＯｘ（ｘ～０．６７及び０．８５）およびＨａｆＳＯｘ：Ｌａ膜に対する透過フーリエ変換赤外（ＦＴＩＲ）分析は、所定温度で５分間加熱した後収集された。ＦＴＩＲスペクトルを用いて２個の官能基を主として検出した。３０００～３６００cm^{-1}の範囲における吸収がヒドロキシル基に帰属され、１０００～１２００cm^{-1}の範囲における吸収が硫酸塩基に帰属される。加熱すると、ヒドロキシル吸収が約３２５℃～約６００℃の範囲にわたり減少する一方、硫酸塩ストレッチが、ＨａｆＳＯｘ膜に対して約６５０℃～７００℃の間で、またＨａｆＳＯｘ：Ｌａ膜に対して約７００℃～７５０℃でほぼ消失する。（硫酸塩からのSiO_2は同じようなエネルギーで吸収するため、硫酸塩吸収に対するプロファイルが僅かに歪曲されるが、スペクトルは定性的に正しい。）

【００４２】
薄膜ＸＲＤデータは、それぞれ図４および図５に示したような所定の温度でそれぞれ５分間加熱した後、ＨａｆＳｏｘ（ｘ～０．６７及び０．８５）およびＨａｆＳＯｘ：２４％Ｌａ膜に対して収集された。両ＨａｆＳＯｘ組成物に対し、膜は約３２５℃～約６５０℃でＸ線アモルファスである。単斜晶HfO_2を約７００℃およびそれ以上で検出する。ＨａｆＳＯｘ：Ｌａ膜は、約３３０℃～約７００℃でアモルファスである一方、立方晶相が約７５０℃から約１０００℃で検出される。立方晶相は、単斜晶HfO_2および$Hf_2La_2O_7$相への分離が開始するので、１１００℃で明らかに不安定である。ＨａｆＳＯｘおよびＨａｆＳＯｘ：Ｌａ膜に関して、硫酸塩の損失が酸化物の結晶化と直接的に相関させることができ、これは粉体の挙動と一致する。

【００４３】
ＨａｆＳＯｘ，ＺｉｒｃＳＯｘおよびその誘導体の膜を、誘電体として使用するのにスピンコーティングによって堆積した。ＭＩＭコンデンサを試験して、１ｋＨｚでの誘電率および損失正接のパラメータと、電界破壊強度を画定した。「破壊」は、電流密度が１０μAcm^{-1}を超える電界として定義する。同様の試験をＨａｆＳＯｘ，ＨａｆＳＯｘ／

Ｌａ，ＺｉｒｃＳＯｘ，ＺＩｒｃＳＯｘ：Ｌａ，ＨａｆＳＯｘ：ＣｅおよびＺｉｒｃＳＯｘ：Ｃａに対して行った。図６は、アルミニウムドット接触が０．０１１ｃｍ^{2}の面積を示すＨａｆＳＯｘ誘電体膜に関する誘電体破壊特性を示す。ＨａｆＳＯｘおよびＺｉｒｃＳＯｘ膜は、４～６ＭＶｃｍ$^{-1}$の破壊電界を有する。３．６ＭＶｃｍ$^{-1}$の破壊電界がＺｉｒｃＳＯｘ：Ｃａで見られた。１ＭＶｃｍ$^{-1}$の印加電界で、６個すべてのものが５０ｎＡｃｍ$^{-2}$未満の漏洩電流を示し、１０ｎＡｃｍ$^{-2}$未満の漏洩電流が多くの組成物で観察された。約９～約１２の誘電率値および１％未満の損失正接がすべてのもので測定された。

【００４４】

ＨａｆＳＯｘ：ＬａまたはＺｉｒｃＳｏｘ：Ｌａをゲート誘電体として、また酸化亜鉛インジウムまたは酸化亜鉛スズをチャネルとして用いて電界効果トランジスタ（ＦＥＴｓ）を製造した。電流変調が達成され、ドレイン対ソース電流がドレイン対ソース電圧の増加で飽和され、10^{6}を超えるオンオフ比が付与され、また、ゲート漏洩電流がｐＡｃｍ$^{-2}$の範囲である。これらの結果は、ＨａｆＳＯｘ：ＬａおよびＺｉｒｃＳＯｘ：Ｌａ膜がデバイス集積に関して十分に強固で、誘電体／チャネル界面品質の必要性も満たしていることを明確に示す。

【００４５】

新しいクラスのアモルファス多成分酸化物誘電体膜として、ＨａｆＳＯｘ，ＺｉｒｃＳＯｘおよびその誘導体を、他の混合系、特に$(MO_2)_{1-x}(Al_2O_3)_x$および$(MO_2)_{1-x}(SiO_2)_x$として表わされ、Ｍ＝ＨｆまたはＺｒであるアルミン酸塩およびケイ酸塩と比較することができる。これらの系のそれぞれに対する様々な膜組成物を従来の気相技術によって堆積させた。２０～５０モル％のAl_2O_3またはSiO_2（誘電体用途に共通な組成として）を有するＨｆまたはＺｒのアルミン酸塩およびケイ酸塩の場合、結晶化が通常約８００℃～約１０００℃で相凝離と同時に起こる。試験したＨａｆＳＯｘ粉体および膜に関して、硫酸塩が分解するので、結晶化が約７００℃で起こる。誘電体として、これらアルミン酸塩およびケイ酸塩は１０～１５の誘電率値を示し、ＨａｆＳＯｘおよびＺｉｒｃＳＯｘに関しては９～１２の値である。この新しいクラスの酸化物硫酸塩材料は、アモルファスで、中間温度で、中間の誘電率の誘導体であると見做すことができる。

【００４６】

走査型電子顕微鏡（ＳＥＭ）およびＸ線反射性（ＸＲＲ）を用いて膜品質をさらに検討する。ＨａｆＳＯｘおよびＨａｆＳＯｘ：Ｌａ膜のＳＥＭ画像を図７および図８に示す。これらの画像は、誘電体試験に通常用いられるような約１５０～約３００ナノメートルの厚さを有する膜に対して、滑らかで高密度の均一な断面を示す。図７は、SiO_2基板７１０と、その上に堆積したＴａ金属の５０６ｎｍ層７１２および１６０ｎｍのＨａｆＳＯｘ膜７１４とを示す。図８は、SiO_2基板８１０と、その上に堆積したＴａ金属の５１２ｎｍ層８１２および１９２ｎｍのＨａｆＳＯｘ／Ｌａ膜８１４とを示す。

【００４７】

より薄い膜製造に関する再現性の厳格な目安として、ＨａｆＳＯｘ／ＺｉｒｃＳｏｘ繰り返しモチーフを有する多層構造体を堆積し、ＸＲＲで分析した。一つのＸＲＲ走査による干渉パターンを図９に示す。定常波調波の典型であるピーク最大値の位置を用いて、繰り返し二重層の厚さを求めた。ＨａｆＳＯｘおよびＺｉｒｘＳＯｘの厚さを独立して系統的に変化させることによって、個々の層の厚さを画定した。ナノ積層体スタック内において、約３ナノメートル程薄い単一層を測定した。回折パターンにおける高次の反射を観察すると、各二重層を粗度を含む０．５未満のばらつきで堆積した。

【００４８】

装置寸法の縮小は、薄く、高い漏洩電流のSiO_2をＳｉ　ＣＭＯＳ技術において誘電体として代替する必要性を導いた。この代替誘電体は、高い誘電率を示さなければならず、より厚い層が低い漏洩電流の同じ装置電気容量を示すことを可能にする。HfO_2およびZrO_2は、その望ましい誘電体特性および熱的特性のために、代替ゲート誘電体とし

て非常に注目されている。HfO_2およびZrO_2誘電体に対する挑戦の一つは、１３ｎｍ以下の厚さを有する滑らかで、高密度で、ピンホールがない超薄膜を製造することである。以前は、超薄膜が、原子層堆積（ＡＬＤ）を用いて形成されていた。ＡＬＤによるいくつかの期待できる結果にも関わらず、この処理は長い堆積時間（１Å／分）を有する真空を用いることを必要とし、これは高いコストで低い処理量となる。これは、HfO_2およびZrO_2の溶液系堆積に対しいくつかの研究を促進した。今まで、これらの膜は、ＡＬＤ膜と同じ均一性および密度に達していない。

【００４９】

交換反応を用いて、ＡＬＤの品質に匹敵し、ＤＲＡＭ（ダイナミックランダムアクセスメモリ）およびＳｉ　ＣＭＯＳ（相補型金属酸化膜半導体）技術に用いるのに適した超薄$M(OH)_x$およびMO_x膜を製造することができる。開示した実施形態に関しては、スピンコーティングを用いる無機凝縮を介して膜を硫酸塩形態で堆積する。例えば、半固体膜を$MO_x \cdot HCl \cdot H_2SO_4$の組成で形成することができる。硫酸塩は、水酸化ナトリウム水溶液を用いるイオン交換によって除去される。

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

【００５０】

生成したヒドロキソおよび／または酸化物膜は、滑らかで、高密度で、ピンホールがない。例えば、約２ナノメートルの厚さを有するHfO_2膜を、ＨａｆＳＯｘ膜から製造することができる。交換した膜に約８００℃まで熱処理を約１０秒～１０分間施して約０．１ナノメートルの膜表面粗さをもたらす。高価な原子層堆積処理を低コストのスピンオンまたはミスト技術と交換する一方、上記膜特性がＣＭＯＳおよび関連する技術における金属－誘電体ゲートの要件を満たす。

【００５１】

堆積した半固体の水和ヒドロキソ膜は、膜形態を破壊することなくアニオン交換をすることができる。例えば、SO_4^{2-}，WO_4^{2-}，PO_4^{3-}，AsO_4^{3-}，SiO_4^{4-}，VO_4^{3-}，AlO_4^{5-}，GaO_4^{5-}のようなオキソアニオンおよびそのプロトン化物、例えばHPO_4^{2-}，$H_2PO_4^-$並びにハロゲン化物F^-，Cl^-，Br^-およびI^-は、膜を金属塩浴、例えば$Na_2SO_4^{2-}$（ａｑ）中に置くことによって選択的に交換させることができる。これは、電子用途と、イオン交換クロマトグラフィおよび濾過のような他の用途のための膜機能を最適化する機会を提供する。

【００５２】

酸化物膜のいくつかの実施形態に関して、基板に直接塗布して複雑な組成、例えば２個またはそれ以上の金属原子を提供し得る単一源の前駆体懸濁液を生成するのが困難である。以下の方法が、かかる懸濁液の生成およびその装置用途に適した品質の膜の堆積用の単一源の前駆体としての使用を可能にする。

【００５３】

前駆体水溶液を合成し、該前駆体を用いて金属酸化物膜を堆積するための一般的な方法を下記に開示する。前駆体水溶液は、非水極性溶媒中での加水分解により凝縮し、続いて堆積用の水性環境に転換されたポリマーまたはオリゴマーの金属ヒドロキソ化合物を備えることに特色を示す。有利な薄膜の電気的および光学的特性と、処理温度は、有害な有機汚染なしに金属水酸化物を濃密な固体酸化物に凝縮することにより達成される。ここに開示した合成方法の実施形態は、一般的な手法、すなわち１）金属塩の極性溶媒への溶解、２）加水分解および凝縮、３）溶媒蒸発、４）H_2Oへの溶解、５）溶液堆積および硬化に従う。

【００５４】

金属カチオン（M^{a+}）および１個以上のアニオン（X^{b-}）を備える１個またはそれ以上の可溶性塩を、脂肪族アルコールまたはニトリルのような非錯化で非水の極性溶媒、特にメタノール、エタノール、アセトニトリルもしくはその混合物のような低級（１０炭素原子もしくはそれ以下）アルキルアルコールおよびニトリルに溶解する。多くの溶媒系

が可能である。特定の用途に適した溶媒は、沸点（通常１５０℃未満）と、低毒性と、所望の溶液相反応に適合し得る酸―塩基およびレドックス特性とを考慮することによって選択することができる。金属源には、簡単なイオンもしくは分子塩（$Zn(NO_3)_2$，$SnCl_4$，など）；オキシもしくはヒドロキシ塩（$ZrO(NO_3)_2$，ZnOHCl，など）；または潜在的に有機塩（$Fe(CH_3CO_2)_2$，$Cu(CHOO)_2$，など）がある。金属カチオンの少なくとも一つは、3^+より大きい形式電荷を有さなければならず、また、このイオン（$a>3$のM^{a+}）の全濃度は、目的酸化物中の金属カチオンの５０モル％を越えるべきである。同時に、ある量のH_2Oが、上述した金属塩の水和物として溶液に純粋な液体または以下で説明する塩基溶液として導入される。水の量は選択したカチオンによって画定される。すなわち、水の典型的な量は、非水極性溶媒の２０モル％を越えない。

【００５５】

次いで、溶液のｐＨが、適切な塩基の添加によるか、または酸化還元機構を介した遊離プロトンの反応によって、最初のｐＨに対し上昇される。上昇したｐＨは、酸性カチオン（$a>3$）により結合したH_2O配位子の加水分解および生成するヒドロキソカチオンの凝縮を起こす。最終溶液のｐＨは、用いた金属カチオンに依存するが、通常約２～９の範囲内にある。これは、以下の技術の一つ、またはそのいくつかもしくはすべての組み合わせを用いて達成することができる。

ａ）NH_4OH，$(NH_4)_3PO_4$，ＣｓＯＨまたは類似化合物を含有する塩基性水溶液の添加。特定の化合物（NH_4OH）を選択して、その後の処理の間に分解または揮発することができる。最終酸化物膜の一部を構成して脱水を伴う独特の形態学的、光学的もしくは電気的な特性を達成することを意図する場合、他のカチオン（例えばＣｓ）または多原子アニオン（例えばPO_4^{3-}）を用いることができる。

ｂ）最終酸化物膜における介在物の類似目安でＣａＯまたはＳｒＯのような少量の塩基性酸化物の添加および溶解

ｃ）H_2O中で塩基性溶液を形成するNH_3または他のガス状化合物の添加

ｄ）H_2への直接還元によるか、又はNO_3^-の還元のような他のプロトン消費酸化還元処理の一部としてプロトンを消費し得るＺｎ，ＡｌまたはＦｅのような電気陽性金属還元剤の添加。然る後、生成したカチオン種を最終酸化物膜に入れ込む。

ｅ）プロトンを消費するか又は対イオンを分解する目的であるが、最終酸化物膜に介在することなく液体形態若しくは可溶性塩としてのN_2H_4，H_2CO又はH_2O_2のような水性またはガス状酸化剤または還元剤の添加。

【００５６】

前記溶液を室温で攪拌し、加熱するか、またはソルボサーマル条件に曝して、所望の最終組成に応じた熱分解および凝縮を促進させることができる。適切な反応時間の後、該溶液は１個またはそれ以上の可溶性オリゴマーまたはポリマーの金属－ヒドロキソカチオン種を含有する。これら種は、実際ホモまたはヘテロ金属とすることができる。凝縮の程度は、入手し得るH_2O（水和およびヒドロキソ配位子）の制限的なモル比によって制限される一方、H_2Oに対する非水溶媒の減少した極性およびサイズが、立体効果または変化した電荷スクリーニング特性によって付加的な凝縮および沈殿処理を防止することができる。

【００５７】

可溶性金属種は、非水溶媒を揮発させることによって分離される。分離した金属－ヒドロキソ化合物は、溶媒、対イオン、および加水分解比のようなある処理考察に応じて結晶性もしくはアモルファスの固体またはゲルを形成することができる。

【００５８】

酸化物膜用の前駆体溶液は、分離した固体をH_2Oに溶解または分散させることによって調製される。生成したゾルまたは溶液は均質で、また熱力学的に安定又は安定でない場合がある。

【００５９】

前駆体溶液を、印刷、スピン、スプレーまたはディップコーティングを含む任意適当な技術を用いて基板に塗布してパターン化または前命的な液膜を形成する。液膜を大気条件下約１００℃から６００℃の温度で約５－２４０分間熱硬化する。真空または二次成形ガス（例えば、H_2およびN_2もしくはＡｒ流）アニールを用いて、所望の化学もしくは光電子工学特性に適するように酸素の化学量論またはカチオン酸化状態を変えることができる。

【００６０】

本明細書に開示した膜の平滑さおよび高い原子密度は、溶液処理を介して純粋な無機ナノ積層体を製造することができる。これらの膜は、さらに以下で説明するように、広範囲の用途を開発するための新しい土台となる。

【００６１】

III．用途

当業者は、ＨａｆＳＯｘおよびＺｉｒｃＳＯｘ化合物およびかかる化合物を備える膜を用いて多くの異なる装置を作成することができ、またかかる化合物を利用する様々な処理を実行することができることが理解できる。金属－有機物前駆体は、無機酸化物の溶液系堆積に広く採用されている。この有機部の存在は、相当な体積変化と通常結晶化および「泥割れ」現象とを導く高温焼却工程を必要とする。これらの問題点は、本発明の開示した実施形態と、適切な無機組成とを用いて、簡単な脱水および重合が膜品質維持を導くアモルファスＨａｆＳＯｘおよびＺｉｒｃＳＯｘ膜を形成することにより排除される。相安定性を解明するため、代表的なＨａｆＳＯｘおよびＨａｆＳＯｘ：Ｌａ粉体と膜を様々な温度で特徴付けた。膜の品質および利用性を検討するために、ＨａｆＳＯｘおよびＺｉｒｃＳＯｘを基にした薄膜を様々形状で堆積した。いくつかの誘導体を用いてキャパシタ誘電体を製造した。ＨａｆＳＯｘ：ＬａおよびＺｉｒｃＳＯｘ：Ｌａを用いて、ＦＥＴ装置におけるゲート誘電体を形成した。ＨａｆＳＯｘおよびＺｉｒｃＳＯｘナノ積層体層は、対の原子層内で再現性と共に顕著な平滑さ示した。ＨａｆＳＯｘ，ＺｉｒｃＳＯｘおよびその誘導体を備える膜の階級は、他のものの中でも、電気絶縁体、防護壁、光学的コーティングおよび／またはフォトリソグラフィー用の無機高分子として有用である。

【００６２】

Ａ．レジスト、インプリントリソグラフィーおよび印刷用のパターン化膜

フォトリソグラフィーを一般に用いてマスク上の幾何学的図形をシリコンウエハまたは他の半導体の表面に転写する。過去４０年間は、フォトリソグラフィー処理は、マイクロ電子業界における装置特性の解明および寸法制御において改良するための原動力であった。これらの利点によって、現在我々の生活の欠かせない部分と考えられる高性能のパーソナルコンピューター、携帯電話、ＣＤプレーヤーおよび他の無数の進化した電子製品が可能となった。これら製品を可能にしたフォトリソグラフィーの進展は、短波長の露光ツールの開発と、ポリマーレジストの解明および形状能力の並外れた進展とに大きく集中した。しかし、より小さくデバイス歩留まりの改良が依然として求められているため、ポリマー系レジスト技術の制限および非能率はより明確になってきている。

【００６３】

リソグラフィーにより実現された最小の形状サイズは、無機材料の電子ビーム書き込みによって製造された。しかし、これら形状を生成するのに必要なビーム投与量は、製造環境での使用の一時的なもの以上を受け取る極端に高いものであった。

【００６４】

ここに開示した膜の堆積および処理の間、積層した膜の相互拡散と、生成する物理的および化学的特性を制御する方法を与える膜の水和レベルを制御することが可能である。高品質な膜と結合した材料溶解度に誘起された修飾を有する制御された相互拡散を用いて、新しいリソグラフィーパターン化法を開発する。この方法論は、２個の異なる膜を堆積および反応させることを含み、二重層拡散として指定される。また、ペルオキシド（O_2^{2-}）のような小さい配位種を水系無機懸濁液および膜に添合して追加の新しいリソグラフィーのパターン化方法を提供することができる。この技術では、エネルギー（例えば、光

、電子ビーム、熱）を膜に付与して、膜の溶解性を変える凝縮反応を起こし、リソグラフィーのパターン化を可能にする。

【００６５】

パターンは、ポジ型またはネガ型フォトレジストを用いて形成することができる。この処理をシリコン基板１０１２、シリカ層１０１４およびレジスト層１０１６を有する積層構造体１０１０を参照して図１０に概略的に示す。ポジ型レジストに関しては、レジスト層１０１６をＵＶ光のようなエネルギー源に露出し、どこであっても下側の材料を除去すべきである。これらレジストでは、ＵＶ光への露出がレジスト層１０１６の化学構造を変えるので、現像剤中で一層可溶となる。その後、露出したレジスト層１０１６を現像剤溶液によって除去して、裸の下側材料の領域を残す。換言すれば、「何を示そうが、行く」ということである。したがって、マスク１０１８は、ウエハ上に残すべきパターンの正確なコピーを含む。

【００６６】

ネガ型レジストは、正反対の挙動を示す。ＵＶ光への露出は、ネガ型レジストの重合を生起し、したがって、溶解が一層難しくなる。その結果、ネガレジスト１０２０が露出された表面上に残り、現像剤溶液が未露出部分だけを除去する。したがって、ネガ型フォトレジストに用いるマスクは、転写すべきパターンの逆（または写真の「ネガ」）を有する。

【００６７】

電子機器製造に現在使用中のレジスト材料は、有機ポリマーである。これらポリマーは、パターン分解能を制限するコイリングおよび形態を示す。本発明の無機薄膜は、新しいレジスト技術の基礎を形成する。ここで、ネガ型レジストは、無機物膜を半固体形状で光または電子ビームに露出し、脱水中に溶媒、とくに水を失わせることにより実現することができる。これは膜を強化し、酸に不溶にする。

【００６８】

ポジ型レジストの一つ実施形態は、二重層システムを用いて作成することができる。二重層の第１層は、ハフニウム酸化物硫酸塩（ＨａｆＳＯｘ）膜上に堆積したギ酸銅膜からなる。ギ酸銅膜は、酸に可溶で、未ドープのＨａｆＳＯｘ膜は酸に不溶である。二重層をマスクを介して光に、または収束した電子ビームに露出させると、２個の膜が露出領域で相互拡散を生起し、これにより予め未ドープのＨａｆＳＯｘ膜を可溶にする。

【００６９】

この処理の一実施形態を図１１に概略的に示す。図１１を参照すると、積層構造体１１１０が、先ずスピンコーティングまたはインクジェットコーティングの適切な材料によって加工装置を画成するのに必要とするような所定のオーダーと厚さで形成される。より詳細には、基板材料１１１２を最初に選択する。当業者は、多くの基板材料のうちどれを使っても本発明のこの実施形態を実現できると理解できるだろう。ほんの一例として、また、限定することなく、適切な基板には、半導体材料、金属、ガラス、高分子材料およびそれらの組み合わせがある。そのようなものとして、レジスト技術が半導体製造における様々な用途にとって有用とすることができる。適切な基板１１１２を選択すると、ＨａｆＳＯｘの第１層１１１４を基板１１１２上に溶液堆積する。その後、Ｃｕ：ＺｉｒｃＳＯｘの層１１１６のような第２層を層１１１４上に溶液堆積する。次いで、積層構造体１１１０に、マスクを介して電子ビーム又は光のようなエネルギー源をもたらす。マスクを介して光又は電子ビームに露出すると、２個の膜が露出領域で相互拡散し、予め未ドープのＨａｆＳＯｘ膜を可溶性にして積層構造体１１２０を生成する。次いで、露出した構造体１１２０を現像する。予め未ドープのＨａｆＳＯｘは可溶性であので、積層構造体１１３０において示すように除去される。

【００７０】

フレキシブルまたはガラス基板上で、構造体１１３０に示したパターンは、インプリントリソグラフィー用、またはグラビア印刷のような一般化された印刷処理用のマスタープレートであると考えることができる。このようにしてＨａｆＳＯｘの硬化パターン化材料

を形成すると、流体制御および送達用装置の製造におけるマイクロおよびナノチャネルアレイを開発する手段を提供する。かかる装置は、医療診断、インク送達および化学合成に適用することができる。

【００７１】

二重層方法の他の実施形態を図１２に示す。この方法は、所定の基板１２１０上にパターン化酸化物を生成する。例えば、基板はガラス、半導体ウエハ、金属、金属合金、プラスチックまたはその組み合わせとすることができる。この方法の第一の工程は、固体の酸または塩基、例えば１個もしくはそれ以上の金属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またはＬｕ含有する水和した硫酸塩、リン酸塩、硝酸塩、ケイ酸塩、アルミン酸塩、ホウ酸塩もしくはその混合物の薄膜１２１２（約１ｎｍ～約１００ｎｍ）を堆積することを含む。加えて、固体の酸／塩基は、１個またはそれ以上のNH_3，ＯＨ，Ｆ，Ｃｌ、Ｂｒ，Ｉを含有することができる。固体の酸／塩基をスピンコーティングまたは印刷により堆積するのが好ましく、物理的堆積及び気相堆積が付加的な選択である。一例として、固体の酸をスピンコーティングにより$HfOCl_2$およびH_2SO_4（ａｑ）の水溶液から堆積することができる。固体の酸を約５０℃で約２分間加熱することにより十分に加熱して構造的に強固な膜１２１２を生成する。印刷操作モードにおいては、基板１２１０を加熱したプラテン（約２５～３００℃）上に置き、酸化物前駆体、例えばギ酸銅を含有するインク１２１４をインクジェットヘッドを介した送達によって、または基板１２１０を前駆体１２１４を含有するテンプレートと接触させることによって所望のパターンで塗布することができる。テンプレートは、ミクロ接触、活版またはグラビア印刷機の一部からなる。加熱条件（約２５０℃以上）下で、前駆体１２１４は酸化物に分解し、続いて固体の酸と反応および相互拡散して生成物１２１６を形成し、これを容易に洗浄又はエッチングしてパターン１２１８を示すことができる。酸化物前駆体は、微細な酸化物のマイクロもしくはナノ粒子を含有するインク懸濁液またはペーストによって交換することができる。微粒子を加熱または加熱することなく適用すると、パターンを示すようにエッチングし得る製品を形成する直接反応をもたらす。

【００７２】

パターン化酸化物を所定の基板１３１０上に生成するための他の実施形態を図１３に示す。最初の工程は、基板上に固体の酸１３１２または塩基を堆積することを含む。次いで、酸化物前駆体１３１４をスピンコーティング、印刷、化学気相または物理気相堆積によりブランケットコートとして塗布する。その後、活性化した前駆体１３１６のパターンを、フォトマスクを介して光のようなエネルギー源に露出することによって形成する。適切な光源としては、特にフィルターなしの重水素放電管または１９３ｎｍで光を放出する光源がある。或いはまた、活性化前駆体１３１６のパターンを、収束したレーザ又は電子ビームで直接書き込むことにより形成する。所要に応じて、活性化しパターン化した構造体１３１６を約１２５℃～約３５０℃の温度に加熱して２層の相互拡散を促進させることができる。次いで、露出領域をエッチングして所望のパターン１３１８を形成することができる。露出感度を改善する手法は、固体酸上に酸化物前駆体の極めて薄い層（約２ｎｍ）を用いることを含む。次いで、前駆体層を化学又は物理的気相堆積のような任意適当な技術によるか、または酸化物ナノ粒子の溶液注型によって堆積する酸化物の層で覆う。この層が相互拡散し、続いて前駆体の薄層を露出する。

【００７３】

上述した方法は、ポジ型レジスト技術と関連する。また、不溶性生成物をもたらす固体の酸／塩基および前駆体を選択することができる。かかる生成物を用いて、少なくとも２つの方法でポジティブ画像を生成することができる。一実施形態においては、２つの層が完全に相互拡散して単一の不溶性層を形成する。印刷または露光および現像に続いて、膜の可溶性部分をその後洗浄又はエッチングしてポジティブパターンを示す。代案の手法においては、相互拡散が前駆体と固体酸／塩基の間の界面でのみ生起して、薄く不溶性の境

界層を形成する。次いで、この境界層を用いて膜スタックのエッチングを制御し、ポジティブ画像を形成する。境界層は感光性である。これは、露光前に前駆体と固体酸／塩基間の反応を防止し、さもなければ容易に接触して相互拡散する。境界層が感光化されたら、反応性の酸化物となる。境界層が「破壊」され、上部層が下部層と相互拡散することができる。

【００７４】

次世代のパターン化は、写真又はインプリントに基づいていようと、通常電子ビームリソグラフィで製造されたマスクまたはテンプレートを用いる。かかるテンプレートまたはマスクの多くは、ハードマスクＨＳＱ（水素シルセスキオキサン）を用いて製造される。ＨＳＱマスクは、様々な電子部品、データ保管およびミクロ電子工学装置を製造するのに広く用いられる。ＨＳＱはまたインプリントリソグラフィー用の硬いマスター／テンプレートとして開発中である。

【００７５】

マスクまたはテンプレートは、ここに開示した膜を図１４に示すような単一層処理に用いて製造することができる。かかる処理の第一の工程は、無機前駆体１４１０の薄膜（約１ｎｍ～約１００ｎｍ）を基板１４１２上に堆積することを含む。無機前駆体１４１０は固体酸または塩基、例えば一個以上の金属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，またはＬｕを含有し、ペルオキシドもしくは類似の配位アニオンと組み合わせた水和硫酸塩、リン酸塩、硝酸塩、ケイ酸塩、アルミン酸塩、ホウ酸塩もしくはその混合物とすることができる。加えて、固体酸／塩基およびペルオキシド混合物は、１個以上のNH_3，ＯＨ，Ｆ，Ｃｌ、Ｂｒ，Ｉを含有することができる。固体酸／塩基をスピンコーティング、液体ミストまたは印刷により堆積するのが好ましく、物理的堆積および気相堆積が付加的な選択である。一例として、固体酸をスピンコーティングにより$HfOCl_2$，H_2SO_4（ａｑ）およびH_2O_2（ａｑ）の水溶液から堆積することができる。固体酸を、たとえば約５０℃～約１２５℃の温度に約１０秒～約１０分間十分に加熱して、構造的に強固な膜を生成する。次いで、かかる膜をフォトマスクを介して露光するか、または画定したレーザーもしくは電子ビームを介して露出し、露出領域に凝縮を誘起する。露出領域１４１４の溶解度は、未露出領域と比較して減少するため、未露出領域を酸または塩基で選択的にエッチングすることができる。使用し得る酸または塩基を例示すると、特に塩酸、硫酸、過酸化水素、水酸化ナトリウムおよびテトラメチル水酸化アンモニウムがある。一般に、用いる酸および塩基の濃度は約０．１Ｍ～約１Ｍの範囲内である。次いで、膜を酸または塩基で現像して未露出領域をエッチングし、続いて、随意的に約１００℃を超える温度で熱硬化する。この方法は、膜にネガティブな画像を作成する。塗布膜を野外露出前に高温に予熱することによって、エッチング差速を誘起してポジティブな画像を実現することができる。図１５は、熱的に予熱した単一層膜に対するエッチング差速を明示する。このグラフは、露出領域が開始時間にしたがって未露出領域より速くエッチングされるように熱処理がエッチング速度に影響することを立証する。

【００７６】

他の実施形態においては、ＨａｆＳＯｘ膜を水酸化ナトリウムおよび過酸化水素の混合物で処理して、アニオン交換および$M(OH)_x/H_2O_2$膜の形成をもたらす。或いはまた、予め調製した$M(OH)_x$膜を過酸化水素水に浸して$M(OH)_x/H_2O_2$膜を形成することができる。次いで、生成した$M(OH)_x/H_2O_2$膜を光または電子ビームへの露出によってパターン化する。これらの技術は、ポリマーレジストなしで複雑なMO_x膜を直接パターン化するための手段を提供する。例えば、HfO_2膜を高ｋの誘電体としてＳｉ　ＣＭＯＳ回路および印刷電子機器用途に用いるために直接パターン化することができる。他の例では、パターン化TiO_2膜を$Ti(OH)_4$のH_2O_2溶液堆積によって形成した$Ti(OH)_x/H_2O_2$膜から生成することができる。

【００７７】

これらの方法は、２層実施形態に用いた拡散を排除し、露光投与量を低くし、またライン－エッジ粗さと限界寸法とを改善する。図１６は、０μｃ／ｃｍ^{2}より大きく少なくとも４００μｃ／ｃｍ^{2}の範囲の投与量レベルで電子ビームを用いる単一層のネガティブトーン処理によりパターン化したＨａｆＳＯｘ膜のＡＦＭ（原子間力顕微鏡）画像である。該画像の右側のナノメートル目盛りは、膜内へエッチングされた容貌の高さを示す。図１６に示すように、かかる容貌が２μＣ／ｃｍ^{2}でのような低い投与量レベルでの電子ビーム露出により書刻された。この投与量レベルは、最も既知の化学的に増幅した高分子レジストに匹敵するもので、無機レジストに対し以前検証されたものより１０００倍低い。容貌は、約２０ｎｍ未満の解像力で作成することができる。加えて、膜は、ＨＳＱに対して検証されたものよりほぼ一桁小さい３ｎｍ未満の構造的完全性（例えば、滑らかで、高密度、ピンホールがない）を明示する。

【００７８】

ポリマーレジストに付随した膜塗布、加熱およびエッチング工程並びに無機材料の真空高温処理工程は、パターン化方法において排除されている。生成したパターン化膜は、電子装置の機能的構成材、下側基板のその後のパターン化用のハードマスク、またはインプリント用テンプレートとすることができる。電子ビーム露出を除いて、すべての処理を大気中の標準環境で行う。いくつかの処理工程の排除を考慮すると、ここに開示した技術は、装置生産歩留まりを改善し、製造コストを下げる新しい方法を提供する。専用の水溶性薬品に頼ると、前記処理も環境に優しく、また洗浄した製品を完全に回収し、リサイクルすることができる。この技術は、多くの発展した技術への用途を有する。その使用は、本明細書に記述したシステムのみに限定されない。

【００７９】

Ｂ．熱エンボス加工リソグラフィー

熱エンボス加工リソグラフィーは、ＨａｆＳＯｘ，ＺｉｒｃＳＯｘおよび関連する材料におけるパターンを形成する他の方法である。この方法は、図１７に概略的に示し、有機高分子でパターンを形成するのに最も一般的に適用されている。ＨａｆＳＯｘおよび関連する組成の半固体形態は、有機高分子と比較してずっと高い機械強度と、化学的安定性と、独特の電気的および光学的特性を有する無機材料をパターン化する機会を提供する。

【００８０】

図１７を参照するに、有機高分子の代わりに、ＨａｆＳＯｘまたは関連する無機材料をスピンコーティングまたはインクジェット印刷により適切な基板１７１２上に溶液堆積して、ＨａｆＳＯｘ層１７１４を形成する。基板１７１２およびＨａｆＳＯｘ層１７１４は、積層構造体１７１０を画成する。ナノメートル、マイクロメートルまたはミリメートルのような所望のサイズスケールの単位容貌を有するスタンプ１７１６を半固体のＨａｆＳＯｘまたは関連する膜層１７１４にプレスして、スタンプ層１７１８を形成する。次いで、スタンプ層１７１８および基板１７１２を加熱してＨａｆＳＯｘを硬化する。その後、スタンプを除去して、パターン化積層構造体１７２０にパターン化ＨａｆＳＯｘ材料を画成する。

【００８１】

Ｃ．測定装置

上述した二重層ポジ型レジスト技術用に開発した薬品を用いて、電子顕微鏡検査のような適当な分野で測定を規格化するのに用いる図１８に示すような物理的ルーラーを製造することができる。この用途においては、酸可溶層１８１２と、酸不溶層１８１４とを交互に配したナノ積層体１８１０を堆積する。酸可溶層は、ハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物、および／またはハフニウムおよび／またはジルコ

ニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物で、Mがハフニウムまたはジルコニウム、xおよびzが固定もしくは可変であり、xが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、zが０．０～３．８の範囲のいずれかの値を取るものの溶液堆積によって形成される。通常、該層に銅をドープする。酸不溶層は、ハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物、および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物で、Mがハフニウムまたはジルコニウム、xおよびzが固定もしくは可変であり、xが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、zが０．０～３．８の範囲のいずれかの値を取るものの溶液堆積によって形成される。

【００８２】

層１８１２および１８１４の幅は、Ｘ線反射性を用いるなどして正確に画定される。次いで、酸可溶層１８１２をエッチングして、電子顕微鏡で物体を正確に測定する際の二次基準として用いることができる指型のパターン１８２０を呈示する。

【００８３】

Ｄ．腐食バリア

前駆体液を金属、合金またはセラミックのような適当な基板上に塗布して腐食バリアを形成することができる。加えて、かかる液を繊維にするか、若しくは鋳型内に置くか、または単独で用いることができる。前記液を、加水分解、アニーリングまたは大気中の熱分解を含む任意適当な処理によって固体で、安定な形態に転換することができる。通常、これは所望の結果を達成するに有効な温度まである時間加熱することを必要とし、例えば通常１００℃以上の温度で少なくとも数秒間、より一般的には少なくとも数分間加熱することが必要である。

【００８４】

膜の原子的に高密度のために、潜在的用途には、限定することはないが、金属および金属／セラミック系熱保護システム用の熱、腐食および酸化保護、有機ベースのディスプレイおよび電子部品、太陽電池、高放射率コーティング、酸化物系セラミックマトリックスシステム用の界面コーティング、りん光体上の保護コーティング、金属およびセラミック系システム用の環境障壁コーティング、複合体およびファイバーレーザー用の繊維、融解金属処理における腐食防止、熱絶縁用モノリシック材料、触媒担体、並びに他の多くのものがある。膜を積層する能力は、一層における欠陥の位置を他の層に対しランダム化して増強した腐食保護を付与する機会を提供する。

【００８５】

Ｅ．光学的コーティング

前駆体液を、個々の層として、また多重層の型で適当な光学的基板上に塗布して、反射防止コーティング、誘電体ミラー、Ｘ線ミラー、干渉フィルター、導波管、平面コーティングおよび傷のつきにくい表面を生成することができる。多重層の周期性は、少なくとも２個の材料組成を交互に堆積することによって達成される。単一層の周期性は、フォトリソグラフィー処理に関して記述したようにエッチングによって達成することができる。アモルファス性質、層間の鋭い界面および誘電定数を制御する能力は、理論的限界近くで性能を実現するための処理を提供する。

【００８６】

選択的に堆積もしくはエッチングした多重層または単一層形態において、周期的な構造体は、回折用途に適切である。単一もしくは多重材料および／または空隙の組合せは、構造体を画成することができる。空隙スペースを使用することによって、所定の構造体内の

物理特性に大きな対比をもたらすことができる。機能特性は、空隙スペースの使用によって強化または実現することができる。同様に、光学的格子を画成することができる。

【００８７】

実質的に滑らかな表面膜をここに開示した方法の実施形態にしたがって堆積することができるため、膜を用いて、大きな粗度を示す金属、セラミックおよびプラスチックのような基板層を平坦化することができる。

【００８８】

Ｆ．発光膜

材料は、多くの発光処理においてエネルギーを吸収し、光子を放出することができる。かかる発光事象は、主要相（またはホスト）のみを含むか、または付加的な要素も含むことができる。単一材料は、多くの発光添加剤用のホストとして機能することができる。開示した膜組成の多くは、スペクトルの紫外部に潜在的に延在する透明度で可視的に透明である。かかる材料は、発光ホスト材料として潜在的によく機能する。該材料に、一例として、限定することなく、Mn^{2+}，Sb^{3+}，Sn^{2+}，Bi^{3+}，Eu^{3+}，Tb^{3+}，Eu^{2+}，Gd^{3+}，Tm^{3+}，およびそれらの組合せを含む一般的な発光イオンを選択的にドーピングして、照明およびディスプレイ用途に有益な発光膜を生成することができる。

【００８９】

Ｇ．プリント電子機器

製造業者は、従来の蒸着およびリソグラフィー処理の制限を排除する新しく、効率的な製造方法を探究している。印刷および関連するマスクのない技術が、裏面電子機器の製造効率における進歩を実現するための経路として広く認められている。

【００９０】

ここに開示した溶液処理した薄膜は、最も進歩した気相処理方法によって達成したものと類似した形態的で装置機能的特性を示す。ここに開示した組成の溶液を、例えばミクロ接触、グラビア印刷、インクジェットプリンタまたは他の適切な手段でインプリントすることができる。生成したインプリント溶液を用いて、約２０ｎＡ／ｃｍ^{2}未満の誘電体漏洩電流密度で約１０ｃｍ^2／Ｖｓの装置移動度を示す安定な無機トランジスタアレイを製造することができる。また、誘電体および半導体インクをガラス基板上に印刷して、約１ｃｍ^2／Ｖｓの移動度と、約１００ｎＡ／ｃｍ^{2}未満の誘電体漏洩電流とを有するトランジスタアレイを製造することができる。ＭＩＭコンデンサアレイは、約５を越える相対誘電定数および約５０ｎＡ／ｃｍ^{2}未満の漏洩電流密度で製造することができる。

【００９１】

ＩＶ.実施例

以下の実施例は、本発明の実用的および／または仮説の実施形態の特定の特徴を例示するために提供する。当業者は、本発明の範囲がこの実施例に述べた特定の特徴に限定されないことを理解することができる。

【００９２】

実施例１

この実施例は、大量の沈殿物用の給源として、または薄膜前駆体として使用するための溶液を調製するのに用いる一般的な方法を開示する。以下の試薬$HfOCl_2 \cdot 8H_2O$（Ａｌｆａ Ａｅｓａｒ，１．５％Ｚｒを除いて９９＋％）；$ZrOCl_2 \cdot 8H_2O$（Ｗａｓｈ Ｃｈａｎｇ 分光写真分析グレード）；$La_2(SO_4)_3$（Ａｌｆａ Ａｅｓａｒ，９９．９％）；$La(NO_3)_3 \cdot 6H_2O$（Ｊｏｈｕｎｓｏｎ 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％）；NH_3（ａｑ）（ＥＭ Ｓｃｉｅｎｃｅ,ＧＲ ＡＣＳ，２８－３０％）を用いた。$HfOCl_2$または$ZrOCl_2$を$La_2(SO_4)_3$，$Ce_2(SO_4)_3$またはＣａＯと一緒にして約０．８Ｍの全金属濃度にし、続いて硫酸塩溶液を加えて約０．５Ｍの全金属

濃度とすることにより、全ての溶液を調製した。これら溶液を、熱誘導沈殿およびスピンコーティング誘電体膜用に直接用いた。所用に応じて、追加の修正を行って、水酸化物沈殿反応またはナノ積層堆積用の前駆体として機能させた。

【００９３】

実施例２

この実施例は、実施例１に従って作成した溶液からの多量な沈殿のために用いた一般的な方法を開示する。溶液のチューブを沸騰水浴に４０分間浸漬することによって沈殿を誘起した。水酸化物誘起沈殿関しては、$HfOCl_2$および$La_2(SO_4)_3$を２３％Ｌａ（金属パーセント）として混合し、続いて$La(NO_3)_3$および$(NH_4)_2SO_4$の溶液を添加して、約０．３９Ｍのハフニウム濃度（［Ｈｆ］）と、約０．１８Ｍのランタン濃度（［Ｌａ］）と、約０．４２Ｍの硫酸塩濃度（$[SO_4]$）とを付与した。次いで、１．９モル当量（全金属に対し）の飽和NH_3（ａｑ）をすばやく添加し、生成した混合物を１分間撹拌する。全沈殿物を上澄み液から、脱イオン水での数回の洗浄を含む吸引濾過によって分離した。濾液を室温で１日乾燥させた。続いて、サンプルを大気中のアルミナるつぼ内で約１００℃～約１５０℃の温度で約１～４時間加熱した。ＸＲＤデータは、Ｃｕ　Ｋα放射線を用いるＳｉｅｍｅｎｓ　Ｄ５０００回折計器で収集した。熱重量データは、サンプル（１０～２０ｍｇ）をＰｔるつぼ内でN_2（ｇ）の流動下通常１０℃／分の速度で加熱し、より高温度で１５分間保持した後ＳｈｉｍａｄｚｕのＴＧＡ－５０で収集した。誘導結合プラズマ原子発光分析（ＩＣＰＡＥＳ）をＪｏｂｉｎ　Ｙｖｏｎ　ＪＹ２０００分析装置を用いて行った。サンプルを２００℃の消化ボンベ内で数時間溶解し、測定可能なレベルまで希釈した。

【００９４】

実施例３

この実施例は、実施例１に従って作成した溶液を用いる薄膜の堆積に用いる一般的な方法を開示する。ＨａｆＳＯｘ，ＺｉｒｃＳＯｘおよびそのＬａ，Ｃｅ，またはＣａを加えた誘導体の薄膜を、３０００ｒｐｍで３０秒間のスピンコーティングによってＳｉ基板上に堆積し、その後すぐに１３５℃で１．５～２分間ホットプレート重合させた（ある誘導体に対しては、３２５℃オーブンで１５秒～２分間のさらなる加熱が必要である）。所定の堆積膜厚さが得られるまでこの処理を繰り返した。３２５℃で５～１０分間の最終オーブンアニーリングを用いた。

【００９５】

ナノ積層体膜用の前駆体は、H_2SO_4を$HfOCl_2$または$ZrOCl_2$に金属に対し４６％の硫酸塩として加えることによって調製された。溶液を０．０３～０．１３Ｍの金属濃度まで希釈した。ＨａｆＳＯｘおよびＺｉｒｃＳＯｘの交互層を、誘電体膜に関して説明したのと同じようにして堆積した。

【００９６】

シリコン基板は、SiO_2またはＴａ金属の表面を有する。５００ナノメートルＴａ表面を誘電体試験に用いた。２００ナノメートルSiO_2表面を他の全ての目的のために用いた。かかる堆積用の表面は、４５℃の溶液（Ｄｅｃｏｎ　Ｌａｂｓ，Ｃｏｎｔｒａｄ　７０）中で４５分間超音波洗浄し、次いで堆積前にミリポア水で表面を十分にすすぐことにより調製した。

【００９７】

ＸＲＤデータは、５０ｋＶおよび２７０ｍＡで回転陽極から発生したＣｕ　Ｋα放射線を用いてＲｉｇａｋｕのＲＡＰＩＤ回折計器で収集された。入射ビーム角度は７．６°であり、回折ビームを画像プレートで収集した。ＸＲＲデータは、Ｃｕ　Ｋα放射線で収集された。１０°（２θ）までの低角度反射は、０．００５°ステップで収集された。透過ＦＴＩＲデータは、未被覆基板を参照として用いるＮｉｃｏｌｅｔ　５ＰＣ分光計で収集された。

【００９８】

ＭＩＭコンデンサ構造体は、堆積した誘電体上にＡｌの円形接点（直径１．２ｍｍ）を

熱的に蒸着することによって完成させた。誘電定数および損失正接のパラメータが得られた。また、底部ゲートトランジスタ構造体を、活性的に加熱することなく無機チャネル材料をスパッタすることによって製造した。その後、ＺＴＯチャネル装置を３２５℃まで１時間加熱した。アルミニウムソースおよびドレイン接点を熱的に蒸着させた。トランジスタの特性解析を行った。

【００９９】

実施例４

この実施例は、約２ｎｍ程の厚さの滑らかで、高密度のピンホールがない超薄ナノ積層体膜を製造するための一般的な方法を開示する。$HfOCl_2 \cdot 8H_2O$または$ZrOCl_2 \cdot 8H_2O$と，H_2O_2（３０％）と、H_2SO_4（ａｑ）とを含有する前駆体溶液を特許文献３に記述されたように調製した。該前駆体溶液は、金属に対して７０％H_2O_2および５０％硫酸塩で約０．０５Ｍ～０．４Ｍの金属イオン濃度を有した。金属イオン濃度における違いは、３ｎｍ～２５ｎｍのコーティング変化ごとの厚さを可能にした。薄膜を、熱成長したSiO_2を有するシリカ基板上に堆積した。基板は、Ｃｏｎｔｒａｄ７０溶液を有する超音波浴を４５℃で６０分間用い、続いて脱イオン水ですすぐことにより清澄にした。膜は、３０００ｒｐｍの回転速度を有するスピンコーターを３０秒間用い、その後１２５℃で１～２分間ホットプレート重合することにより堆積させた。スピンコーティングおよび重合工程は、所定の厚さに達するまで繰り返した。所定の厚さに達した後は、いくつかの膜を結晶化温度まで加熱した。他の膜は、まず０．１Ｍ～０．５ＭＮａＯＨ浴中で１～２分間処理し、その後熱処理の前に脱イオン水浴で１～２分間すすいだ。

【０１００】

Ｘ線回折（ＸＲＤ）分析を用いた薄膜の特性解析は、Ｃｕ　Ｋα放射線を用いるＲｉｇａｋｕのＲ－ａｘｉｓ　ｒａｐｉｄ上で行った。原子間力顕微鏡（ＡＦＭ）測定は、Ｖｅｅｃｏ　ＮＰ－２０　ＳｉＮプローブと接触モードでかつ１．１５Ｈｚの走査周波数で動作するＤｉｇｉｔａｌ　Ｉｎｓｔｒｕｍｅｎｔｓ　Ｎａｎｏｓｃｏｐｅ　ＩＩＩ　Ｍｕｌｔｉｍｏｄｅ　ＡＦＭを用いて行った。Ｘ線反射性（ＸＲＲ）測定は、Ｂｒｕｋｅｒ　Ｄｉｓｃｏｖｅｒ　Ｄ８を用いて行い、膜の表面および界面の粗度を画定するのに用いた。組成分析は、４個の調節可能な波長分散分光計を備えたＣａｍｅｃａ　ＳＸ－５０電子マイクロプローブ上で得た。１２，１６および２２ｋＶの加速電圧を用い、５点にわたって平均化してＯ，Ｃｌ，Ｎａ，ＳおよびＳｉ　Ｋα強度とＺｒおよびＨｆ　Ｌα強度とをモニターした。分析に用いる規格は、ＭｇＯ，Ｈｆ，Ｚｒ，FeS_2（黄鉄鉱），$Ca_5(PO_4)_3Cl$（リン灰石），Ｓｉ，およびSi_3AlNaO_8（曹長石）であった。原料強度に対する修正は、Ｗｉｎｄｏｗｓ（登録商標）自動化および分析パッケージ用のプローブを用いることによって行った。ＳｔｒａｔｅＧＥＭ組成分析ソフトウェアパッケージは、計算値と実験Ｋ比を比較することによって薄膜構造修正に用いた。

【０１０１】

アモルファスで、原子的に平坦で、高密度なピンホールのない薄膜は、堆積したままで交換した膜用のスピンコーティングにより堆積させた。図１９は、約０．１ｎｍの粗度を有する未交換のＨａｆＳＯｘ膜のＡＦＭ画像である。図２０は、ＨａｆＳＯｘのイオン交換および８５０℃での熱処理を行った後のＨａｆＳＯｘのＴＥＭ画像である。未交換膜は、Ｚｒに対しては６００℃、Ｈｆに対しては６５０℃まで滑らかでアモルファスのままであった。しかし、これら温度以上に加熱した後、膜は結晶化し、でこぼこになり表面に火山状の容貌を形成する。図２１は、シリカ上に堆積したHfO_2膜のＡＦＭ画像である。該HfO_2膜は、ＨａｆＳＯｘの熱分解によって形成された。生成した膜は、約５ｎｍの粗度を有し、火山状のピークをもたらす。これら容貌は、SO_3の損失によってほぼ起こった。これは、Ｈｆ硫酸塩粉体の熱的重量分析によって支持され、硫酸塩分解（SO_3（ｇ）→SO_2（ｇ）と１／２O_2（ｇ）が７００℃以上で起こる。

【０１０２】

火山作用を排除するため、膜を０．１～０．５ＭのＮａＯＨ（ａｑ）浴中で１～２分間処理して、加熱する前に膜からSO_4^{2-}およびCl^-アニオンを除去した。ＮａＯＨは

、ジルコニウム塩における他のアニオンに対しヒドロキシアニオンを効果的に交換することがすでに示されている。ＮａＯＨ処理は、４０～４５％の厚さ減少を生起（２～１５ｎｍの層厚を付与）するが、ジルコニアおよびハフニアに対しそれぞれ５００℃または５５０℃以下に加熱したとき、前記処理は膜の平滑さ（～１Å）またはアモルファス性にほとんど影響を与えなかった。

【０１０３】

図２２は、シリカ上に堆積し、その後０．１ＭのＮａＯＨで処理し、４５０℃まで１０分間加熱したＨａｆＳＯｘ膜のＡＦＭ画像である。生成した膜は、約０．１ｎｍの粗度を有した。これら温度以上に加熱した膜は結晶化したが、８５０℃までの温度で滑らかなままであった。

【０１０４】

図２３は、シリカ上に堆積し、その後０．１ＭのＮａＯＨで処理し、８５０℃まで１０分間加熱したHfO_2膜を示す。生成した結晶化膜は、約０．２ｎｍの粗度で滑らかさを維持した。

【０１０５】

結晶化温度降下が、Ｘ線回折プロットにおいて見られた（図２４～２７）。図２４～２７において、基板のピークをソフトウェアで除去した。*は、主要な正方晶相のピークを示す。図２４は、７００℃で正方晶相と単斜晶相との混合物として結晶化した未処理のHfO_2膜のＸＲＤプロットである。HfO_2プロットは、単斜晶相に対する参照プロットである。これに対し、図２５は、５５０℃で単斜晶相のみに結晶化した０．１ＭのＮａＯＨで処理したハフニア膜のＸＲＤプロットである。HfO_2プロットは、単斜晶相に対する参照プロットである。図２６は、６５０℃で単斜晶相および正方晶相の混合物に結晶化した未処理のジルコニウム膜のＸＲＤプロットである。ZrO_2プロットは、単斜晶相に対する参照プロットである。図２７で明らかなように、０．１３ＭのＮａＯＨで処理したジルコニア膜は、５００℃で正方晶相のみに結晶化した。さらに加熱すると、膜は正方晶相と単斜晶相との両方に発達した。HfO_2およびZrO_2の正方晶相は、前述の薄膜研究において観察されている。低い結晶化温度、結晶化および厚さの減少は、ＮａＯＨ処理が薄膜からアニオン（SO_4^{2-}またはCl^-）を除去することを示した。

【０１０６】

０．４ＭのＨｆ溶液から堆積し、３５０℃に５分間加熱した膜の電子プローブ微小部分分析（ＥＰＭＡ）は、組成$HfO_{1.32}(SO_4)_{0.61}Cl_{0.15}$の膜を与えた。膜中の塩素は、急速な熱脱水の結果としての動的トラップの成果である。ＮａＯＨ（ａｑ）浴で処理した膜は、測定可能な硫黄レベルを持たず（０．０１原子％未満）、０．３原子％未満のＣｌが観察された。これは、硫黄および塩素がＮａＯＨ（ａｑ）浴中で膜から除去されたことを裏付けた。ＥＰＭＡも、処理後の膜に残る残留硫黄が０．３原子％未満であることを実証した。

【０１０７】

実施例５

上述した手法の特定実施形態において、水和したインジウムおよびガリウム硝酸塩（$In(NO_3)_3 \cdot 0.5H_2O$および$Ga(NO_3)_3 \cdot 9.5H_2O$）をメタノール（CH_3OH）に溶解した。最終濃度は、[Ｉｎ]＝０．２８８Ｍで、[Ｇａ]＝０．１７０Ｍであった。次いで、亜鉛粉末を溶液に加え、フラスコを密封する。亜鉛の最終濃度は０．２Ｍであった。１～７日の期間にわたって反応させると、粉末が緩徐に酸化し、溶解して０．６５８Ｍの全金属イオン濃度になった。メタノール溶液を空気中にさらし、メタノールを室温で蒸発させた。次いで、溶液中に残っている固体残渣を０．３９５Ｍの全金属濃度までH_2O中に溶解した。この前駆体溶液を、導電性バック接点を有するSiO_2基板上にスピンコーティングし、４５０℃で１～４時間アニーリングした。アニーリング後、透明でアモルファスな$InGa_{0.6}Zn_{0.7}O_{3.15}$半導体膜が、図２８のＳＥＭ画像に示されるように得られた。アルミニウムソースおよびドレイン接点を、シャドーマスクを介して酸化物半導体膜上に熱蒸着させて薄膜トランジスタ（ＴＦＴ）を形成した

。かかるＴＦＴに対する電界効果移動度は、８ｃｍ^{2}Ｖ$^{-1}$ｓ$^{-1}$を超えることが示された。

【０１０８】

実施例６

この実施例は、二重層無機リソグラフィー処理の２つの一般的な方法を開示する。第一の実用的実施形態においては、約３０ｎｍ～約６０ｎｍの厚さのＨａｆＳＯｘ膜をＳｉＯ$_2$／Ｓｉ基板上に堆積した。この基板を約５０℃にセットしたホットプレート上に直接置き、加熱して膜に構造的完全性を付与した。生成した膜は酸不溶性である。次いで、基板をインクジェットプリンターの加熱したプラテン（約５０℃～約２００℃）上に置き、ここでギ酸銅のラインを熱的インクジェットヘッドを介して基板上に印刷した。ギ酸銅を分解し、加熱によりＨａｆＳＯｘ膜に拡散して膜を可溶性にする。水ですすぎ、約３００℃までさらに加熱し、希釈酸で現像すると、図２９に示すように描画ラインが明白に示された。

【０１０９】

他の実用的実施形態においてはまた、パターンをフォトリソグラフィーにより生成した。$HfO_{2-x}(SO_4)_x$二重層膜をフィルターなしの重水素ランプを用いて遠ＵＶ光に露出させて、その後の相互拡散および図３０に示すパターンの現像のためにギ酸銅分解を促進した。形態の大きさを、電子ビーム書刻で約２２ｎｍまで減じた。相互拡散処理を電子ビームエネルギーにより空間的に制御して、パターンおよび対象物をナノスケールで描画することができる。高度に解像されたパターンを、多くのポリマーレジストのものと類似した感度を示す１５０μＣ／ｃｍ^{2}近い電荷線量レベルで形成した。図３１および３２は、約２００μＣ／ｃｍ^{2}の線量レベルで電子ビーム書刻によって形成した２個のパターンである。図３１において、ライン間隔は、電子顕微鏡によって測定して５００ｎｍである。

【０１１０】

実施例７

この実施例は、単一層無機膜をパターン化する一般的な方法を開示する。過酸化物又は関連する配位種を含む単一無機膜を適切な基板上にスピンキャスト、液状ミストまたはインクジェット印刷した。この膜を１００℃未満の適度な温度で加熱して、膜に構造的完全性を付与した。次いで、この膜をフォトマスクを介して高エネルギー光、空間光変調によるマスクなしパターン、所定のレーザービーム、または電子ビームに露出して、パターンまたは他の好ましい膜形態を画成する。写真用にパターン化した膜の２つの例を図３３および３４に示す。図３３は、パターン化$ZrO_{2-x}(SO_4)_x$膜である。図３４はパターン化TiO_2膜である。このTiO_2膜は、厚さ約１５～５０ｎｍである。これは、フィルターなしの重水素ランプを用いてパターン化し、続いて０．１～０．２ＭのＨＣｌで６０秒未満エッチングした。図３５～３７は、電子ビームでパターン化した$HfO_{2-x}(SO_4)_x$膜である。かかる膜は、厚さ約３０～６０ｎｍである。これらを、電子ビームを２００μＣ／ｃｍ^{2}の線量レベルで用いてパターン化し、続いて５～１２ＭのＨＣｌで約１～４分間エッチングした。

【０１１１】

ここに開示した発明の原理を適用し得る多くの可能な実施形態を考慮すると、図示した実施形態が単に本発明の好ましい実施例であり、本発明の範囲を限定することがないと認識すべきである。それどころか、本発明の範囲は、請求項によって画成される。したがって、この範囲内からくるすべておよびこれらの請求項を、本発明として請求する。

【図１】

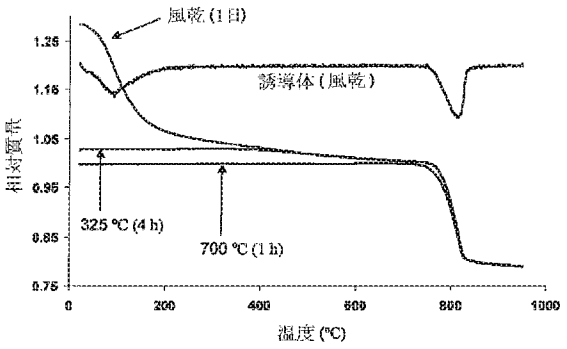


FIG. 1

【図２】

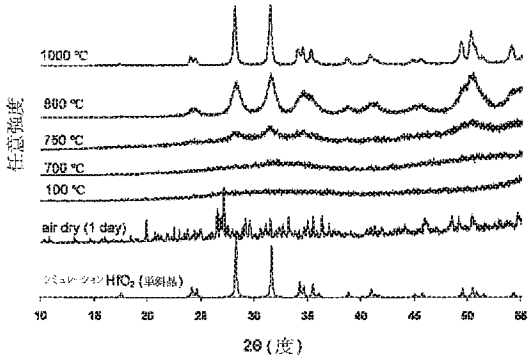


FIG. 2

【図３】

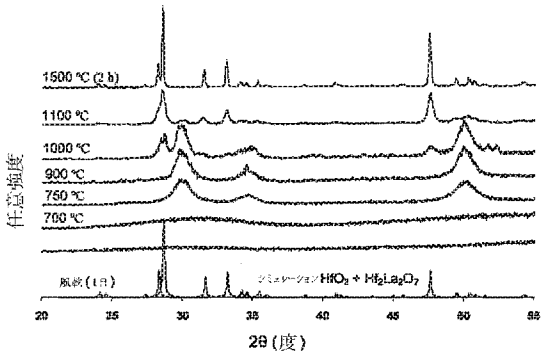


FIG. 3

【図５】

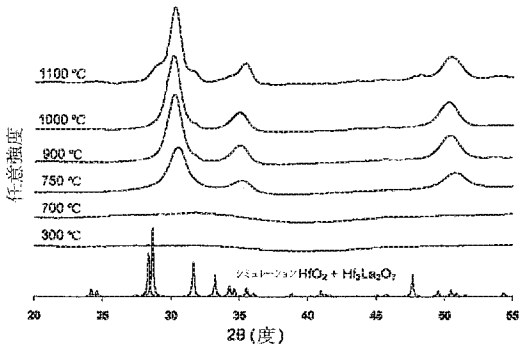


FIG. 5

【図４】

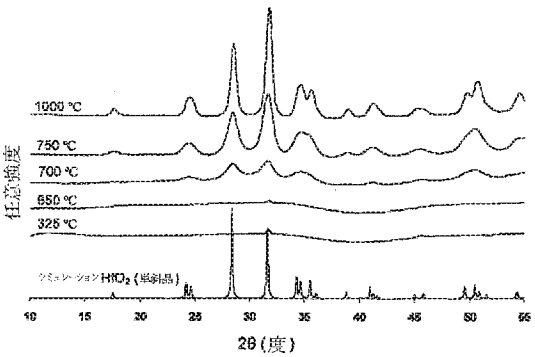


FIG. 4

【図６】

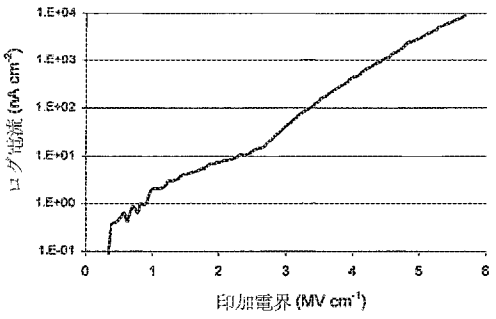


FIG. 6

【図９】

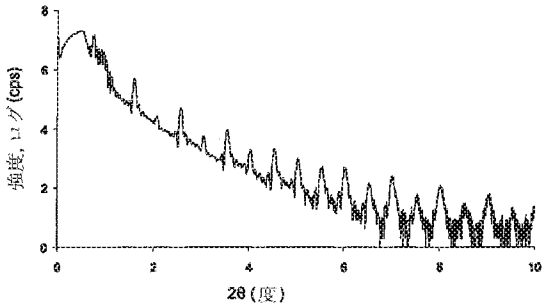


FIG. 9

【図１０】

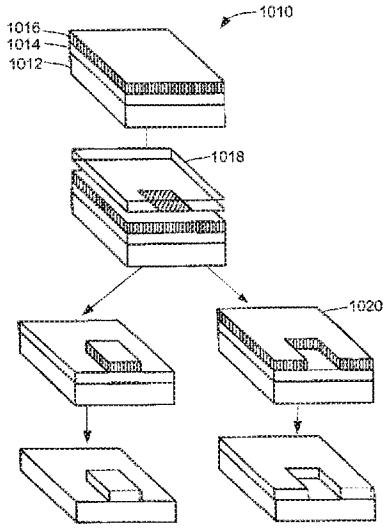


FIG. 10

【図１１】

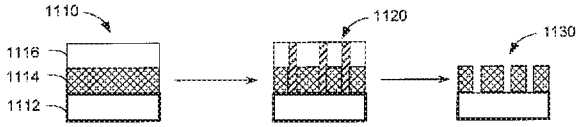


FIG. 11

【図１２】

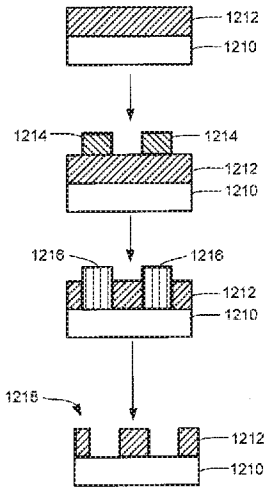


FIG. 12

【図１３】

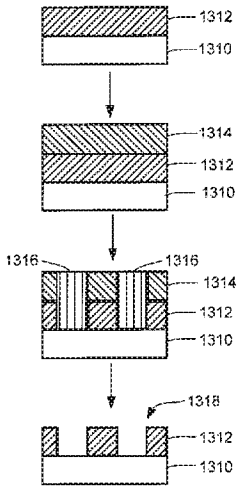


FIG. 13

【図１４】

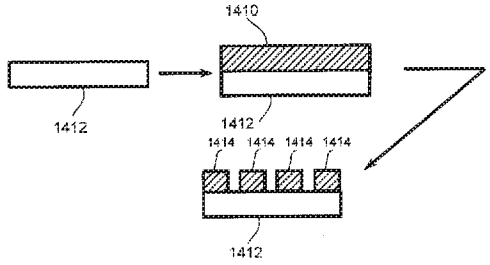


FIG. 14

【図１５】

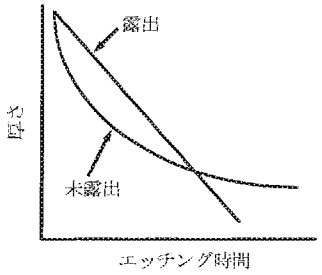


FIG. 15

【図１８】

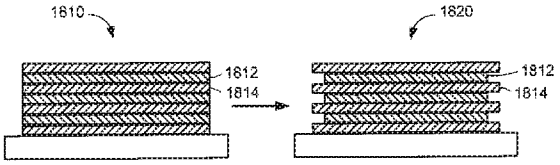


FIG. 18

【図２４】

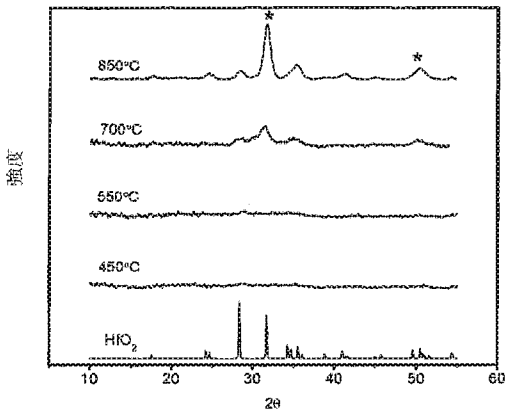


FIG. 24

【図２５】

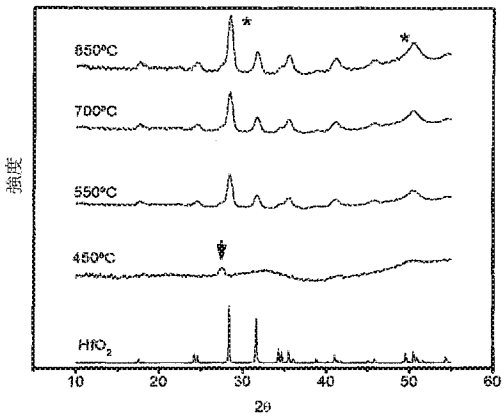


FIG. 25

【図２６】

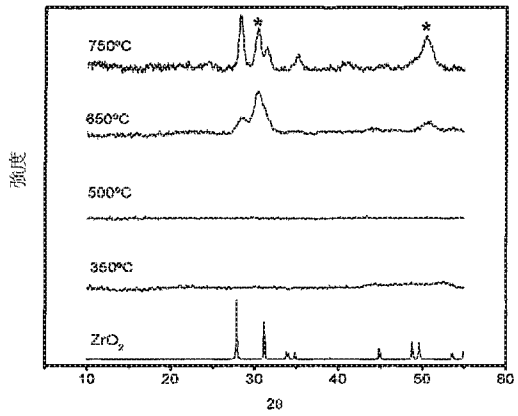


FIG. 26

【図２７】

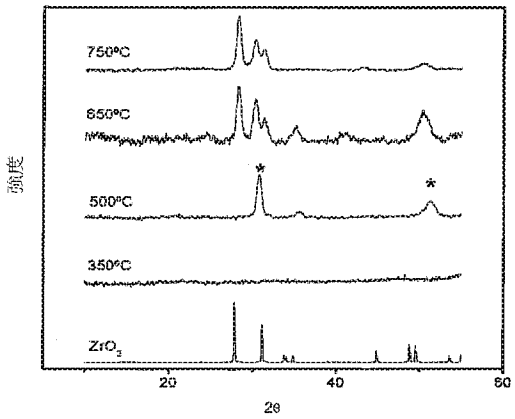


FIG. 27

【図３３】

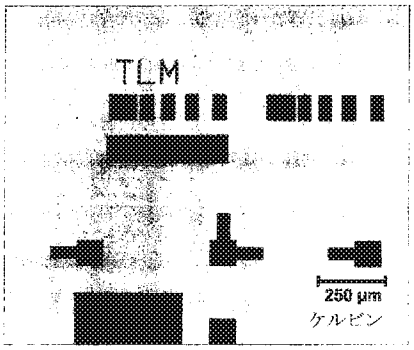


FIG. 33

【図３４】

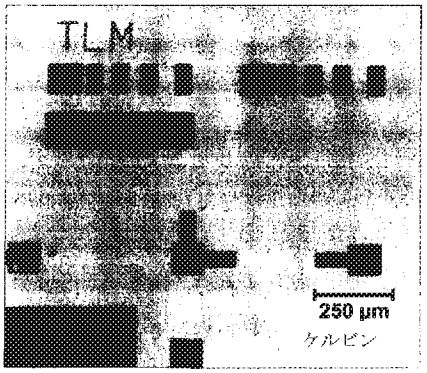


FIG. 34

【図３７】

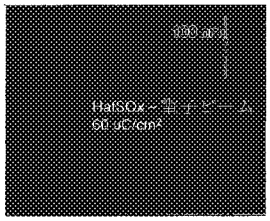


FIG. 37

【図７】

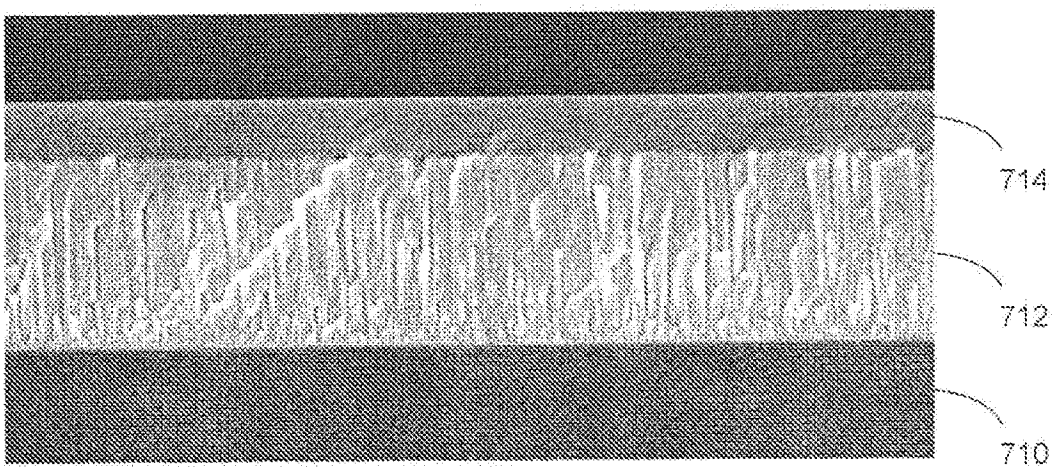


FIG. 7

【図８】

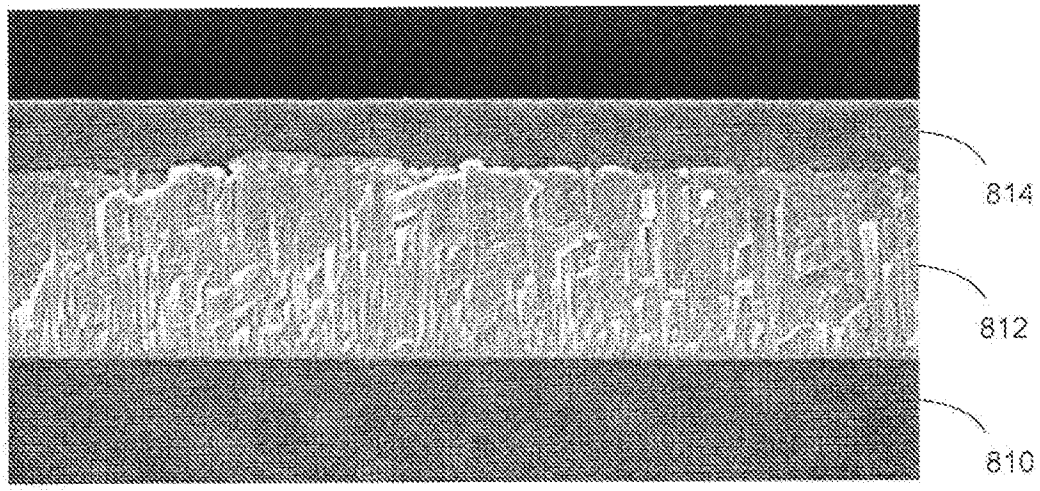


FIG. 8

【図１６】

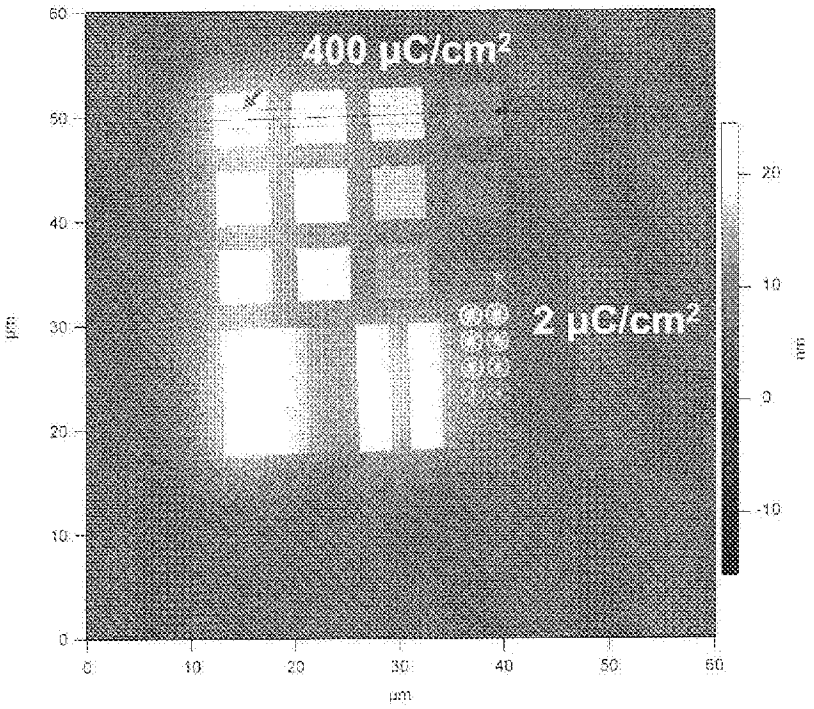


FIG. 16

【図１７】

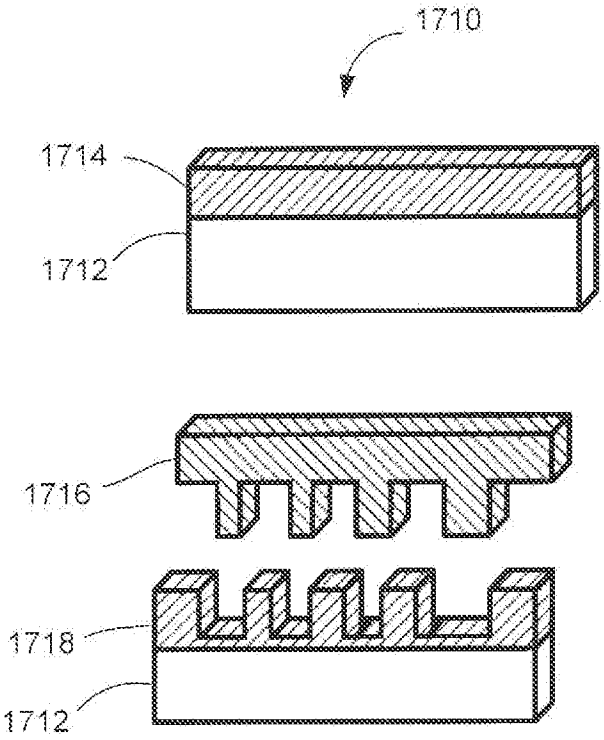


FIG. 17

【図１９】

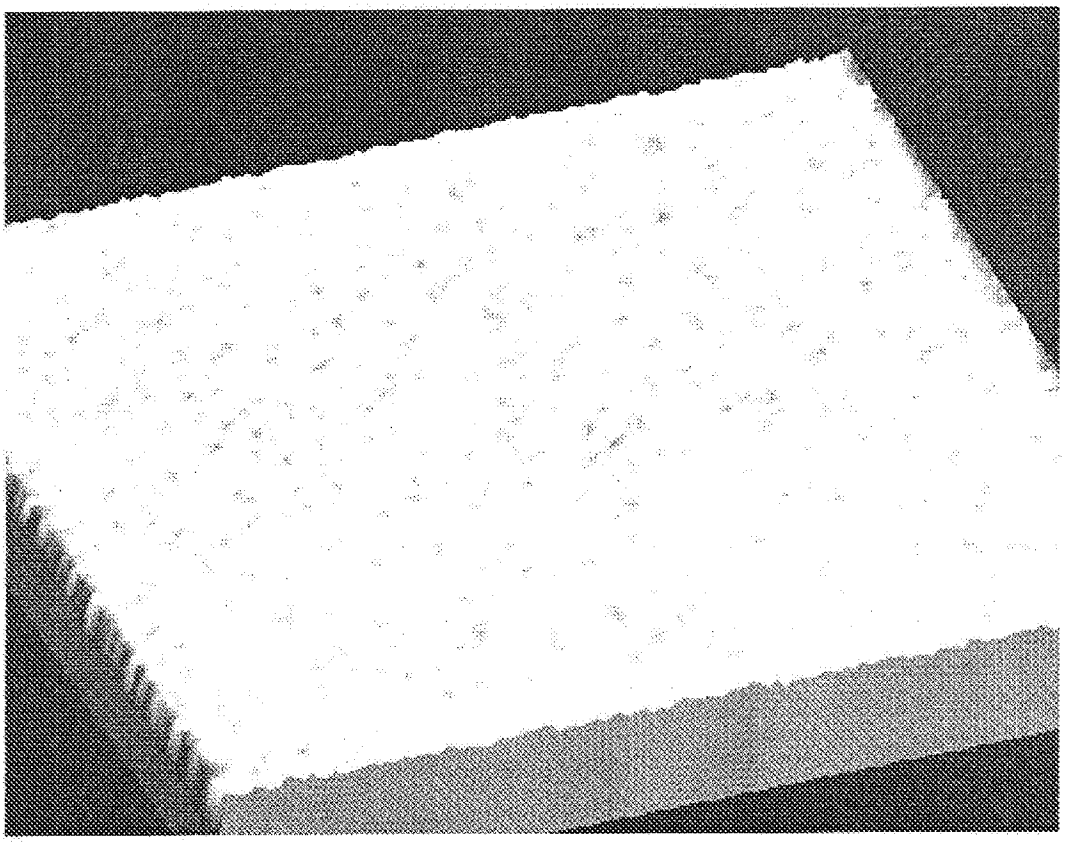


FIG. 19

【図２０】

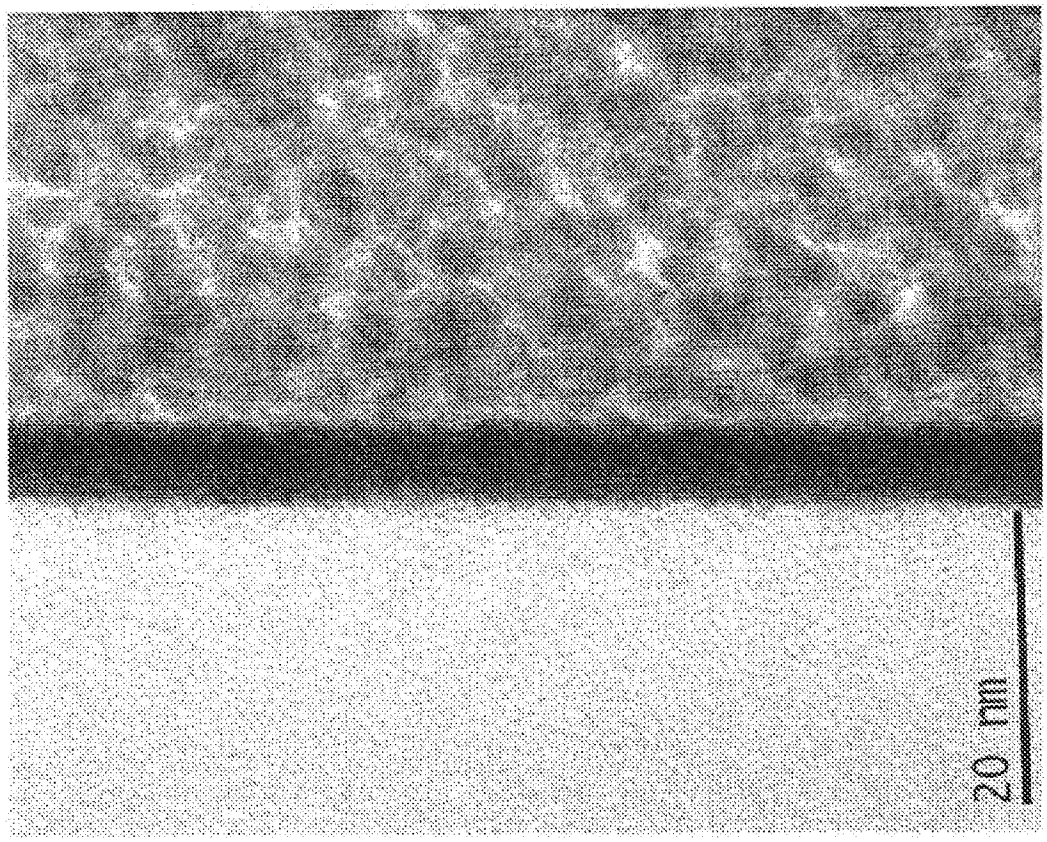


FIG. 20

【図２１】

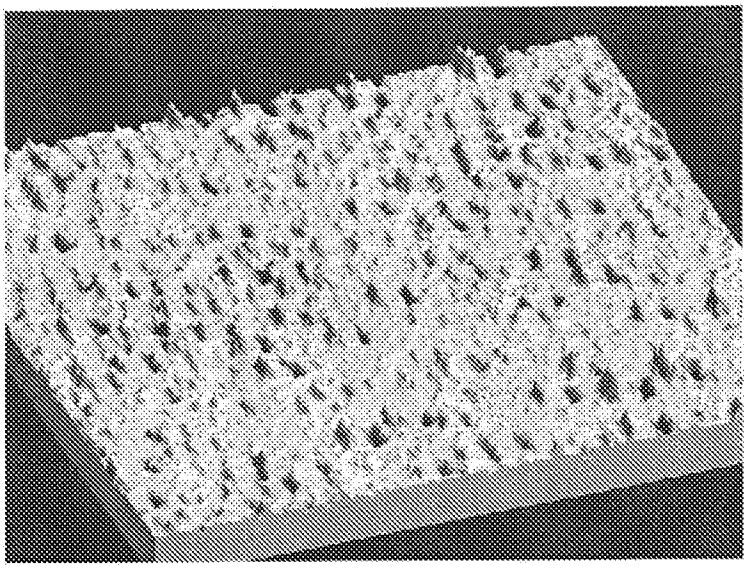


FIG. 21

【図２２】

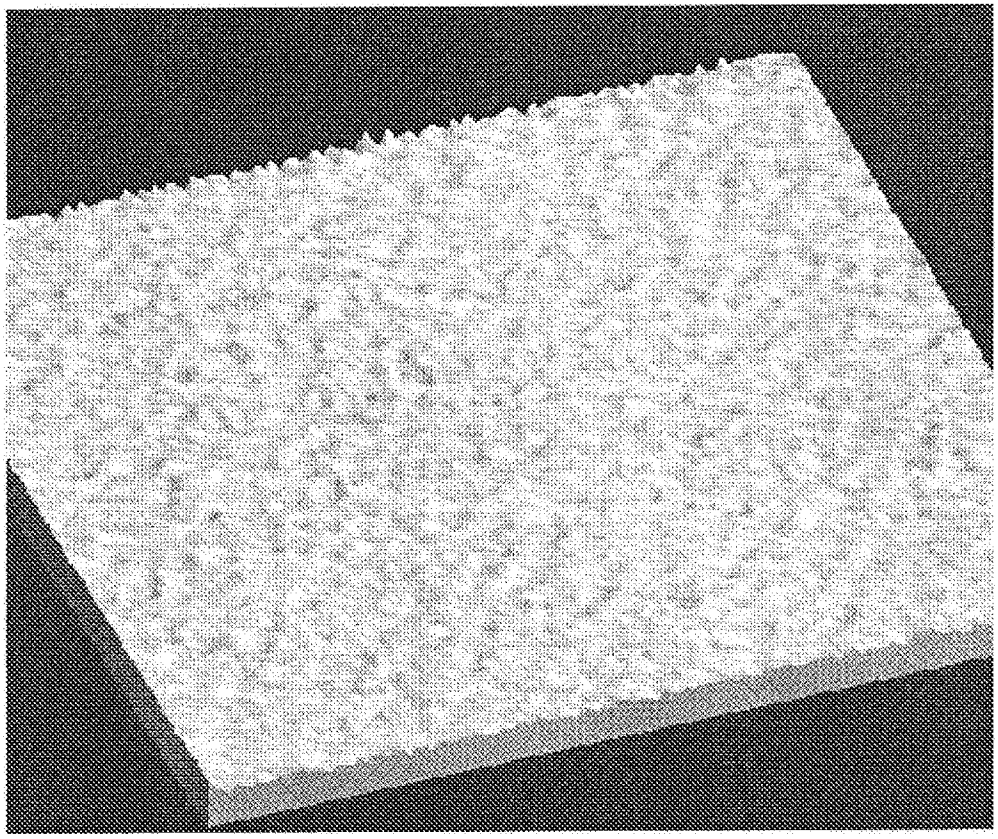


FIG. 22

【図２３】

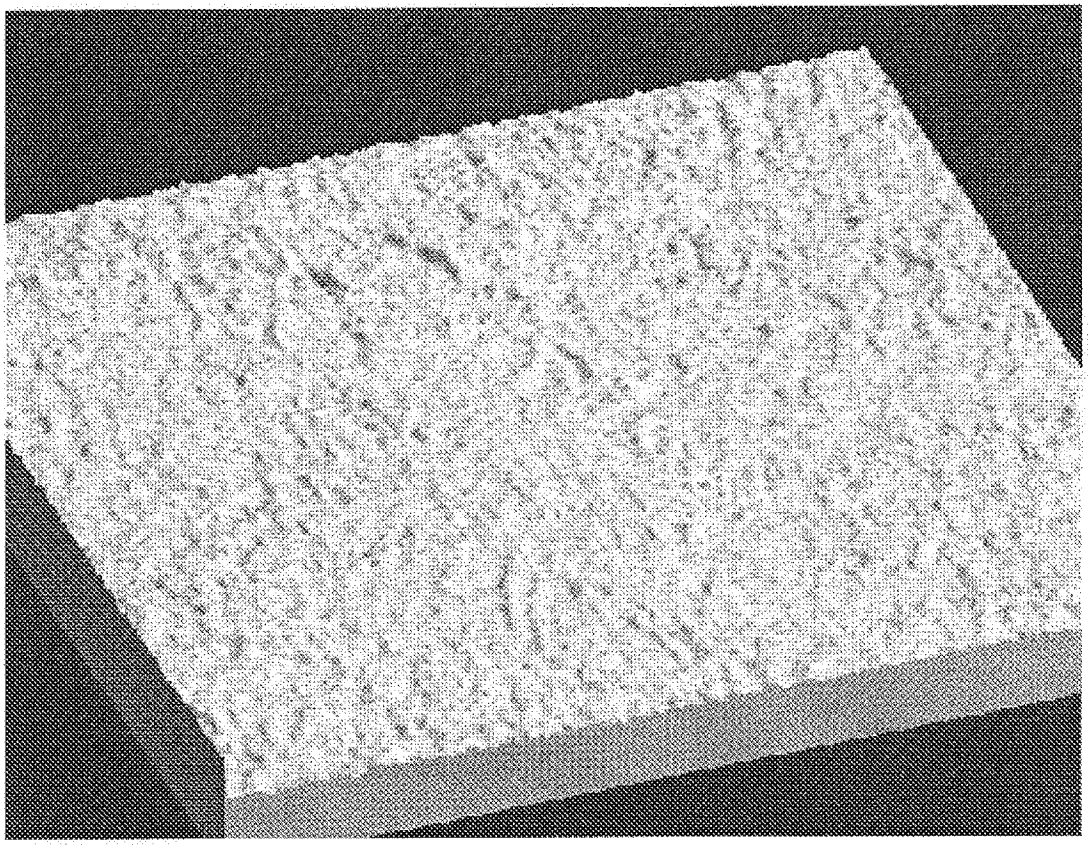


FIG. 23

【図２８】

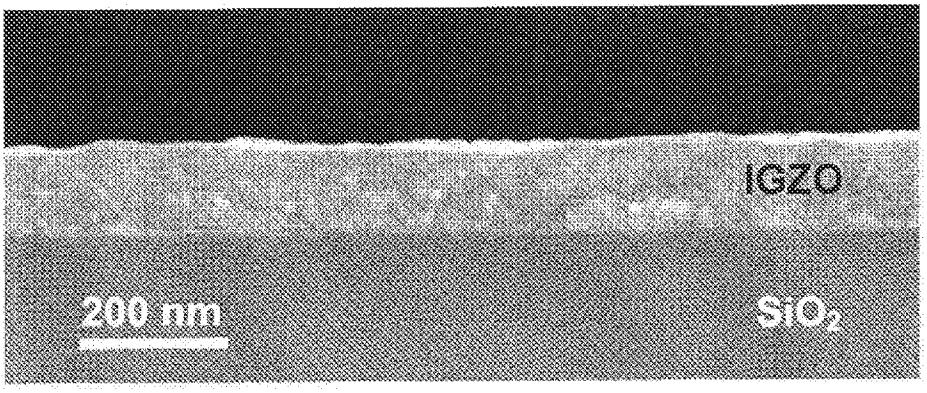


FIG. 28

【図２９】

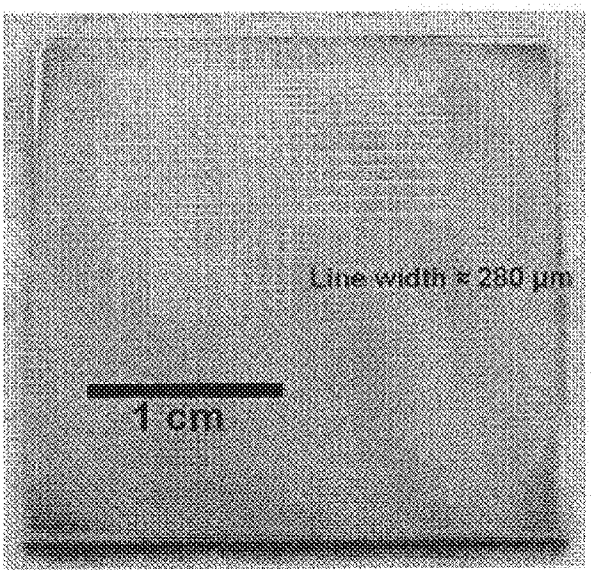


FIG. 29

【図３０】

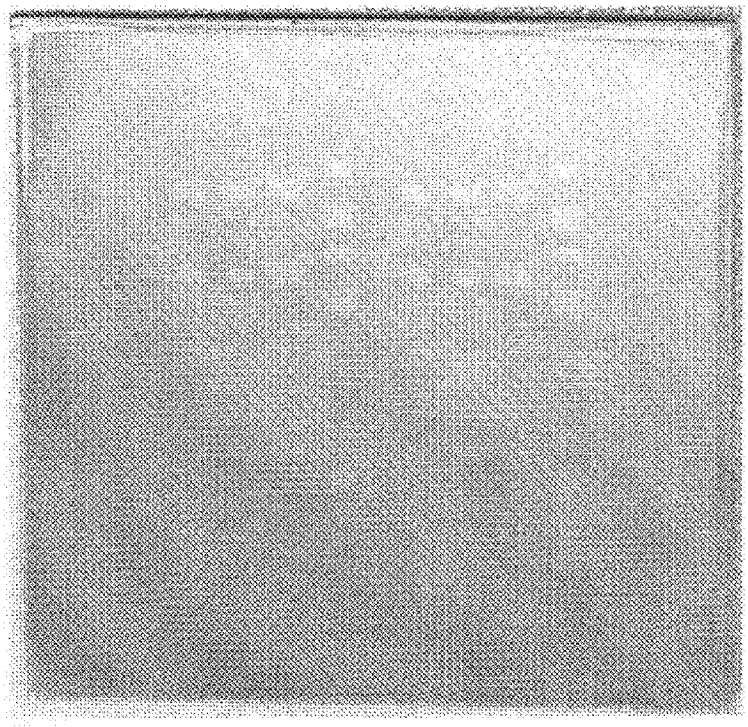


FIG. 30

【図３１】

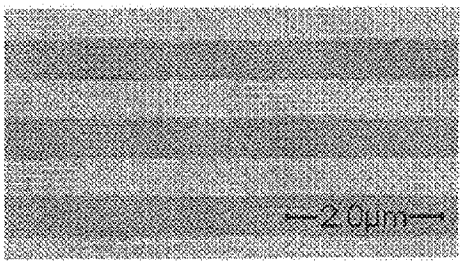


FIG. 31

【図３２】

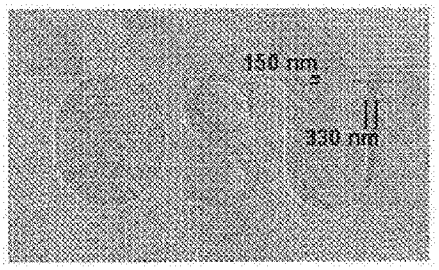


FIG. 32

【図３５】

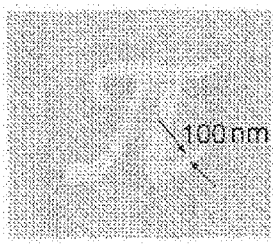


FIG. 35

【図３６】

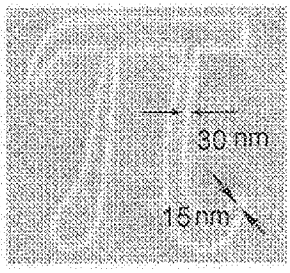


FIG. 36

【国際調査報告】

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
"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
10 April 2008 (10.04.2008)	15 MAY 2008

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (April 2007)

フロントページの続き

(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,IS,IT,LT,LU,LV,MC,MT,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,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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アメリカ合衆国 オレゴン州 ９７３３１ コーヴァリス ギルバート ホール １５３

Ｆターム(参考) 2K009 AA02 CC02 CC03 DD01
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【手続補正書】
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【手続補正１】
【補正対象書類名】特許請求の範囲
【補正対象項目名】全文
【補正方法】変更
【補正の内容】
【特許請求の範囲】
【請求項１】
光学基板と、薄膜または積層体とを備えた装置であって、
前記薄膜または積層体が前記光学基板上のコーティングを形成しており、
前記薄膜または積層体が、少なくとも一つのハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物、および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物で、Ｍがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変で、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、ｚが０．０～３．８の範囲のいずれかの値を取る化合物を含む、
装置。
【請求項２】
前記コーティングが反射防止コーティングであり、および／または前記コーティングが可視光または紫外光を通す請求項１に記載の装置。
【請求項３】
前記コーティングを選択的にドーピングして、Mn^{2+}，Sb^{3+}，Sn^{2+}，Bi^{3+}，Eu^{3+}，Tb^{3+}，Eu^{2+}，Gd^{3+}，Tm^{2+}およびその組み合わせから選択した発光イオンを有するドーピングした発光層を付与する請求項２に記載の光学的装置。
【請求項４】
前記光学基板およびコーティングが誘電体ミラー、Ｘ線ミラー、干渉フィルター、回折格子および／または導波管を画成する請求項１に記載の装置。

【請求項５】
前記薄膜または積層体が、約９～１２の誘電率値、少なくとも６ＭＶｃｍ$^{-1}$までの破壊電界強度、電界強度１ＭＶｃｍ$^{-1}$で１ｎＡｃｍ$^{-2}$近くの漏洩電流を有する請求項１に記載の装置。
【請求項６】
前記化合物がさらにランタンを含み、式$M_{1-z}La_zO_{2-x-z/2}(SO_4)_x$（ＭＳＯｘ：Ｌａ）を有し、Ｍがハフニウムまたはジルコニウムであり、ｘおよびｚが固定または可変で、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲におけるいずれかの値を取り、ｚが０．０～約３．８の範囲におけるいずれかの値を取る請求項１に記載の装置。
【請求項７】
前記化合物がＨａｆＳＯｘ，ＨａｆＳＯｘ／Ｌａ，ＺｉｒｃＳＯｘ，ＺｉｒｃＳＯｘ：Ｌａ，ＨａｆＳＯｘ：Ｃｅ，またはＺｉｒｃＳＯｘ：Ｃａであり、前記装置が５０ｎＡｃｍ$^{-2}$未満の漏洩電流と、約９～約１２の誘電率値を有する請求項１に記載の装置。
【請求項８】
薄膜または積層構造体を設け、該構造体が光学基板と該光学基板上に堆積した１個またはそれ以上の層とを備え、
前記１個またはそれ以上の層の少なくとも一つが、ハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物、および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物からなり、Ｍがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変であり、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、ｚが０．０～３．８の範囲のいずれかの値を取り、
前記構造体をエネルギー源に露出することを備えることを特徴とする装置の製造方法。
【請求項９】
前記薄膜または積層構造体が、光学基板と、パターン化用の第１層と、ハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物からなる第２層とを備え、前記第２層がポジ型レジスト層で、エネルギー源への露出により該レジスト層の材料を現像液に可溶な材料に変換し、前記方法がさらに、前記レジスト層を現像液で処理することにより前記エネルギー源に露出したレジスト層の材料を除去して前記構造体をパターン化することを備える請求項８に記載の方法。
【請求項１０】
前記薄膜または積層構造体が、光学基板と、パターン化用の第１層と、ハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物からなる第２層とを備え、前記第２層がネガ型レジスト層で、エネルギー源への露出により該レジスト層を重合化し、前記方法がさらに、前記構造体を現像液で処理してエネルギー源に未露出の材料を除去することによって前記構造体をパターン化することを備える請求項８に記載の方法。
【請求項１１】
前記ポジ型レジストが二重層からなり、該二重層の第２層が不溶性酸化ハフニウム硫酸塩（ＨａｆＳＯｘ）膜上に堆積した酸可溶のＣｕドープ酸化ジルコニウム硫酸塩（ＺｉｒｃＳＯｘ：Ｃｕ）膜を備え、光または電子ビームからなるエネルギー源へのマスクを介した露出によりＺｉｒｃＳＯｘ：Ｃｕ膜およびＨａｆＳＯｘ膜を露出領域で相互拡散させて、前記ＨａｆＳＯｘ膜を可溶性にする請求項９に記載の方法。
【請求項１２】
前記ハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物が硫酸塩からなり

、該硫酸塩をその後塩基水溶液でのイオン交換によって除去し、前記塩基水溶液がＩ族金属の水酸化物、可溶性のII族金属の水酸化物、可溶性のIII族金属の水酸化物、可溶性のランタニド水酸化物、水酸化アンモニウムおよび／または水性第３アミン、またはその組合せからなる請求項８に記載の方法。

【請求項１３】

半導体材料、金属、ガラス、シリカ、高分子材料またはその組合せからなる適当な光学基板を用意し、

前記光学基板に第１のＨａｆＳＯｘ膜を溶液堆積し、

第２のＺｉｒｃＳＯｘ：Ｃｕ膜を前記第１膜上に溶液堆積して積層構造体を形成し、

前記積層構造体をエネルギー源に露出して、前記ＨａｆＳＯｘ膜および前記ＺｉｒｃＳＯｘ：Ｃｕ膜を露出領域で相互拡散させ、これにより予め未ドープのＨａｆＳＯｘ膜を可溶性にし、

前記露出した構造体を現像してＨａｆＳＯｘ膜を除去することを備える請求項８に記載の方法。

【請求項１４】

前記薄膜または積層構造体が、光学基板と、該光学基板上に堆積した不溶性の酸化ハフニウム硫酸塩（ＨａｆＳＯｘ）の第１層と、前記第１層上に堆積したギ酸銅からなる第２層とを備え、前記第１層および第２層を備える積層構造体を約５０℃～約２００℃の温度に加熱してギ酸銅を分解し、ＨａｆＳＯｘ層と相互拡散させて可溶性の生成物を生成し、該可溶性の生成物を除去する請求項８に記載の方法。

【請求項１５】

前記薄膜または積層構造体が、光学基板と、固体無機酸もしくは塩基を含む第１層とを備え、前記固体無機酸もしくは塩基が原子番号２１～７８を有する金属を含み、前記第１層がさらにペルオキシドまたは他の配位アニオンを含み、前記第１層が酸または塩基に可溶で、該第１層を約５０℃～約１２５℃まで加熱して構造的に硬い膜を生成し、マスクを介してレーザー、電子ビームおよび／または光に露出して膜の露出領域を未露出領域より低い可溶性とし、前記未露出領域を除去してパターンを膜に画成する請求項８に記載の方法。

【請求項１６】

前記膜に電子ビームを０μＣ／ｃｍ^{2}より大きく少なくとも４００μＣ／ｃｍ^2、より一般的には約２μＣ／ｃｍ^{2}から約４００μＣ／ｃｍ^{2}の線量レベルで露出させてパターンを膜に画成する請求項１５に記載の方法。

【請求項１７】

前記パターン化膜の構造的完全性が約３ｎｍ未満である請求項１５に記載の方法。

Espacenet

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

Inventor(s):

Applicant(s):

Classification: **- international:** ***B32B37/06; B32B9/00; C01B13/14; C01G15/00; G02B5/08; H01L21/027; H01L21/316; H01L29/786;*** *G02B1/11*

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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.

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(54)【発明の名称】溶液処理薄膜および積層体、薄膜および積層体を備えた装置、その使用および製造方法

(57)【要約】
ハフニウムおよび／もしくはジルコニウムオキシヒドロキシ化合物を備える薄膜または積層構造体を有する装置およびかかる装置の製造方法を開示する。ハフニウムおよびジルコニウム化合物は、通常ランタンのような他の金属でドープすることができる。電子装置またはそれを作製し得る構成材の例には、限定することなく、絶縁体、トランジスタおよびコンデンサがある。ポジ型もしくはネガ型レジストまたは装置の機能的構成材としての材料を用いて装置をパターン化する方法も開示する。例えば、インプリントリソグラフィー用のマスタープレートを作製することができる。腐食バリアを有する装置の製造方法の実施形態も開示する。光学基板およびコーティングを備える光学的装置の実施形態も開示する。電子顕微鏡を用いて寸法を正確に測定する物理的ルーラーの実施形態も開示する。

【特許請求の範囲】
【請求項１】
少なくとも一つのハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物で、Ｍｔがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変で、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、ｚが０．０～約３．８の範囲のいずれかの値を取る化合物を含む薄膜または積層構造体を備えた装置。
【請求項２】
前記薄膜または積層体が、約９～１２の誘電率値、少なくとも６ＭＶｃｍ$^{-1}$までの破壊電界強度、電界強度１ＭＶｃｍ$^{-1}$でｌｎＡｃｍ$^{-2}$近くの漏洩電流を有する請求項１に記載の装置。
【請求項３】
前記化合物がさらにランタンを含み、式$M_{1-z}La_zO_{2-x-z/2}(SO_4)_x$（ＭＳＯｘ：Ｌａ）を有し、Ｍがハフニウムまたはジルコニウムであり、ｘおよびｚが固定または可変で、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲におけるいずれかの値を取り、ｚが０．０～約３．８の範囲におけるいずれかの値を取る請求項１に記載の装置。
【請求項４】
前記化合物がＨａｆＳＯｘ，ＨａｆＳＯｘ／Ｌａ，ＺｉｒｃＳＯｘ，ＺｉｒｃＳＯｘ：Ｌａ，ＨａｆＳＯｘ：Ｃｅ，またはＺｉｒｃＳＯｘ：Ｃａであり、前記装置が５０ｎＡｃｍ$^{-2}$未満の漏洩電流と、約９～約１２の誘電率値を有する請求項１に記載の装置。
【請求項５】
前記装置がＨａｆＳＯｘ：Ｌａおよび／またはＺｉｒｃＳｏｘ：Ｌａをゲート誘電体として、また酸化亜鉛インジウムおよび／または酸化亜鉛スズをチャネルとして備える電界効果トランジスタであり、該トランジスタが10^6を超えるオン／オフ比と、ｐＡｃｍ$^{-2}$の範囲のゲート漏洩電流を有する請求項１に記載の装置。
【請求項６】
光学基板を更に備え、前記薄膜または積層構造体が前記光学基板上のコーティングを形成する請求項１に記載の装置。
【請求項７】
前記コーティングが反射防止コーティングであり、および／または前記コーティングが可視光または紫外光を通す請求項６に記載の装置。
【請求項８】
前記光学基板およびコーティングが誘電体ミラー、Ｘ線ミラー、干渉フィルター、回折格子および／または導波管を画成する請求項６に記載の装置。
【請求項９】
前記コーティングを選択的にドーピングして、Mn^{2+}，Sb^{3+}，Sn^{2+}，Bi^{3+}，Eu^{3+}，Tb^{3+}，Eu^{2+}，Gd^{3+}，Tm^{2+}およびその組み合わせから選択した発光イオンを有するドーピングした発光層を付与する請求項７に記載の光学的装置。
【請求項１０】
前記装置がインプリントリソグラフィー用のマスタープレートで、前記薄膜または積層構造体をフレキシブルもしくはガラス基板上に堆積し、該薄膜または積層構造体が基板上に堆積したＨａｆＳＯｘの第１層と、ＺｉｒｃＳＯｘ：Ｃｕからなる第２層トを備え、前記第１層および第２層を備える積層構造体をエネルギー源への露出によってパターン化す

る請求項１に記載の装置。
【請求項１１】
マスクを介して光または電子ビームへの露出で、２つの層を露出領域で相互拡散させて、予め未ドープのＨａｆＳＯｘ層を可溶性にし、該可溶性のＨａｆＳＯｘ層を除去してマスタープレートの少なくとも部分的印刷形態を画成する請求項１０に記載のマスタープレート。
【請求項１２】
薄膜または積層構造体を設け、該構造体が基板と該基板上に堆積した１個またはそれ以上の層とを備え、
前記１個またはそれ以上の層の少なくとも一つがハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物からなり、Ｍがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変であり、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、ｚが０．０～約３．８の範囲のいずれかの値を取り、
前記構造体をエネルギー源に露出することを備えることを特徴とする装置の製造方法。
【請求項１３】
前記薄膜または積層構造体が、基板と、パターン化用の第１層と、ハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物からなる第２層とを備え、前記第２層がポジ型レジスト層で、エネルギー源への露出により該レジスト層の材料を現像液に可溶な材料に変換し、前記方法がさらに、前記レジストを現像液で処理することにより前記エネルギー源に露出したレジスト層の材料を除去して前記構造体をパターン化することを備える請求項１２に記載の方法。
【請求項１４】
前記薄膜または積層構造体が、基板と、パターン化用の第１層と、ハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物からなる第２層とを備え、前記第２層がネガ型レジスト層で、エネルギー源への露出により該レジスト層を重合化し、前記方法がさらに、前記構造体を現像液で処理してエネルギー源に未露出の材料を除去することによって前記構造体をパターン化することを備える請求項１２に記載の方法。
【請求項１５】
前記ポジ型レジストが二重層からなり、該二重層の第２層が不溶性酸化ハフニウム硫酸塩（ＨａｆＳＯｘ）膜上に堆積した酸可溶のＣｕドープ酸化ジルコニウム硫酸塩（ＺｉｒｃＳＯｘ：Ｃｕ）膜を備え、光または電子ビームからなるエネルギー源へのマスクを介した露出によりＺｉｒｃＳＯｘ：Ｃｕ膜およびＨａｆＳＯｘ膜を露出領域で相互拡散させて、前記ＨａｆＳＯｘ膜を可溶性にする請求項１３に記載の方法。
【請求項１６】
前記ハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物が硫酸塩からなり、該硫酸塩をその後塩基水溶液でのイオン交換によって除去し、前記塩基水溶液がＩ族金属の水酸化物、可溶性のＩＩ族金属の水酸化物、可溶性のＩＩＩ族金属の水酸化物、可溶性のランタニド水酸化物、水酸化アンモニウムおよび／または水性第３アミン、またはその組合せからなる請求項１２に記載の方法。
【請求項１７】
半導体材料、金属、ガラス、シリカ、高分子材料またはその組合せからなる適当な基板を用意し、
前記基板に第１のＨａｆＳＯｘ膜を溶液堆積し、

第２のＺｉｒｃＳＯｘ：Ｃｕ膜を前記第１膜上に溶液堆積して積層構造体を形成し、
前記積層構造体をエネルギー源に露出して、前記ＨａｆＳＯｘ膜および前記ＺｉｒｃＳＯｘ：Ｃｕ膜を露出領域で相互拡散させ、これにより予め未ドープのＨａｆＳＯｘ膜を可溶性にし、
前記露出した構造体を現像してＨａｆＳＯｘ膜を除去することを備える請求項１２に記載の方法。
【請求項１８】
前記薄膜または積層構造体が基板と、該基板上に堆積した不溶性の酸化ハフニウム硫酸塩（ＨａｆＳＯｘ）の第１層と、前記第１層上に堆積したギ酸銅からなる第２層とを備え、前記第１層および第２層を備える積層構造体を約５０℃～約２００℃の温度に加熱してギ酸銅を分解し、ＨａｆＳＯｘ層と相互拡散させて可溶性の生成物を生成し、該可溶性の生成物を除去する請求項１２に記載の方法。
【請求項１９】
前記薄膜または積層構造体が、基板と、固体無機酸もしくは塩基を含む第１層とを備え、前記固体無機酸もしくは塩基が原子番号２１～７８を有する金属を含み、前記第１層がさらにペルオキシドまたは他の配位アニオンを含み、前記第１層が酸または塩基に可溶で、該第１層を約５０℃～約１２５℃まで加熱して構造的に硬い膜を生成し、マスクを介してレーザー、電子ビームおよび／または光に露出して膜の露出領域を未露出領域より低い可溶性とし、前記未露出領域を除去してパターンをアモルファスまたは結晶化膜に画成する請求項１２に記載の方法。
【請求項２０】
前記膜に電子ビームを０μＣ／ｃｍ^{2}より大きく少なくとも４００μＣ／ｃｍ^2、より一般的には約２μＣ／ｃｍ^{2}から約４００μＣ／ｃｍ^{2}の線量レベルで露出させてパターンを膜に５ｎｍを超えずに広がる線幅で画成する請求項１９に記載の方法。
【請求項２１】
前記パターン化膜はアモルファスまたは結晶化膜であって、構造的完全性が約３ｎｍ未満である請求項１９に記載の方法。
【請求項２２】
前記装置がマイクロまたはナノチャンネルアレイを含み、前記構造体が基板と、第１層と、金属酸化物層である第２層とからなり、前記方法がさらに、前記構造体をパターン化し、
前記構造体をエネルギー源に露出して、前記構造体のパターン化によって生成した所望のパターンを有する耐久性の材料を形成することを備える請求項１２に記載の方法。
【請求項２３】
さらに所定サイズ単位容貌を半固体ハフニウムまたはジルコニウム化合物および関連する有機物を含まない半固体にスタンプして熱または光硬化したスタンプ層を形成することを備える請求項１２に記載の方法。
【請求項２４】
請求項１２の方法にしたがって作製し、金属および金属／セラミック系熱保護システム、有機系のディスプレイおよび電子機器、太陽電池、高放射率コーティング、酸化物系セラミックマトリックスシステム用の界面コーティング、りん光体上の保護コーティング、金属系およびセラミック系システム用の環境障壁コーティングと、複合体およびファイバーレーザー用ファイバー、溶融金属処理における腐食保護、断熱材用モノリシック材料および触媒担体から選択した装置。
【請求項２５】
装置を用意し、
金属酸化物層を備える前記装置上にハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ

酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物で、Ｍがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変であり、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、ｚが０．０～約３．８の範囲のいずれかの値を取る化合物からなる少なくとも一つの腐食バリアを形成し、

前記化合物をエネルギー源に露出して前記腐食バリアを形成することを備えることを特徴とする腐食バリアを有する装置の製造方法。

【請求項２６】

ハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物で、Ｍがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変であり、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、ｚが０．０～約３．８の範囲のいずれかの値を取る化合物からなる組成物を用意し、

前記化合物を有する溶液を形成し、

前記溶液をファイバーにし、

前記ファイバーを固体の安定したファイバーに変換することを備えることを特徴とするファイバーの製造方法。

【請求項２７】

少なくとも２個の金属を備える金属酸化物膜を製造するに当たり、

金属カチオンおよび１個またはそれ以上のアニオンから主としてなる１個またはそれ以上の可溶塩を非錯化で、非水性の極性溶媒に溶解して溶液を作製し、前記金属カチオンの少なくとも１個が3^+以上の形式電荷を有し、3^+以上の形式電荷を有する金属カチオンの濃度が前記金属酸化物膜にける金属カチオンの５０モル％を越え、また前記溶媒が約１５０℃未満の沸点を有し、

前記溶液のｐＨを上げ、該ｐＨの上昇が、塩基水溶液の添加、少量の可溶性塩基酸化物の添加、塩基水溶液を形成し得るガス状化合物の添加、プロトンを消費し膜内に添合し得る電気的陽性の金属の添加、プロトンを消費するか、もしくは対イオンを分解するが膜に添合しない液状またはガス状の酸化剤の添加、またはその組合せからなり、

非水溶性の溶媒を揮発することによって固体を生成し、

前記固体を水に溶解し、

前記溶解した固体を基板上に堆積してパターン化又はブランケット液体膜を形成し、

前記膜を熱で硬化することを備えることを特徴とする金属酸化物膜の製造方法。

【請求項２８】

薄膜または積層構造体を設け、前記構造体が基板と該基板上に堆積した１個またはそれ以上の層とからなり、前記１個またはそれ以上の層の少なくとも一つが金属‐酸膜を備え、前記金属‐酸膜が金属カチオンと酸アニオンとからなり、

前記酸アニオンを塩基水溶液でのイオン交換によって除去し、前記塩基水溶液がＩ族金属の水酸化物、可溶性のＩＩ族金属の水酸化物、可溶性のＩＩＩ族金属の水酸化物、可溶性のランタニド水酸化物、水酸化アンモニウム、および／または水性第３アミン、またはその組み合わせからなり、

前記構造体をエネルギー源に露出し、前記エネルギー源が熱エネルギー源、マイクロ波エネルギー源、光源、またはレーザーからなることを備えることを特徴とする金属酸化物

膜の製造方法。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、電子および光学用途を含む目的用の空間的に定義された構造体を構築するのに有用な無機金属酸化物材料を備えた作品および装置の実施形態と、その製造および使用方法の実施形態とに関するものである。
【０００２】
（政府支援の承認）
本発明の実施形態は、ＤＡＲＰＡ認可番号ＨＲ００１１－０６－１－００４５で連邦政府の補助金を用いて開発した。米国政府は、本発明における特定の権利を有する。
【背景技術】
【０００３】
電子装置は、材料の逐次的な堆積およびエッチングのような反復プロセス工程を用いて現在形成されている。無機材料を有する装置に関して、金属－有機前駆体が無機酸化物の溶液系堆積用に広く用いられてきた。有機部分の存在は、有機材料を除去するための高温焼却工程を必要とする。この工程は、大きな体積変化、結晶化および「泥割れ」現象を生起する場合がある。それに関連した欠陥が、かかる材料のコーティングとしての装置内での機能を阻害する。
【０００４】
電子装置用途に対する材料を溶液処理する方法が特許された。例えば、「有機薄膜トランジスタ構造体および回路用の予備パターン化基板およびその製造方法」の名称の特許文献１には、基板の表面に所望の回路構造を形成して、有機薄膜タランジスタ（ＯＴＦＴ）構造の形成および導電性通路の相互連結に有用な材料を受け取る領域を予備パターン化することが開示されている。特許文献１によると、ＯＴＦＴ材料が、インクジェット印刷のような印刷技術を用いて予備パターン化領域に堆積される。
【０００５】
特許文献２には、薄膜材料を溶液処理してトランジスタを製造することが開示されている。特許文献２は、導電性の溶液処理した薄膜材料接点と、半導体の溶液処理した薄膜材料活性領域と、誘電体の溶液処理した薄膜材料アイソレーションを順次配置して形成し、トランジスタ操作が可能な溶液処理した薄膜構造を形成することを開示する。
【０００６】
特許文献３は、本願明細書に参照して援用するもので、電子用途に有用なハフニウムおよびジルコニウム化合物に関する。特許文献３は、Ｄｏｕｇｌａｓ　Ｋｅｓｚｌｅｒ博士が発明者であり、本明細書で開示する実施形態の発明者でもある。
【先行技術文献】
【特許文献】
【０００７】
【特許文献１】米国特許第６９４６６７７号明細書
【特許文献２】米国特許第６９２７１０８号明細書
【特許文献３】米国特許出願公開第２００５／０２４２３３０号明細書
【発明の概要】
【０００８】
特許文献３は、先行技術の欠陥を解決するような化合物および無機化合物の溶液堆積を開示する。例えば、本発明に係る溶液堆積は、金属－無機堆積技術に必要な有機材料を用いることを回避し、従って有機物焼却および焼却に伴うクラッキングの問題も回避する。
【０００９】
本発明の一つの実施形態は、電子装置のような装置に関するもので、少なくとも１つのハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキ

シタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物及び／又はハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物で、Ｍがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変である化合物を備える薄膜または積層構造体を有する。ｘは約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を有することができる。例えば、ｘはオキシヒドロキシ硫酸塩化合物のような２価の電荷を有する多原子イオンに対して約０．１～約１．７５の範囲のいずれかの値を取ることができる。ｚは０．０～約３．８の範囲のいずれかの値を取ることができる。

【００１０】

特定の実施形態は、式（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）を有するハフニウムもしくはジルコニウムオキシヒドロキシ硫酸塩化合物を備える薄膜または積層体に関するもので、Ｍはハフニウムもしくはジルコニウム、ｘおよびｚは固定もしくは可変で、ｘが約０．１～約１．７５の範囲、ｚが０．０～約３．８の範囲の任意の値を取るものとする。かかる化合物はまた、ＨａｆＳＯｘおよびＺｉｒｃＳＯｘとも呼ぶ。また、ハフニウムおよびジルコニウム化合物を通常カルシウム、セリウム、ランタンまたはそれらの組合せのような他の金属でドーピングすることができる。ある実施形態では、ランタンをドーパントとして用いて式$M_{1-x}La_yO_{2-x-z/2-y/2}(OH)_z(SO_4)_x$（ＭＳＯｘ：Ｌａ）で、その組成および化学量論は上述の通りである化合物を生成する。ランタンをドーピングした化合物の特定例は、$Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$である。他の例としては、ＨａｆＳＯｘ：Ｌａ，ＺｉｒｃＳＯｘ：Ｌａ，ＨａｆＳＯｘ：ＣｅまたはＺｉｒｃＳＯｘ：Ｃａがある。ある実施形態においては、硫酸塩をその後水性塩基でのイオン交換を介して除去して、$M(OH)_x$またはMO_x膜をもたらす。適当な水性塩基には、Ｉ族金属の水酸化物、ＩＩ族金属の水酸化物、ＩＩＩ族金属の水酸化物、ランタノイドの水酸化物、水酸化アンモニウムおよび／または特に水性第３アミンがある。$M(OH)_x$における有機物成分の不在は、例えばマイクロ波およびランプ乾燥によってまたはレーザー処理によってなどの適切な技術を用いた、低温での金属酸化物MO_xへの特異な変換および脱水を可能にする。

【００１１】

ある実施形態は、２個またはそれ以上の金属との錯体組成物を備える酸化物の薄膜または積層体に関するものである。金属カチオンの少なくとも一つは3^+以上の電荷を有し、3^+以上の電荷を有するカチオンの全濃度が対象酸化物における金属カチオンの５０モル％を越える。溶解塩およびある量の水を含む非水溶液を調製する。水の量は、非水溶媒に対し２０モル％未満である。かかる溶液のｐＨは、塩基を加えることによるか、または酸化還元機構を介した遊離プロトンの反応によって、最初の溶液に対し増大させる。最終溶液のｐＨは、用いた金属カチオンに依存するが、一般に約２～９の範囲となる。増大したｐＨは、カチオンに結合した水分子の加水分解および生成したヒドロキソカチオンの濃縮をもたらす。溶媒を蒸発し、生成した固体を水に溶解または分散し、その後基板に液膜として塗布する。次いで、液膜を約１００～６００℃の温度で約５～２４０分間熱硬化する。

【００１２】

本発明に従って作製し得る電子装置、または該装置の構成材の例としては、限定することはないが、電界効果トランジスタにおけるゲート絶縁体のような絶縁体、電界効果トランジスタのようなトランジスタ、ＭＩＭコンデンサのようなコンデンサがある。本実施形態に従って作製した薄膜および積層体は、約９～約１２の範囲の誘電率と、少なくとも３$MVcm^{-1}$から約６$MVcm^{-1}$までの破壊電界と、１$MVcm^{-1}$の電界強度で１$nAcm^{-2}$近くの漏洩電流とを有する。ＺｉｒｃＳＯｘ：Ｃａを用いて作製した装置は、約３．６$MVcm^{-1}$の破壊電界と、約５０$nAcm^{-2}$未満、より一般的には約１０ｎ

Ａｃｍ$^{-2}$未満の漏洩電流とを有する。

【００１３】

電界効果トランジスタは、ＨａｆＳＯｘ：ＬａおよびまたはＺｉｒｃＳＯｘ：Ｌａをゲート絶縁体材料として用いて作製することができる。ある開示された実施形態では、酸化亜鉛インジウムおよびまたは酸化亜鉛スズをチャネルとして用いる。特定の電界効果トランジスタは、10^{6}を超えるオンオフ比およびｎＡｃｍ$^{-2}$のゲート漏洩電流を有する。

【００１４】

本発明の他の実施形態は、無機フォトレジストを用いる装置のパターン化方法に関する。この方法の特定の実施形態は、パターン化すべき構造体をまず用意することを備える。この構造体は、通常半導体材料、金属、ガラス、ポリマー材料またはこれらの組合せのような基板と、シリカのようなパターン化用材料層と、レジスト層とを備える。このレジスト層は、通常ここに開示したハフニウムおよびまたはジルコニウムオキシヒドロキシ化合物を含む。前記構造体を、電子ビームまたは光のようなエネルギー源、特定例では紫外光線に曝す。その後、材料を除去して装置をパターン化するか、または装置の活性なパターン化構成材として保有する。

【００１５】

レジストは、ポジレジストでもネガレジストでもよい。例えば、前記方法は、レジスト層をエネルギー源に曝して、レジスト層ｘ材料を現像液に可溶な材料に変換することを備えることができる。次いで、現像液に可溶な材料を、現像剤を用いて除去する。適切な現像剤には、酸、塩基およびまたは特に超音波攪拌がある。再度一例として、本方法は、エネルギー源に曝したレジスト層材料を除去することを備えることができる。本発明を特定の動作理論に限定することなく、少なくともある実施形態に関しては、エネルギー源へ露出してレジスト層を重合し、エネルギー源への露出前よりも現像液に溶解しにくくすることができる。

【００１６】

ポジレジストの一つの実施形態は、二重層からなる。二重層の第１層は、ハフニウム酸化物硫酸塩（ＨａｆＳＯｘ）膜上に堆積した蟻酸銅膜を備える。この蟻酸銅膜は酸に溶解し、非ドープのＨａｆＳＯｘ膜は酸に溶解しない。二重層をマスクを介して光に露出するか、または集束電子ビームに露出して二つの膜を露出領域で相互拡散し、これにより予め非ドープのＨａｆＳｏｘ膜を可溶性にする。

【００１７】

レジストを作製するための二重層法の他の実施形態は、1個またはそれ以上の金属原子を含有する固形の酸または塩基から成る第１層を基板に堆積することを備える。蟻酸銅のような酸化物前駆体を含む液体懸濁液を前記第１層上に所望のパターンで塗布する。加熱条件下で、前駆体が酸化物に分解する。その後、酸化物が第１層と反応し、相互拡散して、パターンを示すのにエッチングし得る生成物を形成する。代案の実施形態は、加熱または加熱することなく酸化物粒子を第1層上に堆積し、直接反応してエッチングし得る生成物を形成することを備える。さらなる実施形態は、酸化物前駆体の薄層を第１層上に堆積することを備える。次いで、その後、フォトマスクを介した露光、または集束レーザーもしくは電子ビームでの直接書刻によって活性化前駆体のパターンを形成する。

【００１８】

本発明の他の実施形態は、インプリントリソグラフィー用のマスタープレートに関する。該マスタープレートは、フレキシブル基板またはガラス基板のような基板と、少なくとも1個のここに開示したハフニウムおよびまたはジルコニウムオキシヒドロキシ化合物を有する薄膜または積層体の少なくとも一つの層とを備える。マスタープレートの特定実施形態は、基板上に堆積したＨａｆＳＯｘ層と、ＺｉｒｃＳＯｘ：Ｃｕ層のような第２層とを有する。このマスタープレートを、マスクを介した光または電子ビームへの露出のようなエネルギー源への露出によってパターン化して、２つの膜を露出領域で相互拡散させることができる。これは、予め非ドープのＨａｆＳＯｘ膜を可溶性にし、これを除去して

マスタープレートの印刷特性を少なくとも部分的に画成する。

【００１９】

他の実施形態においては、本発明の膜を単一層法に用いてマスクまたはテンプレートを製造することができる。固体酸または塩基のような無機前駆体の薄膜を過酸化物または類似のアニオンと組み合わせて基板上に堆積する。この膜を加熱して構造的に硬い膜を生成する。次いで、フォトマスクを通して、またはレーザーもしくは電子ビームを介して暴露して露出領域に濃縮／架橋結合を誘導する。露出領域の溶解性は、非露出領域に対して減少する。次いで、非露出領域を選択的にエッチングし、膜内にネガティブトーン画像を形成する。また、ポジティブトーン画像は、露出前に膜を高温に予熱することによって形成することができる。いくつかの実施形態において、ＨａｆＳＯｘのような膜を水酸化ナトリウムおよび過酸化水素の混合物で処理することによってＭ（ＯＨ）$_{x}$／$Ｈ_{2}Ｏ_{2}$膜を形成する。次いで、生成した膜を光または電子ビームに露出することによってパターン化する。

【００２０】

また、装置の製造方法を開示し、これは基板、パターン化用材料層、ここに開示したハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物を含む金属酸化物層を備えるパターン化すべき構造体を用意することを備える。この構造体をパターン化し、その後エネルギー源に露出して、構造体のパターン化によって生成した所望のパターンを有する耐久材料を形成する。この方法に従って作製した装置の一実施形態は、マイクロまたはナノチャンネルアレイのようなチャンネルアレイを含むことができる。かかる実施形態に関する装置の製造方法は、所定寸法規模の単位構成を半固体のハフニウムまたはジルコニウム化合物に刻印してスタンプ層を形成することを備えることができる。

【００２１】

腐食バリアを有する装置の製造方法の実施形態も開示する。この方法の開示した実施形態は、装置を用意し、少なくとも1個の腐食バリアを該装置上に形成することを備える。腐食バリアは、通常ここに開示したハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物を含む金属酸化物層からなる。この方法はまた、前記化合物をエネルギー源に露出して腐食バリアを形成することを備えることができる。かかる装置を例示すると、金属および金属／セラミック系の熱保護システム、有機系のディスプレイおよび電子機器、太陽電池、高放射率コーティング、酸化物系セラミックマトリックスシステム用の界面コーティング、りん光体上の保護コーティング、金属およびセラミック系システム用の環境障壁コーティング、複合体およびファイバーレーザ用の繊維、溶融金属処理における腐食保護、熱絶縁用のモノリシック材料及び触媒担体がある。

【００２２】

繊維の製造方法の実施形態も開示する。ここに開示したハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物を有する溶液を形成する。次いで、該溶液を繊維にする。該繊維を、加水分解、アニーリング、大気中での熱分解およびその組み合わせのような任意適当な方法によって固形の安定した形に転換することができる。

【００２３】

光学装置の実施形態も開示する。この装置の特定の開示した実施形態は、光学基板と、ここに開示したハフニウムおよび／またはジルコニウムオキシヒドロキシ化合物を有する基板コーティングとを備える。層は反射防止コーティングとすることができる。光学基板およびコーティングは、例えば、誘電体反射鏡、Ｘ線反射鏡、干渉フィルター、回折格子および／または導波管を画成することができる。光学装置はまた、視覚的に透明又は紫外光に透明であるような透明な層を含むことができる。かかる層を選択的にドーピングして、$Ｍｎ^{2+}$，$Ｓｂ^{3+}$，$Ｓｎ^{2+}$，$Ｂｉ^{3+}$，$Ｅｕ^{3+}$，$Ｔｂ^{3+}$，$Ｅｕ^{2+}$，$Ｇｄ^{3+}$，$Ｔｍ^{3+}$，およびその組合せから選択した発光イオンを有するドーピング層を付与することができる。この層のドーピングを用いて発光層を形成する。

【００２４】

物理的ルーラーの製造方法の実施形態も開示する。ある実施形態は、ここに開示したハ

フニウムおよび／ジルコニウムオキシヒドロキシ化合物の溶液堆積によって、少なくとも一つの酸可溶性層を形成することを備える。少なくとも一つの酸不溶性層を前記酸可溶性層に隣接して形成し、該酸不溶性層をここに開示したハフニウムおよび／ジルコニウムオキシヒドロキシ化合物の溶液堆積によって形成する。これらステップを繰り返して交代層を形成し、前記方法は、交代酸不溶および酸可溶性層の幅を正確に決定することを含む。幅の決定は、Ｘ線反射率のような任意適当な方法を用いて達成することができる。さらに、少なくとも一つの層をエッチングして、対象物を測定するための指状の二次基準パターンを画成する。かかる装置のある実施形態は、電子顕微鏡を用いて寸法を正確に測定するのに有効である。

【００２５】

本発明の前述した、および他の物、特徴および利点は、添付図面を参照して、以下の詳細な説明からより明らかである。

【図面の簡単な説明】

【００２６】

【図１】様々な予備処理およびN_2（気体）を１０℃／分の速度で流しながら加熱したサンプルによるＨａｆＳＯｘ（ｘ＝０．７０）に関する熱重量分析（相対質量対温度）（ＴＧＡ）を示す。

【図２】上述した以外空気中所定温度で１時間加熱後のＨａｆＳＯｘ粉末に対するＸＲＤパターンを示す。

【図３】上述した以外所定温度で1時間加熱後のＨａｆＳＯｘ：３２％Ｌａの粉末に対するＸＲＤパターンを示す

【図４】３１．８°および４５．６°での非常に小さい構成が基板に起因する空気中所定温度で５分間加熱後のＨａｆＳＯｘ膜に対するＸＲＤパターンを示す。

【図５】空気中所定温度で５分間加熱後のＨａｆＳＯｘ：２４％Ｌａ薄膜に対するＸＲＤパターンを示す。

【図６】ＨａｆＳＯｘ膜に対する絶縁破壊特性を示す。

【図７】二酸化ケイ素基板上のタンタル（Ｔａ）金属上に堆積したＨａｆＳＯｘの一実施形態を示すＳＥＭである。

【図８】Ｔａ上に堆積したＨａｆＳＯｘ：２４％Ｌａに対するＳＥＭである。

【図９】１７．６ｎｍの二重層厚を有する１４個の交代層（７個の二重層）を備えるＨａｆＳＯｘ／ＺｉｒｃＳＯｘ多層薄膜に対するＸＲＲパターンを示す。

【図１０】ポジ型またはネガ型フォトレジスト処理を示す概略図である。

【図１１】二重層システムを用いたポジ型レジストを示す概略図で、図示形態は硫酸酸化ハフニウム（ＨａｆＳＯｘ）膜上に堆積したＣｕドープ硫酸酸化ジルコニウム（Ｃｕ：ＺｉｒｃＳＯｘ）膜を備える。

【図１２】基板上にパターン化酸化物を生成するための二重層処理を示す概略図である。

【図１３】基板上にパターン化酸化物を生成するための二重層処理を示す概略図である。

【図１４】基板上にパターン化膜を生成するための単一層処理を示す概略図である。

【図１５】熱的前処理した単一層膜に対する厚さ対エッチング時間のグラフである。

【図１６】電子ビームによってパターン化膜を示す。

【図１７】有機ポリマーに対しより高い機械的強度と、化学的安定性と、独特の電気および光学特性を有する本明細書で開示した半固体形態の化合物を用いるための熱エンボス加工リソグラフィーを示す概略図である。

【図１８】電子顕微鏡のような用途で測定を規格化するのに用いるための物理的ルーラーを作製する一つの方法を示す概略図である。

【図１９】シリカ上に堆積した未交換のＨａｆＳＯｘ膜のＡＦＭ画像である。

【図２０】ＨａｆＳＯｘのイオン交換および８５０℃の熱処理が続くHfO_2のＴＥＭ画像である。

【図２１】シリカ上に堆積し、７００℃以上で加熱後にＨａｆＳＯｘ熱分解デ形成したHfO_2膜のＡＦＭ画像である。

【図２２】シリカ上に堆積し、０．１ＭＮａＯＨで処理し、４５０℃に１０分間加熱したＨａｆＳＯｘ膜のＡＦＭ画像である。
【図２３】シリカ上に堆積し、０．１ＭＮａＯＨで処理し、８５０℃に１０分間加熱したHfO_2のＡＦＭ画像である。
【図２４】未処理の酸化ハフニウム膜のＸＲＤプロットである。
【図２５】処理した酸化ハフニウム膜のＸＲＤプロットである。
【図２６】未処理のジルコニア膜のＸＲＤプロットである。
【図２７】処理したジルコニア膜のＸＲＤプロットである。
【図２８】シリカ上に堆積した酸化インジウムガリウム亜鉛半導体のＳＥＭ画像である。
【図２９】インクジェット印刷および無機拡散反応を介して生成した線パターンを示す。
【図３０】二重層膜をＵＶ光に露出することによって生成したパターンを示す。
【図３１】電子ビーム書刻によってパターン化した膜を示す。
【図３２】電子ビーム書刻によってパターン化した膜を示す。
【図３３】写真的にパターン化した膜を示す。
【図３４】写真的にパターン化した膜を示す。
【図３５】電子ビームによってパターン化した$HfO_{2-x}(SO_4)_x$膜を示す。
【図３６】電子ビームによってパターン化した$HfO_{2-x}(SO_4)_x$膜を示す。
【図３７】電子ビームによってパターン化した$HfO_{2-x}(SO_4)_x$膜を示す。
【発明を実施するための形態】
【００２７】
本発明で開示した実施形態は、電子装置または電子装置の構成材を含む装置に関するもので、無機材料の溶液堆積によって作製することができる。本明細書中での単数用語の不定冠詞及び定冠詞は、特記しない限り複数形も含む。同様に、用語“ｏｒ”は特記しない限り“ａｎｄ”を含むことを意図する。用語「含む」は、「備える」を意味する。本明細書に列挙した百分率は、明示しない限り、原子パーセントである。本明細書において挙げた特許文献および先行技術文献は、特記しない限り、その全てをここに参照して援用する。不一致の場合、用語の説明を有する本発明の明細書は、制御するものとする。本明細書において列挙した材料、方法、および実施例は、実例のためのみであり、限定するものではない。
【００２８】
Ｉ．一般的および特許文献３に記載の金属酸化物硫酸塩材料
本発明の開示は、無機材料の溶液堆積、通常電子用途に有用な金属酸化物硫酸塩無機材料の溶液堆積の方法の実施形態に関するものである。これらの材料の実施形態は、特許文献３に開示されている。この特許文献３の段落００９から段落０１４を以下に言い換える。この言い換えた文書における図の参照は、特許文献３と共に発行された図を参照する。
「図１は、誘電性前駆体材料の製造プロセスの一実施形態を示す。プロセス１０は、一般に金属含有カチオンのような第１の反応体１２を用意し、多原子アニオンのような第２の反応体１４を用意し、次いで多原子アニオンおよび金属含有カチオンを反応させることを備える。金属含有カチオンおよび多原子アニオンは、一緒に反応させる際、水溶液のような溶液内にあるものとする。一実施形態においては、ハフニウムオキシ塩化物（$HfOCl_2(aq)$）のようなハフニウムオキシハロゲン化物の水溶液を用いて金属含有カチオンを付与することができる。硫酸（$H_2SO_4(aq)$）水溶液を用いて硫酸塩（SO_4^{2-}）のような多原子アニオンを付与することができる。所定材料を作製するのに適した方法及び相対量を用いてこれら２個の反応体を一緒に混合することができる。混合物を加熱してもよい。
反応は、前駆体溶液１６を生成することができる。前駆体溶液１６は、基板に塗布することによるように、所望に応じてすぐに使用することができる。随意的には、前駆体溶液１６を少なくとも部分脱水し、次いで塗布する場合がある。上述した例において、前駆体溶液１６はその後ハフニウムオキシヒドロキシ硫酸塩（$HfO_{2-x-2/z}(OH)_2(SO_4)_x$）を形成することができる。この式における変数に関して、ｘおよびｚは固

定または可変であり、いかなる値も取ることができる。例えば、ｘの値は通常約０．１～約１．９であり、ｚの値は０．０～約２．０である。一つの実施形態に対する値は、ｘ＝０．５およびｚ＝０であった。水酸基が金属含有カチオンの一部であり、前記化合物がハフニウムオキシヒドロキシ硫酸塩（$HfO_{2-x-2/z}(OH)_2(SO_4)_x$）からなる場合がある。

他の実施形態において、多原子アニオンは、１個またはそれ以上の硫酸塩（SO_4^{2-}）、ホウ酸塩（BO_3^{3-}）、リン酸塩（PO_4^{3-}）、タングステン酸塩（WO_4^{2-}）およびケイ酸塩（SiO_4^{4-}）を含むことができる。金属含有カチオンは、金属亜酸化物からなる場合があり、１個またはそれ以上のハフニウム（Hf^{4+}）、チタニウム（Ti^{4+}）、ジルコニウム（Zr^{4+}）、セリウム（Ce^{4+}）、スズ（Sn^{4+}）、タンタル（Ta^{5+}）、ニオブ（Nb^{4+}）、イットリウム（Y^{3+}）、モリブデン（Mo^{4+}）、タングステン（W^{6+}）、アルミニウム（Al^{3+}）、ガリウム（Ga^{3+}）、亜鉛（Zn^{2+}）、クロム（Cr^{3+}）、鉄（Fe^{3+}）、ビスマス（Bi^{3+}）、ランタニド類、ハフニウムオキシ水酸化物（$HfO_y(OH)_z^{(4-2y-z)+}$）、ジルコニウムオキシ水酸化物（$ZrO_y(OH)_z^{(4-2y-z)+}$）、チタニウムオキシ水酸化物（$TiO_y(OH)_z^{(4-2y-z)+}$）、タンタルオキシ水酸化物（$TaO_y(OH)_z^{(5-2y-z)+}$）、イットリウムオキシ水酸化物（$YO_y(OH)_z^{(3-2y-z)+}$）、ニオブオキシ水酸化物（$NbO_y(OH)_z^{(4-2y-z)+}$）、モリブデンオキシ水酸化物（$MoO_y(OH)_z^{(4-2y-z)+}$）、タングステンオキシ水酸化物（$WO_y(OH)_z^{(6-2y-z)+}$）、アルミニウムオキシ水酸化物（$AlO_y(OH)_z^{(3-2y-z)+}$）、ガリウムオキシ水酸化物（$GaO_y(OH)_z^{(3-2y-z)+}$）、亜鉛オキシ水酸化物（$ZnO_y(OH)_z^{(2-2y-z)+}$）、クロムオキシ水酸化物（$CrO_y(OH)_z^{(3-2y-z)+}$）、鉄オキシ水酸化物（$FeO_y(OH)_z^{(3-2y-z)+}$）、ビスマスオキシ水酸化物（$BiO_y(OH)_z^{(3-2y-z)+}$）、およびランタニド系列のオキシ水酸化物を含むことができる。ｙの値は、金属カチオンの電荷と、金属カチオンに結合する水酸化物および他の多原子アニオンの量に関係する。

ここに開示した多原子アニオンおよび金属含有カチオンを用いた方法の実施形態は、錯体を形成するための有機物を用いるのを必要としない誘電性前駆体材料、すなわち有機物を含有しないアニオンおよびカチオンの源を形成することになる場合がある。しかし、ある実施形態に対しては所望又は所要に応じて有機材料を用いることができる。例えば、エタノールのような非錯化有機物を前駆体溶液における部分溶媒として用いることができる。錯化有機物が前駆体材料に含まれない場合、該前駆体溶液を基板に塗布したら、前駆体溶液は通常４００℃またはそれ以上の高温度で加熱またはアニーリングしてあらゆる有機材料を分解／燃焼する必要がない。加熱および／または乾燥による前駆体溶液の重合は、多結晶材料でなくアモルファス膜の形成をもたらし、これにより基板上への誘電体材料の溶液を基にした塗布が可能になる。

一般に、本明細書記載の方法の実施形態は、空気中大気圧のような周囲条件で行うことができる。したがって、真空処理は必要ないが、所要に応じて利用し得る。この方法は、約８０℃～約８５０℃のような大気以上の温度、通常約８０℃から最高３５０℃、しばしば最高１００℃で行うことができる。これら低圧低温処理は、開示した方法用のエネルギー必要条件を低減することができる。誘電体膜を処理するのに有用な低温により、膜をプラスチック基板のような低温基板上で処理するか、または溶液として塗布する。生成したアモルファスの非晶質誘電性前駆体溶液は、ウエハのような基板上への前駆体溶液の等角被覆を可能にする。該溶液はまた、インクジェット印刷を用いるなどして所定の特別なパターンで塗布することができるので、マスキングまたはエッチング工程を用いることはない。したがって、本明細書の方法は、基板上のフォトリソグラフィー処理の間材料の形成および除去に用いる危険もしくは有害な材料の利用を撤廃または減少することができる。すなわち、本方法は、既知の方法に対し時間効率が良く環境に優しい。さらに、本明細書の一実施形態に用いるハフニウム酸化物および硫酸塩材料は、有毒材料ではない。

本明細書の方法に用いる材料の実施例には、ハフニウムオキシヒドロキシ硫酸塩（$HfO_{2-x-z/2}(OH)_z(SO_4)_x$）、ハフニウムオキシヒドロキシタングステン酸塩（$HfO_{2-x-z/2}(OH)_z(WO_4)_x$）、ハフニウムオキシヒドロキシホウ酸塩（$HfO_{2-x-z/2}(OH)_z(BO_3)_x$）、ハフニウムオキシヒドロキシリン酸塩（$HfO_{2-x-z/2}(OH)_z(PO_4)_x$）およびハフニウムオキシヒドロキシケイ酸塩（$HfO_{2-x-z/2}(OH)_z(SiO_4)_x$）を含む一群の化合物がある。これら材料は、８０℃程の低温で重合し、約７４０℃まで、さらには１２００℃までアモルファスを保持することができる。材料の重合は、加熱速度の調整、共溶媒の使用、他の適切な方法、およびこれらの方法のすべての組み合わせにより制御することができる。本明細書のアモルファス膜は、粒界での欠陥形成を減少することができ、またアモルファス－結晶転移によりクラック形成を減少することができる。さらに、本明細書の誘電体膜は、適度に高い誘電定数、すなわち有機化合物の誘電定数よりも高い誘電定数を有する。インクジェット印刷の適用のような溶液系処理による高品質の誘電体を形成する能力は、電界効果トランジスタまたはコンデンサのような低コスト電子部品を形成することができる。

図２は、前駆体溶液１６を塗布して誘電体材料を形成する方法の一実施形態を概略的に示す。ハフニウムオキシ硫酸塩のような前駆体溶液１６を塗布器２０によってウエハのような基板１８に塗布する。一実施形態において、塗布器２０はノズル２２を有するインクジェットプリンタとすることができる。前駆体水溶液１６をインクジェットプリンタのノズル２２を通して噴出する。他の実施形態において、塗布器２０は、前駆体溶液の塗布方法がそれぞれスピンコーティング、ディップコーティングまたはスプレーコーティングからなるようにスピン塗装機、ディップ塗装機またはスプレー塗装機とすることができる。前駆体溶液１６のアモルファスな溶液特性により、前駆体溶液１６を塗布した際に、良好な等角被覆を可能にする。基板表面または基板上に堆積した一枚もしくは複数枚の膜上に一度塗布したら、ヒータ２４での加熱によって、もしくは他の脱水デバイスによって前駆体溶液を脱水して、前駆体溶液中の水分を除去または減少させることができる。この脱水工程は、ハフニウムオキシ硫酸塩薄膜のようなアモルファス誘電体材料のウエハ１８上への沈殿をもたらすことができる。

図３は、誘電体材料前駆体溶液１６の一実施態様（図１参照）、特に硫酸（H_2SO_4）とオキシ塩化ハフニウム（$HfOCl_2$）との反応に対して前駆体濃度を異ならせるために可能な溶液濃度を示すグラフである。特に、図３は、全硫酸塩濃度（モル濃度（Ｍ））対全ハフニウム濃度（Ｍ）のグラフを示す。領域２８は、透明な溶液、すなわち、目で見える沈殿物がない溶液を示し、この場合領域２８は過剰な硫酸（H_2SO_4）の領域である。領域３０は、透明な溶液、すなわち、目で見える沈殿物がない溶液を示す。領域３０は、過剰なオキシ塩化ハフニウム（$HfOCl_2$）の領域である。ライン３２は、硫酸およびオキシ塩化ハフニウムがそれぞれ１対１の比（１：１の化学量論的比）である化学量論ラインである。領域３４は、沈殿領域、すなわち目で見える沈殿物を有する溶液を示す。したがって、領域３４またはその一部は、インクジェット印刷の適用によって滑らかで実質的に欠陥のない膜を形成するのに最適でないが、その用途を除外しない溶液を示す場合がある。したがって、前駆体溶液１６（図２参照）をインクジェットプリンタ適用装置２０（図２参照）により塗布する場合、第１および第２反応体の濃度が領域２８または３０の内に入るが、固体領域３４に入らないことが望ましいばあいがある。領域３４の溶液に存在する固体は、ノズル２２をふさぐか、又は滑らかでない膜を形成するか、さもなければ好ましくない前駆体溶液の塗布をもたらす場合がある。換言すれば、領域２８および３０の溶液は、インクジェットプリントヘッドを通して、または滴下方法によって塗布し得る可能な前駆体溶液「インク」を示す。」

【００２９】

ＩＩ．一般的考察

新しい薄膜誘電体およびナノ積層体が、溶液堆積、通常滑らかで高密度な膜の水溶液堆積を用いて開発されてきた。溶液堆積技術には、スピンコーティングおよびインクジェッ

ト印刷がある。溶液堆積に続いて適度な熱処理（Ｔ＜３２５℃）を行うことができる。

【００３０】

さまざまな分析技術を用いて、本発明に従って作製した材料の化学特性を粉末および膜の両方として定義した。膜の品質および機能は、Ｘ線反射率、電子顕微鏡検査法および電子装置における性能によって分析されてきた。誘電特性は、実施形態に関して決定され、約９～約１２の範囲をカバーする誘電率値と、少なくとも６ＭＶｃｍ$^{-1}$までの破壊電界と、電界強度１ＭＶｃｍ$^{-1}$で１ｎＡｃｍ$^{-2}$近くの漏洩電流とを含む。膜の表面滑らかさおよび間隙のない性質は、少なくとも約２ナノメーター程度の薄い個々の層を有する独特なナノ積層構造体の製造を容易にする。比較的高い誘電率の膜は、本発明の開示した実施形態を用いて実現できるが、薄膜の金属－絶縁体－金属（ＭＩＭ）コンデンサおよび薄膜トランジスタ（ＴＦＴ）に高い破壊強度および低い漏洩電流を付与することもできる。絶縁膜の例外的な特性も、独特なナノ積層構造体の形成を可能にする。

【００３１】

アモルファス材料は、薄膜誘電体としての使用に望ましく、粒界を有さず、したがって、微結晶に伴なう粗度および電荷伝導に影響されにくい。ハフニウムおよびジルコニウムの多くの酸化物、例えば簡単な二成分、ケイ酸塩およびアルミン酸塩を、高い誘電率の誘電体用途の候補として検討した。多成分材料においては、誘電率を犠牲にし得るが、結晶化を抑制して純な２成分酸化物に対しより頑丈な破壊特性を生成することができる。これら誘電膜は、しばしば、様々な金属―有機物または金属―塩の前駆体と、原子層堆積（ＡＬＤ）、化学気相堆積（ＣＶＤ）、ゾル－ゲル処理、またはその組み合わせのような技術とを用いて形成される。しかし、溶液堆積法によって高密度でアモルファスである有用な誘電体膜を形成するには、堆積およびその後の処理中に結晶化およびクラッキングを抑制する必要がある。

【００３２】

本発明に開示したある実施形態は、金属酸化物膜の開発に関するものである。金属酸化物は、それぞれ式$HfO_{2-x}(SO_4)_x$および$ZrO_{2-x}(SO_4)_x$を有し、それぞれ０．１≦ｘ≦１．５であるハフニウムおよびジルコニウム硫酸塩系を参照することによって通常例示される。これら化合物は、ここにそれぞれ頭文字$HafSO_x$および$ZircSO_x$で表さす。これら系の化学的および物理的特性を定義するため、$HafSO_x$およびそのＬａ置換誘導体$HafSO_x$：Ｌａのようなドーピングされた類似物を、粉末および薄膜として両方作製する。$HafSO_x$、$ZircSO_x$およびその選択した誘導体の薄膜誘電特性は、コンデンサおよびＴＦＴを組み立てることにより評価される。これら分析によって、高品質で高密度の膜が生成し得ることが示された。混合$HafSO_x$／$ZircSO_x$ナノ積層体の膜厚および製作は、現在スピンコーティング法によって制御し得る。

【００３３】

多くの相および結晶構造体が、$HfO_2-SO_3-H_2O$および$ZrO_2-SO_3-H_2O$系の検討から報告されている。いくつかの構造体は、水和度並びに金属原子、硫酸塩基および水の凝縮に伴った構造的次元の変動を示す式$Hf(SO_4)_2\cdot nH_2O$または$Zr(SO_4)_2\cdot nH_2O$の簡単な水和物として特徴付けられる。硫酸塩に対し金属が豊富な既知の材料としては、$Zr_2(OH)_2(SO_4)_3\cdot 4H_2O$と；$Hf(OH)_xSO_4$およびその水和物と；$Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}\cdot 33H_2O$および$Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$と；$Zr_3O_5(SO_4)_{13}$およびその水和物とがある。これら構造体の全て（可能であれば$Zr_3O_5SO_4$は除く）は、室温および水素の結合又は脱水の変化をもたらす温和な加熱下の両方で大気に施した際に不安定になりがちである。これによって、脱水及び凝縮処理を用いてアモルファス膜を開発するのが可能になる。

【００３４】

ハフニウムに対する硫酸塩の選択した画分（変数ｘ）を有する水溶液から出発して、ＨａｆＳＯｘ沈殿物を加熱によって生起する。図１は、風乾したＨａｆＳＯｘ沈殿物の熱重

量分析（ＴＧＡ）である。ＴＧＡは、サンプルの重量（質量）の変化を温度の関数として測定するのに用いる温度分析技術である。風乾したＨａｆＳＯｘ沈殿物を加熱すると、３つの領域に質量損失を生じる。同様の特徴が、他のＨａｆＳＯｘ誘導体においても観察される。約２００℃の温度以下での大きな質量損失は、結合した水の損失に起因する。約２００℃～約７００℃の温度範囲における質量損失は、主に水としてより強固に結合したヒドロキシル基の排除に起因する。約７００℃以上で開始する急な質量損失は、SO_3（ｇ）→SO_2＋１／２O_2（ｇ）に従う硫酸塩分解に起因する。脱水ＨａｆＳＯｘ粉末が７００℃から９５０℃の間でHfO_2に完全に転換すると仮定すると、硫酸塩画分は、質量損失から計算できる。サンプルの質量損失を決定することにより、母溶液における硫酸塩の増大レベルが、沈殿物における硫酸塩の増大レベルをもたらすことがわかった。とくに、硫酸塩対ハフニウムの比が、それぞれ$HfO_{1.54}(SO_4)_{0.46}$および$HfO_{1.29}(SO_4)_{0.71}$の脱水式に対し約４６％～約７１％まで変化した。H_2SO_4（ａｑ）または$(NH_4)_xSO_4$（ａｑ）を硫酸塩源として使用していても、同じ最大量の硫酸塩組成物が沈殿したが、４６％未満の硫酸塩レベルを有する生成物は検討しなかった。熱重量プロファイルにおいていくらかばらつきが観察されたが、硫酸塩損失の開始は、すべてのサンプルで７２０℃以上で起こった。誘導体に対するこれら加熱曲線の定義し得る値としてのピーク位置は、試験したサンプルでは７９３℃から８１７℃間での分解を示した。最高分解温度は、硫酸塩源としてH_2SO_4（ａｑ）を用いて最大硫酸塩含有量を有するサンプルで観察された。

【００３５】

再び図１を参照するに、最大硫酸塩含有量のサンプルもＴＧＡ測定の前に加熱した。水と関連した質量損失を減じ、予熱したサンプルおよび規格のサンプルの両方で算出した硫酸塩含有量は類似していた。この７０～７１％硫酸塩含有量は、報告した結晶$Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}33H_2O$および；$Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}S\cdot 33H_2O$の組成を再現する。ＴＧＡ研究より、Ａｈｍｅｄ，Ｆｊｅｌｖａｇ，およびＫｊｅｋｓｈｕｓ（Ａｃｔａ Ｃｈｅｍ．Ｓｃａｎｄ．，５３，２４（１９９９））もまた、$Hf_{18}O_{23}(SO_4)_{13}$および$Zr_{18}O_{23}(SO_4)_{13}$に対する硫酸塩分解が、この研究内においてＨｆおよびＺｒ二硫酸塩に対するものよりも高く、また他者により報告された基本の硫酸塩$Hf(OH)_2(SO_4)\cdot H_2O$および$Zr_3O_5SO_4$に対するものよりも高い温度で起こることを見い出した。増大した熱安定性に加えて、約１３：１８の硫酸塩対金属の比が、この系内で特別な安定性を示す。また、この組成が溶液処理および加熱を要求する目的に関して適切な場合がある。

【００３６】

硫酸塩$La_2O_2SO_4$は、１３００℃を超える分解温度を有する。ランタン（Ｌａ）をＨａｆＳＯｘ母溶液に加えて、修正した脱水特性および、一例として熱安定性である熱的特性のような修飾した物理的性質を有する付加的な化合物を生成する。混合金属システム、すなわち$Hf_{1-z}La_zO_{2-x-z/2}(SO_4)_x$（ＨａｆＳＯｘ：Ｌａ）は、かかる化合物を例示する。かかる化合物を生成するためには、前駆体材料および２３％Ｌａ（全金属）を含む溶液を加熱して沈殿物を形成する。化学分析は、わずか３％のＬａが生成物に見い出されることを示された。ＴＧＡから、７１％の硫酸塩対金属の比が認められ、８２０℃での分解（誘導体ピークとして）が、最大硫酸塩含有量と一致することを見い出した。次いで、NH_3（ａｑ）を、３２％Ｌａ含有構成種の塩溶液に加えることによって共沈澱を誘導した。生成物の化学組成を分析して、母溶液に存在するものと同じＬａ画分を示した。この式に対する熱分解は、未ドーピングのＨａｆＳＯｘと著しく異なった。毎分２℃／分の緩徐な速度で加熱する場合でも、加熱特性は急変せず、一定質量が１０００℃までの加熱で達成されないが、硫酸塩に起因した質量欠損が７００℃以上で明白である。この加熱速度に関して、分解（誘導体ピークとして）が約８７０℃で起こるが、この値は加熱条件による。酸化物への完全分解は、１５００℃まで加熱して、乾燥沈殿物用の式$Hf_{0.68}La_{0.32}O_{1.48}(SO_4)_{0.36}$を得ることにより達成される。

【００３７】
ＸＲＤデータを沈殿したＨａｆＳＯｘ粉末に対して収集して、結晶質相に対する温度範囲を確立する。風乾後、複雑な回折パターンを最大硫酸塩含有量および硫酸塩源としてのH_2SO_4（aq）を有するサンプルに対して記録し、他のサンプルは該パターンを示さないか、または拡散回折を示した。ＨａｆＳＯｘ（ｘ＝０．７０）に対するＸＲＤデータを図２に示す。サンプルを約１００℃～約７００℃で１時間加熱風乾後、該物質はアモルファスとなった。単斜晶HfO_2の結晶ピーク特性が、７５０℃およびそれ以上で１時間加熱後に観察される。硫酸塩損失の開始がＴＧＡによって７２０℃で起こるので、結晶化が硫酸塩損失と一致することがわかった。３％Ｌａの含有は、１０００℃までの温度に対して類似の回折プロファイルを発生する。

【００３８】
ＨａｆＳＯｘ：３２％Ｌａに対するＸＲＤデータを図３に示す。沈澱物および７００℃まで加熱した沈殿物は共にＸ線アモルファスである。未置換のＨａｆＳＯｘと同様に、検出可能な結晶質相が７００℃～７５０℃（１時間加熱）で形成され、これは硫酸塩が分解し始める温度間隔である。３２％Ｌａで置換しても、単斜晶HfO_2は検出される相ではない。むしろ、回折プロファイルは立方晶（または正方晶）HfO_2と一致し、HfO_2の相がランタニド原子包含によってしばしば安定化される。高温加熱は、適切な状態図の考察から予想した通り、$Hf_2La_2O_7$および単斜晶HfO_2を生成する。中間温度酸化物相は、１０～３７％のランタンが９００℃で立方晶ジルコニアを安定化し、１０５０℃で相分離が起こることを発見したＺｈａｎｇ，Ｋｅｒｓｈａｗ，ＤｗｉｇｈｔおよびＷｏｌｄ（Ｊ．Ｓｏｌｉｄ Ｓｔａｔｅ Ｃｈｅｍ．，７２，１３１（１９８８））によるZrO_2－La_2O_3系での研究と一致した。

【００３９】
約２００ナノメートル～約３００ナノメートルの厚さを有するＨａｆＳＯｘおよびＨａｆＳＯｘ：Ｌａ薄膜を、材料特性のために作製した。かかる膜に関する組成を、Ｈｆ，Ｌａ，ＣｌおよびＳの相対濃度に基づく電子プローブ微小分析（ＥＰＭＡ）で画定した。酸素レベルは、この方法では正確ではないので、脱水した式で表した。３２５℃で加熱（５分間）した２個の代表的なＨａｆＳＯｘ膜は、ハフニウムに対し６７％および８５％の硫酸塩を示す$HfO_{0.985}(SO_4)_{0.67}Cl_{0.69}$および$HfO_{0.915}(SO_4)_{0.85}Cl_{0.47}$と画定した。８５％硫酸塩膜をさらに６５０℃に加熱（５分間）し、$HfO_{1.275}(SO_4)_{0.71}Cl_{0.03}$と画定した。また、３３０℃で加熱（５分間）したＨａｆＳＯｘ：Ｌａ膜は、$Hf_{0.76}La_{0.24}O_{0.73}(SO_4)_{0.96}Cl_{0.38}$と画定した。６５０℃に加熱したＨａｆＳＯｘに関して、硫酸塩比を７１％まで減ずると、最大硫酸塩を有する加熱沈殿したＨａｆＳＯｘ粉体の組成と一致する。ＨａｆＳＯｘ：Ｌａに関して、Ｌａ（２４％）の測定画分は、前駆体溶液における２３％Ｌａ濃度とよく一致する。

【００４０】
ＨａｆＳＯｘ（ｘ～０．６７及び０．８５）およびＨａｆＳＯｘ：Ｌａ膜に対する透過フーリエ変換赤外（ＦＴＩＲ）分析は、所定温度で５分間加熱した後収集された。ＦＴＩＲスペクトルを用いて２個の官能基を主として検出した。３０００～３６００cm^{-1}の範囲における吸収がヒドロキシル基に帰属され、１０００～１２００cm^{-1}の範囲における吸収が硫酸塩基に帰属される。加熱すると、ヒドロキシル吸収が約３２５℃～約６００℃の範囲にわたり減少する一方、硫酸塩ストレッチが、ＨａｆＳＯｘ膜に対して約６５０℃～７００℃の間で、またＨａｆＳＯｘ：Ｌａ膜に対して約７００℃～７５０℃でほぼ消失する。（硫酸塩からのSiO_2は同じようなエネルギーで吸収するため、硫酸塩吸収に対するプロファイルが僅かに歪曲されるが、スペクトルは定性的に正しい。）

【００４１】
薄膜ＸＲＤデータは、それぞれ図４および図５に示したような所定の温度でそれぞれ５分間加熱した後、ＨａｆＳｏｘ（ｘ～０．６７及び０．８５）およびＨａｆＳＯｘ：２４％Ｌａ膜に対して収集された。両ＨａｆＳＯｘ組成物に対し、膜は約３２５℃～約６５０

℃でＸ線アモルファスである。単斜晶HfO_2を約７００℃およびそれ以上で検出する。ＨａｆＳＯｘ：Ｌａ膜は、約３３０℃～約７００℃でアモルファスである一方、立方晶相が約７５０℃から約１０００℃で検出される。立方晶相は、単斜晶HfO_2および$Hf_2La_2O_7$相への分離が開始するので、１１００℃で明らかに不安定である。ＨａｆＳＯｘおよびＨａｆＳＯｘ：Ｌａ膜に関して、硫酸塩の損失が酸化物の結晶化と直接的に相関させることができ、これは粉体の挙動と一致する。

【００４２】

ＨａｆＳＯｘ，ＺｉｒｃＳＯｘおよびその誘導体の膜を、誘電体として使用するのにスピンコーティングによって堆積した。ＭＩＭコンデンサを試験して、１ｋＨｚでの誘電率および損失正接のパラメータと、電界破壊強度を画定した。「破壊」は、電流密度が$10\ \mu Acm^{-1}$を超える電界として定義する。同様の試験をＨａｆＳＯｘ，ＨａｆＳＯｘ／Ｌａ，ＺｉｒｃＳＯｘ，ＺＩｒｃＳＯｘ：Ｌａ，ＨａｆＳＯｘ：ＣｅおよびＺｉｒｃＳＯｘ：Ｃａに対して行った。図６は、アルミニウムドット接触が$0.011\ cm^2$の面積を示すＨａｆＳＯｘ誘電体膜に関する誘電体破壊特性を示す。ＨａｆＳＯｘおよびＺｉｒｃＳＯｘ膜は、４～６$MVcm^{-1}$の破壊電界を有する。３．６$MVcm^{-1}$の破壊電界がＺｉｒｃＳＯｘ：Ｃａで見られた。１$MVcm^{-1}$の印加電界で、６個すべてのものが５０$nAcm^{-2}$未満の漏洩電流を示し、１０$nAcm^{-2}$未満の漏洩電流が多くの組成物で観察された。約９～約１２の誘電率値および１％未満の損失正接がすべてのもので測定された。

【００４３】

ＨａｆＳＯｘ：ＬａまたはＺｉｒｃＳｏｘ：Ｌａをゲート誘電体として、また酸化亜鉛インジウムまたは酸化亜鉛スズをチャネルとして用いて電界効果トランジスタ（ＦＥＴｓ）を製造した。電流変調が達成され、ドレイン対ソース電流がドレイン対ソース電圧の増加で飽和され、10^6を超えるオンオフ比が付与され、また、ゲート漏洩電流が$pAcm^{-2}$の範囲である。これらの結果は、ＨａｆＳＯｘ：ＬａおよびＺｉｒｃＳＯｘ：Ｌａ膜がデバイス集積に関して十分に強固で、誘電体／チャネル界面品質の必要性も満たしていることを明確に示す。

【００４４】

新しいクラスのアモルファス多成分酸化物誘電体膜として、ＨａｆＳＯｘ，ＺｉｒｃＳＯｘおよびその誘導体を、他の混合系、特に$(MO_2)_{1-x}(Al_2O_3)_x$および$(MO_2)_{1-x}(SiO_2)_x$として表わされ、Ｍ＝ＨｆまたはＺｒであるアルミン酸塩およびケイ酸塩と比較することができる。これらの系のそれぞれに対する様々な膜組成物を従来の気相技術によって堆積させた。２０～５０モル％のAl_2O_3またはSiO_2（誘電体用途に共通な組成として）を有するＨｆまたはＺｒのアルミン酸塩およびケイ酸塩の場合、結晶化が通常約８００℃～約１０００℃で相凝離と同時に起こる。試験したＨａｆＳＯｘ粉体および膜に関して、硫酸塩が分解するので、結晶化が約７００℃で起こる。誘電体として、これらアルミン酸塩およびケイ酸塩は１０～１５の誘電率値を示し、ＨａｆＳＯｘおよびＺｉｒｃＳＯｘに関しては９～１２の値である。この新しいクラスの酸化物硫酸塩材料は、アモルファスで、中間温度で、中間の誘電率の誘導体であると見做すことができる。

【００４５】

走査型電子顕微鏡（ＳＥＭ）およびＸ線反射性（ＸＲＲ）を用いて膜品質をさらに検討する。ＨａｆＳＯｘおよびＨａｆＳＯｘ：Ｌａ膜のＳＥＭ画像を図７および図８に示す。これらの画像は、誘電体試験に通常用いられるような約１５０～約３００ナノメートルの厚さを有する膜に対して、滑らかで高密度の均一な断面を示す。図７は、SiO_2基板７１０と、その上に堆積したＴａ金属の５０６ｎｍ層７１２および１６０ｎｍのＨａｆＳＯｘ膜７１４とを示す。図８は、SiO_2基板８１０と、その上に堆積したＴａ金属の５１２ｎｍ層８１２および１９２ｎｍのＨａｆＳＯｘ／Ｌａ膜８１４とを示す。

【００４６】

より薄い膜製造に関する再現性の厳格な目安として、ＨａｆＳＯｘ／ＺｉｒｃＳｏｘ繰

り返しモチーフを有する多層構造体を堆積し、ＸＲＲで分析した。一つのＸＲＲ走査による干渉パターンを図９に示す。定常波調波の典型であるピーク最大値の位置を用いて、繰り返し二重層の厚さを求めた。ＨａｆＳＯｘおよびＺｉｒｘＳＯｘの厚さを独立して系統的に変化させることによって、個々の層の厚さを画定した。ナノ積層体スタック内において、約３ナノメートル程薄い単一層を測定した。回折パターンにおける高次の反射を観察すると、各二重層を粗度を含む０．５未満のばらつきで堆積した。

【００４７】

装置寸法の縮小は、薄く、高い漏洩電流のSiO_2をＳｉ　ＣＭＯＳ技術において誘電体として代替する必要性を導いた。この代替誘電体は、高い誘電率を示さなければならず、より厚い層が低い漏洩電流の同じ装置電気容量を示すことを可能にする。HfO_2およびZrO_2は、その望ましい誘電体特性および熱的特性のために、代替ゲート誘電体として非常に注目されている。HfO_2およびZrO_2誘電体に対する挑戦の一つは、１３ｎｍ以下の厚さを有する滑らかで、高密度で、ピンホールがない超薄膜を製造することである。以前は、超薄膜が、原子層堆積（ＡＬＤ）を用いて形成されていた。ＡＬＤによるいくつかの期待できる結果にも関わらず、この処理は長い堆積時間（１Å／分）を有する真空を用いることを必要とし、これは高いコストで低い処理量となる。これは、HfO_2およびZrO_2の溶液系堆積に対しいくつかの研究を促進した。今まで、これらの膜は、ＡＬＤ膜と同じ均一性および密度に達していない。

【００４８】

交換反応を用いて、ＡＬＤの品質に匹敵し、ＤＲＡＭ（ダイナミックランダムアクセスメモリ）およびＳｉ　ＣＭＯＳ（相補型金属酸化膜半導体）技術に用いるのに適した超薄$M(OH)_x$およびMO_x膜を製造することができる。開示した実施形態に関しては、スピンコーティングを用いる無機凝縮を介して膜を硫酸塩形態で堆積する。例えば、半固体膜を$MO_x \cdot HCl \cdot H_2SO_4$の組成で形成することができる。硫酸塩は、水酸化ナトリウム水溶液を用いるイオン交換によって除去される。

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

【００４９】

生成したヒドロキソおよび／または酸化物膜は、滑らかで、高密度で、ピンホールがない。例えば、約２ナノメートルの厚さを有するHfO_2膜を、ＨａｆＳＯｘ膜から製造することができる。交換した膜に約８００℃まで熱処理を約１０秒～１０分間施して約０．１ナノメートルの膜表面粗さをもたらす。高価な原子層堆積処理を低コストのスピンオンまたはミスト技術と交換する一方、上記膜特性がＣＭＯＳおよび関連する技術における金属－誘電体ゲートの要件を満たす。

【００５０】

堆積した半固体の水和ヒドロキソ膜は、膜形態を破壊することなくアニオン交換をすることができる。例えば、SO_4^{2-}，WO_4^{2-}，PO_4^{3-}，AsO_4^{3-}，SiO_4^{4-}，VO_4^{3-}，AlO_4^{5-}，GaO_4^{5-}のようなオキソアニオンおよびそのプロトン化物、例えばHPO_4^{2-}，$H_2PO_4^-$並びにハロゲン化物F^-，Cl^-，Br^-およびI^-は、膜を金属塩浴、例えば$Na_2SO_4^{2-}$（ａｑ）中に置くことによって選択的に交換させることができる。これは、電子用途と、イオン交換クロマトグラフィおよび濾過のような他の用途のための膜機能を最適化する機会を提供する。

【００５１】

酸化物膜のいくつかの実施形態に関して、基板に直接塗布して複雑な組成、例えば２個またはそれ以上の金属原子を提供し得る単一源の前駆体懸濁液を生成するのが困難である。以下の方法が、かかる懸濁液の生成およびその装置用途に適した品質の膜の堆積用の単一源の前駆体としての使用を可能にする。

【００５２】

前駆体水溶液を合成し、該前駆体を用いて金属酸化物膜を堆積するための一般的な方法を下記に開示する。前駆体水溶液は、非水極性溶媒中での加水分解により凝縮し、続いて

堆積用の水性環境に転換されたポリマーまたはオリゴマーの金属ヒドロキソ化合物を備えることに特色を示す。有利な薄膜の電気的および光学的特性と、処理温度は、有害な有機汚染なしに金属水酸化物を濃密な固体酸化物に凝縮することにより達成される。ここに開示した合成方法の実施形態は、一般的な手法、すなわち１）金属塩の極性溶媒への溶解、２）加水分解および凝縮、３）溶媒蒸発、４）H_2Oへの溶解、５）溶液堆積および硬化に従う。

【００５３】

金属カチオン（M^{a+}）および１個以上のアニオン（X^{b-}）を備える１個またはそれ以上の可溶性塩を、脂肪族アルコールまたはニトリルのような非錯化で非水の極性溶媒、特にメタノール、エタノール、アセトニトリルもしくはその混合物のような低級（１０炭素原子もしくはそれ以下）アルキルアルコールおよびニトリルに溶解する。多くの溶媒系が可能である。特定の用途に適した溶媒は、沸点（通常１５０℃未満）と、低毒性と、所望の溶液相反応に適合し得る酸―塩基およびレドックス特性とを考慮することによって選択することができる。金属源には、簡単なイオンもしくは分子塩（$Zn(NO_3)_2$，$SnCl_4$，など）；オキシもしくはヒドロキシ塩（$ZrO(NO_3)_2$，ZnOHCl，など）；または潜在的に有機塩（$Fe(CH_3CO_2)_2$，$Cu(CHOO)_2$，など）がある。金属カチオンの少なくとも一つは、3^+以上の形式電荷を有さなければならず、また、このイオン（$a \geqq 3$のM^{a+}）の全濃度は、目的酸化物中の金属カチオンの５０モル％を越えるべきである。同時に、ある量のH_2Oが、上述した金属塩の水和物として溶液に純粋な液体または以下で説明する塩基溶液として導入される。水の量は選択したカチオンによって画定される。すなわち、水の典型的な量は、非水極性溶媒の２０モル％を越えない。

【００５４】

次いで、溶液のｐＨが、適切な塩基の添加によるか、または酸化還元機構を介した遊離プロトンの反応によって、最初のｐＨに対し上昇される。上昇したｐＨは、酸性カチオン（$a \geqq 3$）により結合したH_2O配位子の加水分解および生成するヒドロキソカチオンの凝縮を起こす。最終溶液のｐＨは、用いた金属カチオンに依存するが、通常約２～９の範囲内にある。これは、以下の技術の一つ、またはそのいくつかもしくはすべての組み合わせを用いて達成することができる。

ａ）NH_4OH，$(NH_4)_3PO_4$，ＣｓＯＨまたは類似化合物を含有する塩基性水溶液の添加。特定の化合物（NH_4OH）を選択して、その後の処理の間に分解または揮発することができる。最終酸化物膜の一部を構成して脱水を伴う独特の形態学的、光学的もしくは電気的な特性を達成することを意図する場合、他のカチオン（例えばＣｓ）または多原子アニオン（例えばPO_4^{3-}）を用いることができる。

ｂ）最終酸化物膜における介在物の類似目安でＣａＯまたはＳｒＯのような少量の塩基性酸化物の添加および溶解

ｃ）H_2O中で塩基性溶液を形成するNH_3または他のガス状化合物の添加

ｄ）H_2への直接還元によるか、又はNO_3^-の還元のような他のプロトン消費酸化還元処理の一部としてプロトンを消費し得るＺｎ，ＡｌまたはＦｅのような電気陽性金属還元剤の添加。然る後、生成したカチオン種を最終酸化物膜に入れ込む。

ｅ）プロトンを消費するか又は対イオンを分解する目的であるが、最終酸化物膜に介在することなく液体形態若しくは可溶性塩としてのN_2H_4，H_2CO又はH_2O_2のような水性またはガス状酸化剤または還元剤の添加。

【００５５】

前記溶液を室温で攪拌し、加熱するか、またはソルボサーマル条件に曝して、所望の最終組成に応じた熱分解および凝縮を促進させることができる。適切な反応時間の後、該溶液は１個またはそれ以上の可溶性オリゴマーまたはポリマーの金属－ヒドロキソカチオン種を含有する。これら種は、実際ホモまたはヘテロ金属とすることができる。凝縮の程度は、入手し得るH_2O（水和およびヒドロキソ配位子）の制限的なモル比によって制限される一方、H_2Oに対する非水溶媒の減少した極性およびサイズが、立体効果または変化

した電荷スクリーニング特性によって付加的な凝縮および沈殿処理を防止することができる。

【００５６】

可溶性金属種は、非水溶媒を揮発させることによって分離される。分離した金属－ヒドロキソ化合物は、溶媒、対イオン、および加水分解比のようなある処理考察に応じて結晶性もしくはアモルファスの固体またはゲルを形成することができる。

【００５７】

酸化物膜用の前駆体溶液は、分離した固体をH_2Oに溶解または分散させることによって調製される。生成したゾルまたは溶液は均質で、また熱力学的に安定又は安定でない場合がある。

【００５８】

前駆体溶液を、印刷、スピン、スプレーまたはディップコーティングを含む任意適当な技術を用いて基板に塗布してパターン化または前命的な液膜を形成する。液膜を大気条件下約１００℃から６００℃の温度で約５－２４０分間熱硬化する。真空または二次成形ガス（例えば、H_2およびN_2もしくはＡｒ流）アニールを用いて、所望の化学もしくは光電子工学特性に適するように酸素の化学量論またはカチオン酸化状態を変えることができる。

【００５９】

本明細書に開示した膜の平滑さおよび高い原子密度は、溶液処理を介して純粋な無機ナノ積層体を製造することができる。これらの膜は、さらに以下で説明するように、広範囲の用途を開発するための新しい土台となる。

【００６０】

ＩＩＩ．用途

当業者は、ＨａｆＳＯｘおよびＺｉｒｃＳＯｘ化合物およびかかる化合物を備える膜を用いて多くの異なる装置を作製することができ、またかかる化合物を利用する様々な処理を実行することができることが理解できる。金属－有機物前駆体は、無機酸化物の溶液系堆積に広く採用されている。この有機部の存在は、相当な体積変化と通常結晶化および「泥割れ」現象とを導く高温焼却工程を必要とする。これらの問題点は、本発明の開示した実施形態と、適切な無機組成とを用いて、簡単な脱水および重合が膜品質維持を導くアモルファスＨａｆＳＯｘおよびＺｉｒｃＳＯｘ膜を形成することにより排除される。相安定性を解明するため、代表的なＨａｆＳＯｘおよびＨａｆＳＯｘ：Ｌａ粉体と膜を様々な温度で特徴付けた。膜の品質および利用性を検討するために、ＨａｆＳＯｘおよびＺｉｒｃＳＯｘを基にした薄膜を様々形状で堆積した。いくつかの誘導体を用いてキャパシタ誘電体を製造した。ＨａｆＳＯｘ：ＬａおよびＺｉｒｃＳＯｘ：Ｌａを用いて、ＦＥＴ装置におけるゲート誘電体を形成した。ＨａｆＳＯｘおよびＺｉｒｃＳＯｘナノ積層体層は、対の原子層内で再現性と共に顕著な平滑さ示した。ＨａｆＳＯｘ，ＺｉｒｃＳＯｘおよびその誘導体を備える膜の階級は、他のものの中でも、電気絶縁体、防護壁、光学的コーティングおよび／またはフォトリソグラフィー用の無機高分子として有用である。

【００６１】

Ａ．レジスト、インプリントリソグラフィーおよび印刷用のパターン化膜

フォトリソグラフィーを一般に用いてマスク上の幾何学的図形をシリコンウエハまたは他の半導体の表面に転写する。過去４０年間は、フォトリソグラフィー処理は、マイクロ電子業界における装置特性の解明および寸法制御において改良するための原動力であった。これらの利点によって、現在我々の生活の欠かせない部分と考えられる高性能のパーソナルコンピューター、携帯電話、ＣＤプレーヤーおよび他の無数の進化した電子製品が可能となった。これら製品を可能にしたフォトリソグラフィーの進展は、短波長の露光ツールの開発と、ポリマーレジストの解明および形状能力の並外れた進展とに大きく集中した。しかし、より小さくデバイス歩留まりの改良が依然として求められているため、ポリマー系レジスト技術の制限および非能率はより明確になってきている。

【００６２】

リソグラフィーにより実現された最小の形状サイズは、無機材料の電子ビーム書き込みによって製造された。しかし、これら形状を生成するのに必要なビーム投与量は、製造環境での使用の一時的なもの以上を受け取る極端に高いものであった。

【００６３】

ここに開示した膜の堆積および処理の間、積層した膜の相互拡散と、生成する物理的および化学的特性を制御する方法を与える膜の水和レベルを制御することが可能である。高品質な膜と結合した材料溶解度に誘起された修飾を有する制御された相互拡散を用いて、アモルファスおよび結晶化膜を用いる新しいリソグラフィーパターン化法を開発する。この方法論は、２個の異なる膜を堆積および反応させることを含み、二重層拡散として指定される。また、ペルオキシド（O_2^{2-}）のような小さい配位種を水系無機懸濁液および膜に添合して追加の新しいリソグラフィーのパターン化方法を提供することができる。この技術では、エネルギー（例えば、光、電子ビーム、熱）を膜に付与して、膜の溶解性を変える凝縮反応を起こし、リソグラフィーのパターン化を可能にする。

【００６４】

パターンは、ポジ型またはネガ型フォトレジストを用いて形成することができる。この処理をシリコン基板１０１２、シリカ層１０１４およびレジスト層１０１６を有する積層構造体１０１０を参照して図１０に概略的に示す。ポジ型レジストに関しては、レジスト層１０１６をＵＶ光のようなエネルギー源に露出し、どこであっても下側の材料を除去すべきである。これらレジストでは、ＵＶ光への露出がレジスト層１０１６の化学構造を変えるので、現像剤中で一層可溶となる。その後、露出したレジスト層１０１６を現像剤溶液によって除去して、裸の下側材料の領域を残す。換言すれば、「何を示そうが、行く」ということである。したがって、マスク１０１８は、ウエハ上に残すべきパターンの正確なコピーを含む。

【００６５】

ネガ型レジストは、正反対の挙動を示す。ＵＶ光への露出は、ネガ型レジストの重合を生起し、したがって、溶解が一層難しくなる。その結果、ネガレジスト１０２０が露出された表面上に残り、現像剤溶液が未露出部分だけを除去する。したがって、ネガ型フォトレジストに用いるマスクは、転写すべきパターンの逆（または写真の「ネガ」）を有する。

【００６６】

電子機器製造に現在使用中のレジスト材料は、有機ポリマーである。これらポリマーは、パターン分解能を制限するコイリング、形態、および拡散化学特性を示す。本発明の無機薄膜は、新しいレジスト技術の基礎を形成する。ここで、ネガ型レジストは、無機物膜を半固体形状で光または電子ビームに露出し、脱水中に溶媒、とくに水、またはO_2^{2-}のような小さい配位子を失わせることにより実現することができる。これは膜を強化し、酸に不溶にする。

【００６７】

ポジ型レジストの一つ実施形態は、二重層システムを用いて作製することができる。二重層の第１層は、ハフニウム酸化物硫酸塩（ＨａｆＳＯｘ）膜上に堆積したギ酸銅膜からなる。ギ酸銅膜は、酸に可溶で、未ドープのＨａｆＳＯｘ膜は酸に不溶である。二重層をマスクを介して光に、または収束した電子ビームに露出させると、２個の膜が露出領域で相互拡散を生起し、これにより予め未ドープのＨａｆＳＯｘ膜を可溶にする。

【００６８】

この処理の一実施形態を図１１に概略的に示す。図１１を参照すると、積層構造体１１１０が、先ずスピンコーティングまたはインクジェットコーティングの適切な材料によって加工装置を画成するのに必要とするような所定のオーダーと厚さで形成される。より詳細には、基板材料１１１２を最初に選択する。当業者は、多くの基板材料のうちどれを使っても本発明のこの実施形態を実現できると理解できるだろう。ほんの一例として、また、限定することなく、適切な基板には、半導体材料、金属、ガラス、高分子材料およびそれらの組み合わせがある。そのようなものとして、レジスト技術が半導体製造における様

々な用途にとって有用とすることができる。適切な基板１１１２を選択すると、ＨａｆＳＯｘの第１層１１１４を基板１１１２上に溶液堆積する。その後、Ｃｕ：ＺｉｒｃＳＯｘの層１１１６のような第２層を層１１１４上に溶液堆積する。次いで、積層構造体１１１０に、マスクを介して電子ビーム又は光のようなエネルギー源をもたらす。マスクを介して光又は電子ビームに露出すると、２個の膜が露出領域で相互拡散し、予め未ドープのＨａｆＳＯｘ膜を可溶性にして積層構造体１１２０を生成する。次いで、露出した構造体１１２０を現像する。予め未ドープのＨａｆＳＯｘは可溶性であので、積層構造体１１３０において示すように除去される。

【００６９】

フレキシブルまたはガラス基板上で、構造体１１３０に示したパターンは、インプリントリソグラフィー用、またはグラビア印刷のような一般化された印刷処理用のマスタープレートであると考えることができる。このようにしてＨａｆＳＯｘの硬化パターン化材料を形成すると、流体制御および送達用装置の製造におけるマイクロおよびナノチャネルアレイを開発する手段を提供する。かかる装置は、医療診断、インク送達および化学合成に適用することができる。

【００７０】

二重層方法の他の実施形態を図１２に示す。この方法は、所定の基板１２１０上にパターン化酸化物を生成する。例えば、基板はガラス、半導体ウエハ、金属、金属合金、プラスチックまたはその組み合わせとすることができる。この方法の第一の工程は、固体の酸または塩基、例えば１個もしくはそれ以上の金属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またはＬｕ含有する水和した硫酸塩、リン酸塩、硝酸塩、ケイ酸塩、アルミン酸塩、ホウ酸塩もしくはその混合物の薄膜１２１２（約１ｎｍ～約１００ｎｍ）を堆積することを含む。加えて、固体の酸／塩基は、１個またはそれ以上のNH_3，ＯＨ，Ｆ，Ｃｌ、Ｂｒ，Ｉを含有することができる。固体の酸／塩基をスピンコーティングまたは印刷により堆積するのが好ましく、物理的堆積及び気相堆積が付加的な選択である。一例として、固体の酸をスピンコーティングにより$HfOCl_2$およびH_2SO_4（ａｑ）の水溶液から堆積することができる。固体の酸を約５０℃で約２分間加熱することにより十分に加熱して構造的に強固な膜１２１２を生成する。印刷操作モードにおいては、基板１２１０を加熱したプラテン（約２５～３００℃）上に置き、酸化物前駆体、例えばギ酸銅を含有するインク１２１４をインクジェットヘッドを介した送達によって、または基板１２１０を前駆体１２１４を含有するテンプレートと接触させることによって所望のパターンで塗布することができる。テンプレートは、ミクロ接触、活版またはグラビア印刷機の一部からなる。加熱条件（約２５０℃以上）下で、前駆体１２１４は酸化物に分解し、続いて固体の酸と反応および相互拡散して生成物１２１６を形成し、これを容易に洗浄又はエッチングしてパターン１２１８を示すことができる。酸化物前駆体は、微細な酸化物のマイクロもしくはナノ粒子を含有するインク懸濁液またはペーストによって交換することができる。微粒子を加熱または加熱することなく適用すると、パターンを示すようにエッチングし得る製品を形成する直接反応をもたらす。

【００７１】

パターン化酸化物を所定の基板１３１０上に生成するための他の実施形態を図１３に示す。最初の工程は、基板上に固体の酸１３１２または塩基を堆積することを含む。次いで、酸化物前駆体１３１４をスピンコーティング、印刷、化学気相または物理気相堆積によりブランケットコートとして塗布する。その後、活性化した前駆体１３１６のパターンを、フォトマスクを介して光のようなエネルギー源に露出することによって形成する。適切な光源としては、特にフィルターなしの重水素放電管または１９３ｎｍで光を放出する光源がある。或いはまた、活性化前駆体１３１６のパターンを、収束したレーザ又は電子ビームで直接書き込むことにより形成する。所要に応じて、活性化しパターン化した構造体１３１６を約１２５℃～約３５０℃の温度に加熱して２層の相互拡散を促進させることが

できる。次いで、露出領域をエッチングして所望のパターン１３１８を形成することができる。露出感度を改善する手法は、固体酸上に酸化物前駆体の極めて薄い層（約２ｎｍ）を用いることを含む。次いで、前駆体層を化学又は物理的気相堆積のような任意適当な技術によるか、または酸化物ナノ粒子の溶液注型によって堆積する酸化物の層で覆う。この層が相互拡散し、続いて前駆体の薄層を露出する。

【００７２】

上述した方法は、ポジ型レジスト技術と関連する。また、不溶性生成物をもたらす固体の酸／塩基および前駆体を選択することができる。かかる生成物を用いて、少なくとも２つの方法でポジティブ画像を生成することができる。一実施形態においては、２つの層が完全に相互拡散して単一の不溶性層を形成する。印刷または露光および現像に続いて、膜の可溶性部分をその後洗浄又はエッチングしてポジティブパターンを示す。代案の手法においては、相互拡散が前駆体と固体酸／塩基の間の界面でのみ生起して、薄く不溶性の境界層を形成する。次いで、この境界層を用いて膜スタックのエッチングを制御し、ポジティブ画像を形成する。境界層は感光性である。これは、露光前に前駆体と固体酸／塩基間の反応を防止し、さもなければ容易に接触して相互拡散する。境界層が感光化されたら、反応性の酸化物となる。境界層が「破壊」され、上部層が下部層と相互拡散することができる。

【００７３】

次世代のパターン化は、写真又はインプリントに基づいていようと、通常電子ビームリソグラフィで製造されたマスクまたはテンプレートを用いる。かかるテンプレートまたはマスクの多くは、ハードマスクＨＳＱ（水素シルセスキオキサン）を用いて製造される。ＨＳＱマスクは、様々な電子部品、データ保管およびミクロ電子工学装置を製造するのに広く用いられる。ＨＳＱはまたインプリントリソグラフィー用の硬いマスター／テンプレートとして開発中である。

【００７４】

マスクまたはテンプレートは、ここに開示した膜を図１４に示すような単一層処理に用いて製造することができる。かかる処理の第一の工程は、無機前駆体１４１０の薄膜（約１ｎｍ～約１００ｎｍ）を基板１４１２上に堆積することを含む。無機前駆体１４１０は固体酸または塩基、例えば一個以上の金属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，またはＬｕを含有し、ペルオキシドもしくは類似の配位アニオンと組み合わせた水和硫酸塩、リン酸塩、硝酸塩、ケイ酸塩、アルミン酸塩、ホウ酸塩もしくはその混合物とすることができる。加えて、固体酸／塩基およびペルオキシド混合物は、１個以上のNH_3，ＯＨ，Ｆ，Ｃｌ、Ｂｒ，Ｉを含有することができる。固体酸／塩基をスピンコーティング、液体ミストまたは印刷により堆積するのが好ましく、物理的堆積および気相堆積が付加的な選択である。一例として、固体酸をスピンコーティングにより$HfOCl_2$，H_2SO_4（ａｑ）およびH_2O_2（ａｑ）の水溶液から堆積することができる。固体酸を、たとえば約５０℃～約１２５℃の温度に約１０秒～約１０分間十分に加熱して、構造的に強固な膜を生成する。次いで、かかる膜をフォトマスクを介して露光するか、または画定したレーザーもしくは電子ビームを介して露出し、露出領域に凝縮を誘起する。露出領域１４１４の溶解度は、未露出領域と比較して減少するため、未露出領域を酸または塩基で選択的にエッチングすることができる。使用し得る酸または塩基を例示すると、特に塩酸、硫酸、過酸化水素、水酸化ナトリウムおよびテトラメチル水酸化アンモニウムがある。一般に、用いる酸および塩基の濃度は約０．１Ｍ～約１Ｍの範囲内である。次いで、膜を酸または塩基で現像して未露出領域をエッチングし、続いて、随意的に約１００℃を超える温度で熱硬化する。この方法は、膜にネガティブな画像を作製する。多くの組成について、生成したパターン化膜はアモルファスであり、一般的に結晶化膜に伴なう制限なしに高分解能、小限界寸法パターン化を実現する手段を提供する。塗布膜を野外露出前に高温に予熱することによって、エッチング差速を誘起してポジティブな画像を実現することがで

きる。図１５は、熱的に予熱した単一層膜に対するエッチング差速を明示する。このグラフは、露出領域が開始時間にしたがって未露出領域より速くエッチングされるように熱処理がエッチング速度に影響することを立証する。

【００７５】

他の実施形態においては、ＨａｆＳＯｘ膜を水酸化ナトリウムおよび過酸化水素の混合物で処理して、アニオン交換およびＭ（ＯＨ）$_x$／H_2O_2膜の形成をもたらす。或いはまた、予め調製したＭ（ＯＨ）$_x$膜を過酸化水素水に浸してＭ（ＯＨ）$_x$／H_2O_2膜を形成することができる。次いで、生成したＭ（ＯＨ）$_x$／H_2O_2膜を光または電子ビームへの露出によってパターン化する。これらの技術は、ポリマーレジストなしで簡単または複雑なMO_x膜を直接パターン化するための手段を提供する。例えば、HfO_2膜を高ｋの誘電体としてＳｉ　ＣＭＯＳ回路および印刷電子機器用途に用いるために直接パターン化することができる。他の例では、パターン化TiO_2膜をＴｉ（ＯＨ）$_4$のH_2O_2溶液堆積によって形成したＴｉ（ＯＨ）$_x$／H_2O_2膜から生成することができる。

【００７６】

これらの方法は、２層実施形態に用いた拡散を排除し、露光投与量を低くし、またライン－エッジ粗さと限界寸法とを改善する。図１６は、０μｃ／ｃｍ^{2}より大きく少なくとも４００μｃ／ｃｍ^{2}の範囲の投与量レベルで電子ビームを用いる単一層のネガティブトーン処理によりパターン化したＨａｆＳＯｘ膜のＡＦＭ（原子間力顕微鏡）画像である。該画像の右側のナノメートル目盛りは、膜内へエッチングされた容貌の高さを示す。図１６に示すように、かかる容貌が２μＣ／ｃｍ^{2}でのような低い投与量レベルでの電子ビーム露出により書刻された。この投与量レベルは、最も既知の化学的に増幅した高分子レジストに匹敵するもので、無機レジストに対し以前検証されたものより１０００倍低い。容貌は、約２０ｎｍ未満の解像力で作製することができる。加えて、膜は、ＨＳＱに対して検証されたものよりほぼ一桁小さい３ｎｍ未満の構造的完全性（例えば、滑らかで、高密度、ピンホールがない）を明示する。

【００７７】

ポリマーレジストに付随した膜塗布、加熱およびエッチング工程並びに無機材料の真空高温処理工程は、パターン化方法において排除されている。生成したパターン化膜は、電子装置の機能的構成材、下側基板のその後のパターン化用のハードマスク、またはインプリント用テンプレートとすることができる。電子ビーム露出を除いて、すべての処理を大気中の標準環境で行う。いくつかの処理工程の排除を考慮すると、ここに開示した技術は、装置生産歩留まりを改善し、製造コストを下げる新しい方法を提供する。専用の水溶性薬品に頼ると、前記処理も環境に優しく、また洗浄した製品を完全に回収し、リサイクルすることができる。この技術は、多くの発展した技術への用途を有する。その使用は、本明細書に記述したシステムのみに限定されない。

【００７８】

Ｂ．インプリントリソグラフィー

熱エンボス加工および光開始インプリントリソグラフィーは、ＨａｆＳＯｘ，ＺｉｒｃＳＯｘおよび関連する材料におけるパターンを形成する付加的な方法である。熱エンボス加工方法は、図１７に概略的に示し、有機高分子でパターンを形成するのに最も一般的に適用されている。ＨａｆＳＯｘおよび関連する組成の半固体形態は、有機高分子と比較してずっと高い機械強度と、化学的安定性と、独特の電気的および光学的特性を有する無機材料をパターン化する機会を提供する。

【００７９】

図１７を参照するに、有機高分子の代わりに、ＨａｆＳＯｘまたは関連する無機材料をスピンコーティングまたはインクジェット印刷により適切な基板１７１２上に溶液堆積して、ＨａｆＳＯｘ層１７１４を形成する。基板１７１２およびＨａｆＳＯｘ層１７１４は、積層構造体１７１０を画成する。ナノメートル、マイクロメートルまたはミリメートルのような所望のサイズスケールの単位容貌を有するスタンプ１７１６を半固体のＨａｆＳＯｘまたは関連する膜層１７１４にプレスして、スタンプ層１７１８を形成する。次いで

、スタンプ層１７１８および基板１７１２を加熱してＨａｆＳＯｘを硬化する。その後、スタンプを除去して、パターン化積層構造体１７２０にパターン化ＨａｆＳＯｘ材料を画成する。

【００８０】

或いはまた、過酸化物または関連する小さく弱い配位子をＨａｆＳＯｘ，ＺｉｒｃＳＯｘ，および関連する材料に加えることができる。その次に、スタンピング工程の間に、膜を短波長光に露出させ、パターン化膜の化学凝縮および硬化を促進することができる。その後、スタンプを除去してパターン化膜を画成する。この技術は、ポリマー材料にインプリントするのによく用いられるステップアンドフラッシュインプリントリソグラフィー（ＳＦＩＬ）の新たな技術革新を示す。

【００８１】

Ｃ．測定装置

上述した二重層ポジ型レジスト技術用に開発した薬品を用いて、電子顕微鏡検査のような適当な分野で測定を規格化するのに用いる図１８に示すような物理的ルーラーを製造することができる。この用途においては、酸可溶層１８１２と、酸不溶層１８１４とを交互に配したナノ積層体１８１０を堆積する。酸可溶層は、ハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物、および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物で、Ｍがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変であり、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、ｚが０．０～３．８の範囲のいずれかの値を取るものの溶液堆積によって形成される。通常、該層に銅をドープする。酸不溶層は、ハフニウムおよび／またはジルコニウムオキシヒドロキシ硫酸塩（$MO_{2-x-z/2}(OH)_z(SO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシタングステン酸塩（$MO_{2-x-z/2}(OH)_z(WO_4)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシホウ酸塩（$MO_{2-3x/2-z/2}(OH)_z(BO_3)_x$）化合物、ハフニウムおよび／またはジルコニウムオキシヒドロキシリン酸塩（$MO_{2-3x/2-z/2}(OH)_z(PO_4)_x$）化合物、および／またはハフニウムおよび／またはジルコニウムオキシヒドロキシケイ酸塩（$MO_{2-2x-z/2}(OH)_z(SiO_4)_x$）化合物で、Ｍがハフニウムまたはジルコニウム、ｘおよびｚが固定もしくは可変であり、ｘが約０．１～約３．５／（多原子イオン電荷）の範囲のいずれかの値を取り、ｚが０．０～３．８の範囲のいずれかの値を取るものの溶液堆積によって形成される。

【００８２】

層１８１２および１８１４の幅は、Ｘ線反射性を用いるなどして正確に画定される。次いで、酸可溶層１８１２をエッチングして、電子顕微鏡で物体を正確に測定する際の二次基準として用いることができる指型のパターン１８２０を呈示する。

【００８３】

Ｄ．腐食バリア

前駆体液を金属、合金またはセラミックのような適当な基板上に塗布して腐食バリアを形成することができる。加えて、かかる液を繊維にするか、若しくは鋳型内に置くか、または単独で用いることができる。前記液を、加水分解、アニーリングまたは大気中の熱分解を含む任意適当な処理によって固体で、安定な形態に転換することができる。通常、これは所望の結果を達成するに有効な温度まである時間加熱することを必要とし、例えば通常１００℃以上の温度で少なくとも数秒間、より一般的には少なくとも数分間加熱することが必要である。

【００８４】
膜の原子的に高密度のために、潜在的用途には、限定することはないが、金属および金属／セラミック系熱保護システム用の熱、腐食および酸化保護、有機ベースのディスプレイおよび電子部品、太陽電池、高放射率コーティング、酸化物系セラミックマトリックスシステム用の界面コーティング、りん光体上の保護コーティング、金属およびセラミック系システム用の環境障壁コーティング、複合体およびファイバーレーザー用の繊維、融解金属処理における腐食防止、熱絶縁用モノリシック材料、触媒担体、並びに他の多くのものがある。膜を積層する能力は、一層における欠陥の位置を他の層に対しランダム化して増強した腐食保護を付与する機会を提供する。

【００８５】
Ｅ．光学的コーティング
前駆体液を、個々の層として、また多重層の型で適当な光学的基板上に塗布して、反射防止コーティング、誘電体ミラー、Ｘ線ミラー、干渉フィルター、導波管、平面コーティングおよび傷のつきにくい表面を生成することができる。多重層の周期性は、少なくとも２個の材料組成を交互に堆積することによって達成される。単一層の周期性は、フォトリソグラフィー処理に関して記述したようにエッチングによって達成することができる。アモルファス性質、層間の鋭い界面および誘電定数を制御する能力は、理論的限界近くで性能を実現するための処理を提供する。

【００８６】
選択的に堆積もしくはエッチングした多重層または単一層形態において、周期的な構造体は、回折用途に適切である。単一もしくは多重材料および／または空隙の組合せは、構造体を画成することができる。空隙スペースを使用することによって、所定の構造体内の物理特性に大きな対比をもたらすことができる。機能特性は、空隙スペースの使用によって強化または実現することができる。同様に、光学的格子を画成することができる。

【００８７】
実質的に滑らかな表面膜をここに開示した方法の実施形態にしたがって堆積することができるため、膜を用いて、大きな粗度を示す金属、セラミックおよびプラスチックのような基板層を平坦化することができる。

【００８８】
Ｆ．発光膜
材料は、多くの発光処理においてエネルギーを吸収し、光子を放出することができる。かかる発光事象は、主要相（またはホスト）のみを含むか、または付加的な要素も含むことができる。単一材料は、多くの発光添加剤用のホストとして機能することができる。開示した膜組成の多くは、スペクトルの紫外部に潜在的に延在する透明度で可視的に透明である。かかる材料は、発光ホスト材料として潜在的によく機能する。該材料に、一例として、限定することなく、Mn^{2+}，Sb^{3+}，Sn^{2+}，Bi^{3+}，Eu^{3+}，Tb^{3+}，Eu^{2+}，Gd^{3+}，Tm^{3+}，およびそれらの組合せを含む一般的な発光イオンを選択的にドーピングして、照明およびディスプレイ用途に有益な発光膜を生成することができる。

【００８９】
Ｇ．プリント電子機器
製造業者は、従来の蒸着およびリソグラフィー処理の制限を排除する新しく、効率的な製造方法を探究している。印刷および関連するマスクのない技術が、裏面電子機器の製造効率における進歩を実現するための経路として広く認められている。

【００９０】
ここに開示した溶液処理した薄膜は、最も進歩した気相処理方法によって達成したものと類似した形態的で装置機能的特性を示す。ここに開示した組成の溶液を、例えばミクロ接触、グラビア印刷、インクジェットプリンタまたは他の適切な手段でインプリントすることができる。生成したインプリント溶液を用いて、約２０ｎＡ／cm^2未満の誘電体漏洩電流密度で約１０cm^2／Ｖｓの装置移動度を示す安定な無機トランジスタアレイを製

造することができる。また、誘電体および半導体インクをガラス基板上に印刷して、約５ｃｍ^2／Ｖｓの移動度と、約１００ｎＡ／ｃｍ^{2}未満の誘電体漏洩電流とを有するトランジスタアレイを製造することができる。ＭＩＭコンデンサアレイは、約５を越える相対誘電定数および約５０ｎＡ／ｃｍ^{2}未満の漏洩電流密度で製造することができる。

【実施例】

【００９１】

ＩＶ．実施例

以下の実施例は、本発明の実用的および／または仮説の実施形態の特定の特徴を例示するために提供する。当業者は、本発明の範囲がこの実施例に述べた特定の特徴に限定されないことを理解することができる。

【００９２】

（実施例１）

この実施例は、大量の沈殿物用の給源として、または薄膜前駆体として使用するための溶液を調製するのに用いる一般的な方法を開示する。以下の試薬$HfOCl_2 \cdot 8H_2O$（Ａｌｆａ　Ａｅｓａｒ，１．５％Ｚｒを除いて９９＋％）；$ZrOCl_2 \cdot 8H_2O$（Ｗａｓｈ　Ｃｈａｎｇ　分光写真分析グレード）；$La_2(SO_4)_3$（Ａｌｆａ　Ａｅｓａｒ，９９．９％）；$La(NO_3)_3 \cdot 6H_2O$（Ｊｏｈｕｎｓｏｎ　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％）；NH_3（ａｑ）（ＥＭ　Ｓｃｉｅｎｃｅ，ＧＲ　ＡＣＳ，２８－３０％）を用いた。$HfOCl_2$または$ZrOCl_2$を$La_2(SO_4)_3$，$Ce_2(SO_4)_3$またはＣａＯと一緒にして約０．８Ｍの全金属濃度にし、続いて硫酸塩溶液を加えて約０．５Ｍの全金属濃度とすることにより、全ての溶液を調製した。これら溶液を、熱誘導沈殿およびスピンコーティング誘電体膜用に直接用いた。所用に応じて、追加の修正を行って、水酸化物沈殿反応またはナノ積層堆積用の前駆体として機能させた。

【００９３】

（実施例２）

この実施例は、実施例１に従って作製した溶液からの多量な沈殿のために用いた一般的な方法を開示する。溶液のチューブを沸騰水浴に４０分間浸漬することによって沈殿を誘起した。水酸化物誘起沈殿関しては、$HfOCl_2$および$La_2(SO_4)_3$を２３％Ｌａ（金属パーセント）として混合し、続いて$La(NO_3)_3$および$(NH_4)_2SO_4$の溶液を添加して、約０．３９Ｍのハフニウム濃度（［Ｈｆ］）と、約０．１８Ｍのランタン濃度（［Ｌａ］）と、約０．４２Ｍの硫酸塩濃度（$[SO_4]$）とを付与した。次いで、１．９モル当量（全金属に対し）の飽和NH_3（ａｑ）をすばやく添加し、生成した混合物を１分間攪拌する。全沈殿物を上澄み液から、脱イオン水での数回の洗浄を含む吸引濾過によって分離した。濾液を室温で１日乾燥させた。続いて、サンプルを大気中のアルミナるつぼ内で約１００℃～約１５０℃の温度で約１～４時間加熱した。ＸＲＤデータは、Ｃｕ　Ｋα放射線を用いるＳｉｅｍｅｎｓのＤ５０００回折計器で収集した。熱重量データは、サンプル（１０～２０ｍｇ）をＰｔるつぼ内でN_2（ｇ）の流動下通常１０℃／分の速度で加熱し、より高温度で１５分間保持した後ＳｈｉｍａｄｚｕのＴＧＡ－５０で収集した。誘導結合プラズマ原子発光分析（ＩＣＰＡＥＳ）をＪｏｂｉｎ　Ｙｖｏｎ　ＪＹ２０００分析装置を用いて行った。サンプルを２００℃の消化ボンベ内で数時間溶解し、測定可能なレベルまで希釈した。

【００９４】

（実施例３）

この実施例は、実施例１に従って作製した溶液を用いる薄膜の堆積に用いる一般的な方法を開示する。ＨａｆＳＯｘ，ＺｉｒｃＳＯｘおよびそのＬａ，Ｃｅ，またはＣａを加えた誘導体の薄膜を、３０００ｒｐｍで３０秒間のスピンコーティングによってＳｉ基板上に堆積し、その後すぐに１３５℃で１．５～２分間ホットプレート重合させた（ある誘導

体に対しては、３２５℃オーブンで１５秒～２分間のさらなる加熱が必要である）。所定の堆積膜厚さが得られるまでこの処理を繰り返した。３２５℃で５～１０分間の最終オーブンアニーリングを用いた。

【００９５】

ナノ積層体膜用の前駆体は、H_2SO_4を$HfOCl_2$または$ZrOCl_2$に金属に対し４６％の硫酸塩として加えることによって調製された。溶液を０．０３～０．１３Ｍの金属濃度まで希釈した。ＨａｆＳＯｘおよびＺｉｒｃＳＯｘの交互層を、誘電体膜に関して説明したのと同じようにして堆積した。

【００９６】

シリコン基板は、SiO_2またはＴａ金属の表面を有する。５００ナノメートルＴａ表面を誘電体試験に用いた。２００ナノメートルSiO_2表面を他の全ての目的のために用いた。かかる堆積用の表面は、４５℃の溶液（Ｄｅｃｏｎ　Ｌａｂｓ，Ｃｏｎｔｒａｄ７０）中で４５分間超音波洗浄し、次いで堆積前にミリポア水で表面を十分にすすぐことにより調製した。

【００９７】

ＸＲＤデータは、５０ｋＶおよび２７０ｍＡで回転陽極から発生したＣｕ　Ｋα放射線を用いてＲｉｇａｋｕのＲＡＰＩＤ回折計器で収集された。入射ビーム角度は７．６°であり、回折ビームを画像プレートで収集した。ＸＲＲデータは、Ｃｕ　Ｋα放射線で収集された。１０°（２θ）までの低角度反射は、０．００５°ステップで収集された。透過ＦＴＩＲデータは、未被覆基板を参照として用いるＮｉｃｏｌｅｔ　５ＰＣ分光計で収集された。ＥＰＭＡを収集した。

【００９８】

ＭＩＭコンデンサ構造体は、堆積した誘電体上にＡｌの円形接点（直径１．２ｍｍ）を熱的に蒸着することによって完成させた。誘電定数および損失正接のパラメータが得られた。また、底部ゲートトランジスタ構造体を、活性的に加熱することなく無機チャネル材料をスパッタすることによって製造した。その後、ＺＴＯチャネル装置を３２５℃まで１時間加熱した。アルミニウムソースおよびドレイン接点を熱的に蒸着させた。トランジスタの特性解析を行った。

【００９９】

（実施例４）

この実施例は、約２ｎｍ程の厚さの滑らかで、高密度のピンホールがない超薄ナノ積層体膜を製造するための一般的な方法を開示する。$HfOCl_2 \cdot 8H_2O$または$ZrOCl_2 \cdot 8H_2O$と，H_2O_2（３０％）と、H_2SO_4（ａｑ）とを含有する前駆体溶液を特許文献３に記述されたように調製した。該前駆体溶液は、金属に対して７０％H_2O_2および５０％硫酸塩で約０．０５Ｍ～０．４Ｍの金属イオン濃度を有した。金属イオン濃度における違いは、３ｎｍ～２５ｎｍのコーティング変化ごとの厚さを可能にした。薄膜を、熱成長したSiO_2を有するシリカ基板上に堆積した。基板は、Ｃｏｎｔｒａｄ７０溶液を有する超音波浴を４５℃で６０分間用い、続いて脱イオン水ですすぐことにより清澄にした。膜は、３０００ｒｐｍの回転速度を有するスピンコーターを３０秒間用い、その後１２５℃で１～２分間ホットプレート重合することにより堆積させた。スピンコーティングおよび重合工程は、所定の厚さに達するまで繰り返した。所定の厚さに達した後は、いくつかの膜を結晶化温度まで加熱した。他の膜は、まず０．１Ｍ～０．５ＭＮａＯＨ浴中で１～２分間処理し、その後熱処理の前に脱イオン水浴で１～２分間すすいだ。

【０１００】

Ｘ線回折（ＸＲＤ）分析を用いた薄膜の特性解析は、Ｃｕ　Ｋα放射線を用いるＲｉｇａｋｕのＲ－ＡＸＩＳ　ＲＡＰＩＤ上で行った。原子間力顕微鏡（ＡＦＭ）測定は、Ｖｅｅｃｏ　ＮＰ－２０　ＳｉＮプローブと接触モードでかつ１．１５Ｈｚの走査周波数で動作するＤｉｇｉｔａｌ　Ｉｎｓｔｒｕｍｅｎｔｓ　Ｎａｎｏｓｃｏｐｅ　ＩＩＩ　Ｍｕｌｔｉｍｏｄｅ　ＡＦＭを用いて行った。Ｘ線反射性（ＸＲＲ）測定は、Ｂｒｕｋｅｒ　Ｄｉｓｃｏｖｅｒ　Ｄ８を用いて行い、膜の表面および界面の粗度を画定するのに用いた。

組成分析は、４個の調節可能な波長分散分光計を備えたＣａｍｅｃａ　ＳＸ－５０電子マイクロプローブ上で得た。１２，１６および２２ｋＶの加速電圧を用い、５点にわたって平均化してＯ，Ｃｌ，Ｎａ，ＳおよびＳｉ　Ｋα強度とＺｒおよびＨｆ　Ｌα強度とをモニターした。分析に用いる規格は、ＭｇＯ，Ｈｆ，Ｚｒ，FeS_2（黄鉄鉱），$Ca_5(PO_4)_3Cl$（リン灰石），Ｓｉ，およびSi_3AlNaO_8（曹長石）であった。原料強度に対する修正は、Ｗｉｎｄｏｗｓ自動化および分析パッケージ用のプローブを用いることによって行った。ＳｔｒａｔｅＧＥＭ組成分析ソフトウェアパッケージは、計算値と実験Ｋ比を比較することによって薄膜構造修正に用いた。

【０１０１】

アモルファスで、原子的に平坦で、高密度なピンホールのない薄膜は、堆積したままで交換した膜用のスピンコーティングにより堆積させた。図１９は、約０．１ｎｍの粗度を有する未交換のＨａｆＳＯｘ膜のＡＦＭ画像である。図２０は、ＨａｆＳＯｘのイオン交換および８５０℃での熱処理を行った後のＨａｆＳＯｘのＴＥＭ画像である。未交換膜は、Ｚｒに対しては６００℃、Ｈｆに対しては６５０℃まで滑らかでアモルファスのままであった。しかし、これら温度以上に加熱した後、膜は結晶化し、でこぼこになり、表面に火山状の容貌を形成する。図２１は、シリカ上に堆積したHfO_2膜のＡＦＭ画像である。該HfO_2膜は、ＨａｆＳＯｘの熱分解によって形成された。生成した膜は、約５ｎｍの粗度を有し、火山状のピークをもたらす。これら容貌は、SO_3の損失によってほぼ起こった。これは、Ｈｆ硫酸塩粉体の熱的重量分析によって支持され、硫酸塩分解（SO_3（ｇ）→SO_2（ｇ）と$1/2O_2$（ｇ）が７００℃以上で起こる。

【０１０２】

火山作用を排除するため、膜を０．１～０．５ＭのＮａＯＨ（ａｑ）浴中で１～２分間処理して、加熱する前に膜からSO_4^{2-}およびCl^-アニオンを除去した。ＮａＯＨは、ジルコニウム塩における他のアニオンに対しヒドロキシアニオンを効果的に交換することがすでに示されている。ＮａＯＨ処理は、４０～４５％の厚さ減少を生起（２～１５ｎｍの層厚を付与）するが、ジルコニアおよびハフニアに対しそれぞれ５００℃または５５０℃以下に加熱したとき、前記処理は膜の平滑さ（～１Å）またはアモルファス性にほとんど影響を与えなかった。

【０１０３】

図２２は、シリカ上に堆積し、その後０．１ＭのＮａＯＨで処理し、４５０℃まで１０分間加熱したＨａｆＳＯｘ膜のＡＦＭ画像である。生成した膜は、約０．１ｎｍの粗度を有した。これら温度以上に加熱した膜は結晶化したが、８５０℃までの温度で滑らかなままであった。

【０１０４】

図２３は、シリカ上に堆積し、その後０．１ＭのＮａＯＨで処理し、８５０℃まで１０分間加熱したHfO_2膜を示す。生成した結晶化膜は、約０．２ｎｍの粗度で滑らかさを維持した。

【０１０５】

結晶化温度降下が、Ｘ線回折プロットにおいて見られた（図２４～２７）。図２４～２７において、基板のピークをソフトウェアで除去した。*は、主要な正方晶相のピークを示す。図２４は、７００℃で正方晶相と単斜晶相との混合物として結晶化した未処理のHfO_2膜のＸＲＤプロットである。HfO_2プロットは、単斜晶相に対する参照プロットである。これに対し、図２５は、５５０℃で単斜晶相のみに結晶化した０．１ＭのＮａＯＨで処理したハフニア膜のＸＲＤプロットである。HfO_2プロットは、単斜晶相に対する参照プロットである。図２６は、６５０℃で単斜晶相および正方晶相の混合物に結晶化した未処理のジルコニウム膜のＸＲＤプロットである。ZrO_2プロットは、単斜晶相に対する参照プロットである。図２７で明らかなように、０．１３ＭのＮａＯＨで処理したジルコニア膜は、５００℃で正方晶相のみに結晶化した。さらに加熱すると、膜は正方晶相と単斜晶相との両方に発達した。HfO_2およびZrO_2の正方晶相は、前述の薄膜研究において観察されている。低い結晶化温度、結晶化および厚さの減少は、ＮａＯＨ処理

が薄膜からアニオン（SO_4^{2-}またはCl^-）を除去することを示した。

【０１０６】

０．４Ｍの$HfO_{1.32}(SO_4)_{0.61}Cl_{0.15}$溶液から堆積し、３５０℃に５分間加熱した膜の電子プローブ微小部分分析（ＥＰＭＡ）は、組成$HfO_{1.32}(SO_4)_{0.61}Cl_{0.15}$の膜を与えた。膜中の塩素は、急速な熱脱水の結果としての動的トラップの成果である。ＮａＯＨ（ａｑ）浴で処理した膜は、測定可能な硫黄レベルを持たず（０．０１原子％未満）、０．３原子％未満のＣｌが観察された。これは、硫黄および塩素がＮａＯＨ（ａｑ）浴中で膜から除去されたことを裏付けた。ＥＰＭＡも、処理後の膜に残る残留硫黄が０．３原子％未満であることを実証した。

【０１０７】

（実施例５）

上述した手法の特定実施形態において、水和したインジウムおよびガリウム硝酸塩（$In(NO_3)_3 \cdot 0.5H_2O$および$Ga(NO_3)_3 \cdot 9.5H_2O$）をメタノール（CH_3OH）に溶解した。最終濃度は、[Ｉｎ]＝０．２８８Ｍで、[Ｇａ]＝０．１７０Ｍであった。次いで、亜鉛粉末を溶液に加え、フラスコを密封する。亜鉛の最終濃度は０．２Ｍであった。１～７日の期間にわたって反応させると、粉末が緩徐に酸化し、溶解して０．６５８Ｍの全金属イオン濃度になった。メタノール溶液を空気中にさらし、メタノールを室温で蒸発させた。次いで、溶液中に残っている固体残渣を０．３９５Ｍの全金属濃度までH_2O中に溶解した。この前駆体溶液を、導電性バック接点を有するSiO_2基板上にスピンコーティングし、４５０℃で１～４時間アニーリングした。アニーリング後、透明でアモルファスな$InGa_{0.6}Zn_{0.7}O_{3.15}$半導体膜が、図２８のＳＥＭ画像に示されるように得られた。アルミニウムソースおよびドレイン接点を、シャドーマスクを介して酸化物半導体膜上に熱蒸着させて薄膜トランジスタ（ＴＦＴ）を形成した。かかるＴＦＴに対する電界効果移動度は、$8\,cm^2\,V^{-1}\,s^{-1}$を超えることが示された。

【０１０８】

（実施例６）

この実施例は、二重層無機リソグラフィー処理の２つの一般的な方法を開示する。第一の実用的実施形態においては、約３０ｎｍ～約６０ｎｍの厚さの$HfSO_x$膜をSiO_2／Ｓｉ基板上に堆積した。この基板を約５０℃にセットしたホットプレート上に直接置き、加熱して膜に構造的完全性を付与した。生成した膜は酸不溶性である。次いで、基板をインクジェットプリンターの加熱したプラテン（約５０℃～約２００℃）上に置き、ここでギ酸銅のラインを熱的インクジェットヘッドを介して基板上に印刷した。ギ酸銅を分解し、加熱により$HfSO_x$膜に拡散して膜を可溶性にする。水ですすぎ、約３００℃までさらに加熱し、希釈酸で現像すると、図２９に示すように描画ラインが明白に示された。

【０１０９】

他の実用的実施形態においてはまた、パターンをフォトリソグラフィーにより生成した。$HfO_{2-x}(SO_4)_x$二重層膜をフィルターなしの重水素ランプを用いて遠ＵＶ光に露出させて、その後の相互拡散および図３０に示すパターンの現像のためにギ酸銅分解を促進した。形態の大きさを、電子ビーム書刻で約２２ｎｍまで減じた。相互拡散処理を電子ビームエネルギーにより空間的に制御して、パターンおよび対象物をナノスケールで描画することができる。高度に解像されたパターンを、多くのポリマーレジストのものと類似した感度を示す$150\,\mu C/cm^2$近い電荷線量レベルで形成した。図３１および３２は、約$200\,\mu C/cm^2$の線量レベルで電子ビーム書刻によって形成した２個のパターンである。図３１において、ライン間隔は、電子顕微鏡によって測定して５００ｎｍである。

【０１１０】

（実施例７）

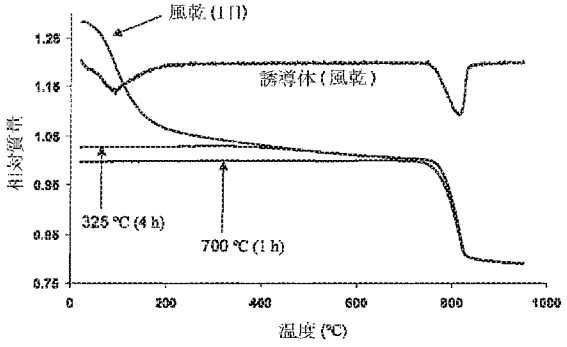
この実施例は、単一層無機膜をパターン化する一般的な方法を開示する。過酸化物又は

関連する配位種を含む単一無機膜を適切な基板上にスピンキャスト、液状ミストまたはインクジェット印刷した。この膜を１００℃未満の適度な温度で加熱して、膜に構造的完全性を付与した。次いで、この膜をフォトマスクを介して高エネルギー光、空間光変調によるマスクなしパターン、所定のレーザービーム、または電子ビームに露出して、パターンまたは他の好ましい膜形態を画成する。写真用にパターン化した膜の２つの例を図３３および３４に示す。図３３は、パターン化$ZrO_{2-x}(SO_4)_x$膜である。図３４はパターン化TiO_2膜である。このTiO_2膜は、厚さ約１５～５０ｎｍである。これは、フィルターなしの重水素ランプを用いてパターン化し、続いて０．１～０．２ＭのＨＣｌで６０秒未満エッチングした。図３５～３７は、電子ビームでパターン化した$HfO_{2-x}(SO_4)_x$膜である。かかる膜は、厚さ約３０～６０ｎｍである。これらを、電子ビームを２００$\mu C/cm^2$の線量レベルで用いてパターン化し、続いて５～１２ＭのＨＣｌで約１～４分間エッチングした。

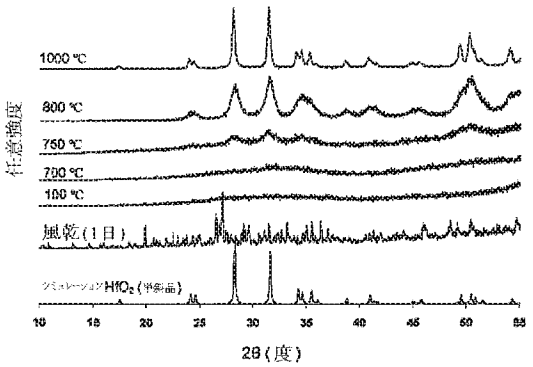
【０１１１】

ここに開示した発明の原理を適用し得る多くの可能な実施形態を考慮すると、図示した実施形態が単に本発明の好ましい実施例であり、本発明の範囲を限定することがないと認識すべきである。それどころか、本発明の範囲は、請求項によって画成される。したがって、この範囲内からくるすべておよびこれらの請求項を、本発明として請求する。

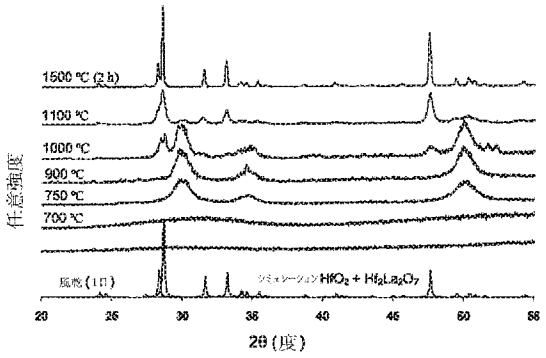
【図１】



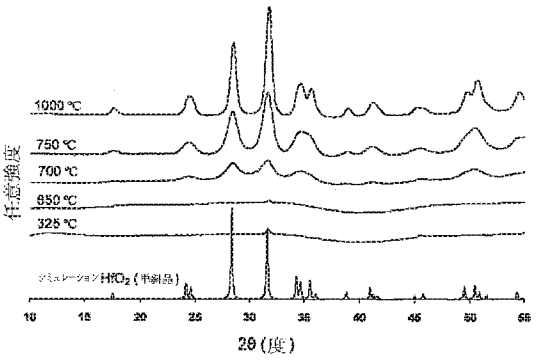
【図２】



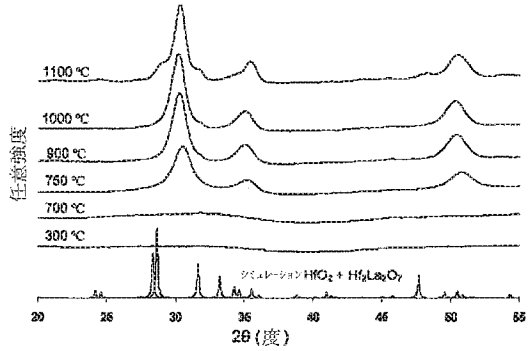
【図３】



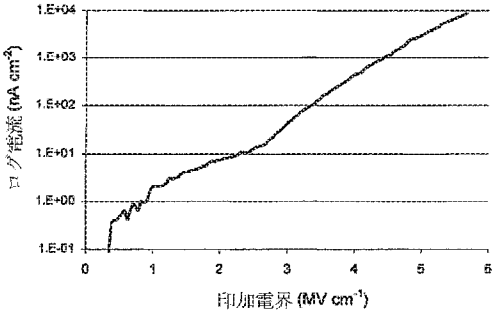
【図４】



【図５】



【図６】



【図７】

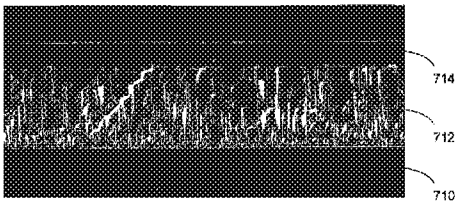


FIG. 7

【図８】

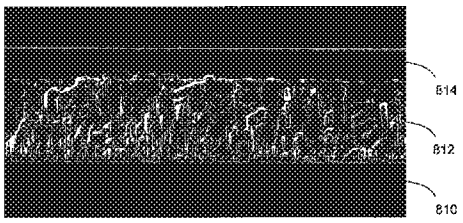
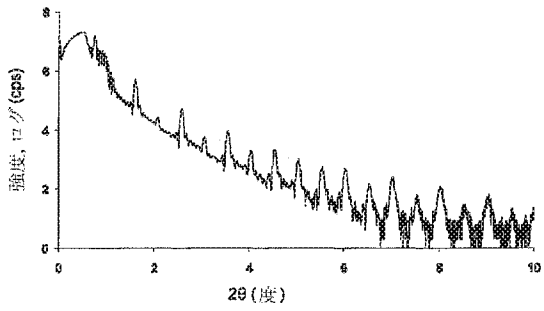


FIG. 8

【図９】



【図１０】

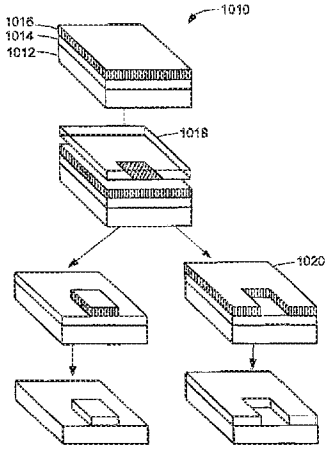


FIG. 10

【図１１】

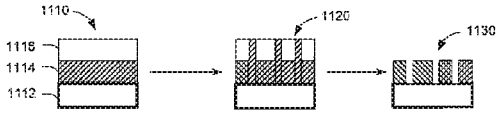


FIG. 11

【図１２】

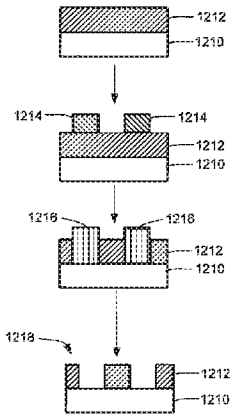


FIG. 12

【図１３】

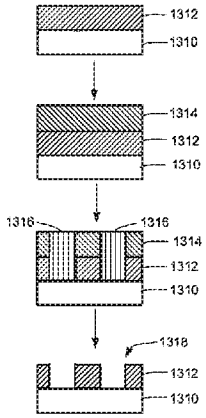


FIG. 13

【図１４】

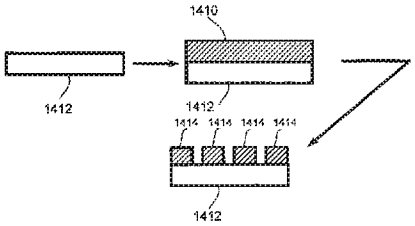
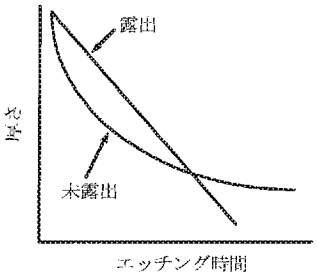


FIG. 14

【図１５】



【図１６】

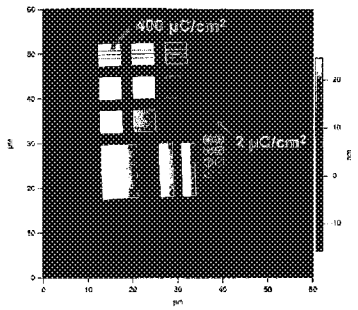


FIG. 16

【図１７】

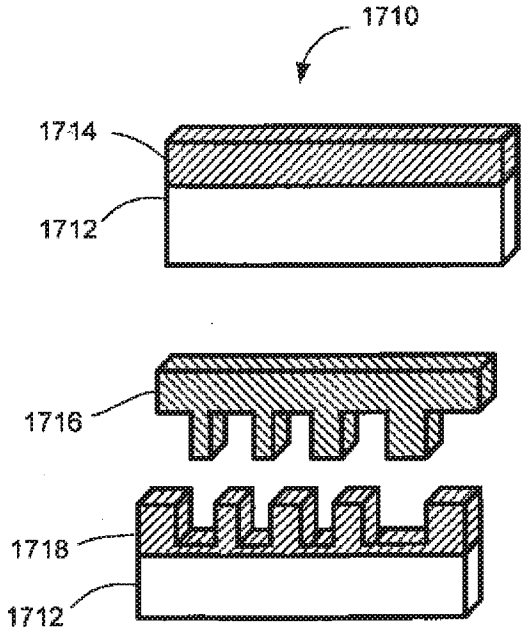


FIG. 17

【図１８】

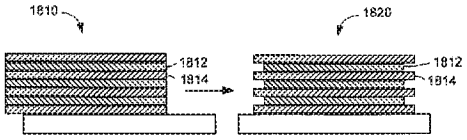


FIG. 18

【図１９】

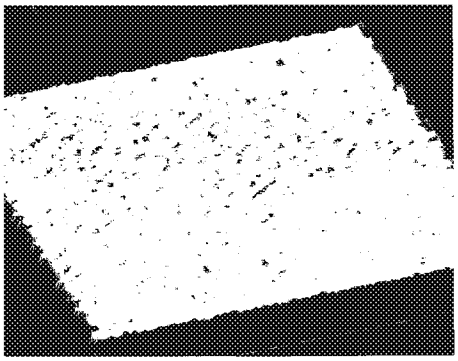


FIG. 19

【図２０】

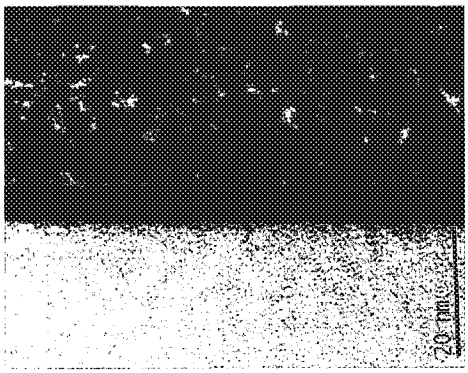


FIG. 20

【図２１】

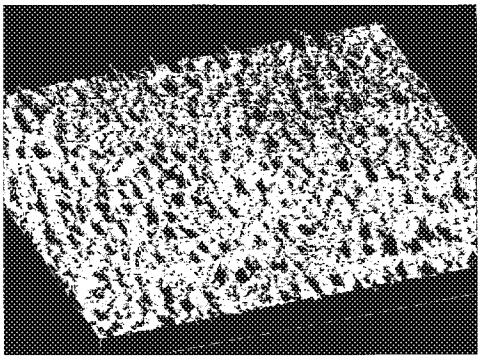


FIG. 21

【図２２】

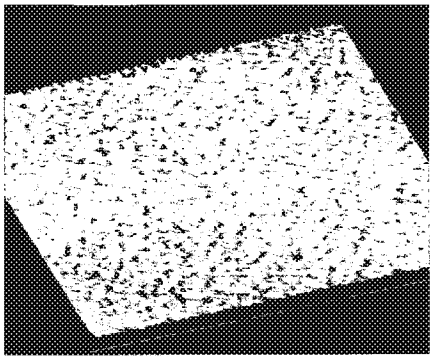


FIG. 22

【図２３】

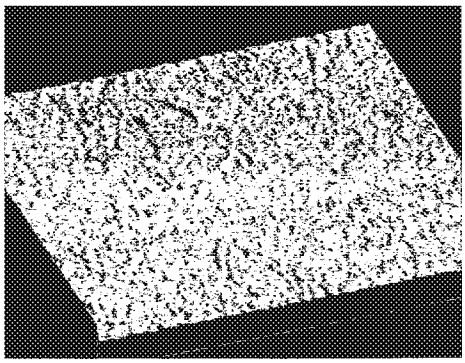
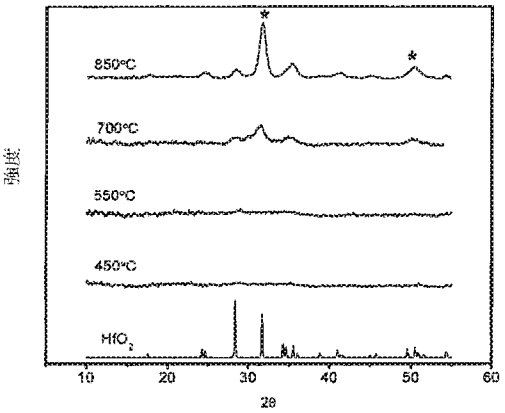
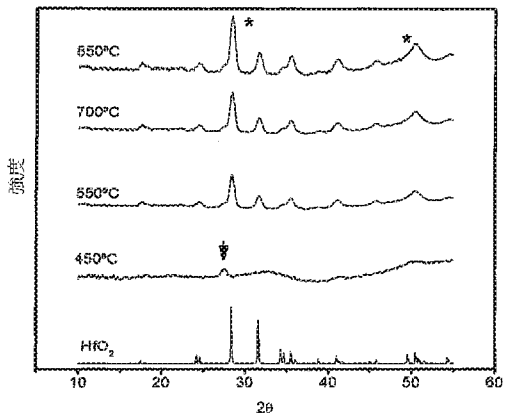


FIG. 23

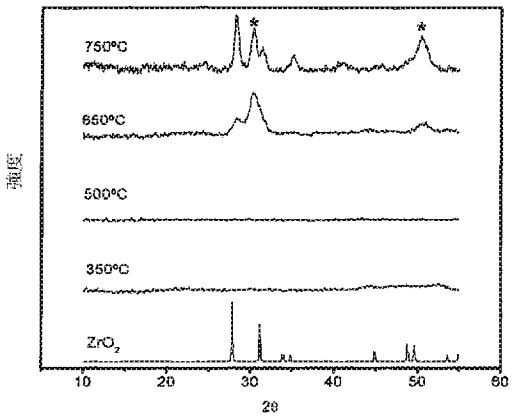
【図２４】



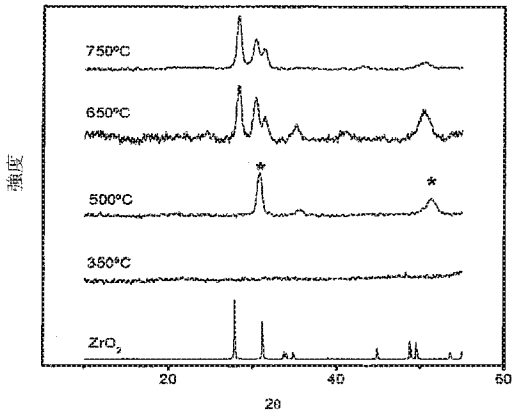
【図２５】



【図２６】



【図２７】



【図２８】

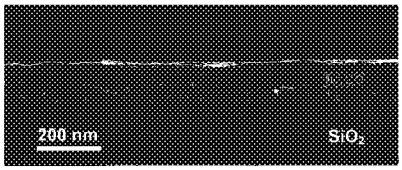


FIG. 28

【図２９】

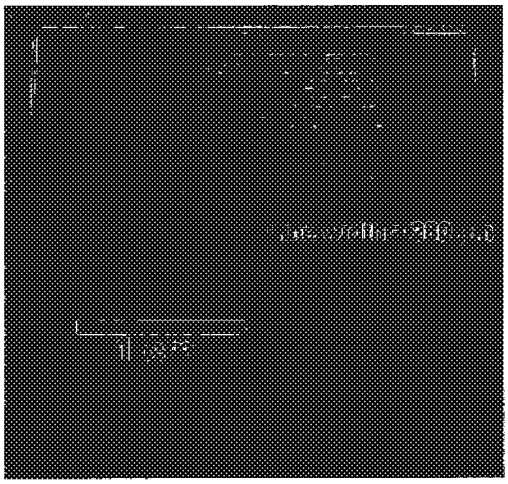


FIG. 29

【図３０】

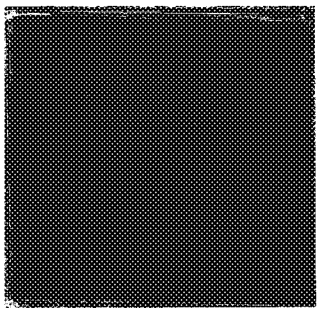


FIG. 30

【図３１】

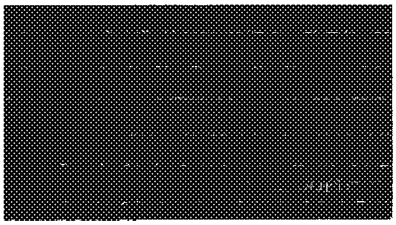


FIG. 31

【図３２】

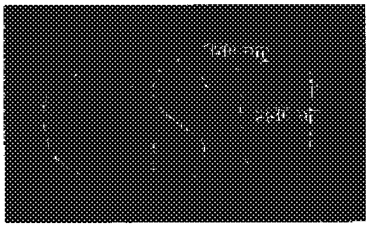
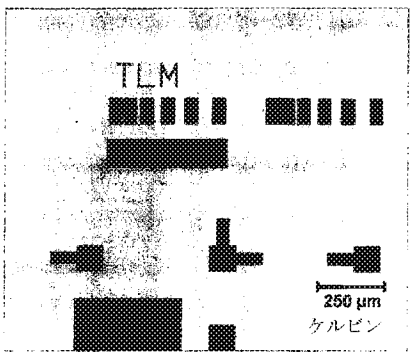
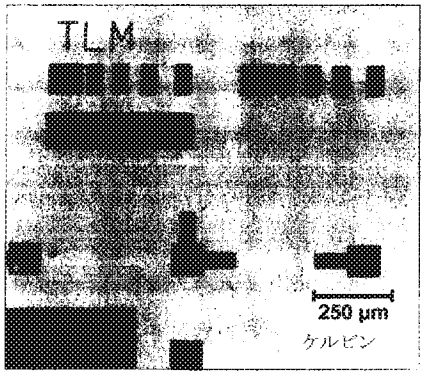


FIG. 32

【図３３】



【図３４】



【図３５】

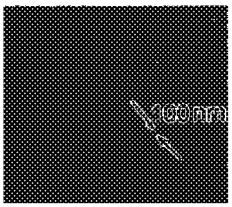


FIG. 35

【図３６】

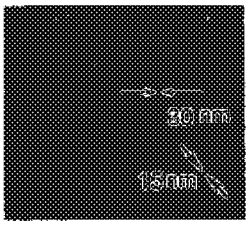
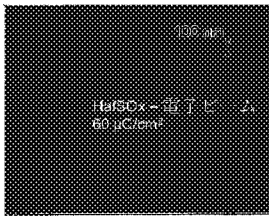


FIG. 36

【図３７】



【手続補正書】
【提出日】平成22年11月25日(2010.11.25)
【手続補正１】
【補正対象書類名】特許請求の範囲
【補正対象項目名】全文
【補正方法】変更
【補正の内容】
【特許請求の範囲】
【請求項１】
少なくとも２個の金属を備える金属酸化物膜を製造するに当たり、
金属カチオンおよび１個またはそれ以上のアニオンから主としてなる１個またはそれ以上の可溶塩を非錯化で、非水性の極性溶媒に溶解して溶液を作製し、前記金属カチオンの少なくとも１個が3^+の形式電荷を有し、3^+の形式電荷を有する金属カチオンの濃度が前記金属酸化物膜にける金属カチオンの５０モル％を越え、また前記溶媒が約１５０℃未満の沸点を有し、
前記溶液のｐＨを上げ、該ｐＨの上昇が、塩基水溶液の添加、少量の可溶性塩基酸化物の添加、塩基水溶液を形成し得るガス状化合物の添加、プロトンを消費し膜内に添合し得る電気的陽性の金属の添加、プロトンを消費するか、もしくは対イオンを分解するが膜に添合しない液状またはガス状の酸化剤の添加、またはその組合せからなり、
非水溶性の溶媒を揮発することによって固体を生成し、
前記固体を水に溶解し、
前記溶解した固体を基板上に堆積してパターン化又はブランケット液体膜を形成し、
前記膜を熱で硬化することを備えることを特徴とする金属酸化物膜の製造方法。
【請求項２】
薄膜または積層構造体を設け、前記構造体が基板と該基板上に堆積した１個またはそれ

以上の層とからなり、前記１個またはそれ以上の層の少なくとも一つが金属‐酸膜を備え、前記金属‐酸膜が金属カチオンと酸アニオンとからなり、
前記酸アニオンを塩基水溶液でのイオン交換によって除去し、前記塩基水溶液がＩ族金属の水酸化物、可溶性のＩＩ族金属の水酸化物、可溶性のＩＩＩ族金属の水酸化物、可溶性のランタニド水酸化物、水酸化アンモニウム、および／または水性第３アミン、またはその組み合わせからなり、
前記構造体をエネルギー源に露出し、前記エネルギー源が熱エネルギー源、マイクロ波エネルギー源、光源、またはレーザーからなることを備えることを特徴とする金属酸化物膜の製造方法。
【請求項３】
前記溶液のｐＨが２～９まで上昇する請求項１に記載の方法。
【請求項４】
前記１個またはそれ以上の可溶性塩を硝酸インジウム水和物、硝酸ガリウム水和物、またはその組み合わせから選択し、前記方法がさらに前記溶液に亜鉛を加えることを備える請求項１に記載の方法。
【請求項５】
請求項１に記載の方法により製造した金属酸化物膜。
【請求項６】
請求項１に記載の方法により製造した金属酸化物膜を備える装置。
【請求項７】
前記金属酸化物膜が半導体である請求項６に記載の装置。
【請求項８】
前記装置が薄膜トランジスタである請求項６に記載の装置。
【手続補正書】
【提出日】平成23年3月24日(2011.3.24)
【手続補正１】
【補正対象書類名】特許請求の範囲
【補正対象項目名】全文
【補正方法】変更
【補正の内容】
【特許請求の範囲】
【請求項１】
少なくとも２個の金属を備える金属酸化物膜を製造するに当たり、
金属カチオンおよび１個またはそれ以上のアニオンから主としてなる１個またはそれ以上の可溶塩を非錯化で、非水性の極性溶媒に溶解して溶液を作製し、前記金属カチオンの少なくとも１個が3^{+}の形式電荷を有し、3^{+}の形式電荷を有する金属カチオンの濃度が前記金属酸化物膜にける金属カチオンの５０モル％を越え、また前記溶媒が約１５０℃未満の沸点を有し、
前記溶液のｐＨを上げ、該ｐＨの上昇が、塩基水溶液の添加、少量の可溶性塩基酸化物の添加、塩基水溶液を形成し得るガス状化合物の添加、プロトンを消費し膜内に添合し得る電気的陽性の金属の添加、プロトンを消費するか、もしくは対イオンを分解するが膜に添合しない液状またはガス状の酸化剤の添加、またはその組合せからなり、
非水溶性の溶媒を揮発することによって固体を生成し、
前記固体を水に溶解し、
前記溶解した固体を基板上に堆積してパターン化又はブランケット液体膜を形成し、
前記膜を熱で硬化することを備えることを特徴とする金属酸化物膜の製造方法。
【請求項２】
薄膜または積層構造体を設け、前記構造体が基板と該基板上に堆積した１個またはそれ以上の層とからなり、前記１個またはそれ以上の層の少なくとも一つが金属‐酸膜を備え、前記金属‐酸膜が金属カチオンと酸アニオンとからなり、

前記酸アニオンを塩基水溶液でのイオン交換によって除去し、前記塩基水溶液がＩ族金属の水酸化物、可溶性のＩＩ族金属の水酸化物、可溶性のＩＩＩ族金属の水酸化物、可溶性のランタニド水酸化物、水酸化アンモニウム、および／または水性第３アミン、またはその組み合わせからなり、

前記構造体をエネルギー源に露出し、前記エネルギー源が熱エネルギー源、マイクロ波エネルギー源、光源、またはレーザーからなることを備えることを特徴とする金属酸化物膜の製造方法。

【請求項３】

前記溶液のｐＨが２～９まで上昇する請求項１に記載の方法。

【請求項４】

前記１個またはそれ以上の可溶性塩を硝酸インジウム水和物、硝酸ガリウム水和物、またはその組み合わせから選択し、前記方法がさらに前記溶液に亜鉛を加えることを備える請求項１に記載の方法。

【請求項５】

請求項１に記載の方法により製造した金属酸化物膜。

【請求項６】

請求項１に記載の方法により製造した金属酸化物膜を備える装置。

【請求項７】

前記金属酸化物膜が半導体である請求項６に記載の装置。

【請求項８】

前記装置が薄膜トランジスタである請求項６に記載の装置。

【請求項９】

水と、金属亜酸化物カチオンと、多原子アニオンと、ペルオキシド基を有する配位種とを含む、水性無機パターン化組成物であって、

前記組成物が、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、Ｎｄ、Ｐｍ、Ｓｍ、Ｅｕ、Ｇｄ、Ｔｂ、Ｄｙ、Ｈｏ、Ｅｒ、Ｔｍ、Ｙｂ、Ｌｕ又はそれらの組み合わせを含む、

水性組成物。

【請求項１０】

前記金属亜酸化物カチオンが、ZrO^{+2}カチオン、HfO^{+2}カチオン又はそれらの組み合わせを含む、請求項９に記載の水性組成物。

【請求項１１】

前記多原子アニオンが、タングステン酸塩、リン酸塩、硝酸塩、ケイ酸塩、アルミン酸塩、ホウ酸塩又はそれらの組み合わせを含む、請求項９に記載の水性組成物。

【請求項１２】

前記多原子アニオンが硫酸塩を含む、請求項９に記載の水性組成物。

【請求項１３】

更に、NH_3、OH^-、F^-、Cl^-、Br^-、I^-、又はそれらの組み合わせを含む、請求項９に記載の水性組成物。

【請求項１４】

コーティング組成物を有する基板を準備する工程であって、該コーティング組成物が金属亜酸化物カチオンと、多原子アニオンと、ペルオキシド基を有する配位種とを含み、該コーティング組成物が、更に、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、Ｎｄ、Ｐｍ、Ｓｍ、Ｅｕ、Ｇｄ、Ｔｂ、Ｄｙ、Ｈｏ、Ｅｒ、Ｔｍ、Ｙｂ、Ｌｕ又はそれらの組み合わせを含む、工程と、

前記コーティングの第１の部分を放射線に露出させ、前記コーティングの第２の部分を放射線に露出させないようなパターンで、前記コーティング組成物を放射線に露出させ、それによって露光されパターン化されたコーティングを形成する工程と、

を含む、基板上に無機金属のパターンを形成する方法。
【請求項１５】
前記放射線が電子ビーム又は紫外光を含む、請求項１４に記載の方法。
【請求項１６】
前記放射線にコーティング組成物を露出させることが、前記露光されたコーティング組成物の第１の部分を濃縮する、請求項１４に記載の方法。
【請求項１７】
前記金属亜酸化物カチオンが、ZrO^{+2}カチオン、HfO^{+2}カチオン又はそれらの組み合わせを含み、
前記多原子アニオンが硫酸塩アニオンを含み、
前記コーティング組成物が、更に、F^-、Cl^-、Br^-、I^-、又はそれらの組み合わせを含む、
請求項１４に記載の方法。
【請求項１８】
更に、放射線への露出後に、前記コーティング組成物の露光されていない第２の部分を除去するエッチング工程を含む、請求項１４に記載の方法。
【請求項１９】
前記エッチングをテトラメチル水酸化アンモニウムで行う、請求項１８に記載の方法。
【請求項２０】
更に、放射線への露出前に、前記コーティング組成物を加熱する工程を含む、請求項１４に記載の方法。
【請求項２１】
前記コーティング組成物を前記放射線パターンに露出させた後で且つ前記露光されたコーティング組成物を酸又は塩基でエッチングして前記コーティング組成物の露光されていない第２の部分を除去する前に、前記コーティング組成物を約１００℃を超える温度に加熱する、請求項１４に記載の方法。
【請求項２２】
更に、前記露光されたコーティング組成物を、塩酸、硫酸、過酸化水素、水酸化ナトリウム、又はテトラメチル水酸化アンモニウムから選択される組成物と接触させ、前記材料の一部を除去して、前記パターンを形成する工程を含む、請求項１４に記載の方法。
【請求項２３】
前記コーティング組成物の厚さが約１ｎｍから約１００ｎｍである、請求項１４に記載の方法。
【請求項２４】
更に、前記露光されたコーティング組成物を現像して、前記露光された材料を除去する工程を含む、請求項２３に記載の方法。
【請求項２５】
前記コーティング組成物を有する基板を準備することが、コーティングされた基板を得ることを含む、請求項１４に記載の方法。
【請求項２６】
前記コーティング組成物を有する基板を準備することが、
水と、金属亜酸化物カチオンと、多原子アニオンと、ペルオキシド基を有する配位種とを含む水性組成物であって、該組成物が、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、Ｎｄ、Ｐｍ、Ｓｍ、Ｅｕ、Ｇｄ、Ｔｂ、Ｄｙ、Ｈｏ、Ｅｒ、Ｔｍ、Ｙｂ、Ｌｕ又はそれらの組み合わせを含む、水性組成物を形成することと、
前記組成物を前記基板の上に堆積させることと、
を含む、請求項１４に記載の方法。
【請求項２７】
金属亜酸化物カチオンと、多原子アニオンと、ペルオキシド基を有する配位種とを含む

水性溶液を混合して、無機パターン化組成物を形成する工程を含み、
前記組成物が、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、Ｎｄ、Ｐｍ、Ｓｍ、Ｅｕ、Ｇｄ、Ｔｂ、Ｄｙ、Ｈｏ、Ｅｒ、Ｔｍ、Ｙｂ、Ｌｕ又はそれらの組み合わせを含む、
無機パターン化組成物の形成方法。
【請求項２８】
前記配位種が過酸化水素を含む、請求項２７に記載の方法。
【請求項２９】
前記多原子アニオンが硫酸塩アニオンを含む、請求項２７に記載の方法。
【請求項３０】
前記金属亜酸化物カチオンが、ZrO^{+2}カチオン、HfO^{+2}カチオン又はそれらの組み合わせを含み、
前記多原子アニオンが、硫酸塩、リン酸塩、硝酸塩、ケイ酸塩、アルミン酸塩、ホウ酸塩又はそれらの組み合わせを含む、
請求項２７に記載の方法。

【国際調査報告】

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
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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 6,197,886 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
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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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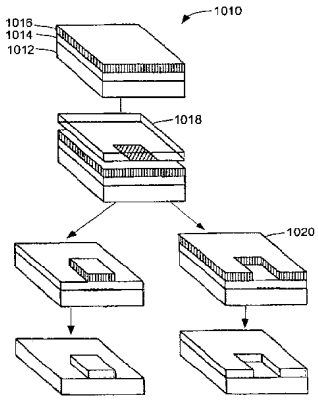
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(54) Title: SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THEIR USE AND MANUFACTURE



(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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— *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

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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 ($T < 325\ ^{o}C$).

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 ($x \sim 0.67$ & 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 ($Fe(CH_3CO_2)_2$, $Cu(CHOO)_2$, 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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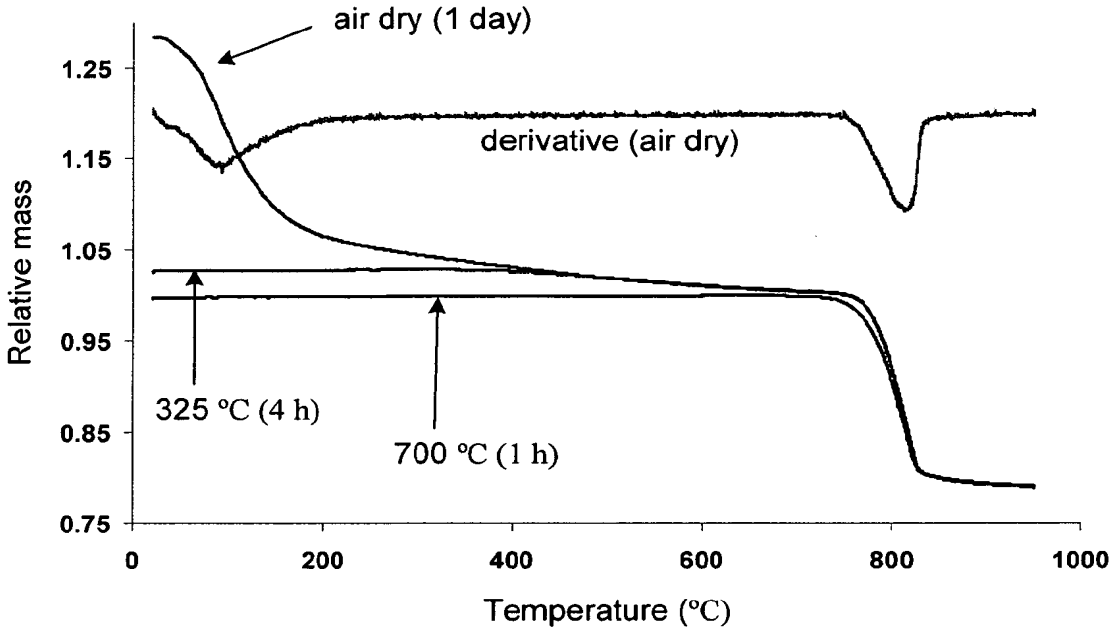


FIG. 1

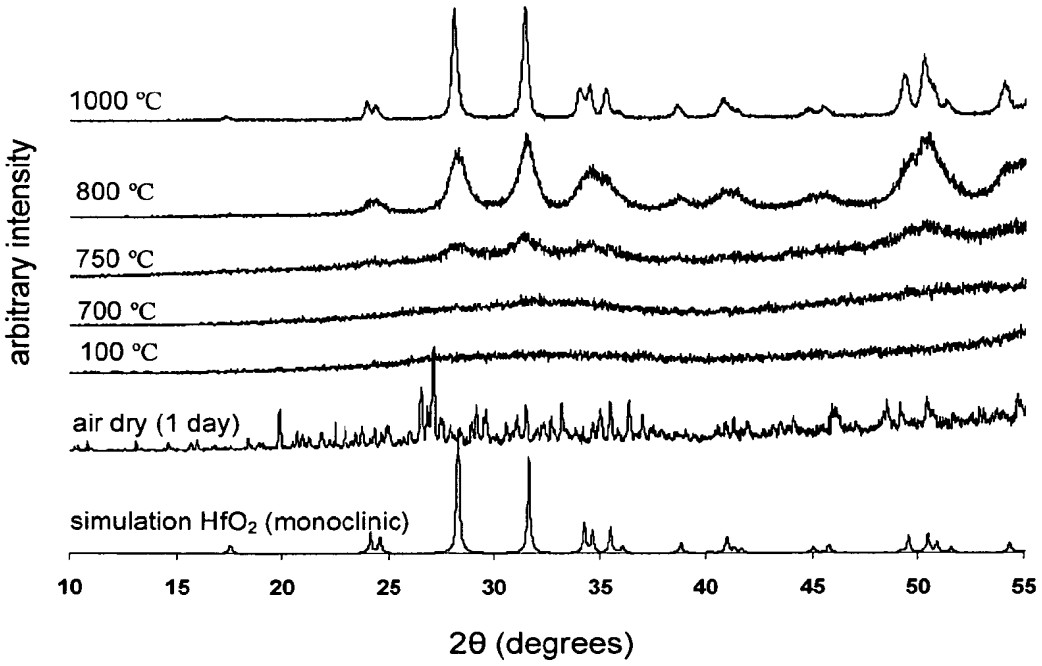


FIG. 2

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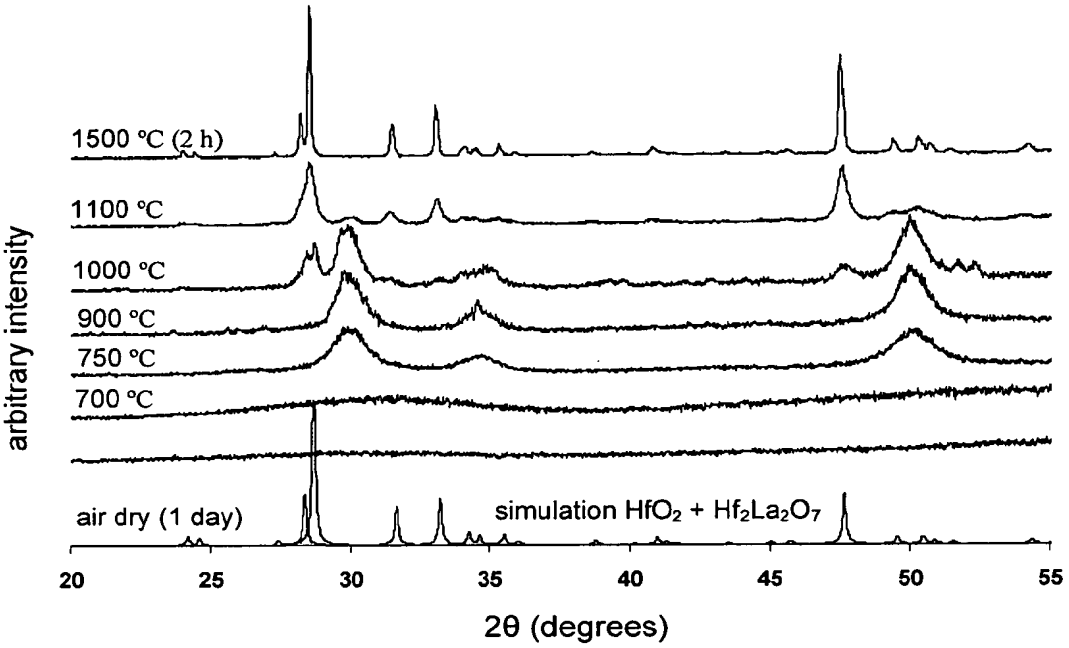


FIG. 3

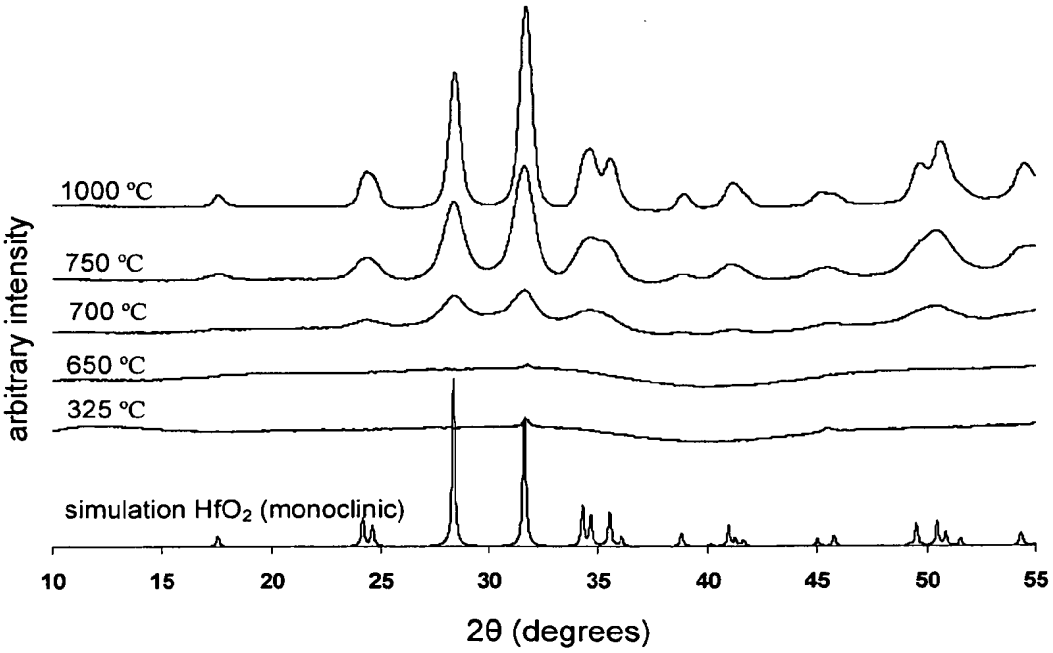


FIG. 4

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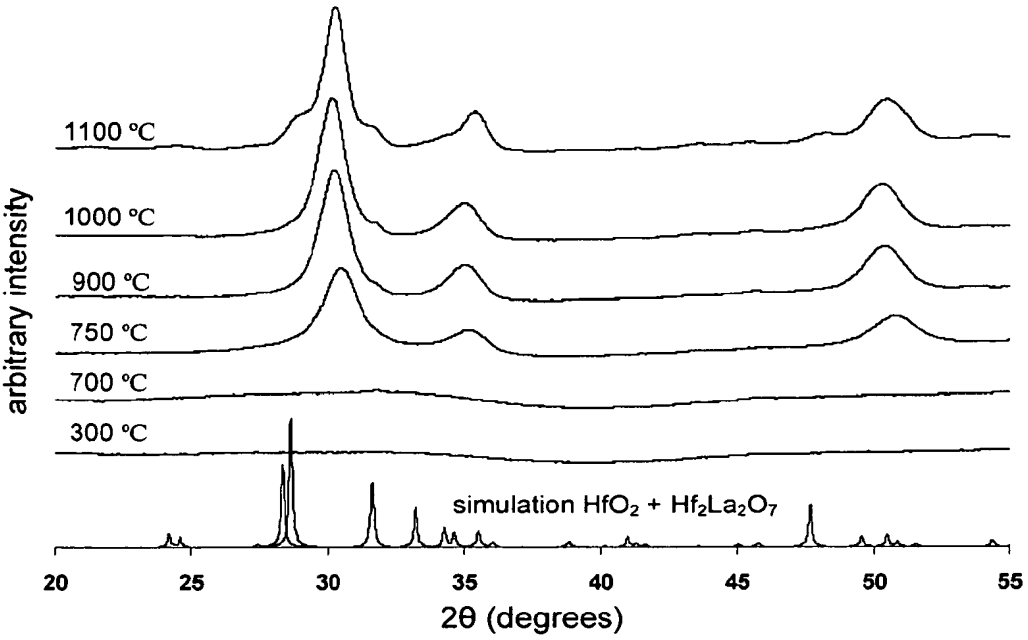


FIG. 5

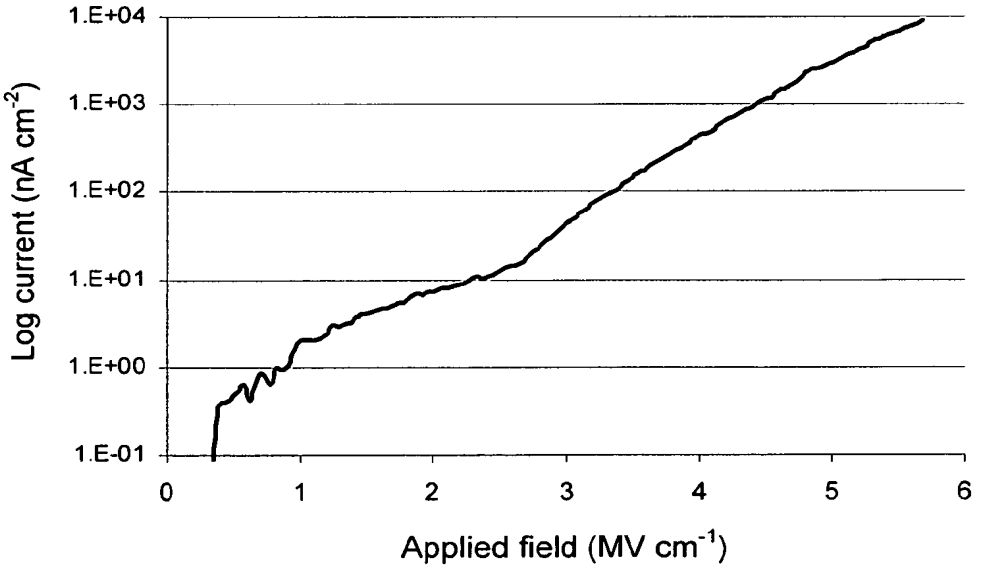


FIG. 6

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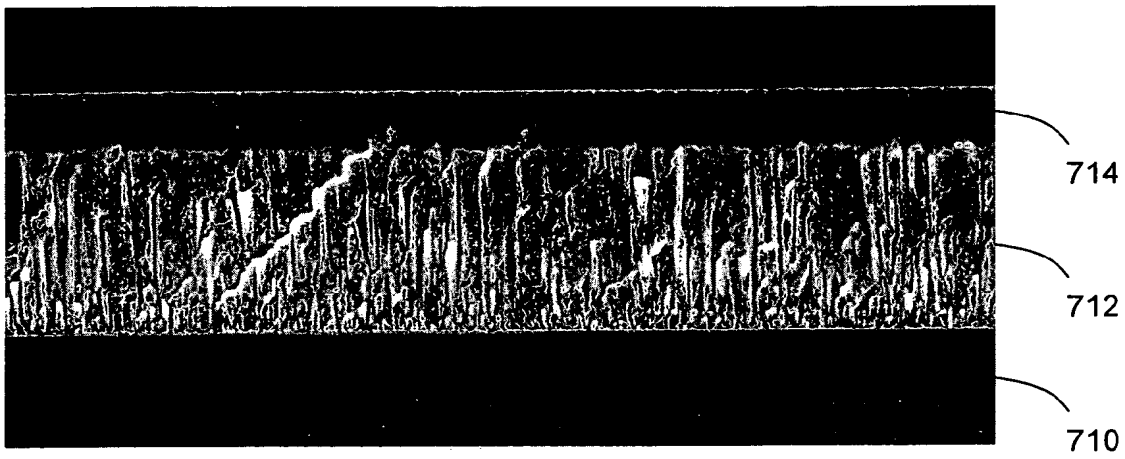


FIG. 7

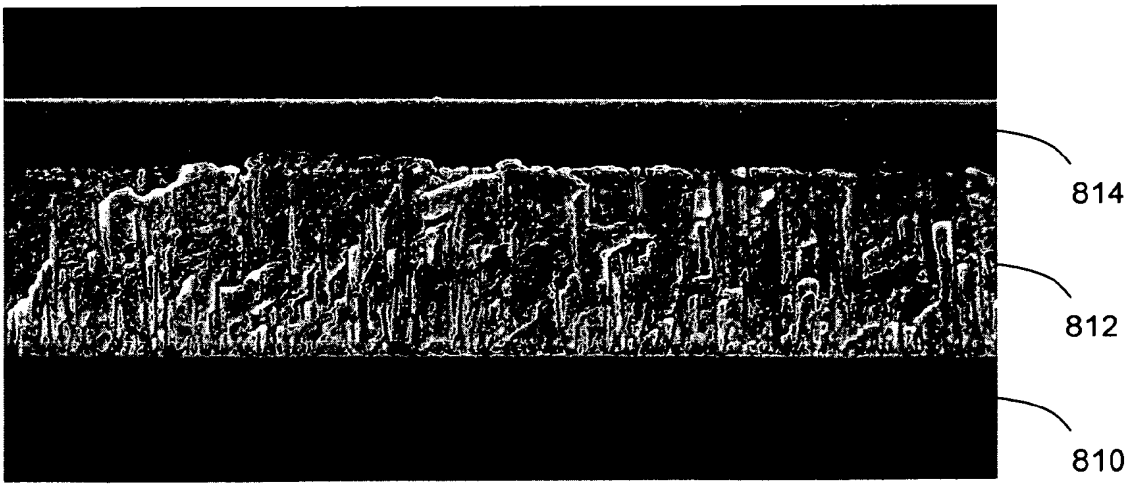


FIG. 8

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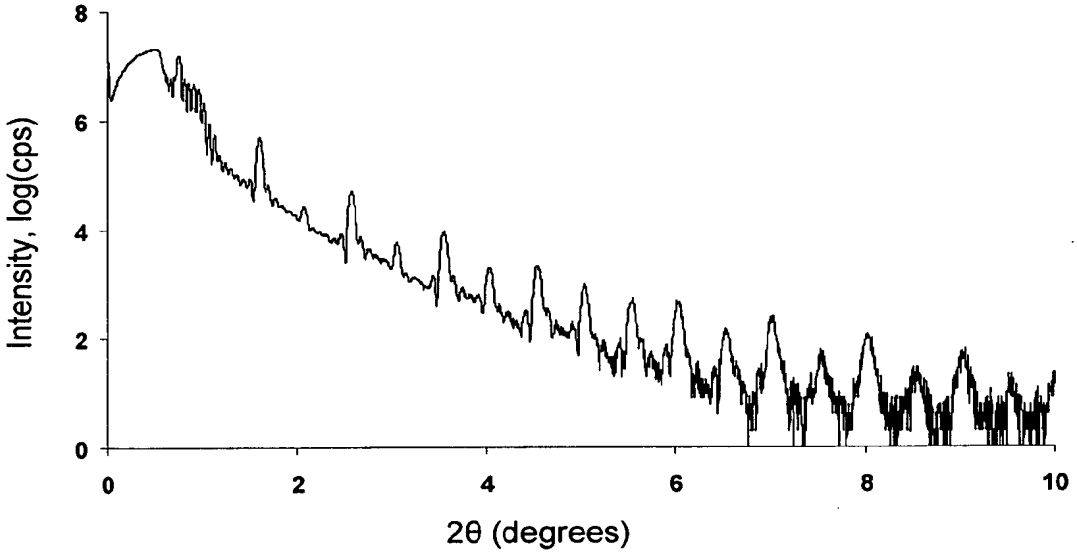


FIG. 9

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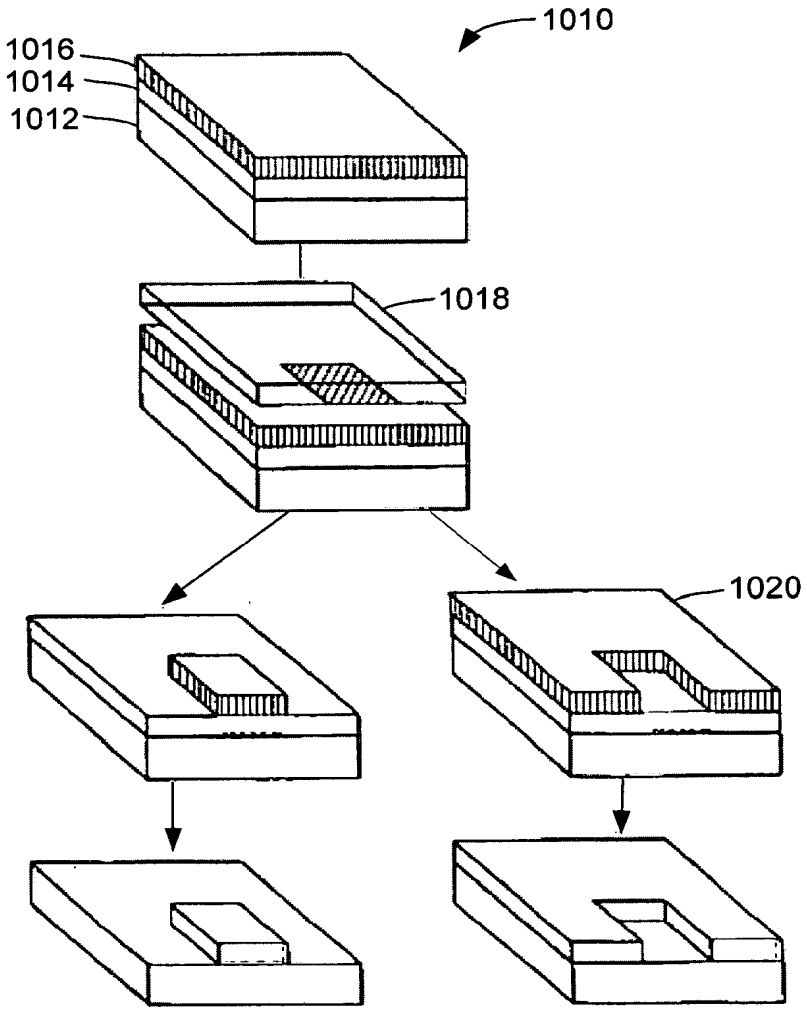


FIG. 10

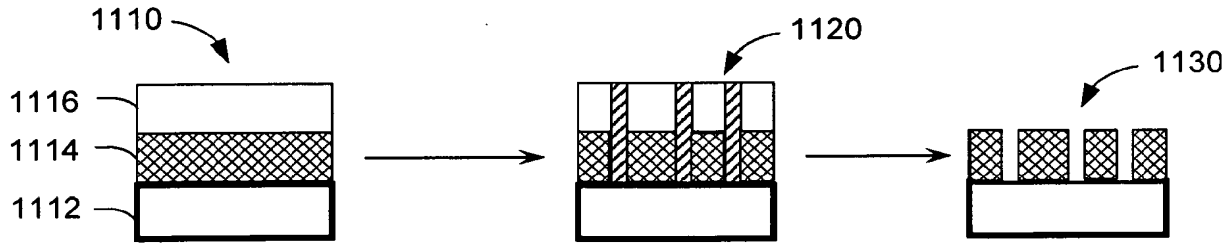


FIG. 11

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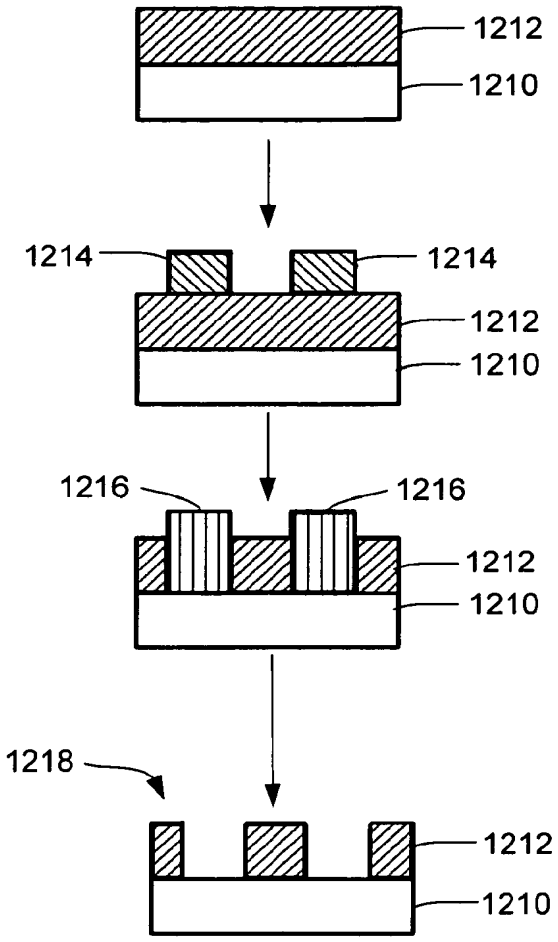


FIG. 12

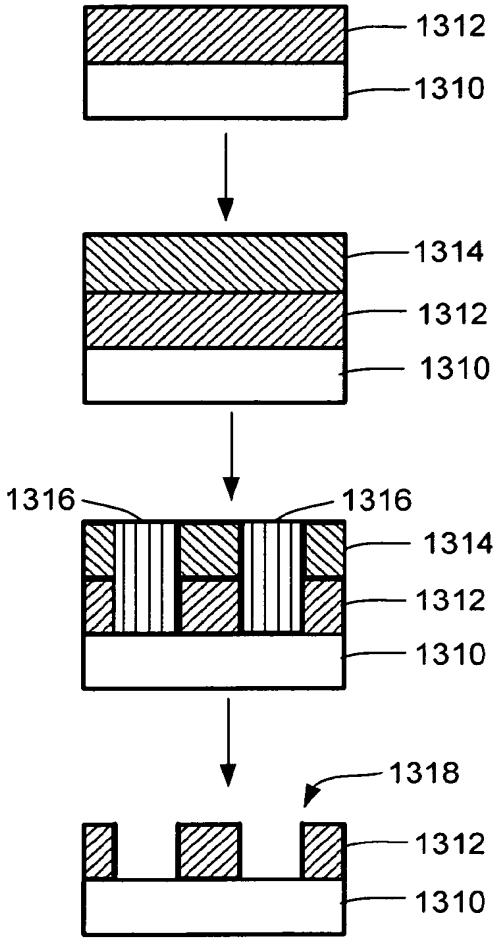


FIG. 13

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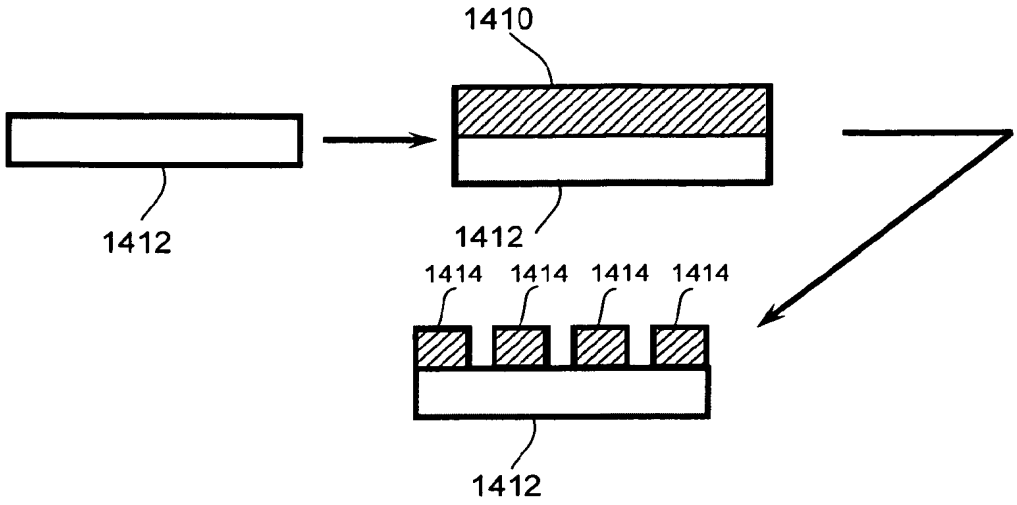


FIG. 14

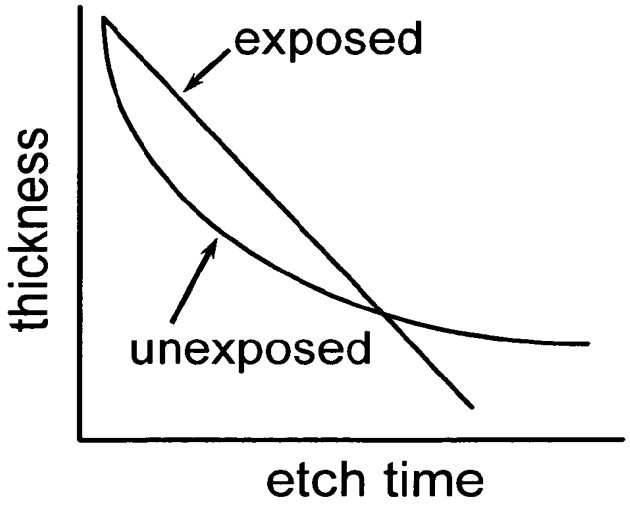


FIG. 15

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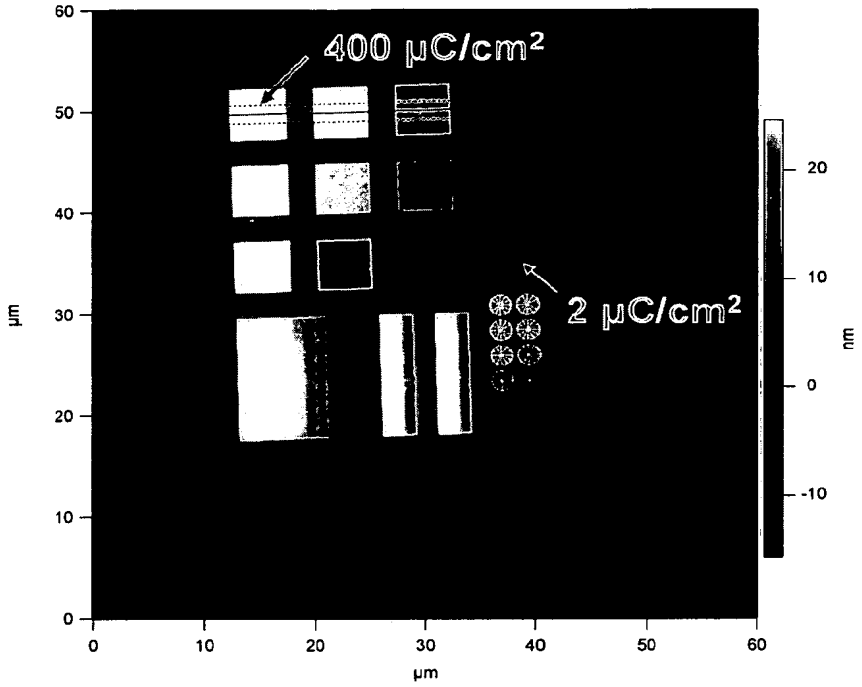


FIG. 16

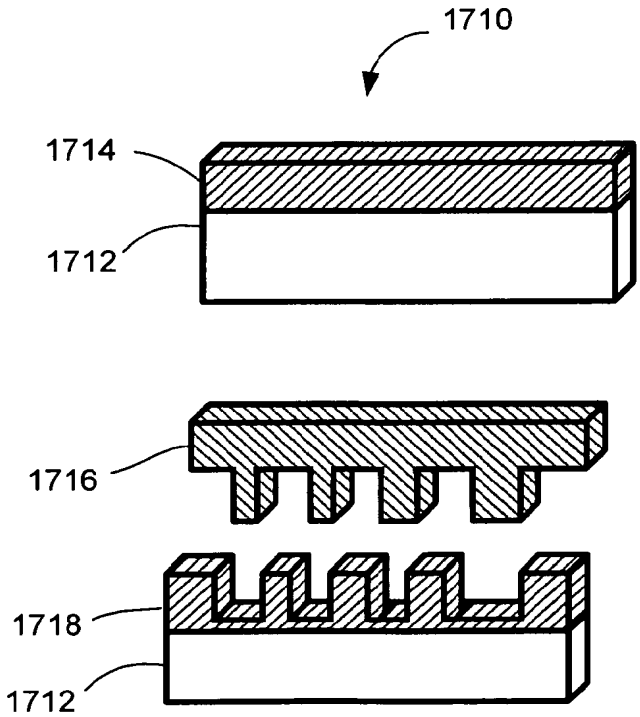


FIG. 17

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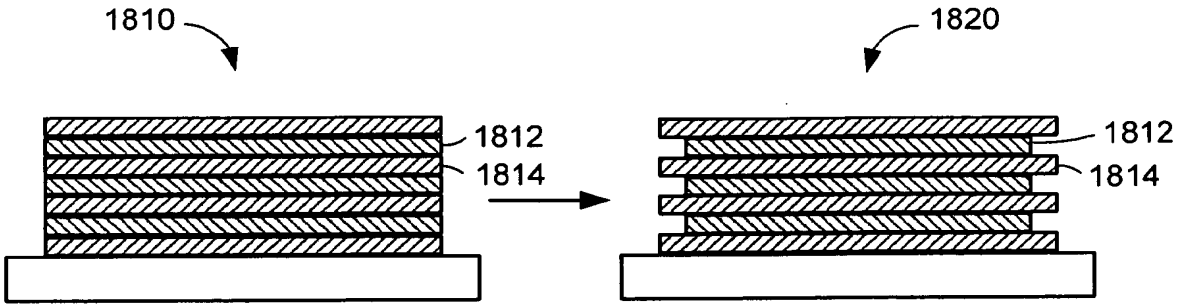


FIG. 18

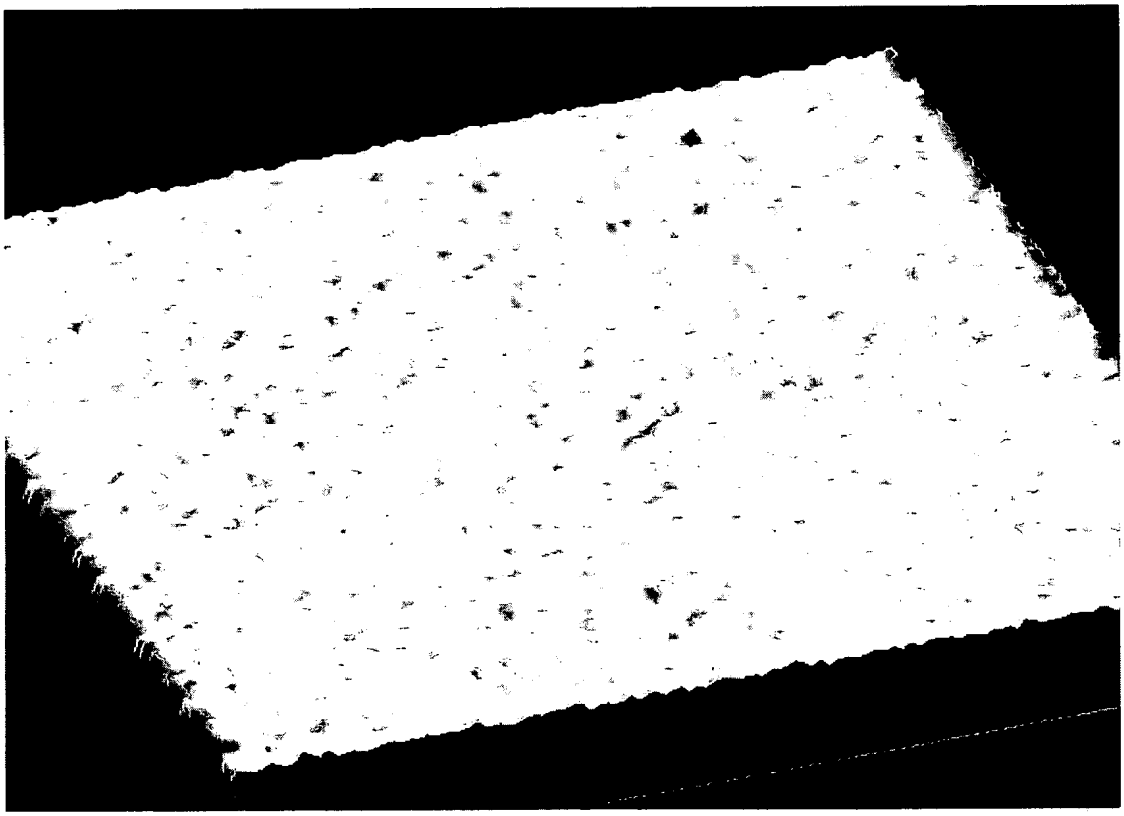


FIG. 19

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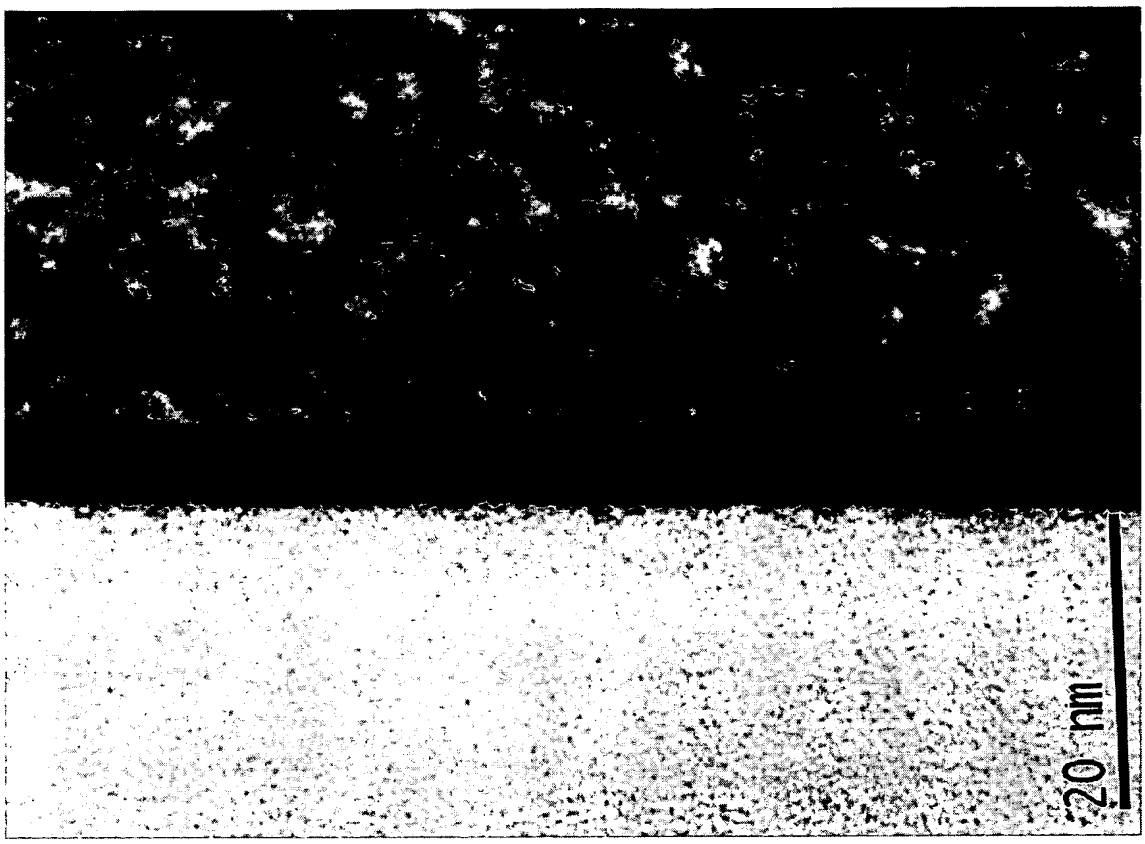


FIG. 20

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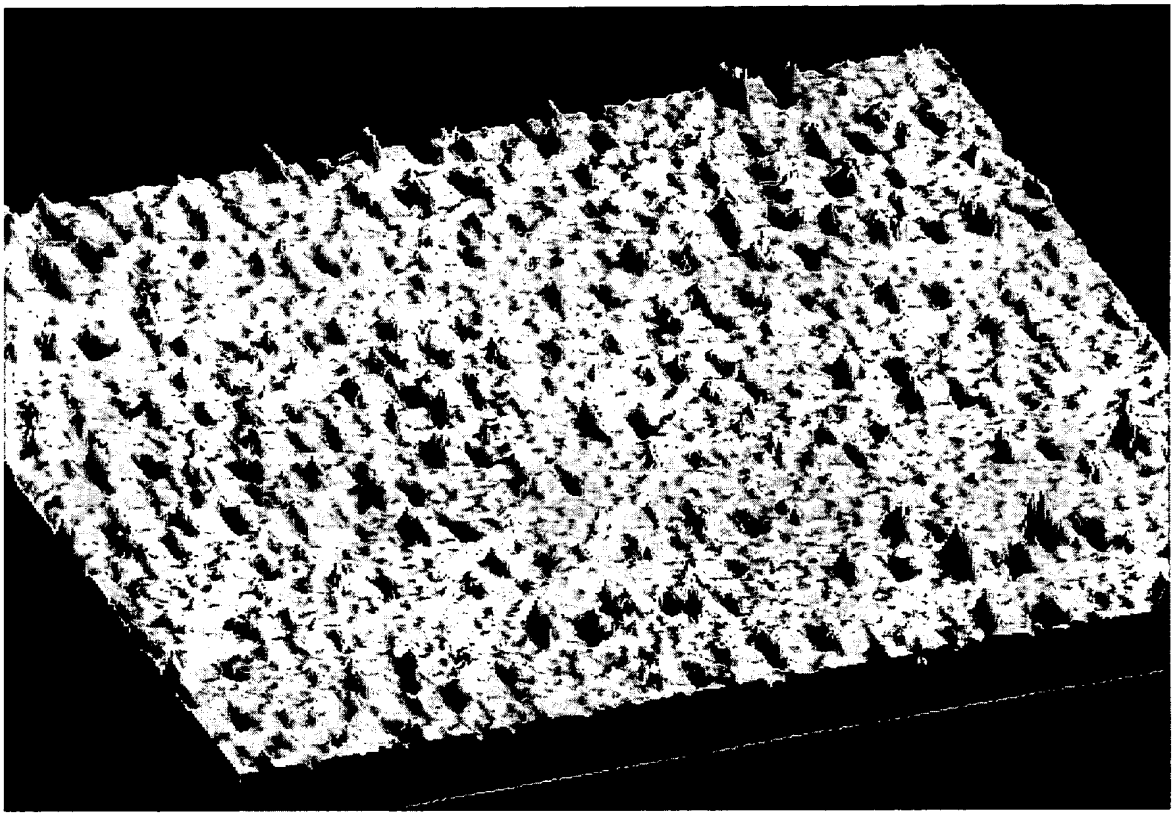


FIG. 21

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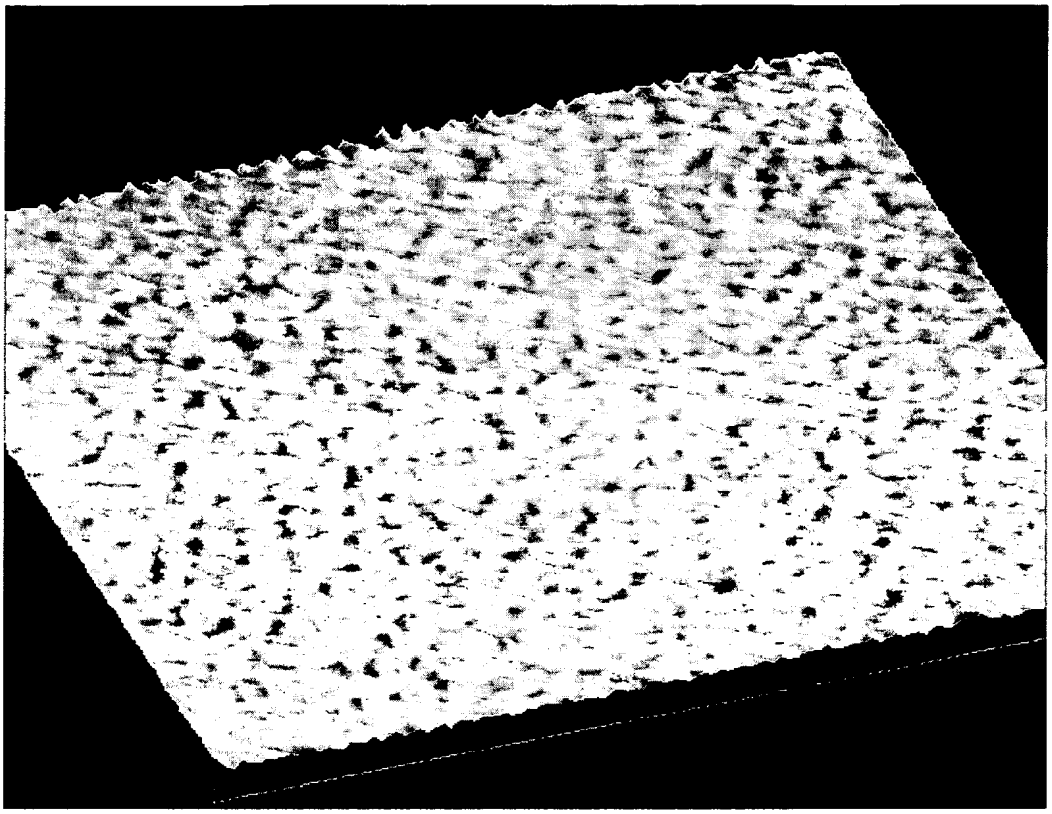


FIG. 22

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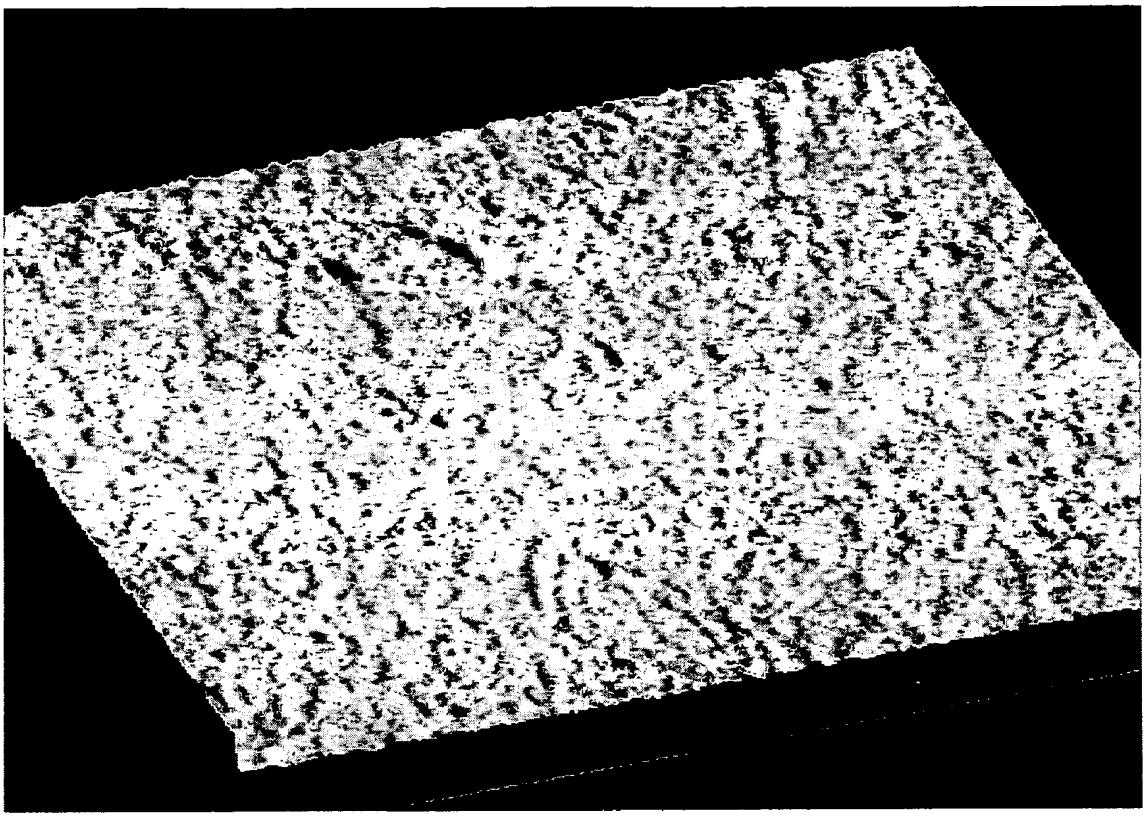


FIG. 23

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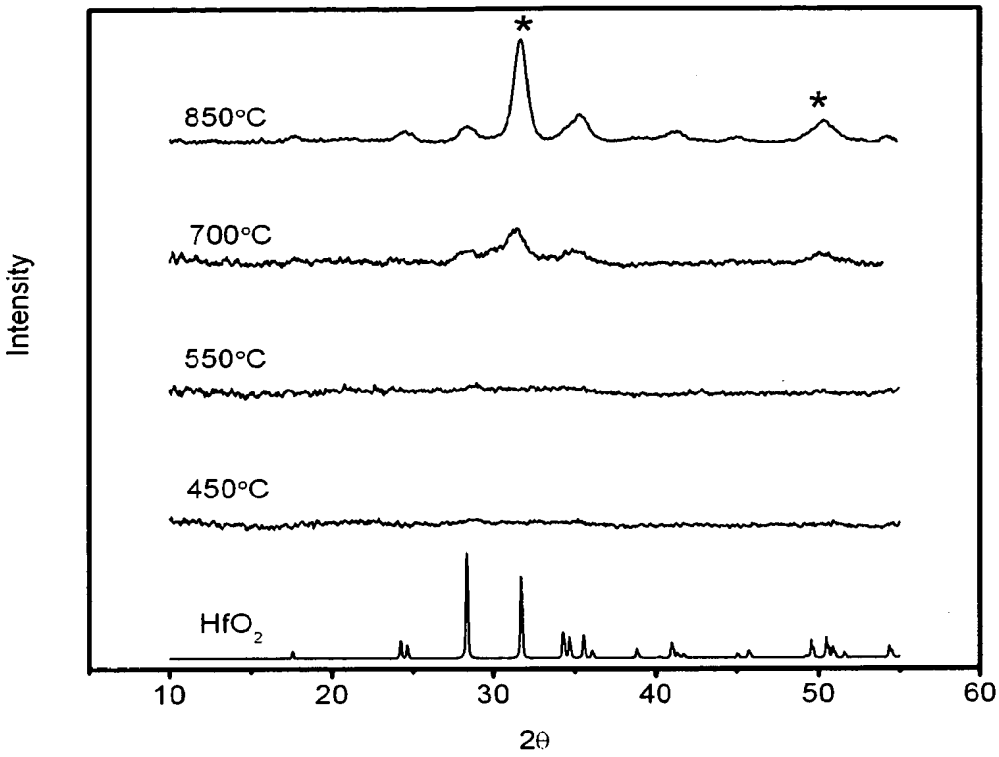


FIG. 24

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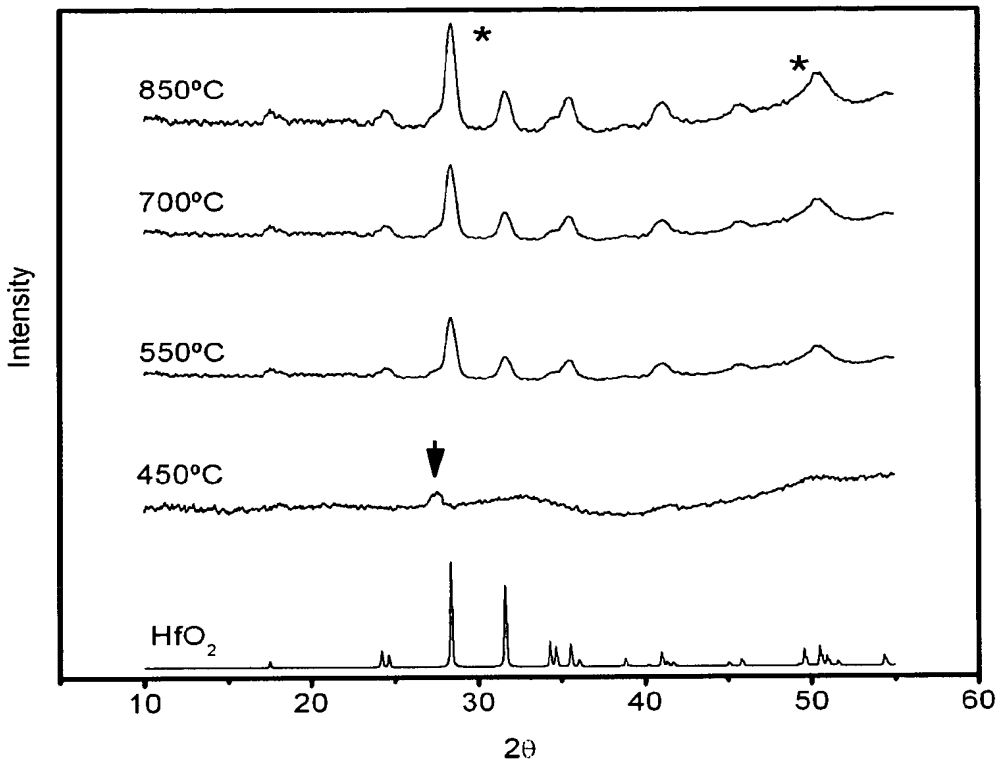


FIG. 25

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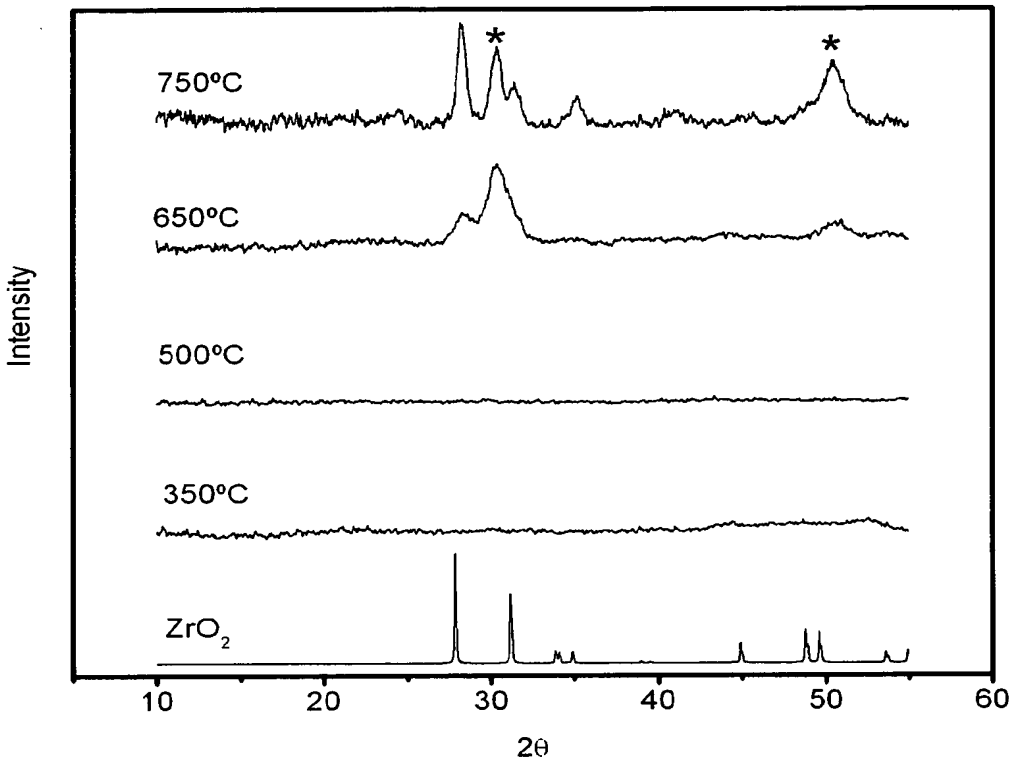


FIG. 26

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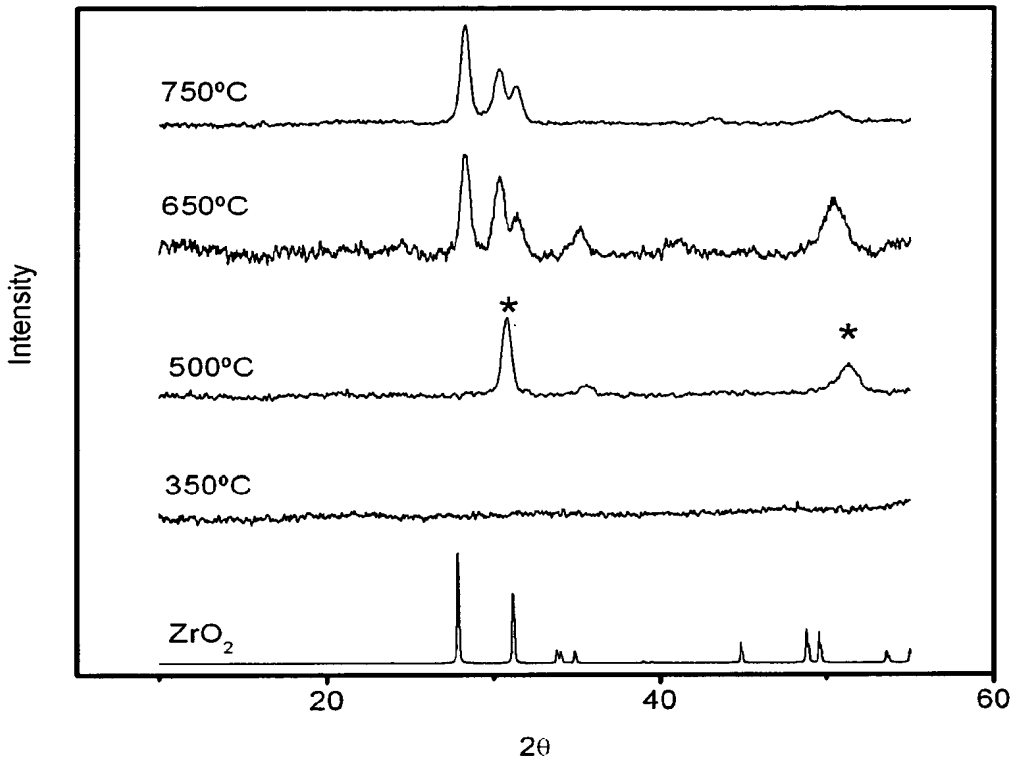


FIG. 27

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FIG. 28

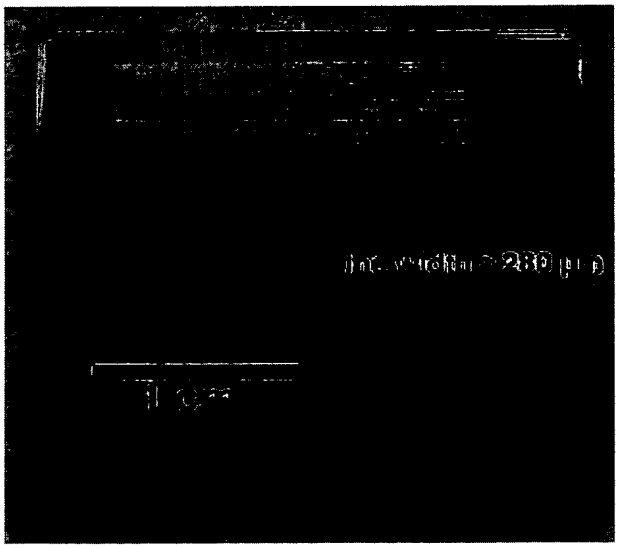


FIG. 29

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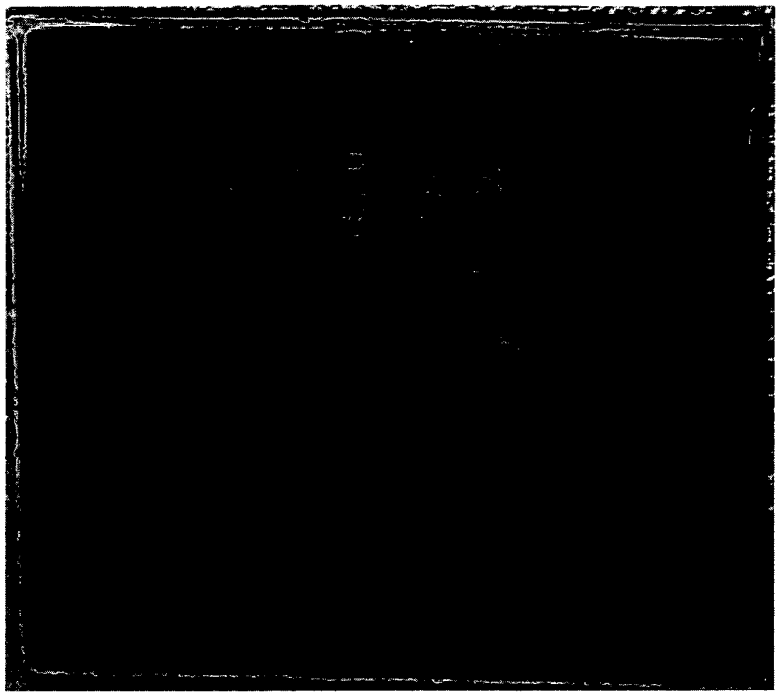


FIG. 30



FIG. 31

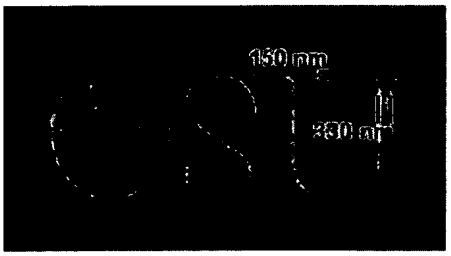


FIG. 32

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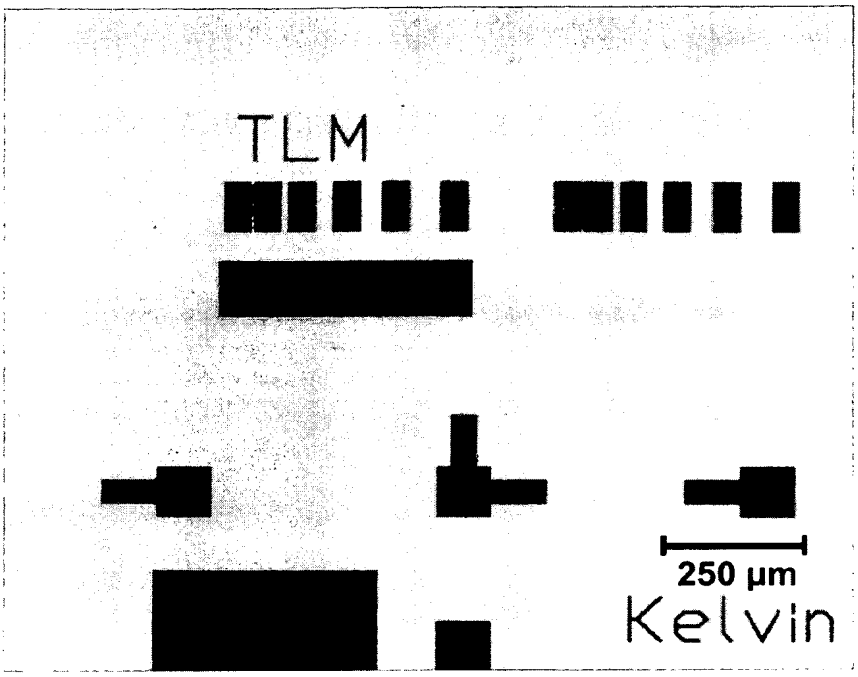


FIG. 33

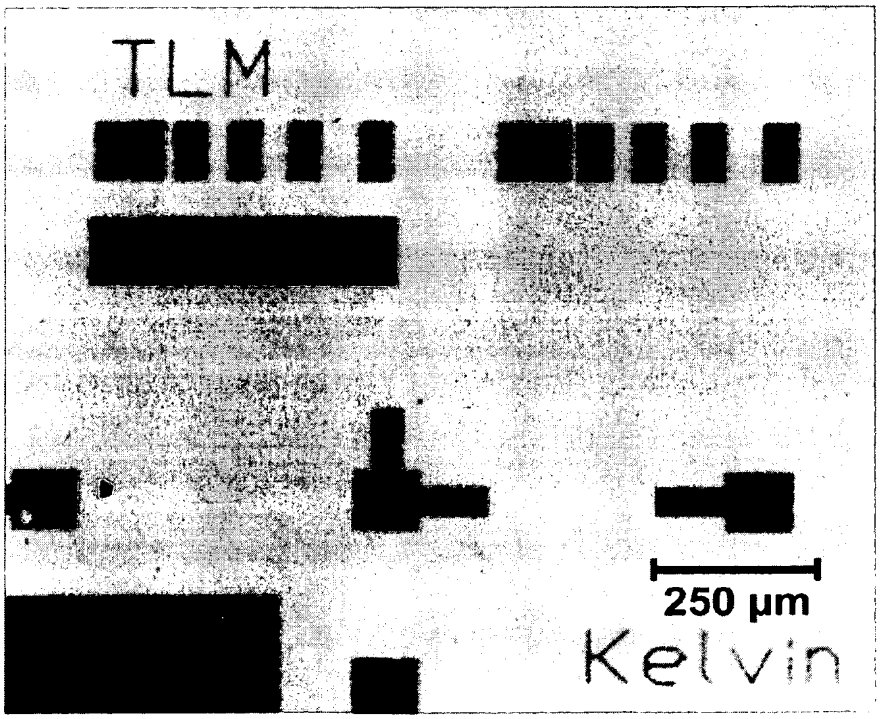


FIG. 34

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FIG. 35

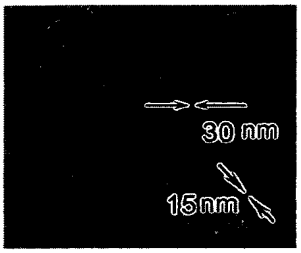


FIG. 36

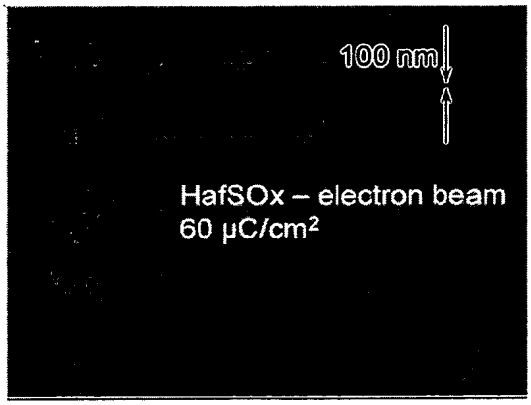


FIG. 37

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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:
"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
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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(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

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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 ($T < 325\ ^{o}C$).

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 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

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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.

Lam Research Ex. 1007 - Page 380 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

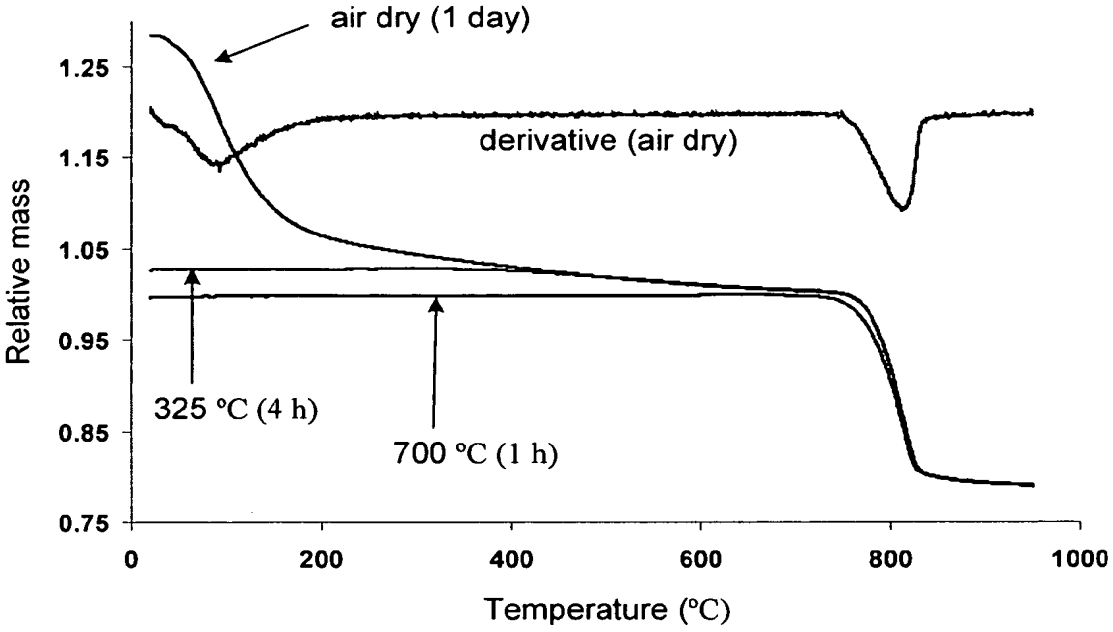

air dry (1 day)
derivative (air dry)
325 °C (4 h)
700 °C (1 h)
Relative mass
1.25
1.15
1.05
0.95
0.85
0.75
0
200
400
600
800
1000
Temperature (°C)

FIG. 1

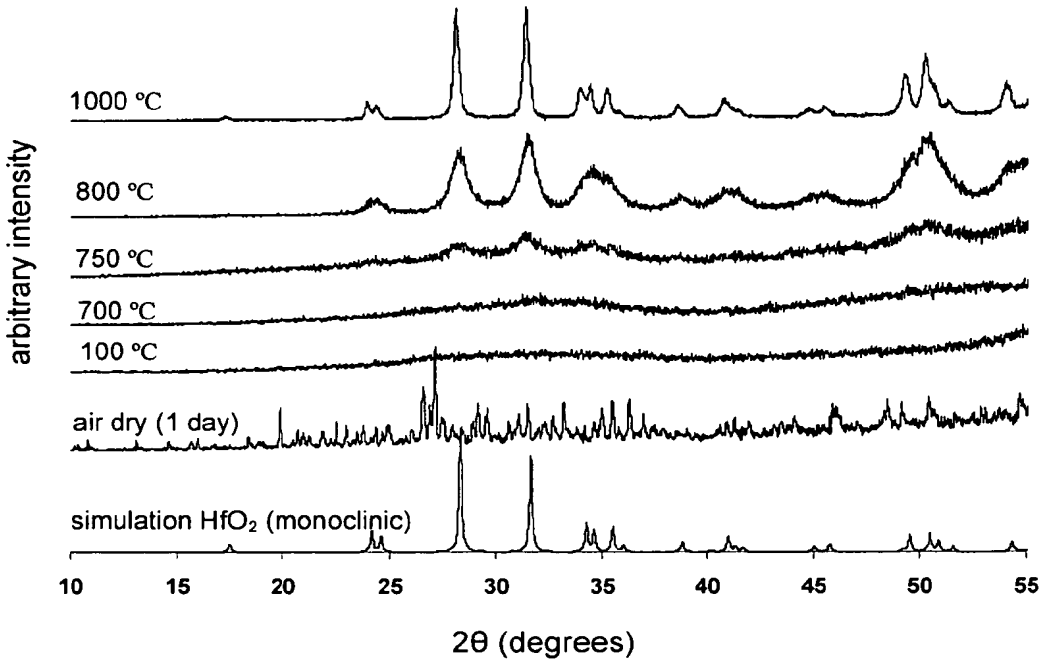

1000 °C
800 °C
750 °C
700 °C
100 °C
air dry (1 day)
simulation HfO2 (monoclinic)
arbitrary intensity
10
15
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 2

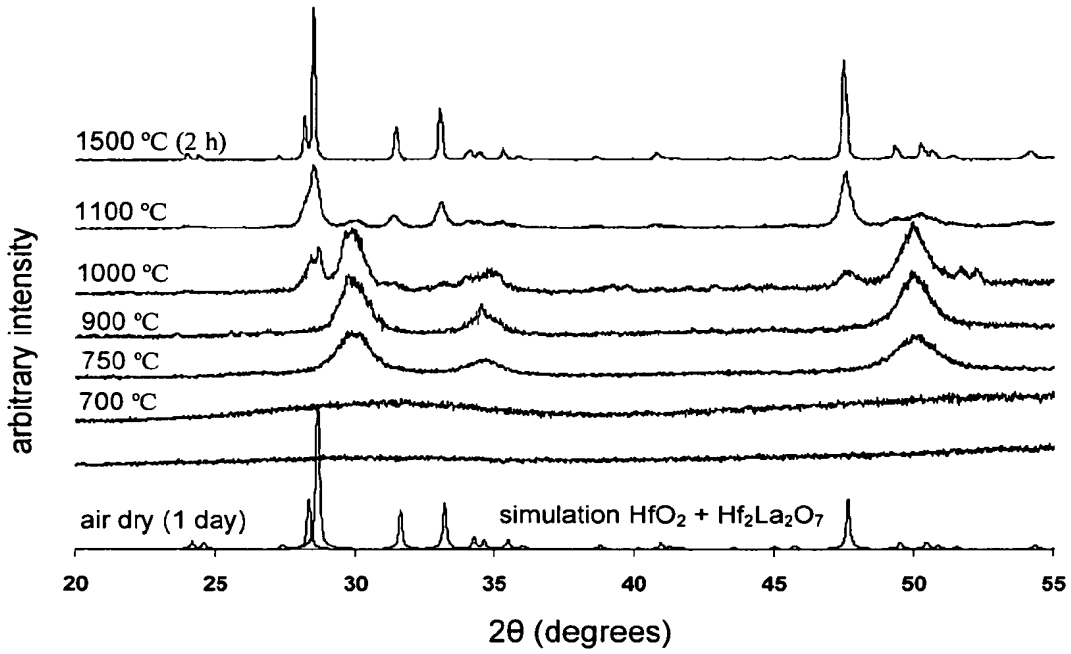

1500 °C (2 h)
1100 °C
1000 °C
900 °C
750 °C
700 °C
air dry (1 day)
simulation HfO_2 + $Hf_2La_2O_7$
arbitrary intensity
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 3

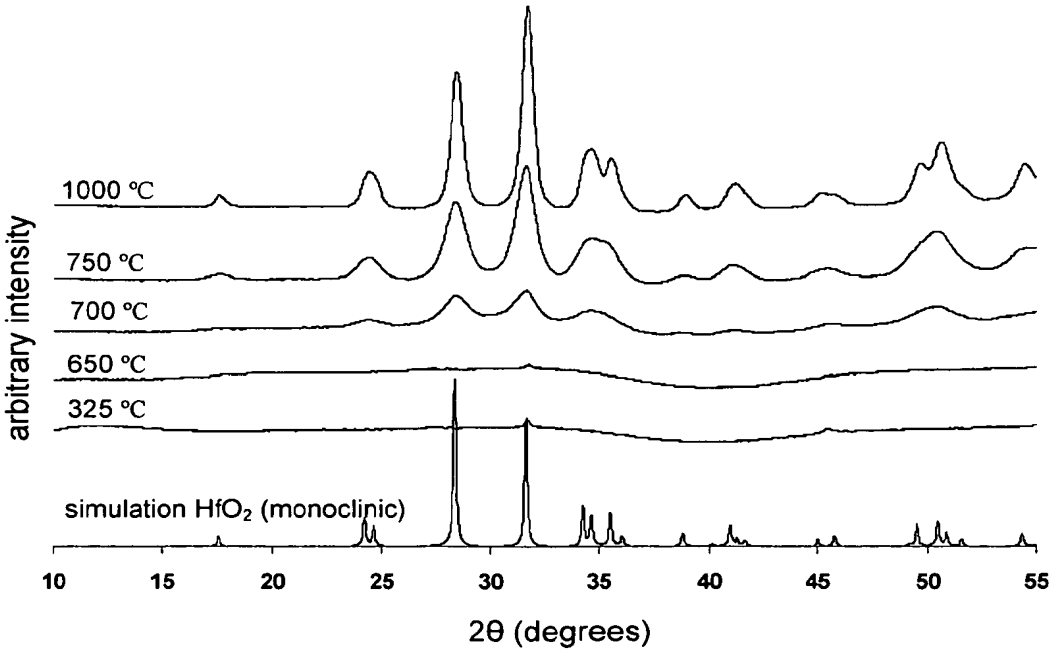

1000 °C
750 °C
700 °C
650 °C
325 °C
simulation HfO_2 (monoclinic)
arbitrary intensity
10
15
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 4

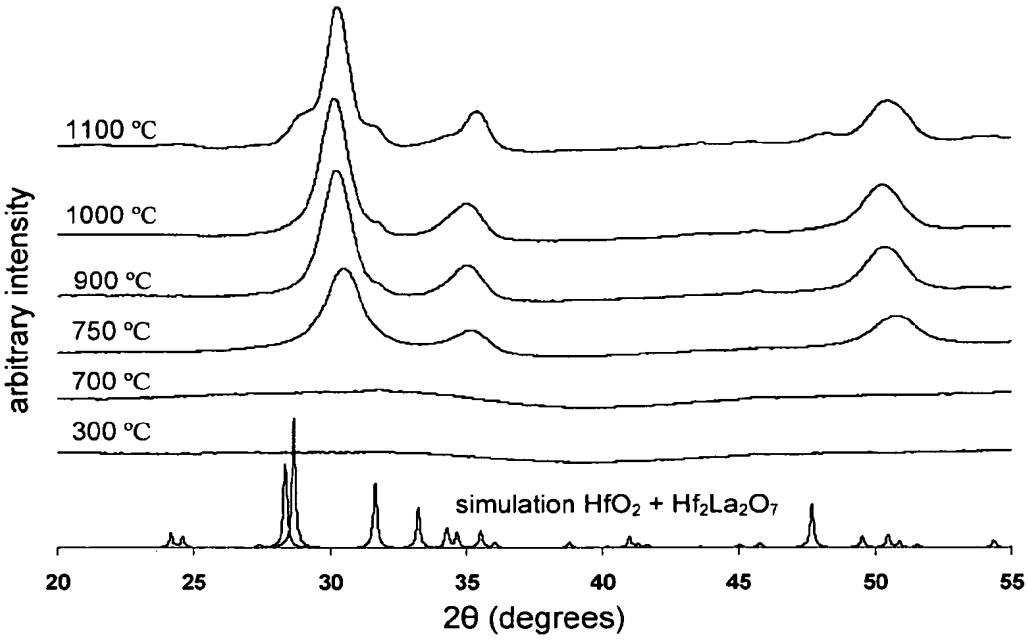

1100 °C
1000 °C
900 °C
750 °C
700 °C
300 °C
simulation HfO_2 + $Hf_2La_2O_7$
arbitrary intensity
20
25
30
35
40
45
50
55
2θ (degrees)

FIG. 5

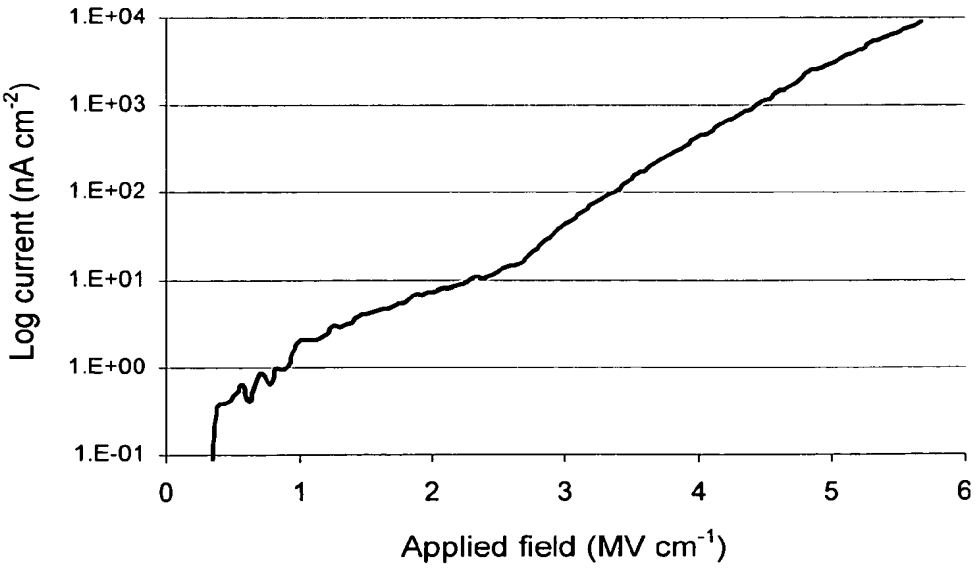

1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
Log current (nA cm^{-2})
0
1
2
3
4
5
6
Applied field (MV cm^{-1})

FIG. 6

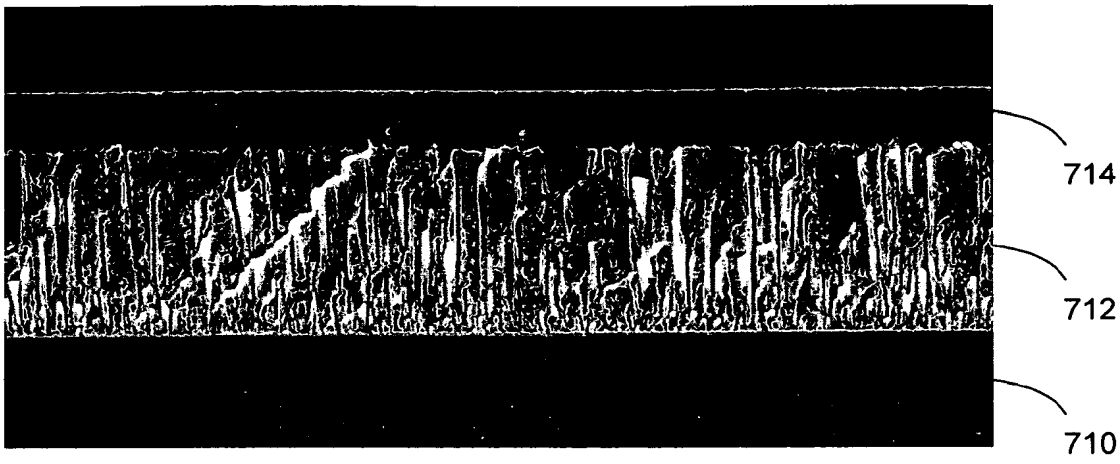


FIG. 7

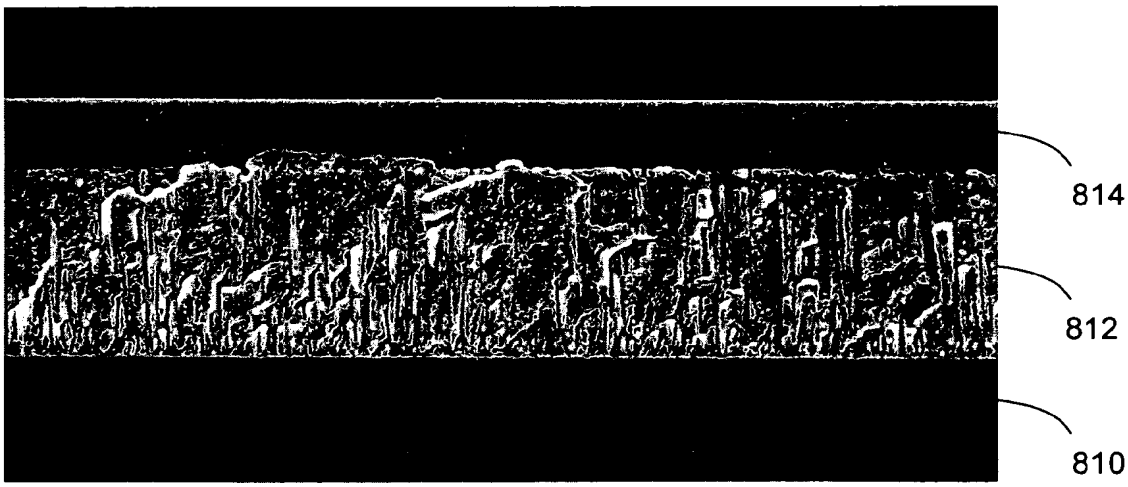


FIG. 8

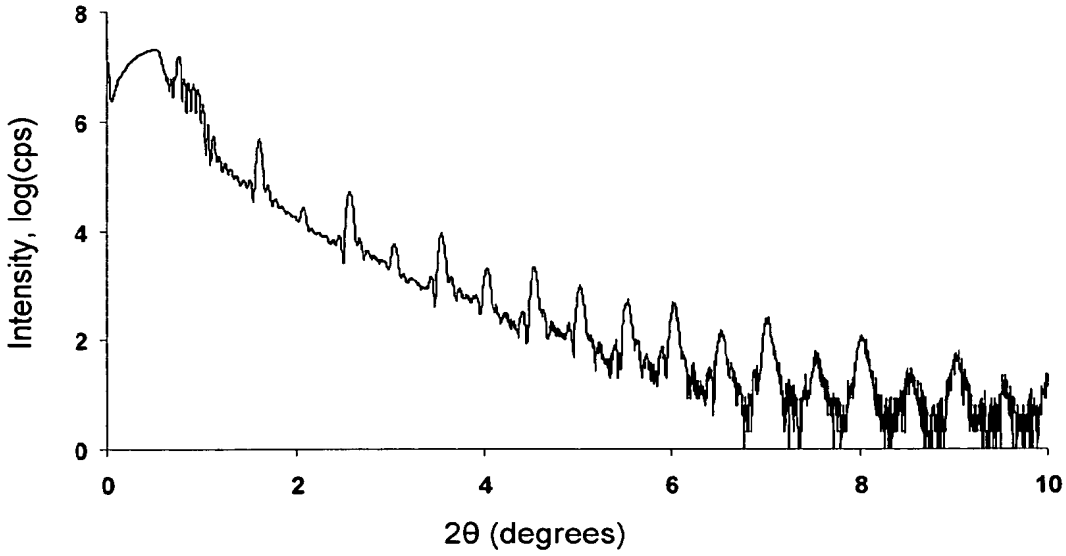


FIG. 9

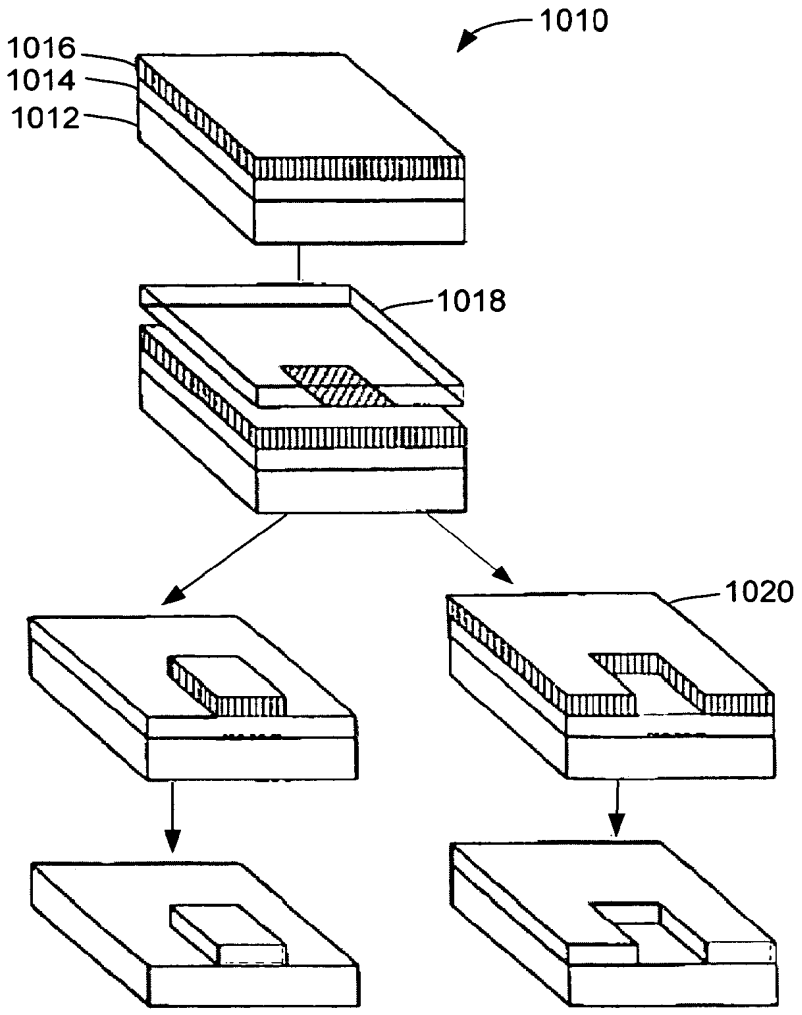


FIG. 10

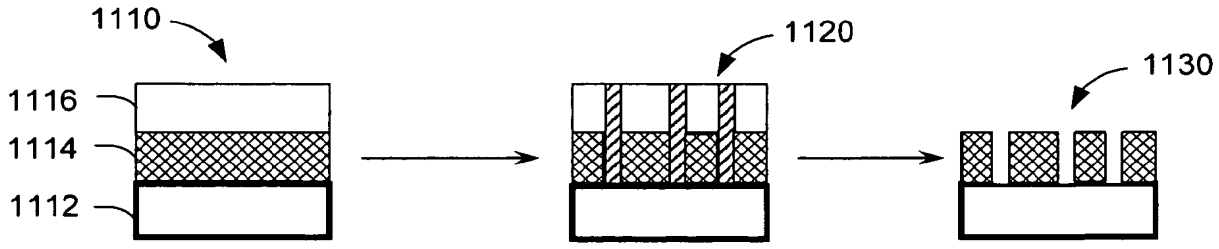


FIG. 11

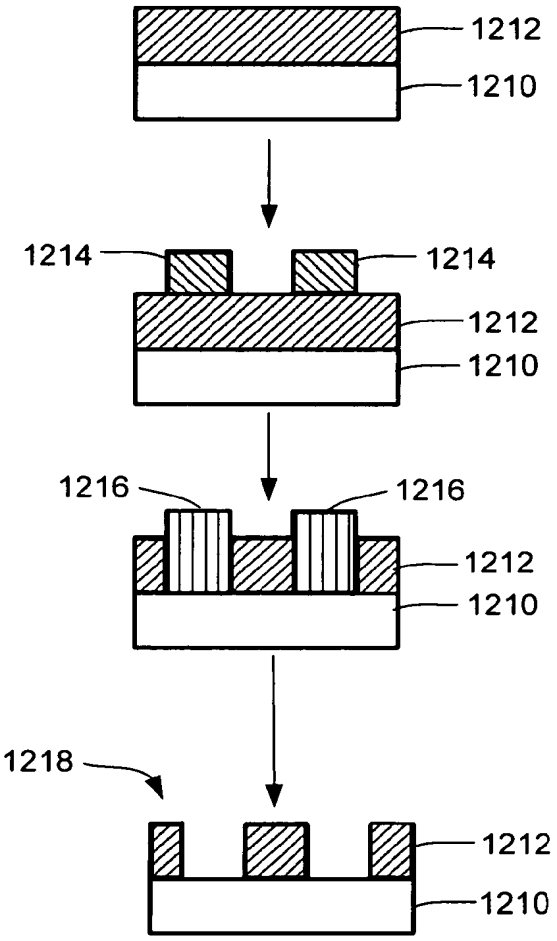

1212
1210
1214
1214
1212
1210
1216
1216
1212
1210
1218
1212
1210

FIG. 12

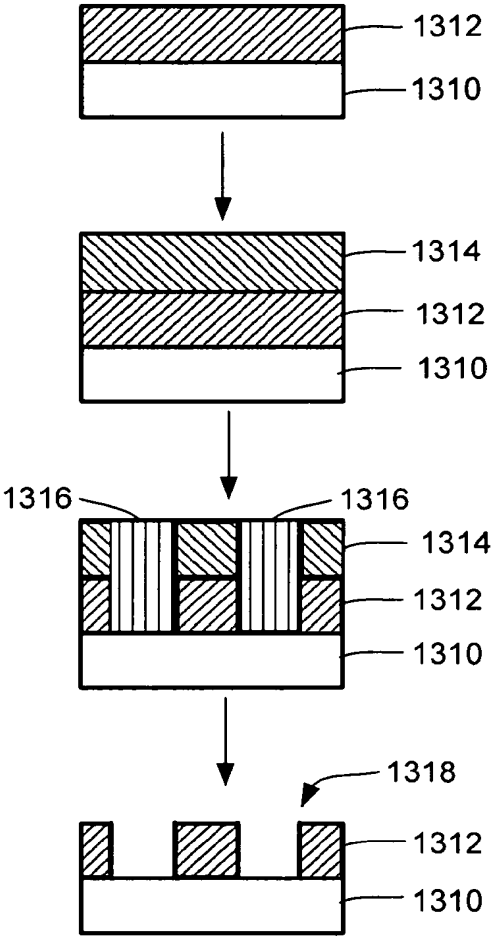

1312
1310
1314
1312
1310
1316
1316
1314
1312
1310
1318
1312
1310

FIG. 13

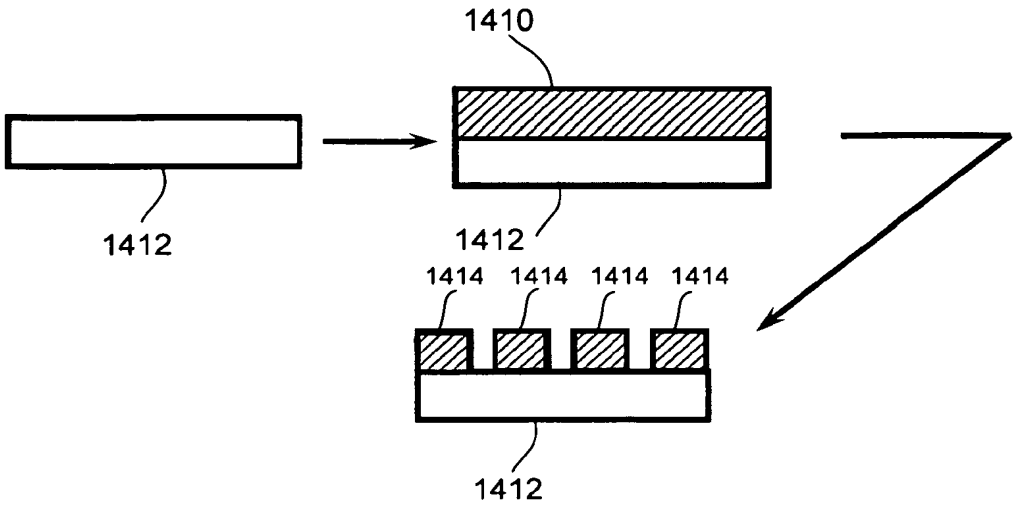

1410
1412
1412
1414
1414
1414
1414
1412

FIG. 14

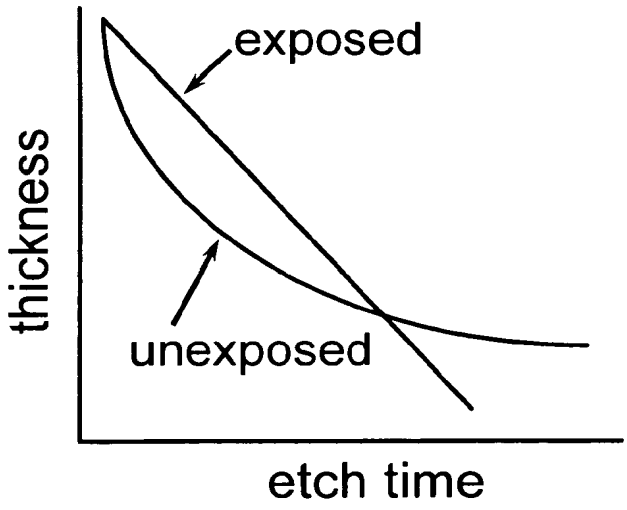

exposed
thickness
unexposed
etch time

FIG. 15

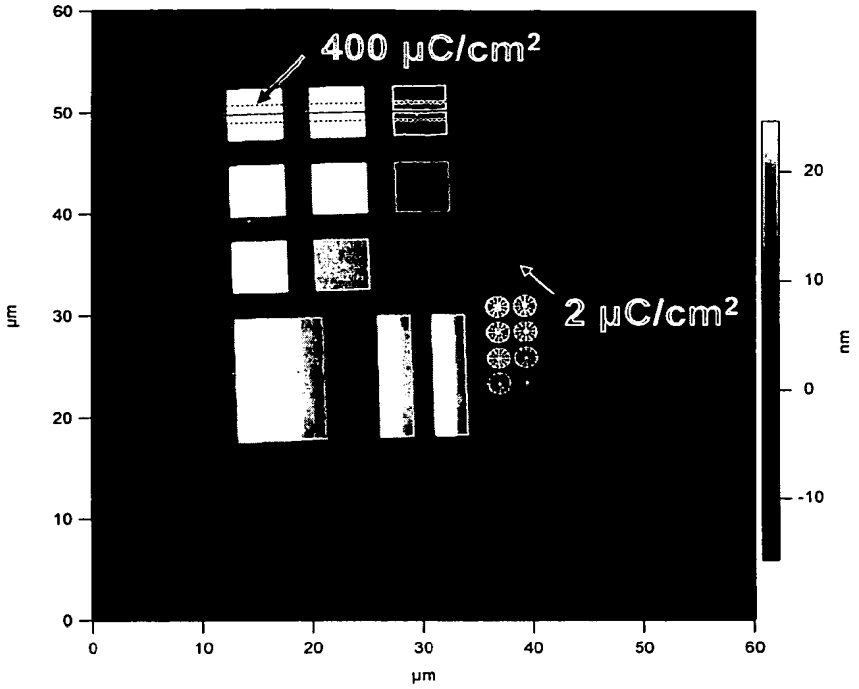

400 µC/cm²
2 µC/cm²
µm
nm
0
10
20
30
40
50
60
-10

FIG. 16

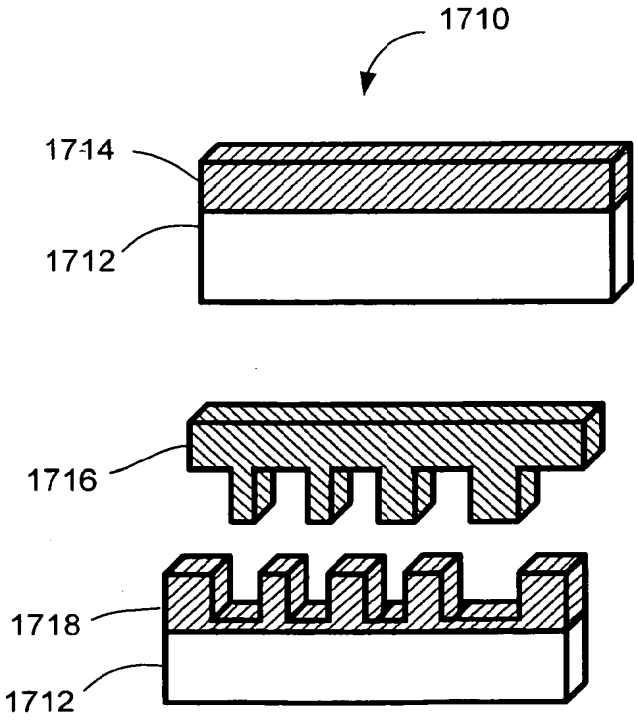

1710
1714
1712
1716
1718
1712

FIG. 17

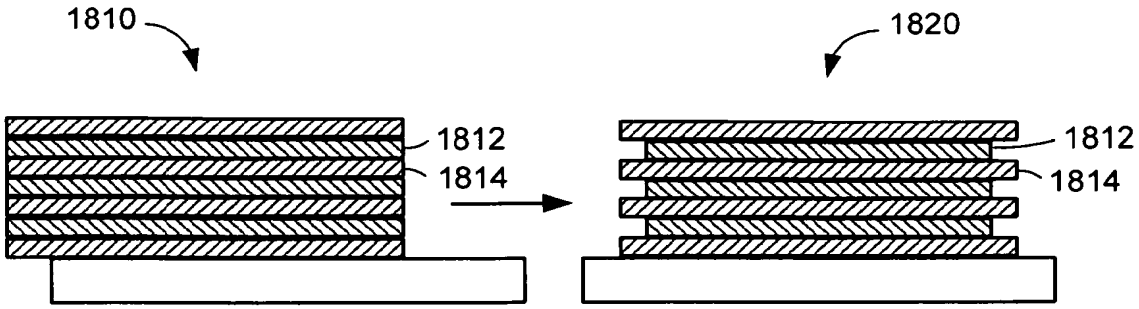


FIG. 18

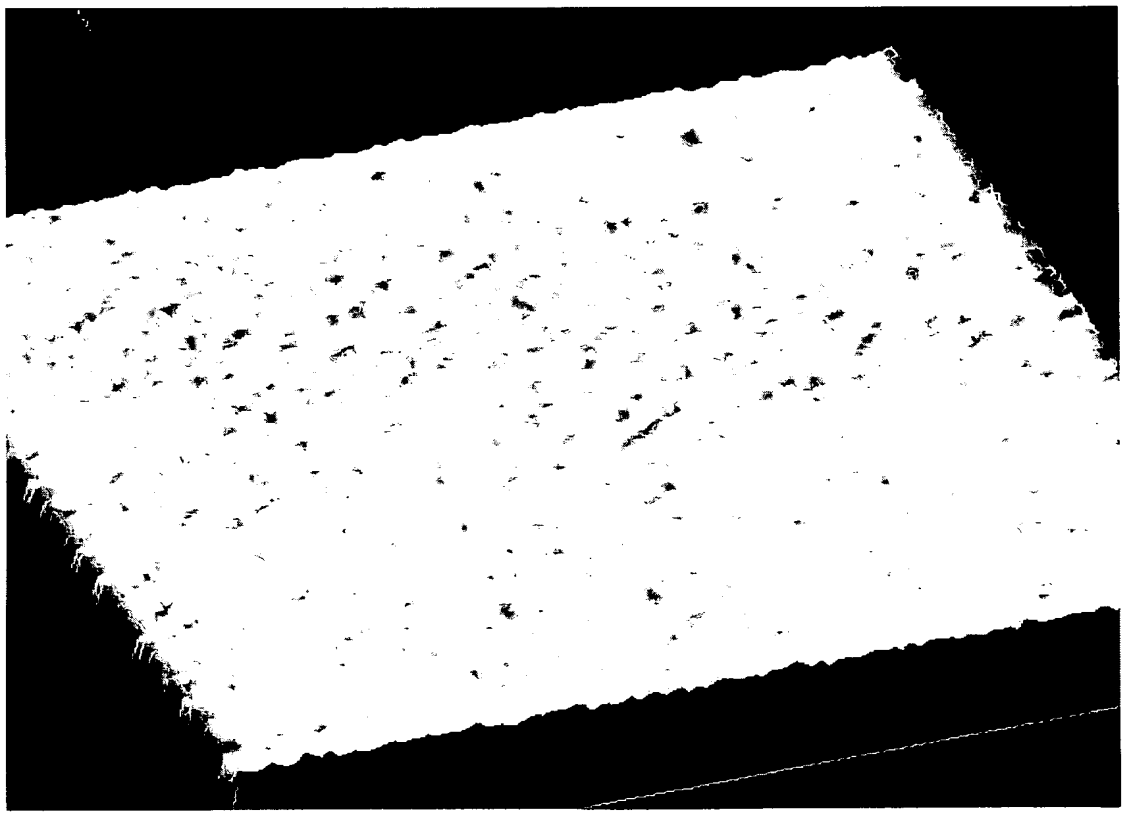


FIG. 19

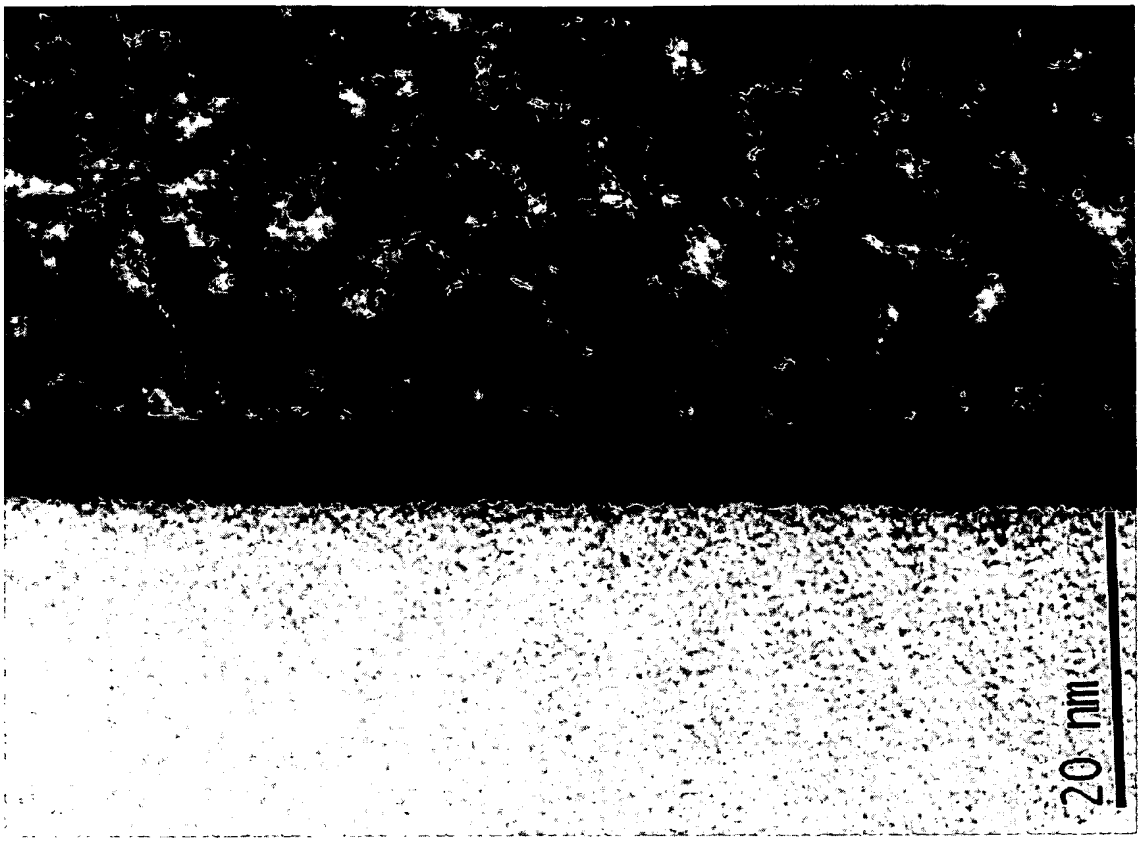


FIG. 20

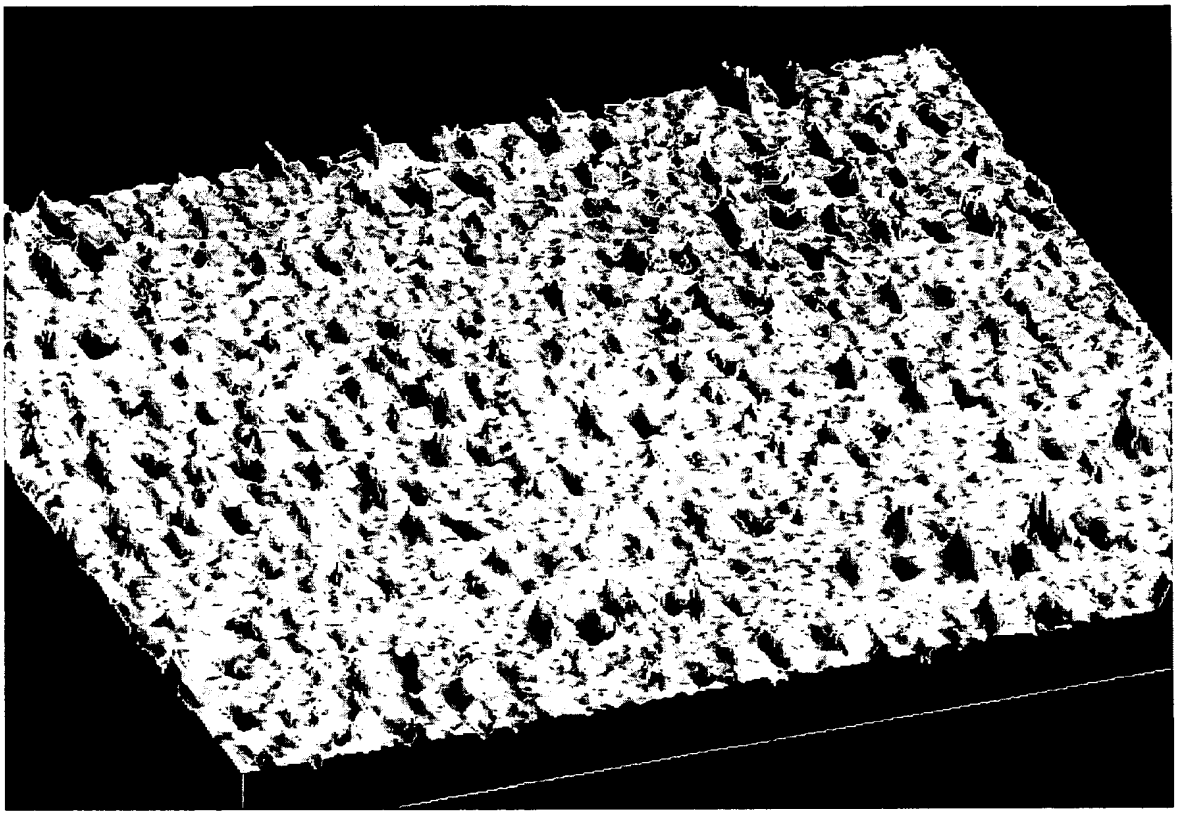


FIG. 21

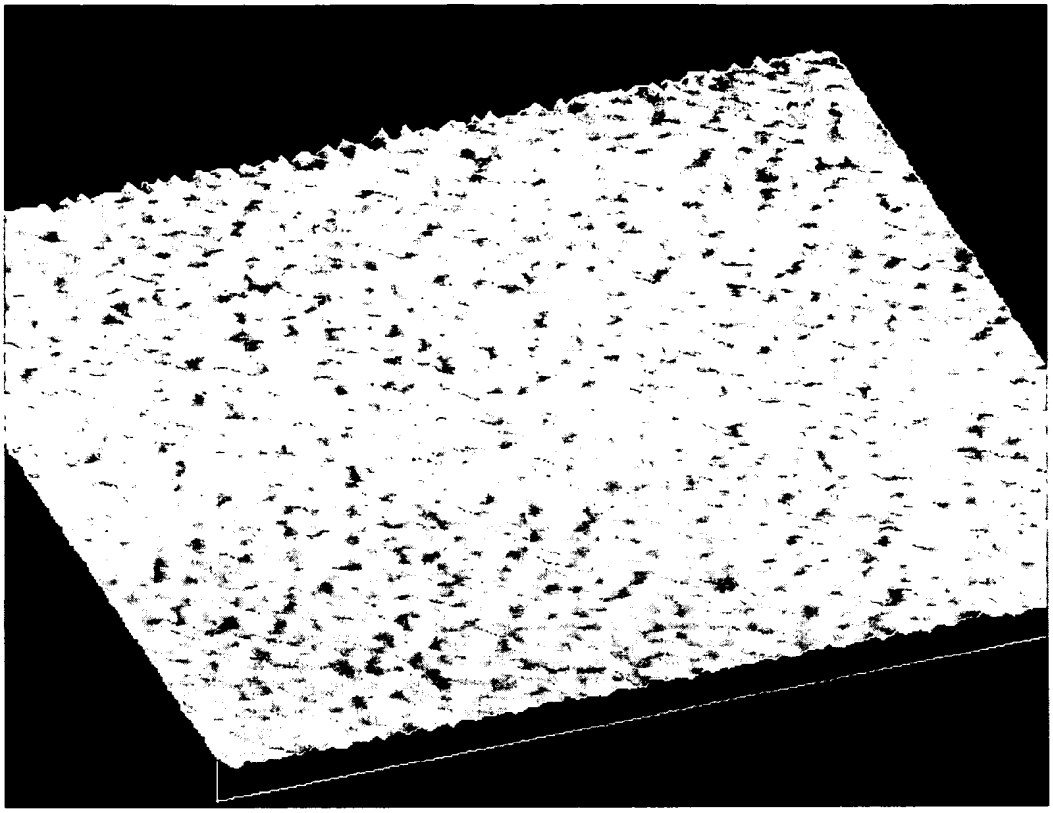


FIG. 22

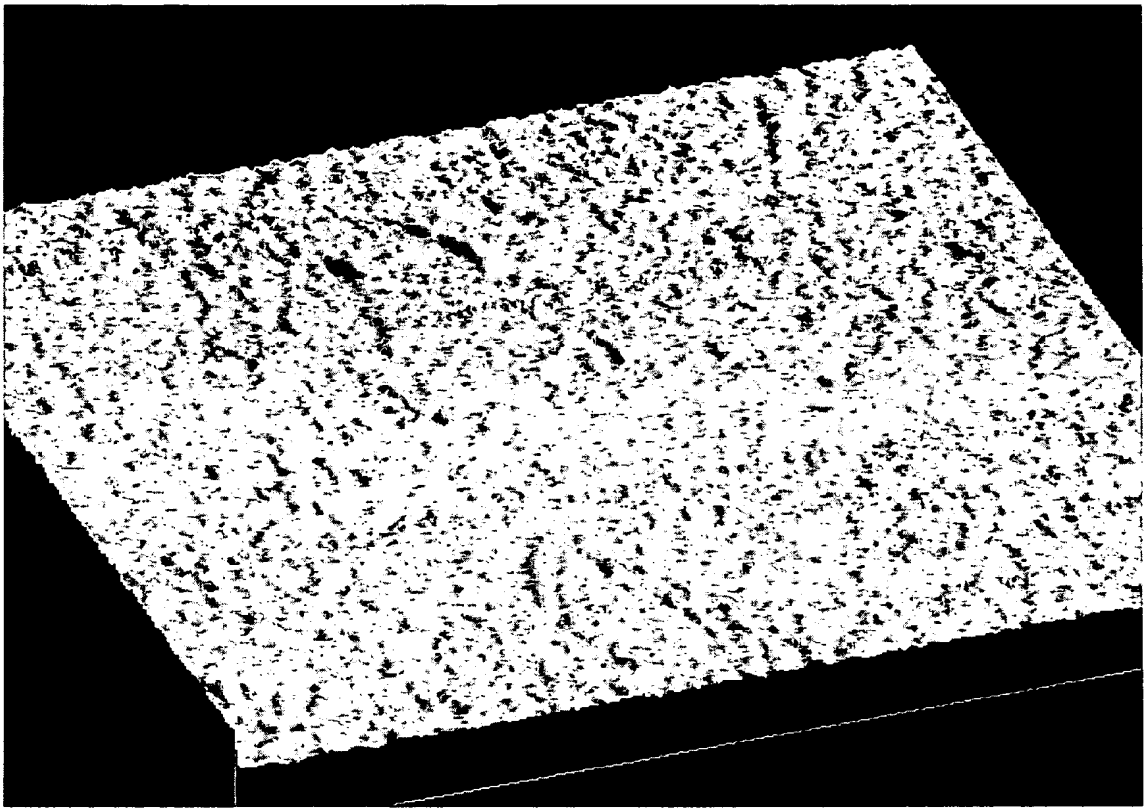


FIG. 23

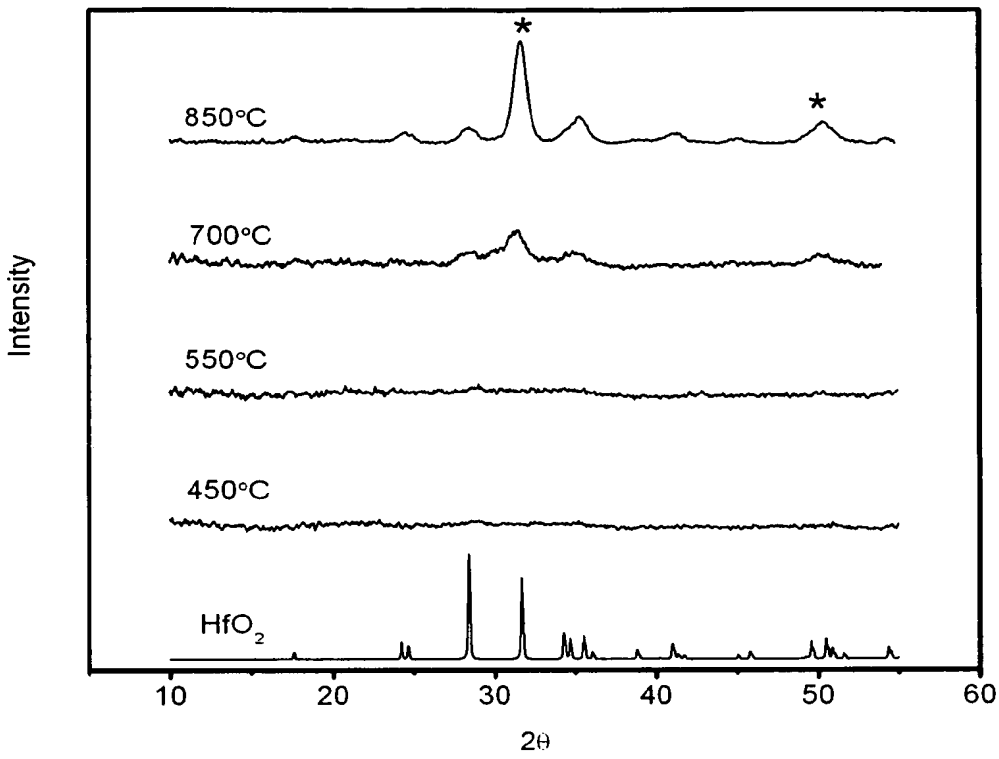


FIG. 24

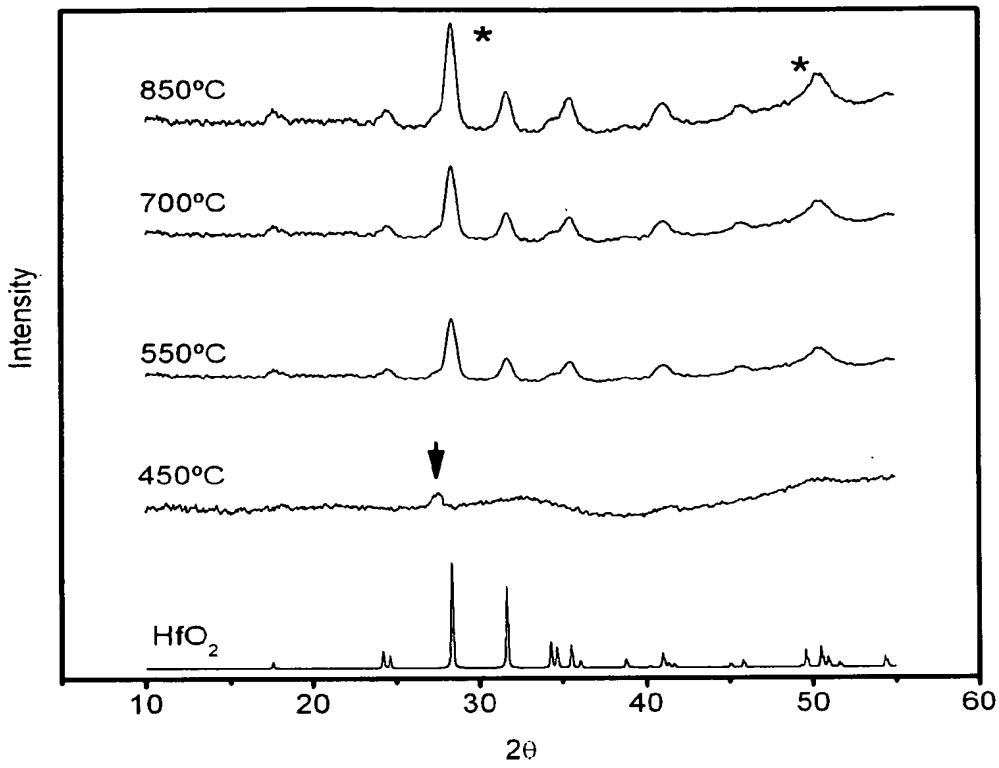


FIG. 25

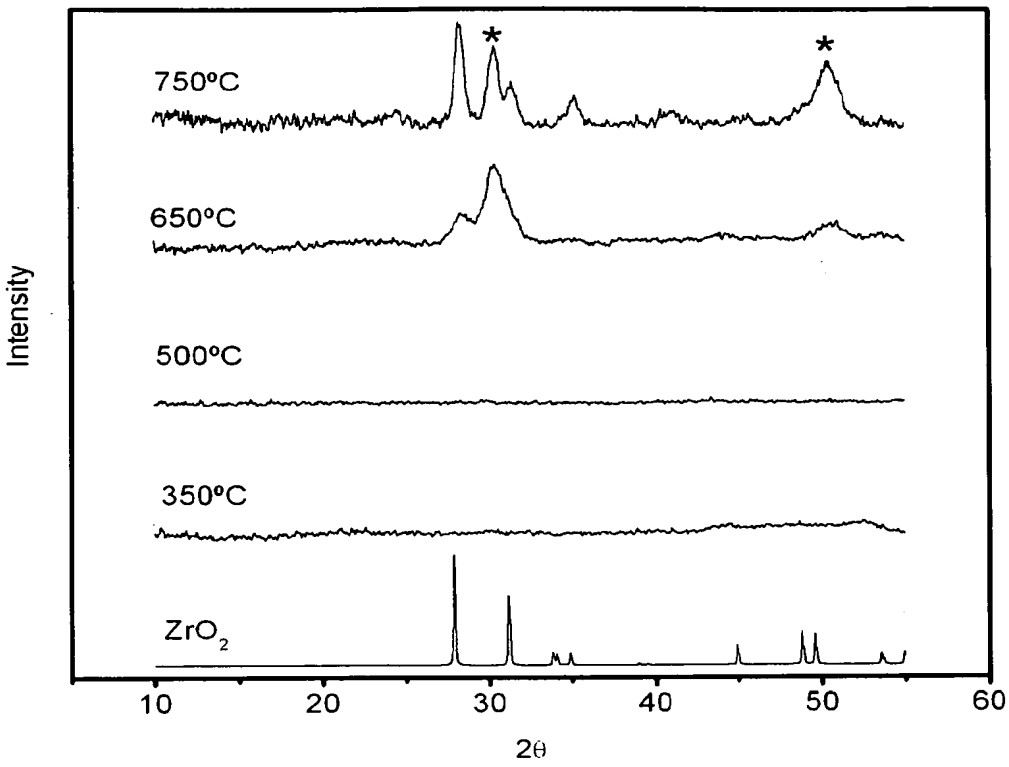


FIG. 26

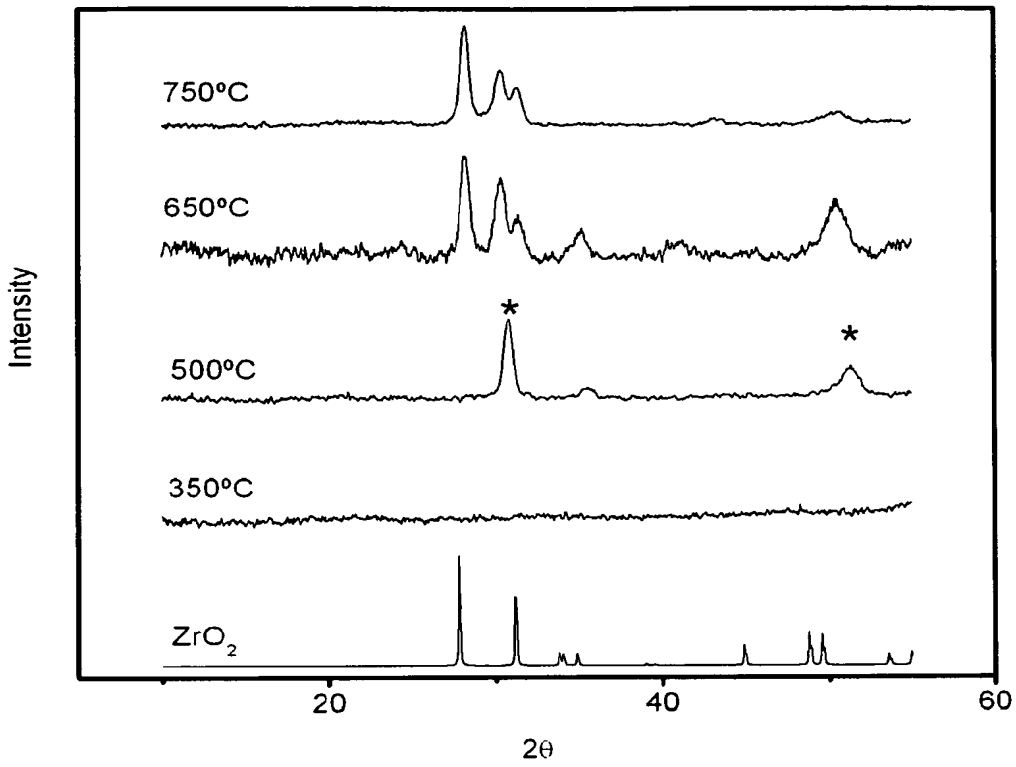


FIG. 27

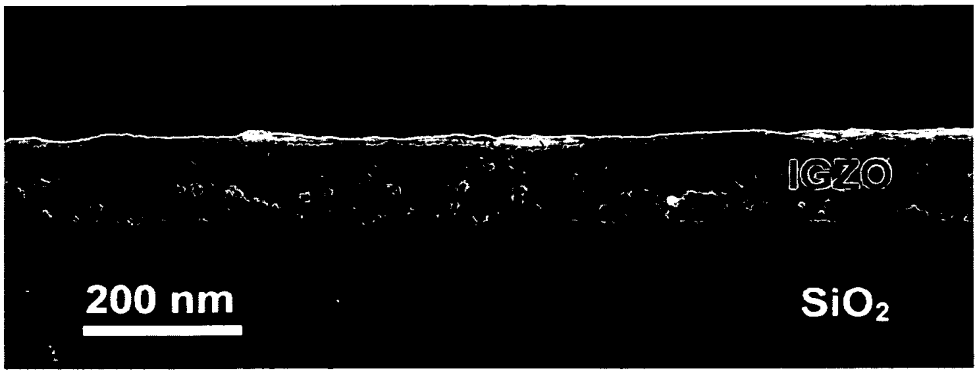


FIG. 28

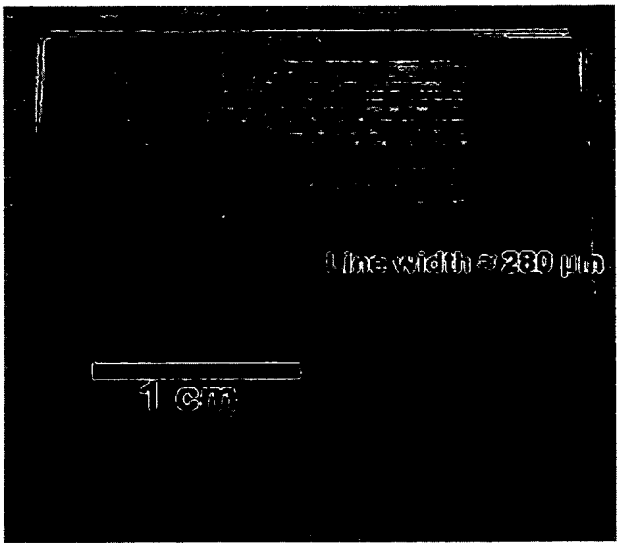


FIG. 29

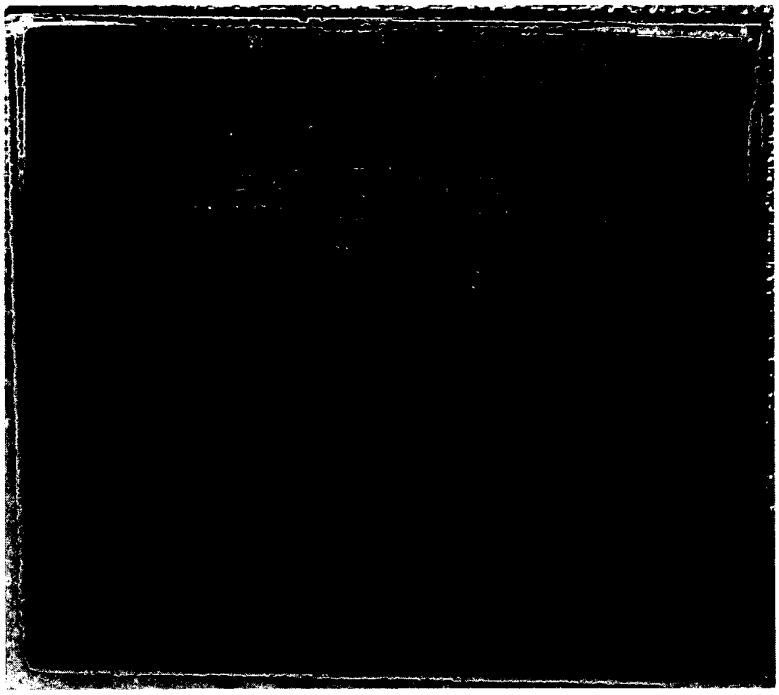


FIG. 30



FIG. 31

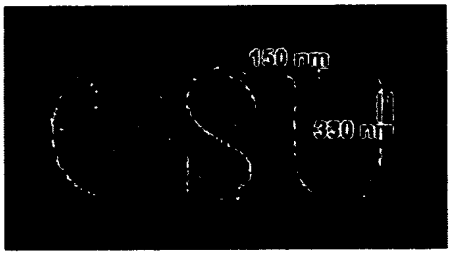


FIG. 32

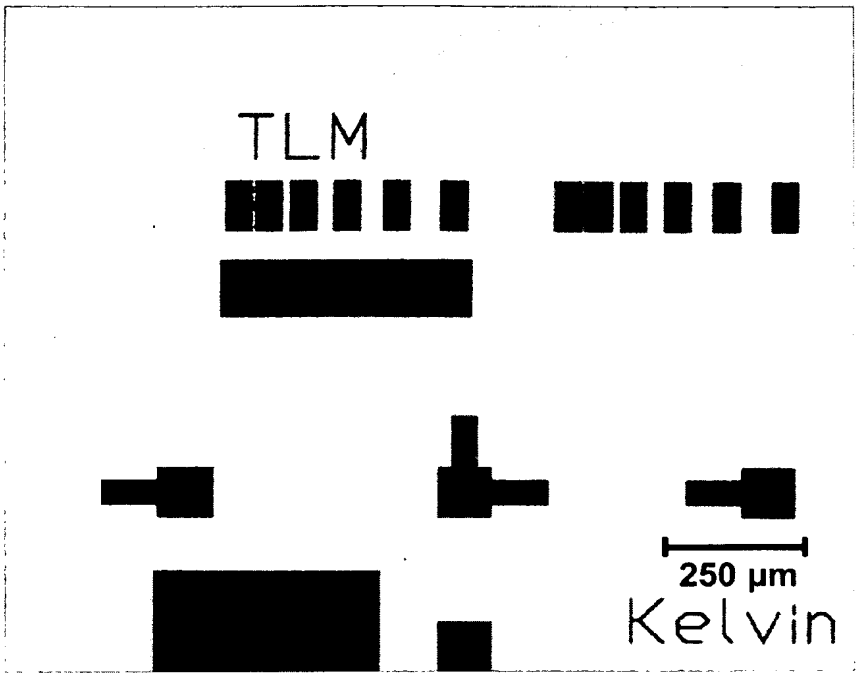


FIG. 33

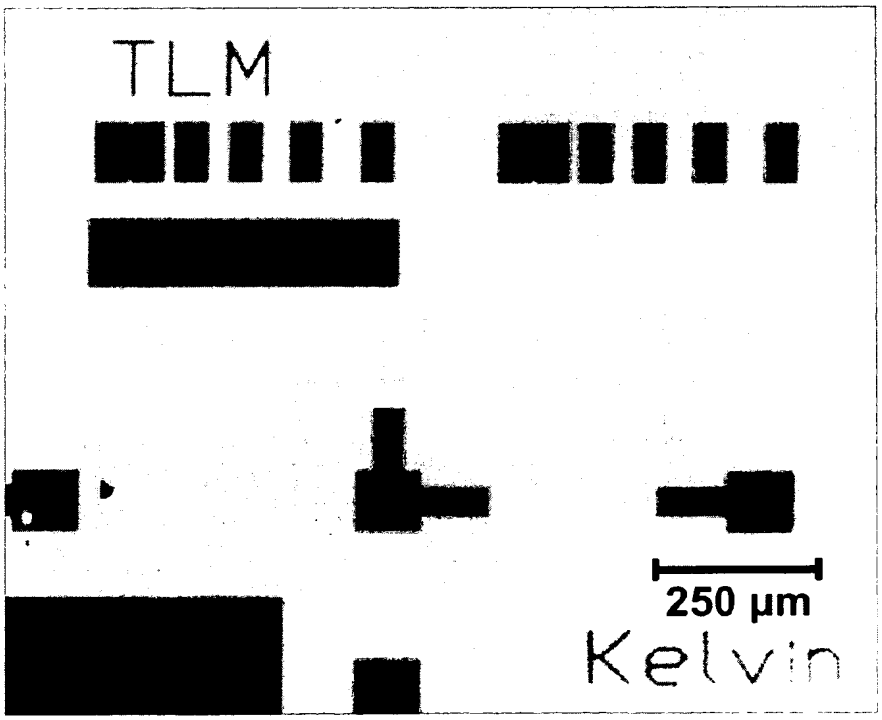


FIG. 34

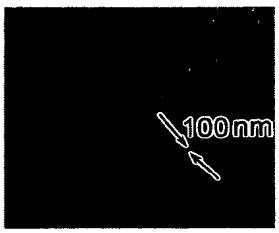


FIG. 35

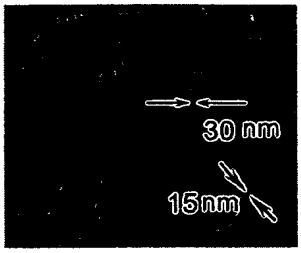


FIG. 36

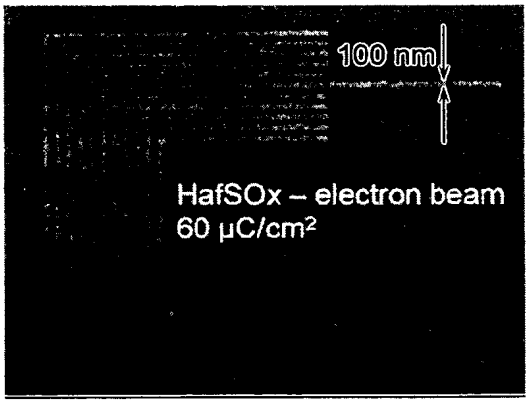


FIG. 37

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)

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. (Original) A structure comprising a substrate and a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands and wherein the coating material has an average thickness from about 5 nm to about 30 nm, wherein exposure of the coating material to UV, EUV and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material.

2. (Original) The structure of claim 1 wherein the metal ions comprise metal suboxide ions.

3. (Original) The structure of claim 1 wherein the metal of the metal ions comprises 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.

4. (Original) The structure of claim 1 wherein the radiation sensitive ligands comprise peroxide ligands.

5. (Original) The structure of claim 1 wherein the coating material further comprises polyatomic anions.

6. (Original) The structure of claim 1 wherein the average thickness is from about 5 nm to about 25 nm.

7. (Original) The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists.

8-20. (Cancelled)

21. (New) The structure of claim 1 having a metal ion to radiosensitive ligand ratio of at least about 2.

22. (New) The structure of claim 1 wherein the coating material has been heated to temperatures from about 45°C to about 150°C.

23. (New) The structure of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous solvent.

24. (New) The structure of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent.

25. (New) The structure of claim 1 wherein the coating material can be effectively patterned with UV radiation or EUV radiation at a dose of no more than about 100 mJ/cm^2.

Lam Research Ex. 1007 - Page 405 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.: 5063.02US04
Stowers et al.	Confirmation No.: 1074
Application No.: 14/858,612	Examiner: Robinson, Chanceity N.
Filed: September 18, 2015	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 June 30, 2016, please enter the following amendments and consider the following remarks. This document has 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.

September 30, 2016
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
L1	5	(("8415000") or ("9281207")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 15:28
L2	1	(14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:05
L3	1	2 and (thickness)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:05
L4	5	(("2001154366") or ("2010508560") or ("2011524627")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:47
L5	15	(("2001154366") or ("2010508560") or ("2011524627") or ("2008082448") or ("2009120169")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:49
L6	2	5 and (aqueous and organic)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/10/16 17:36
S1	1	(14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/16 13:02
S2	66252	(metal adj ions) and (ligands)	US-PGPUB;	OR	ON	2016/06/16

			USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			13:02
S3	29121	(UV or ultraviolet or electron-beam or EUV) and S2	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:03
S4	6581	S3 and ((alter$1 or change$1) with chemical)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S5	5760	S4 and substrate	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S6	1990	S5 and peroxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S7	85	S5 and (peroxide with ligand)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S8	65	S7 and anion	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S9	14	S8 and polyatomic and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S10	14	S9 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/327 OR G03F7/0002 OR G03F7/11 OR G03F7/09 OR G03F7/2002 OR G03F7/2037 OR G03F7/30 OR G03F7/2004 OR G03F7/32 OR H01L29/7869 OR H01L27/1225 OR	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT;	OR	ON	2016/06/16 13:07

		H01L21/02181 OR H01L21/02189 OR H01L21/02192 OR H01L21/02194 OR H01L21/02282 OR H01L21/0337 OR H01L21/28194 OR H01L29/4908 OR B32B2457/14 OR B32B9/005 OR B82Y10/00 OR B82Y40/00 OR C01G1/10 OR C01G25/006 OR C01G25/06 OR C01G27/006 OR C01G27/06).CPC.)	IBM_TDB			
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S13	123950	substrate and (metal adj ion)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
S14	19	radiation adj sensitive adj ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
S15	14	S13 and S14	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
S16	13	S15 and (UV or EUV or electron-beam or ultraviolet)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
S17	6	S16 and differential	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:19
S18	4	S17 and peroxide	US-PGPUB; USPAT; USOCR; FPRS;	OR	ON	2016/06/27 14:19

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S20	1	S19 and about	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:22
S21	1	S20 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/327).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:23
S22	6	("2009120169").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 14:48
S23	0	S22 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 15:10
S24	0	S22 and nm	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 15:10

EAST Search History (Interference)

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Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14858612	STOWERS ET AL.
	Examiner	Art Unit
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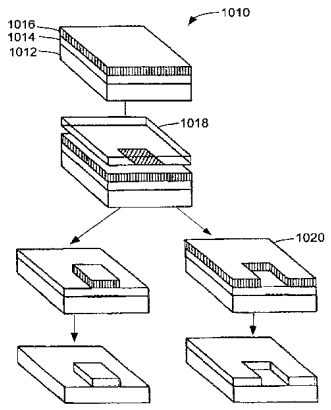
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(54) Title: SOLUTION PROCESSED THIN FILMS AND LAMINATES, DEVICES COMPRISING SUCH THIN FILMS AND LAMINATES, AND METHOD FOR THEIR USE AND MANUFACTURE



(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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— *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

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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 ($T < 325\ ^{o}C$).

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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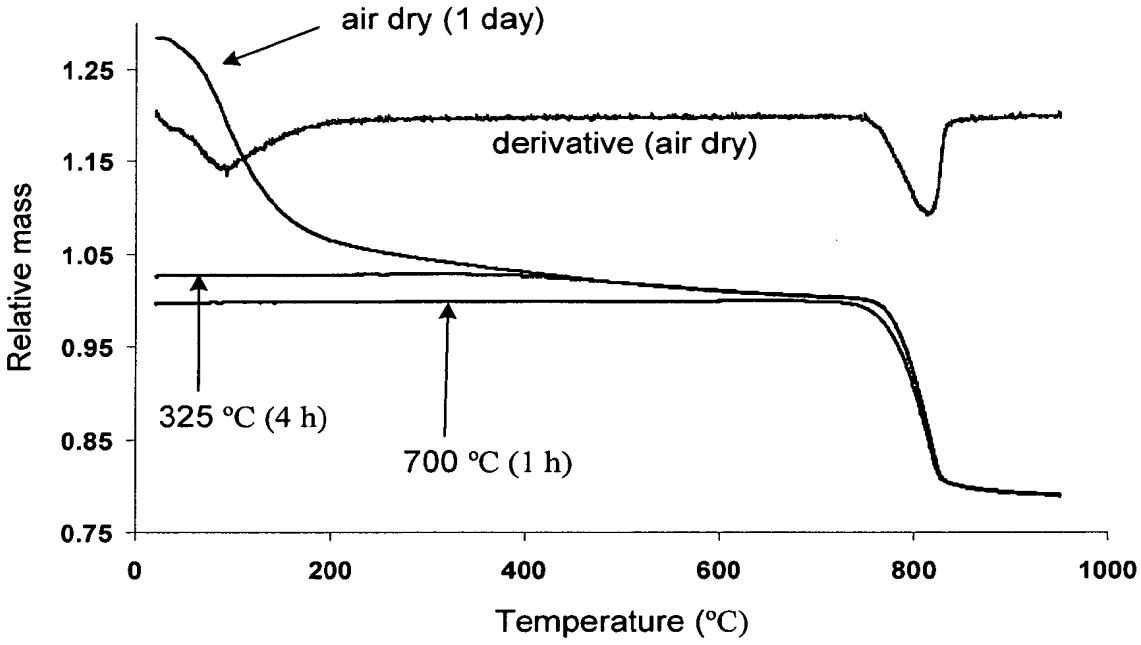


FIG. 1

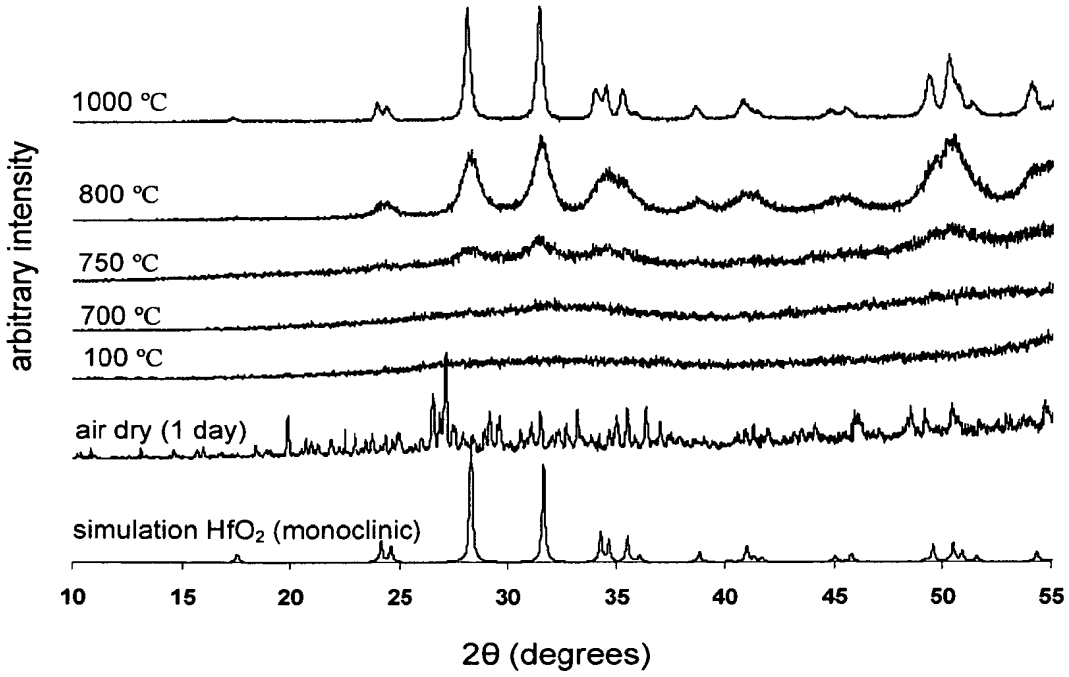


FIG. 2

Lam Research Ex. 1007 - Page 464 Lam Research Corp. v. Entegris, Inc. IPR2020-00033 - U.S. Patent No. 9,823,564

SUBSTITUTE SHEET (RULE 26)

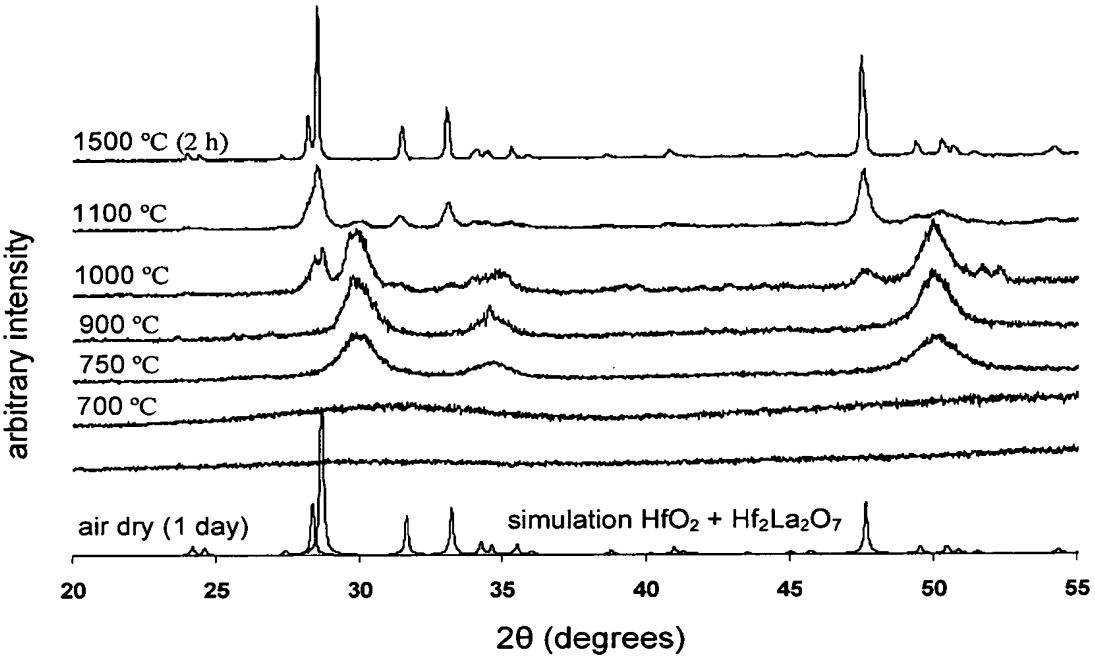


FIG. 3

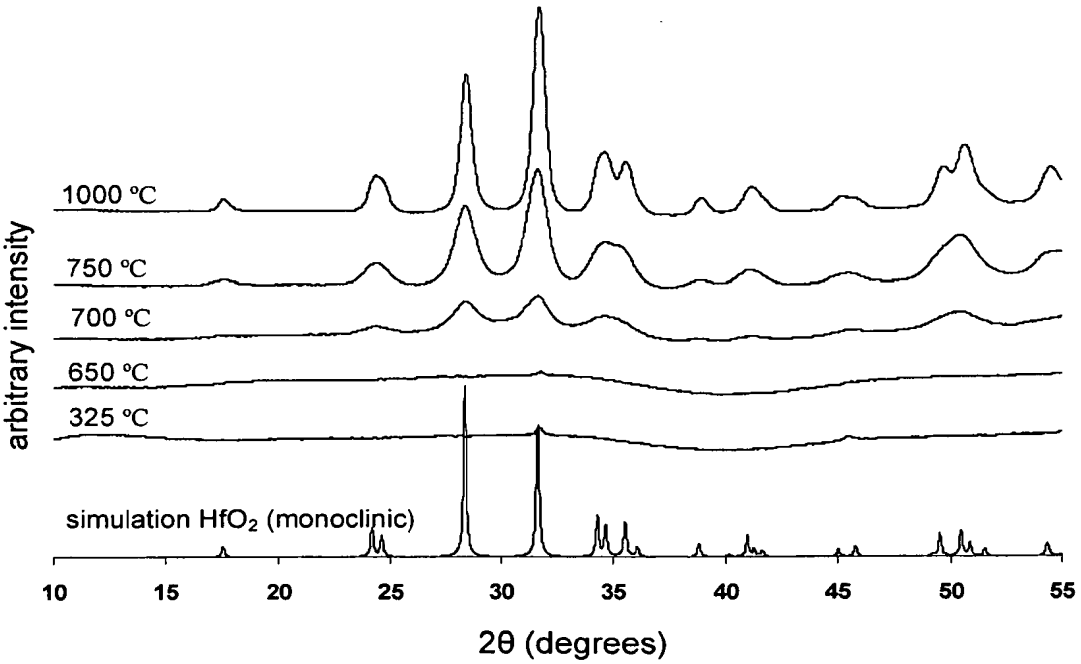


FIG. 4

Lam Research Ex. 1007 - Page 465 Lam Research Corp. v. Impria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

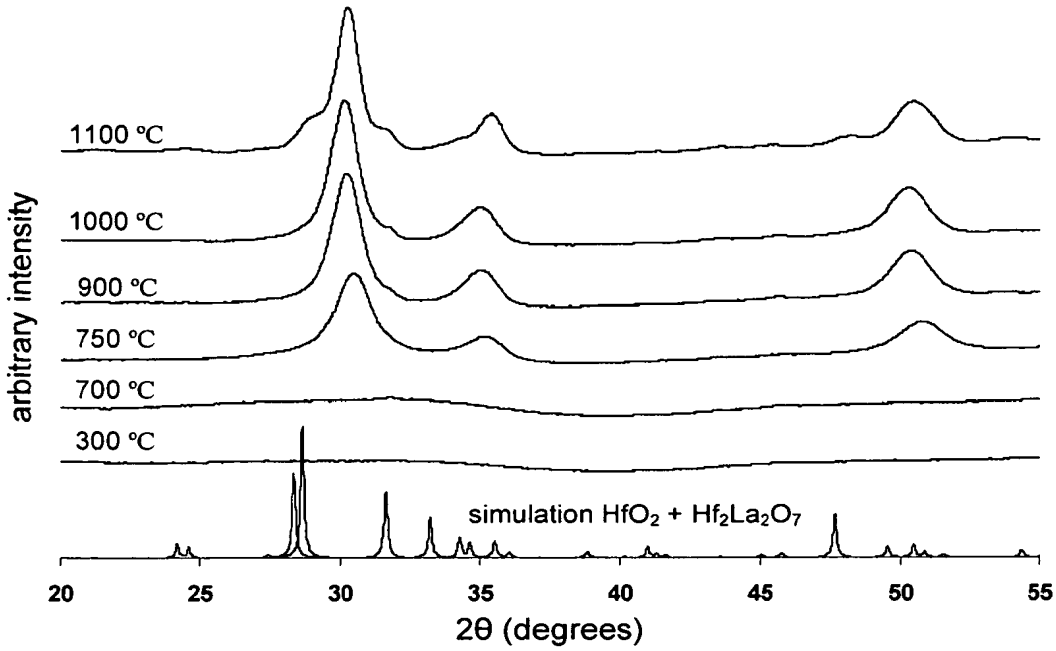


FIG. 5

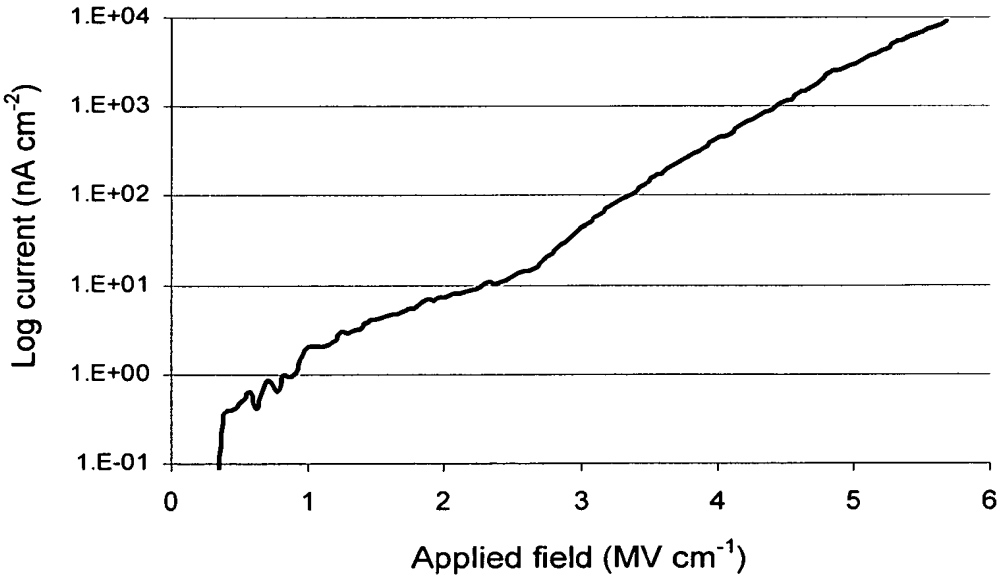


FIG. 6

Lam Research Ex. 1007 - Page 466 Lam Research Corp. v. Impria Corp. IPR2024-00833 - U.S. Patent No. 9,823,564

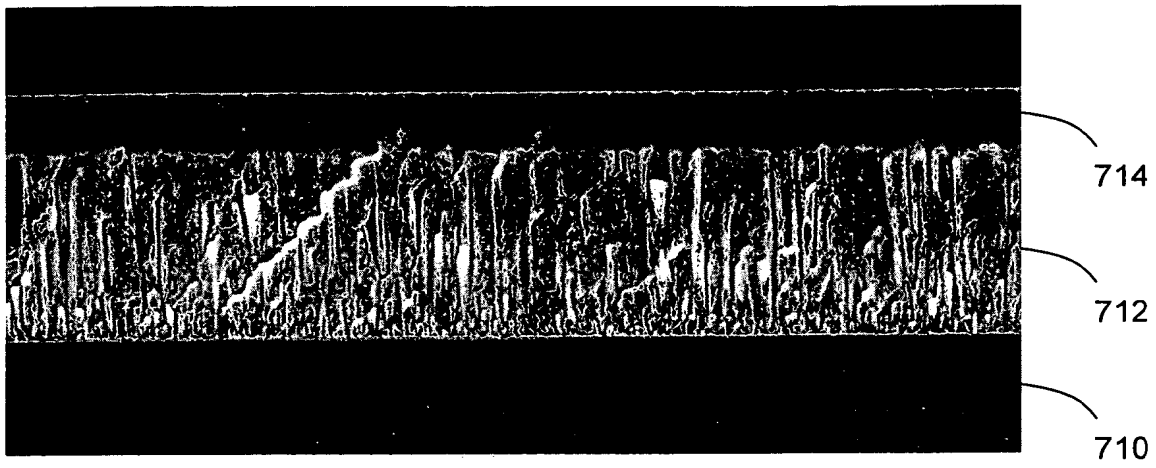


FIG. 7

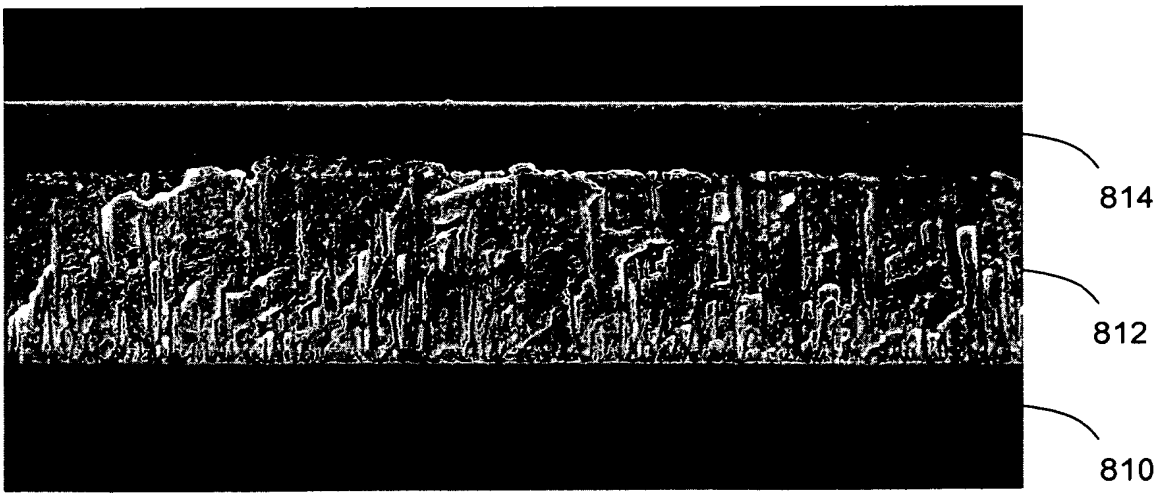


FIG. 8

Lam Research Ex. 1007 - Page 467 Lam Research Corp. v. Inpria Corp. IPR2024-00633 - U.S. Patent No. 9,823,564

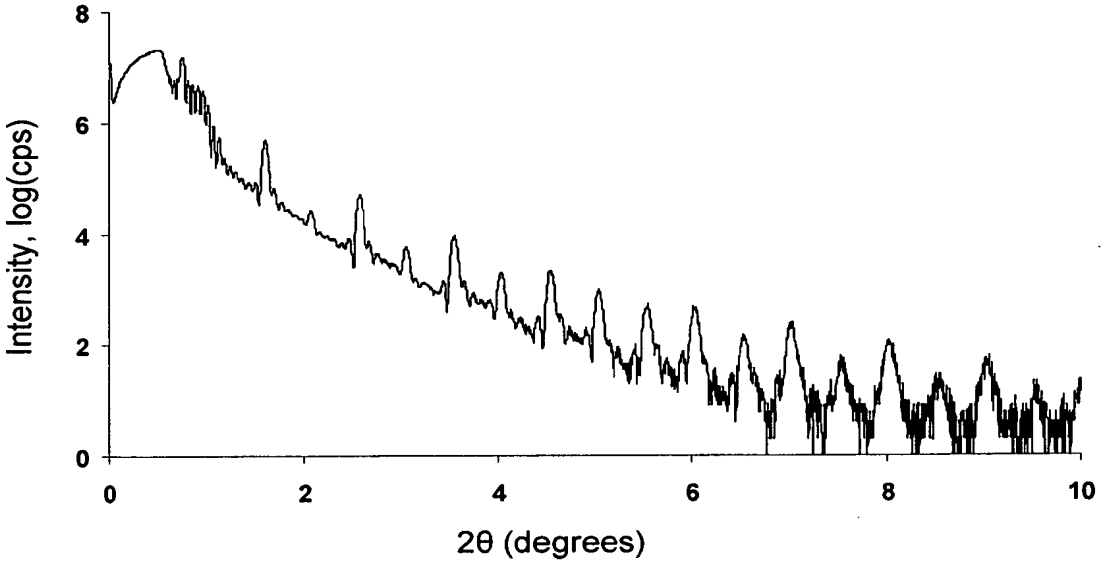


FIG. 9

Lam Research Ex. 1007 - Page 468 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

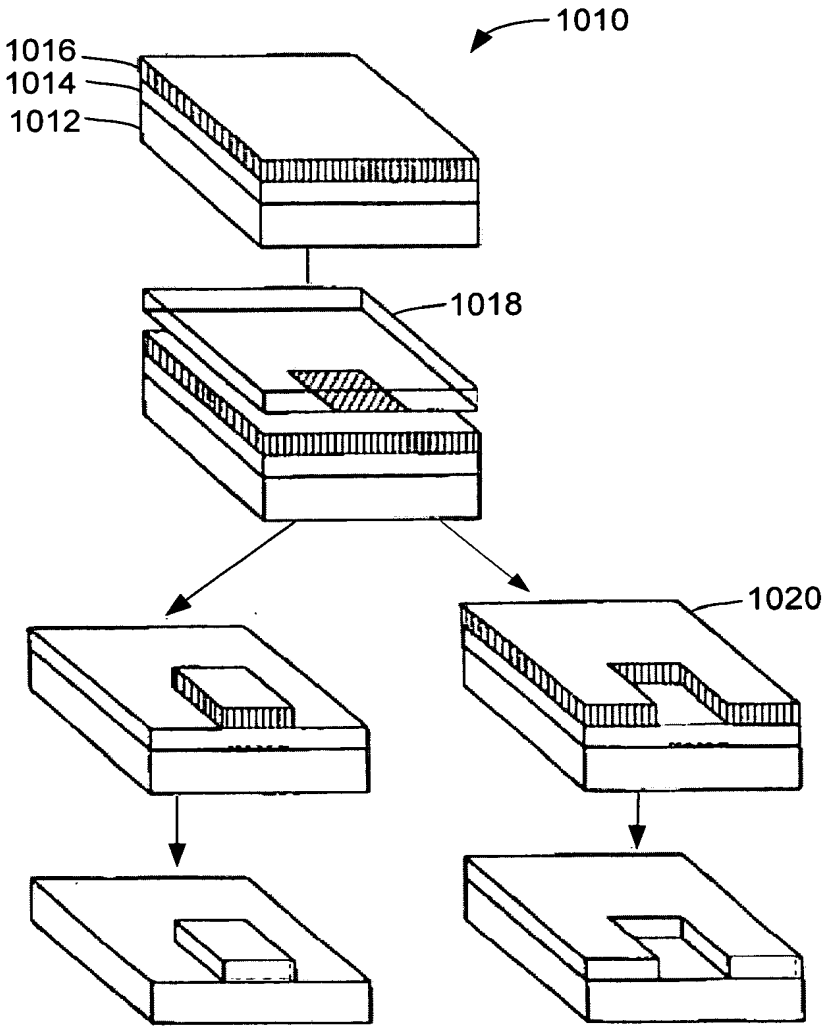


FIG. 10

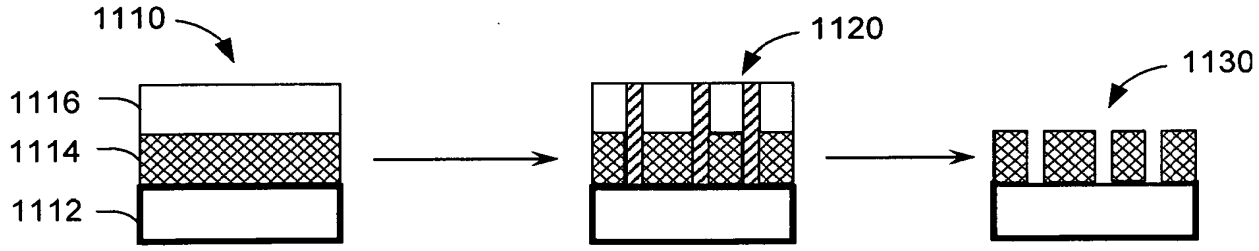


FIG. 11

Lam Research Ex. 1007 - Page 469 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

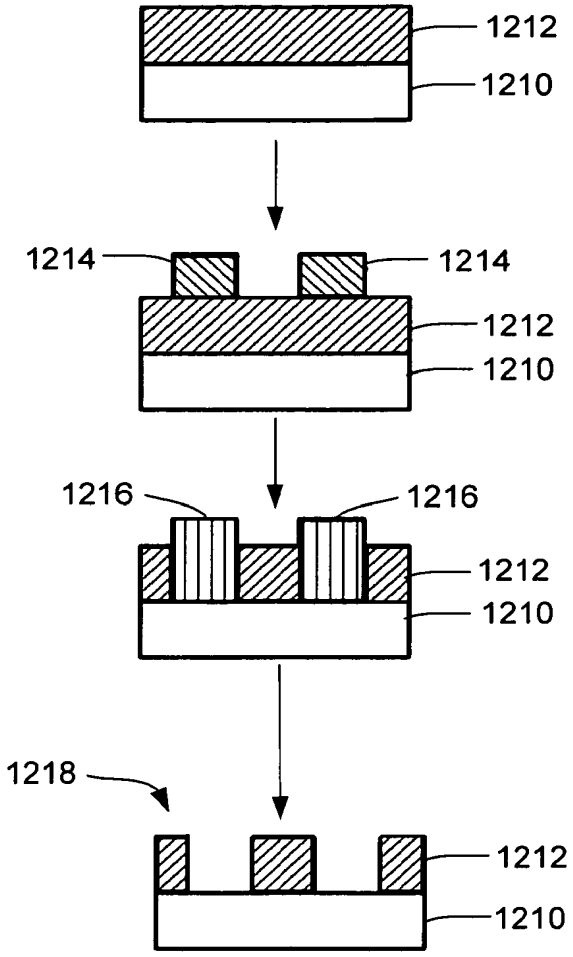


FIG. 12

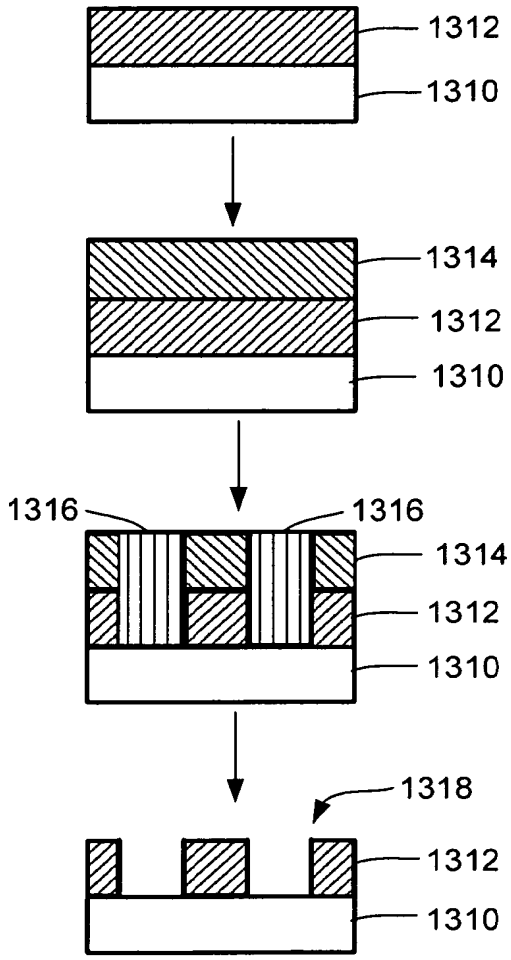


FIG. 13

Lam Research Ex. 1007 - Page 470 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

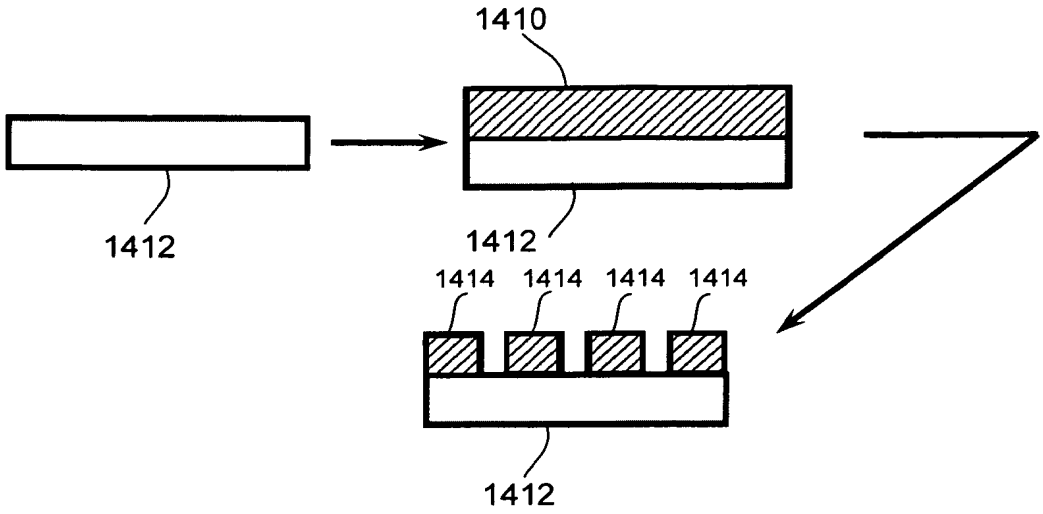


FIG. 14

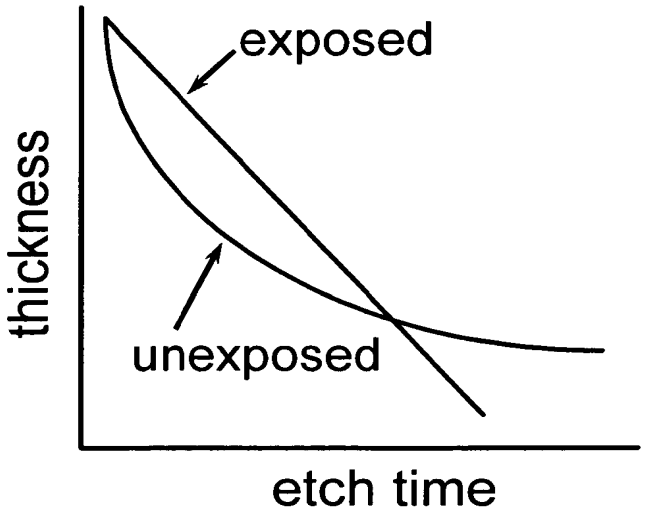


FIG. 15

Lam Research Ex. 1007 - Page 471 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

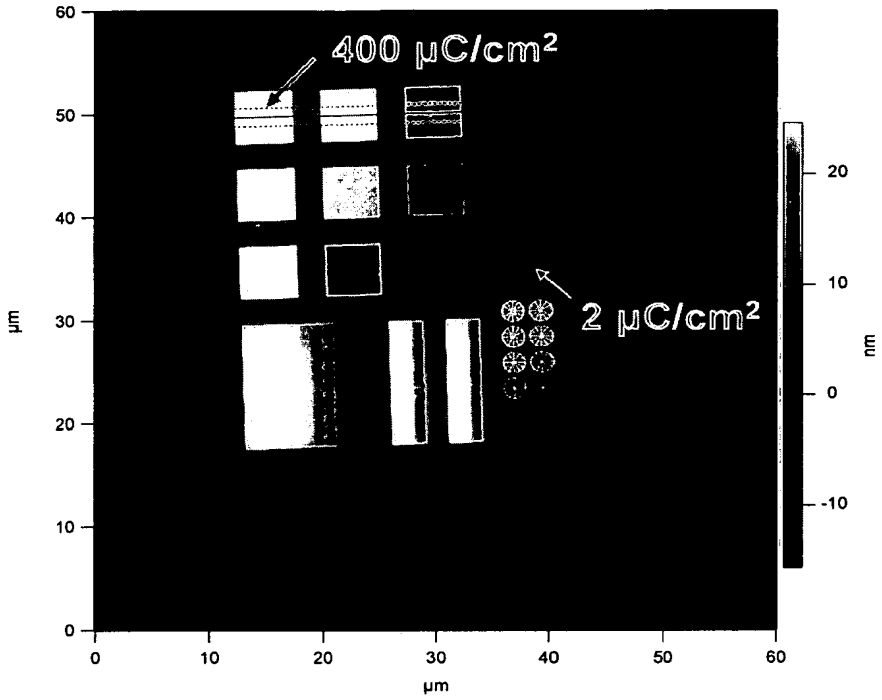


FIG. 16

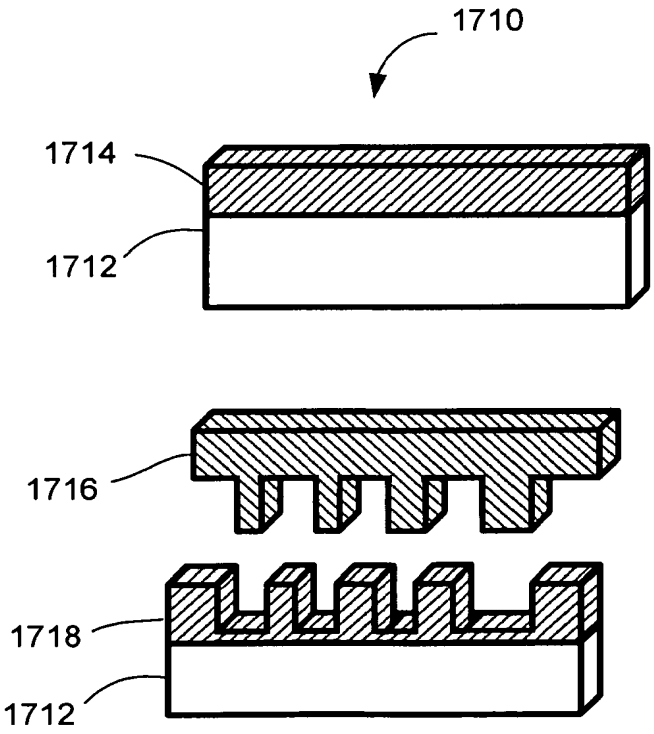


FIG. 17

Lam Research Ex. 1007 - Page 472 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

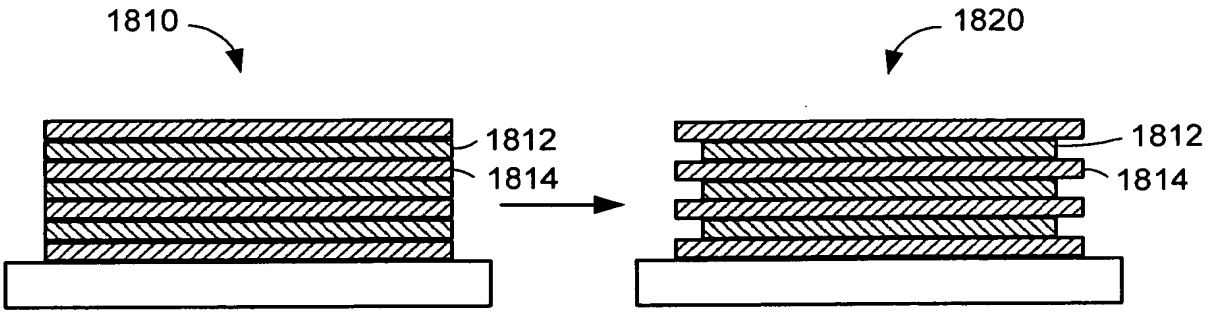


FIG. 18

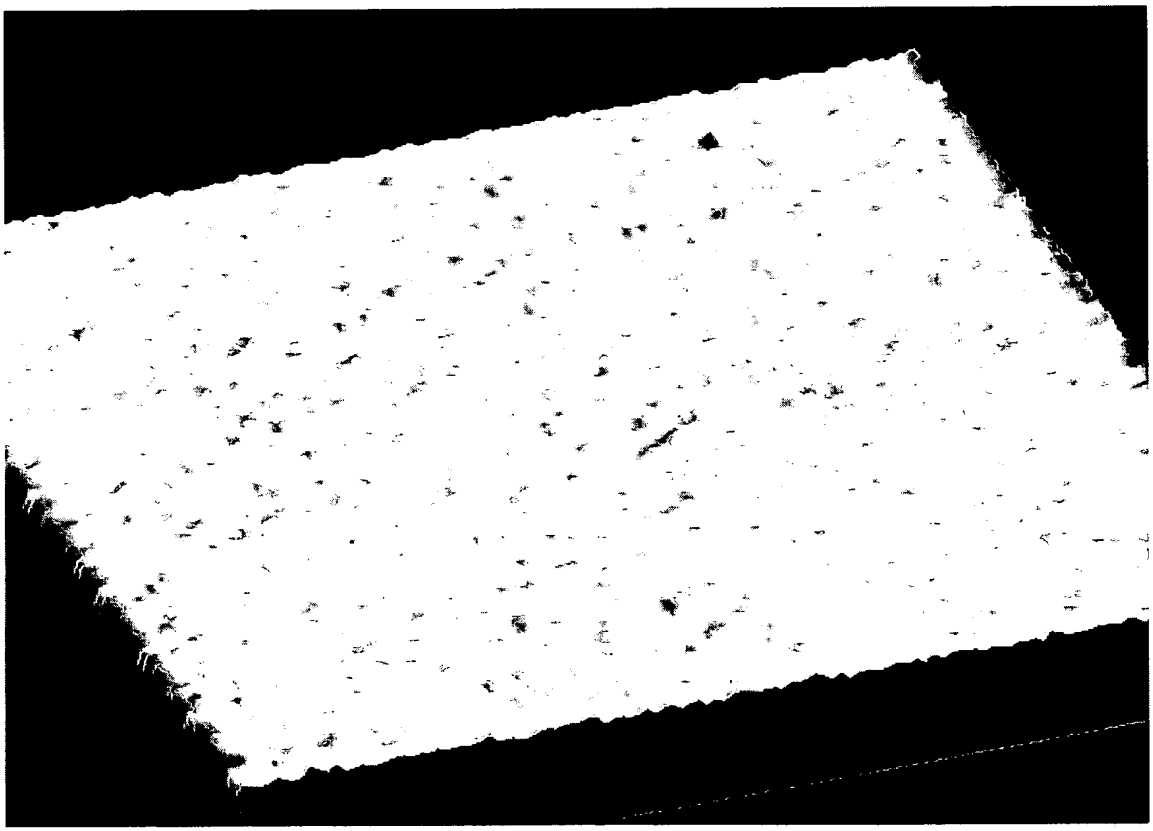


FIG. 19

Lam Research Ex. 1007 - Page 473 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

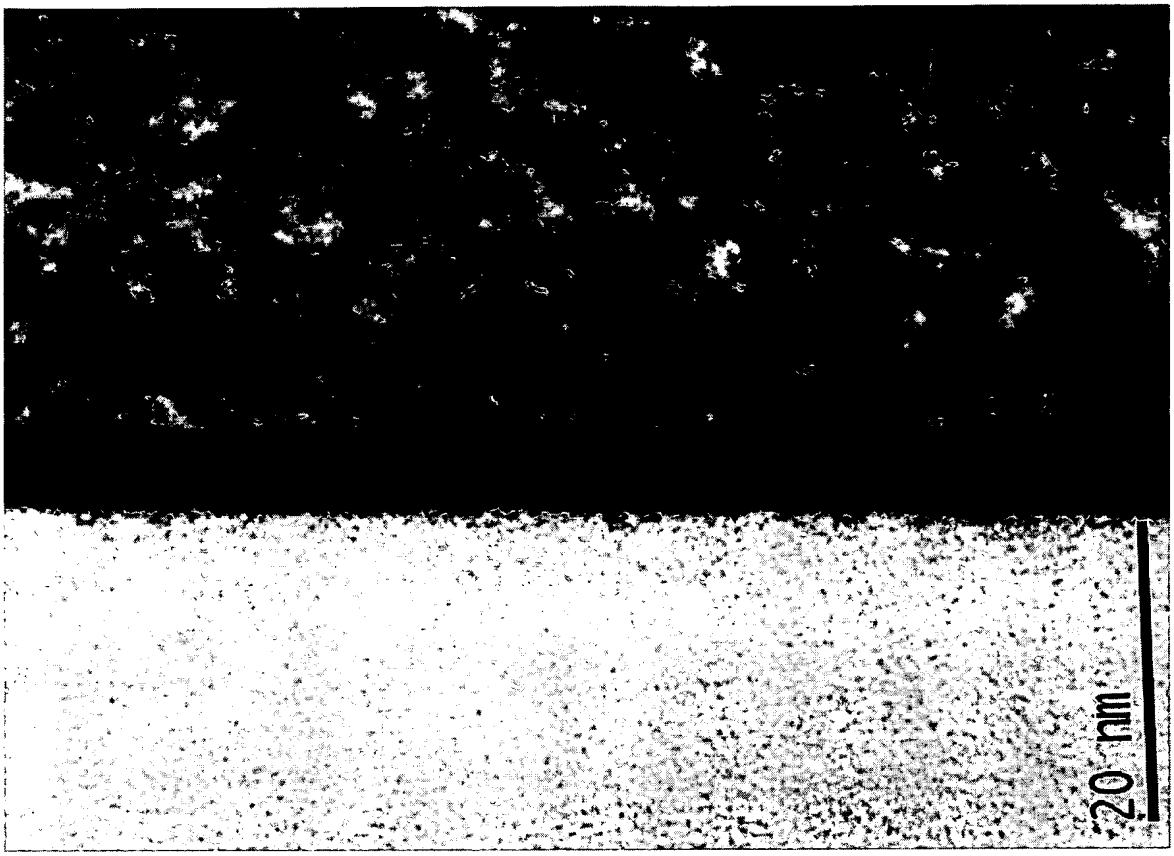


FIG. 20

Lam Research Ex. 1007 - Page 474 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

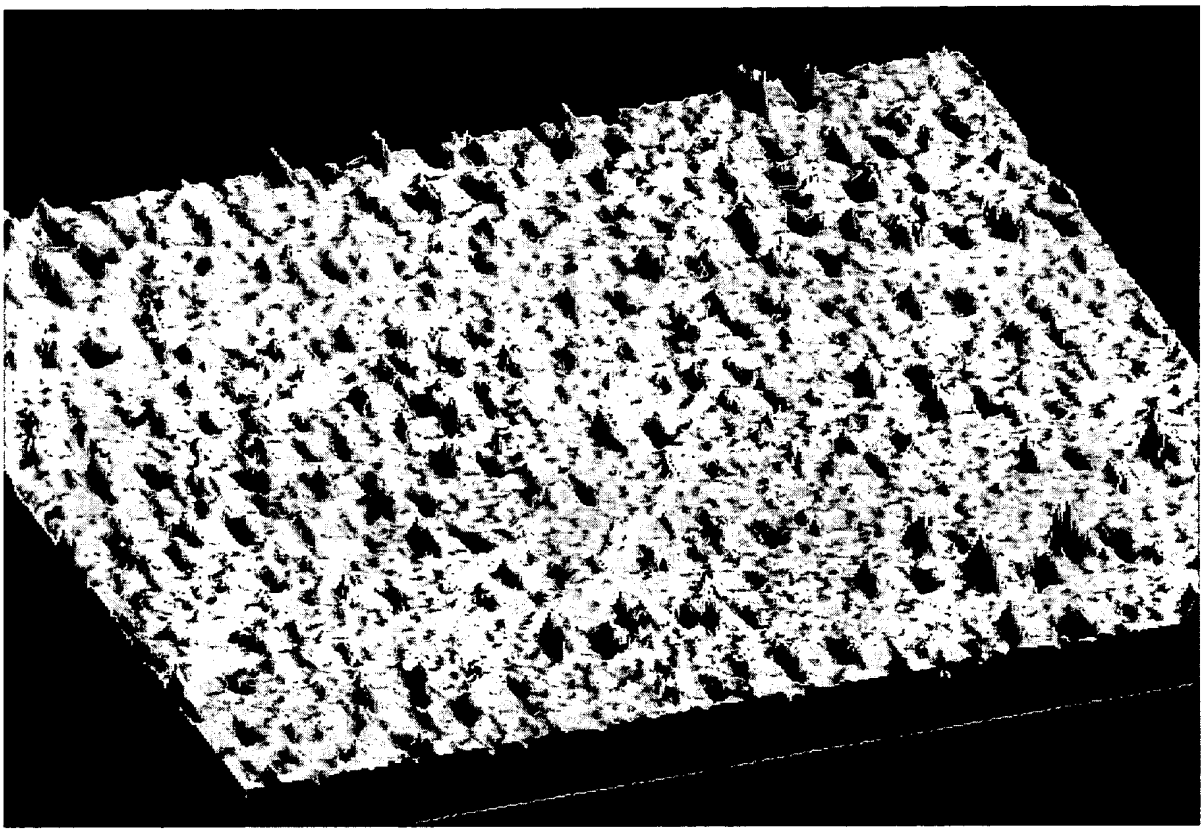


FIG. 21

Lam Research Ex. 1007 - Page 475 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

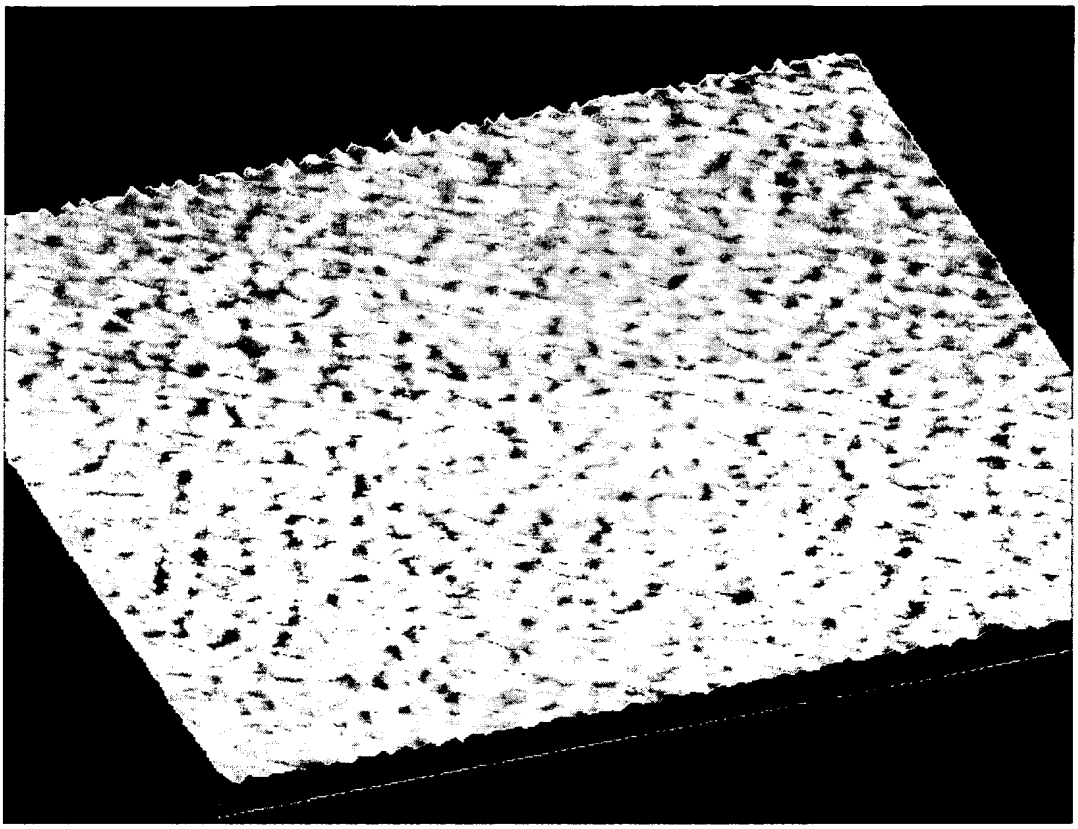


FIG. 22

Lam Research Ex. 1007 - Page 476 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

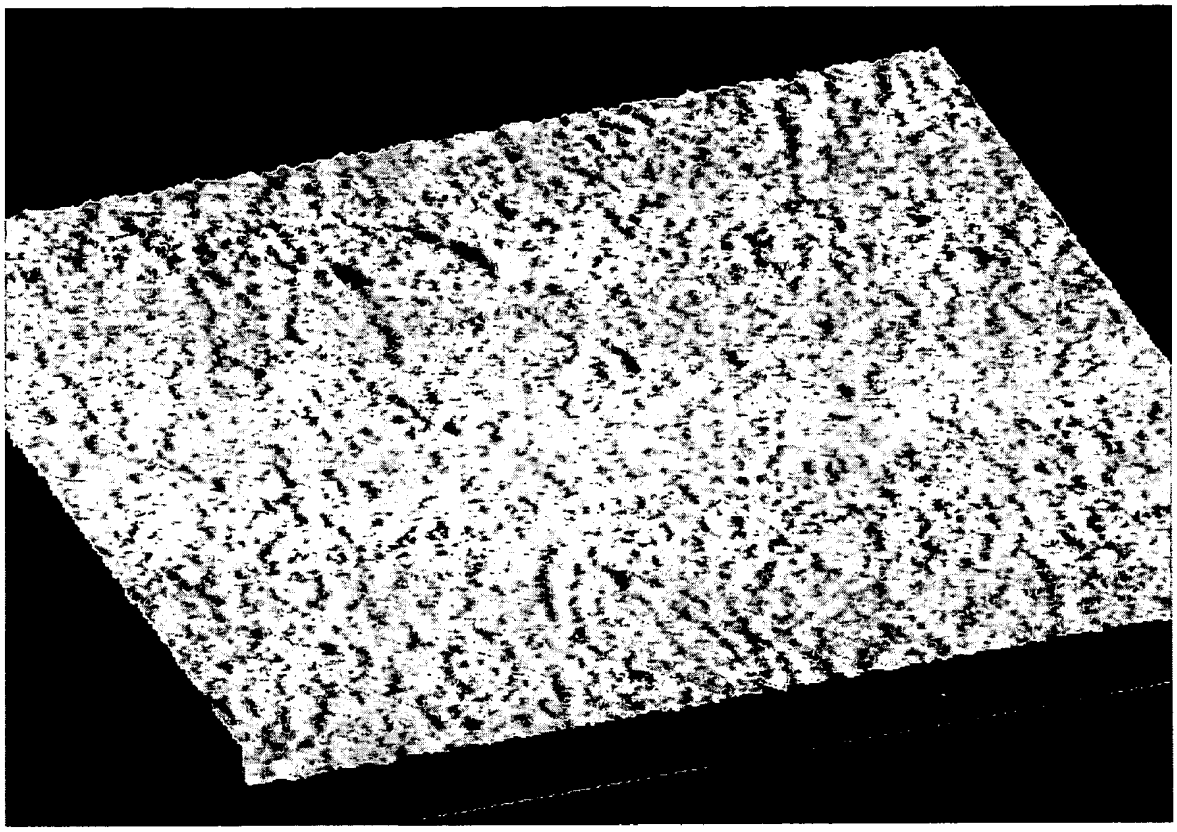


FIG. 23

Lam Research Ex. 1007 - Page 477 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

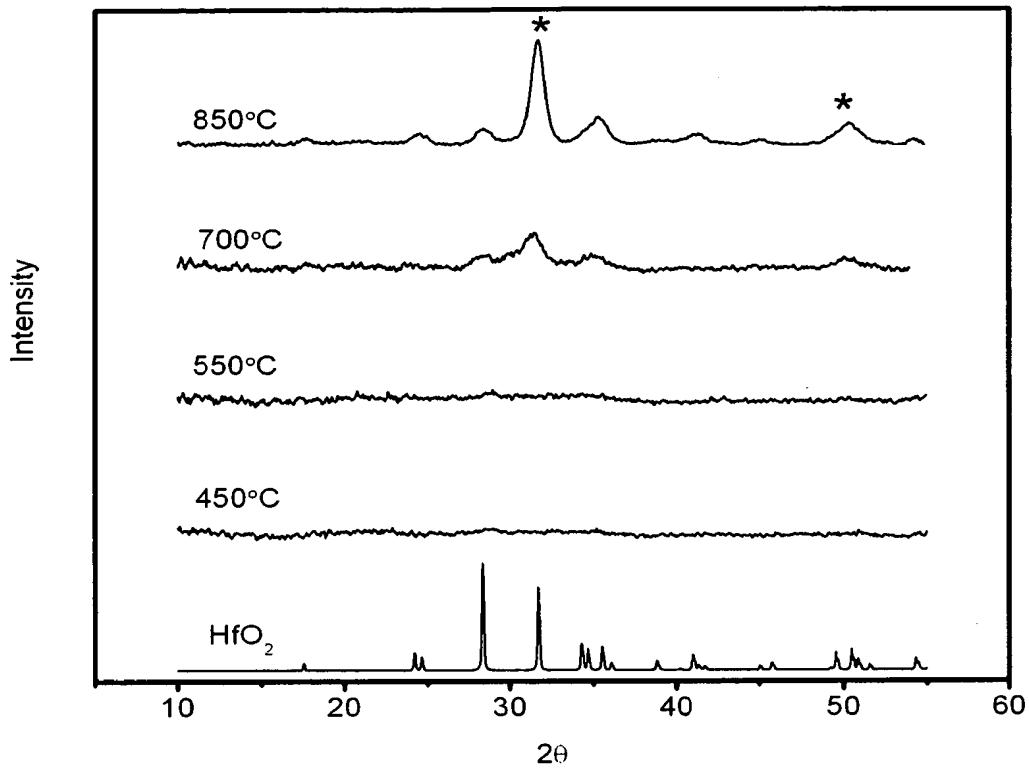


FIG. 24

Lam Research Ex. 1007 - Page 478 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

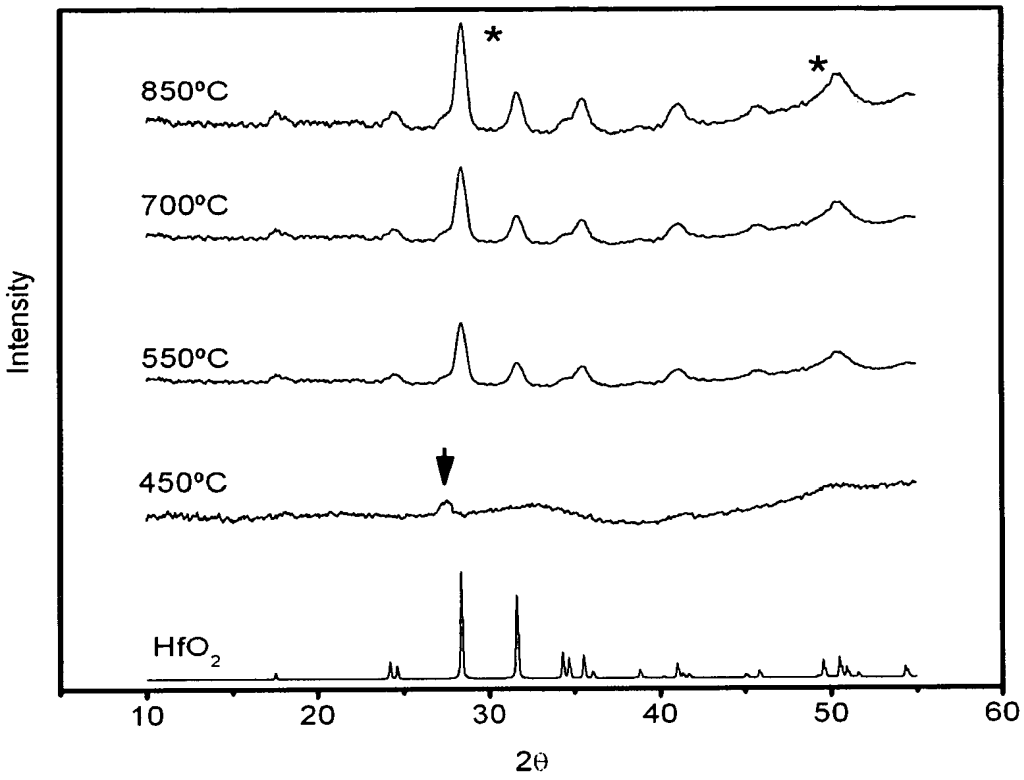


FIG. 25

Lam Research Ex. 1007 - Page 479 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

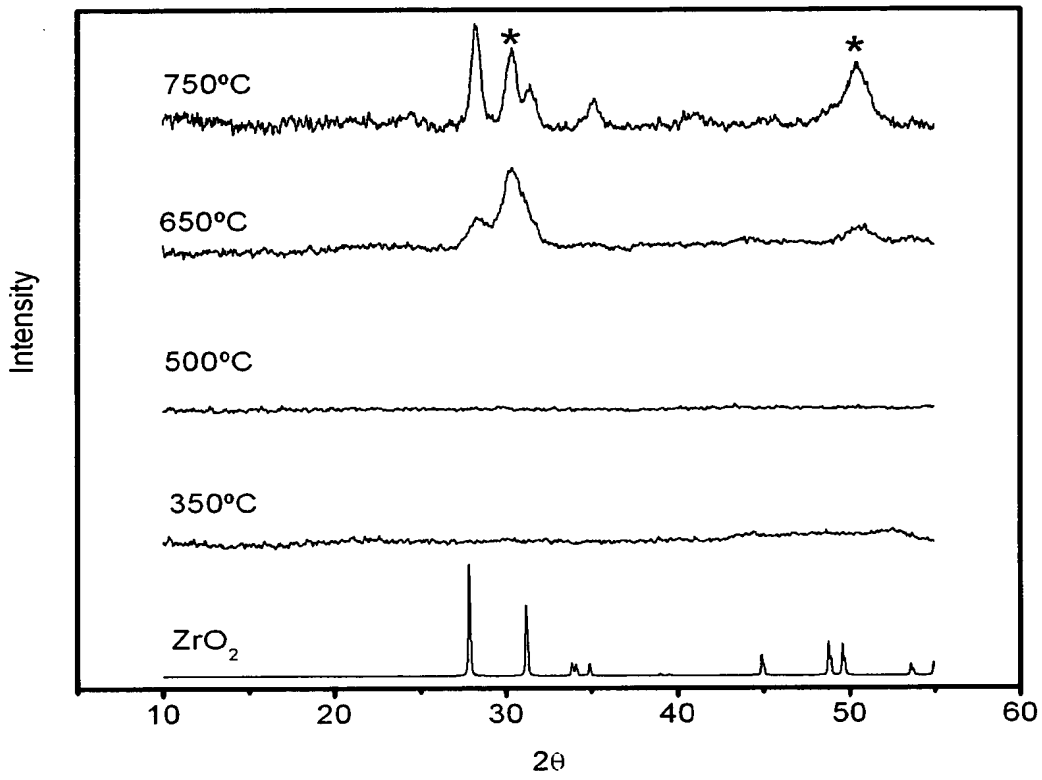


FIG. 26

Lam Research Ex. 1007 - Page 480 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

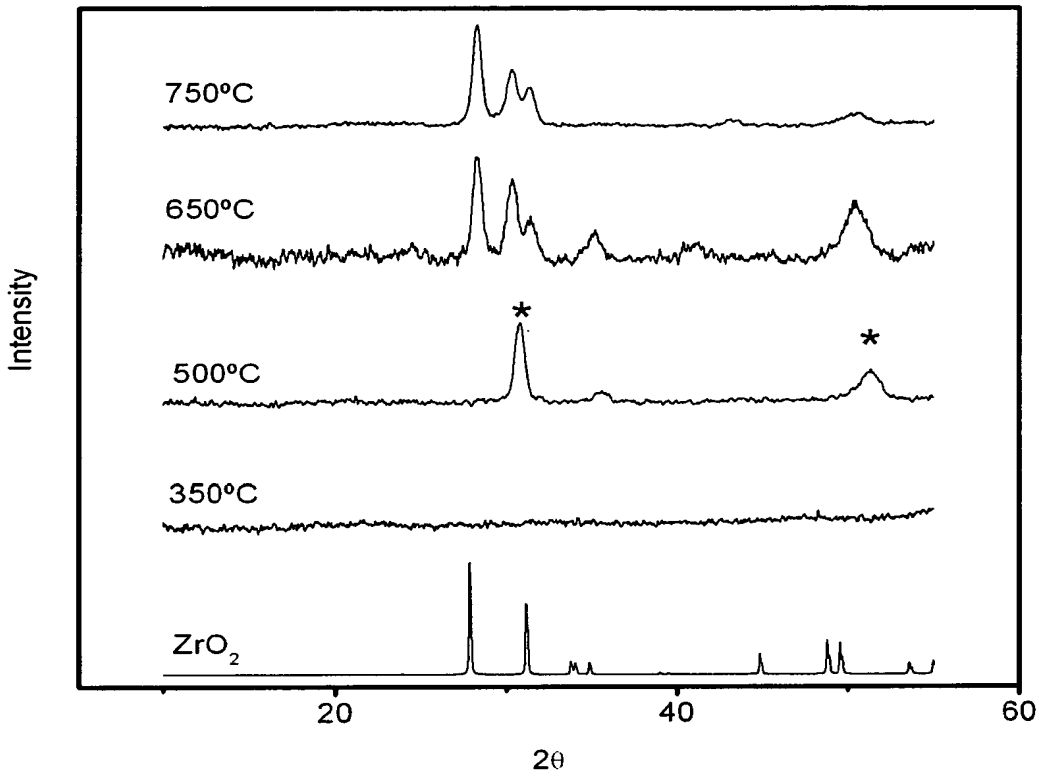


FIG. 27

Lam Research Ex. 1007 - Page 481 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564



FIG. 28

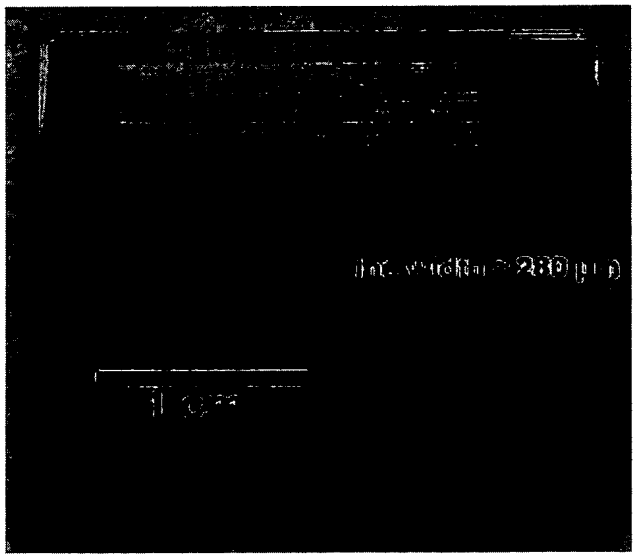


FIG. 29

Lam Research Ex. 1007 - Page 482 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

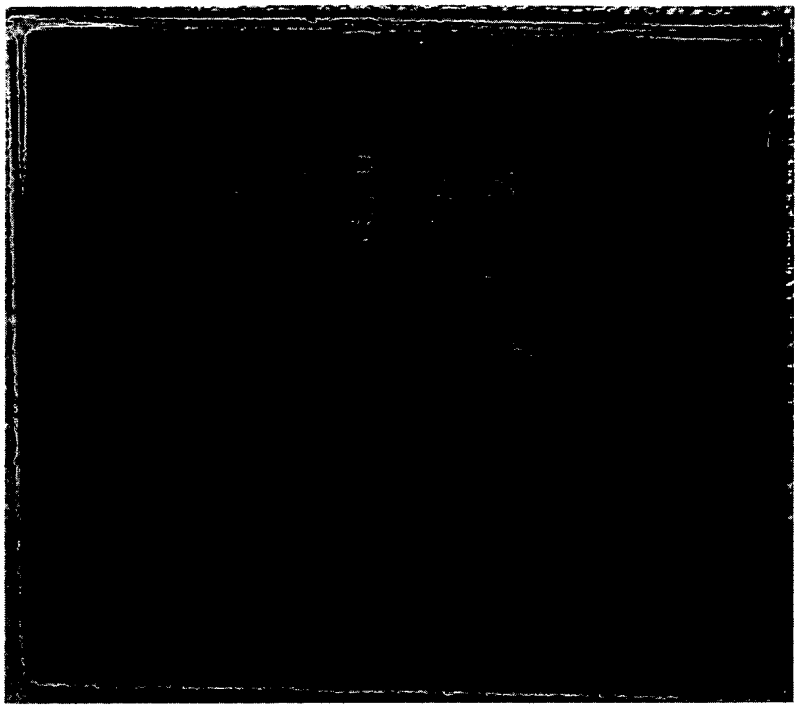


FIG. 30



FIG. 31

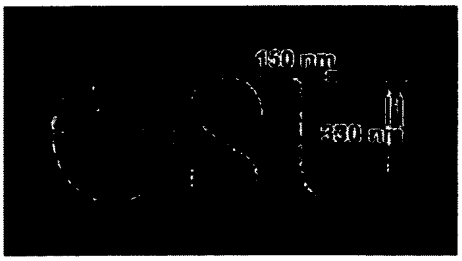


FIG. 32

Lam Research Ex. 1007 - Page 483 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

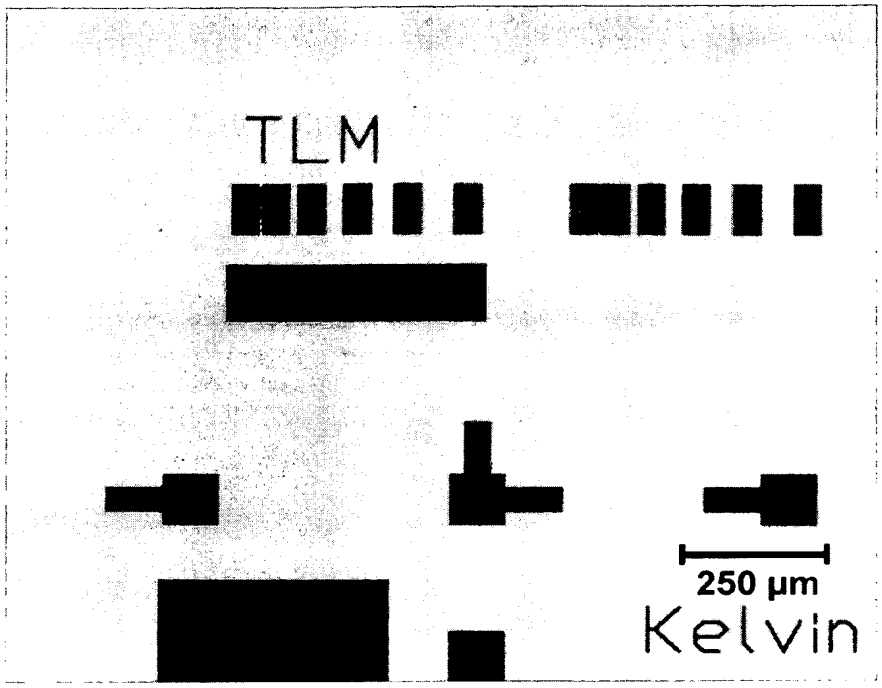


FIG. 33

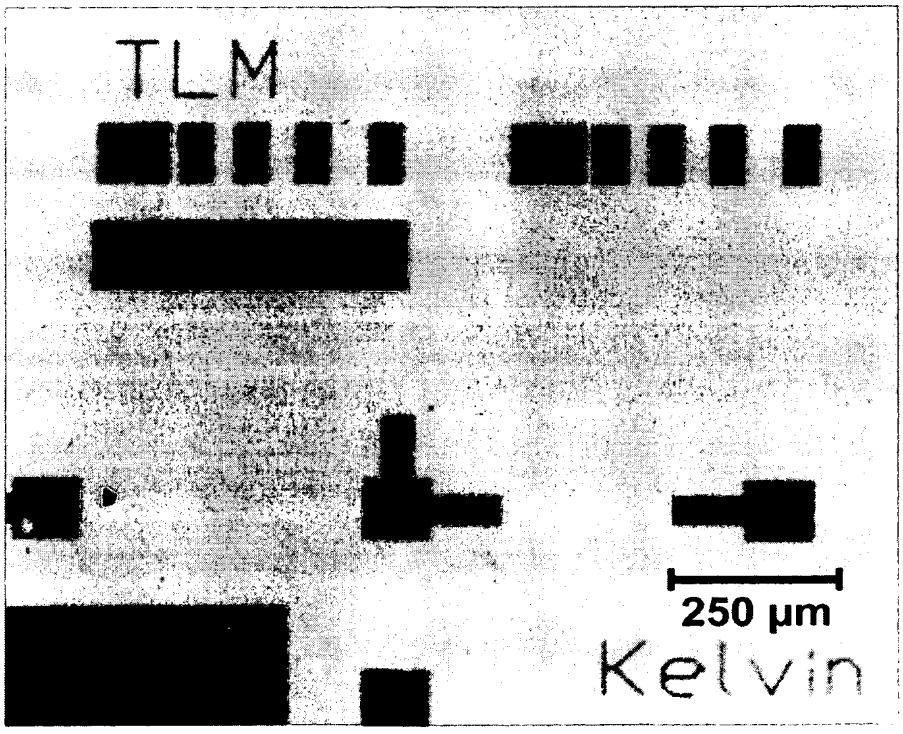


FIG. 34

Lam Research Ex. 1007 - Page 484 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

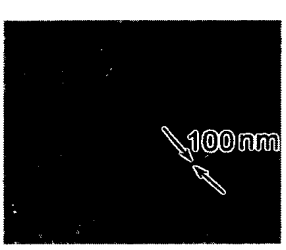


FIG. 35

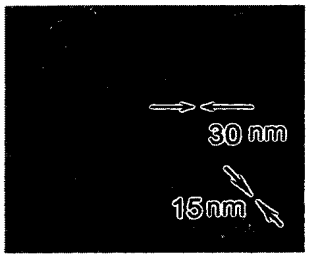


FIG. 36

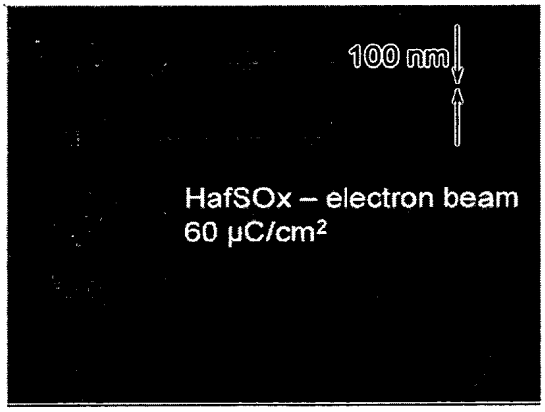


FIG. 37

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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

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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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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/858,612	09/18/2015	Jason K. Stowers	5063.02US04	1074

62274 7590 10/18/2016

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Moore Lake Plaza, Suite 205
1250 East Moore Lake Drive
Fridley, MN 55432

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ART UNIT	PAPER NUMBER
1722	

MAIL DATE	DELIVERY MODE
10/18/2016	PAPER

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The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No. 14/858,612	Applicant(s) STOWERS ET AL.	
	Examiner CHANCEITY ROBINSON	Art Unit 1722	AIA (First Inventor to File) Status No

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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 *09/30/2016*.

☐ 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) *1-7 and 21-25* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-7 and 21-25* 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 *09/30/2016*.

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 September 30, 2016 received. Claims 8-20 have been canceled. Claims 21-25 have been added as new.

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 June 30, 2016.

Claim Rejections - 35 USC § 112

4. Claims 1-7 and 21-25 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. Instant claims 1-7 and 21-26 recite the term, "about". The term "about" in claims 1, 6, 21, 22 and 25 is a relative term which renders the claim indefinite. The term "about" is not defined by the claim, the specification does not provide a standard for ascertaining the requisite degree, and one of ordinary skill in the art would not be reasonably apprised of the scope of the invention. Appropriate correction is required.

Double Patenting

5. Claims 1-7 and 21-25 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-17 of U.S. Patent No. 8,415,000 B2. Although the claims at issue are not identical, they are not patentably distinct from each other because both the instant claims and patent '000 have claims drawn to a structure

comprising a substrate a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands (patterned inorganic material). Both the instant claims and patent ‘000 recite open claim language; therefore, other components may be comprised in their respective invention.

6. Claims 1-7 and 21-25 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-19 of U.S. Patent No. 9,281,207 B2. Although the claims at issue are not identical, they are not patentably distinct from each other because both the instant claims and patent ‘207 have claims drawn to a structure comprising a substrate a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands. Both the instant claims and patent ‘207 recite open claim language; therefore, other components may be comprised in their respective invention.

Claim Rejections - 35 USC § 103

7. Claims 1-7 and 21-25 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) in view of Meyers et al. (WO 2008/082448 A1).

Regarding claims 1-7 and 21-25, Stowers et al. disclose a structure comprising a substrate and a coating material an aqueous precursor solutions 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 the coating material has an average thickness 35 nm (about 30 nm), wherein exposure of the coating material to UV , EUV, and/or electron-beam radiation alters the chemical properties of the coating material creating

an exposed coating material with differential dissolution rates between exposed and unexposed regions of the coating material (see introduction section).

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.

Further regards to claims, Stowers et al. teach a method of making a structure by exposing, spin coating and heating the coating material. However, Meyers et al. teach it is well-known to one of ordinary skill in the art to heat the coating material of a patterning structure (examples, abstract, and pages 30-31) to a temperature about 50 to about 200℃ (see claim 18), which encompasses the instant claimed range from about 45 to about 150℃. Also, Meyers et al. teach the structure us exposed at an electron beam at a dose level of from greater than 0 $\mu C/cm^2$ to at least 400 $\mu C/cm^2$ to define a pattern in the structure (claim 20), which encompasses the instant claimed range of no more than about 100 mJ/cm^2 . Stowers et al. and Meyers et al. are analogous art in patterned structures field. Therefore, it would have been obvious to one of ordinary skill in the art at the time of invention to modify and include the specific heating range and dosage level to structure process of Stowers et al. in view of aiding in imaging and patterning.

Stowers et al. do not explicitly disclose the structure having a metal ion to radiosensitive ligand ratio is at least about 2. Stowers et al. recognize that metal ion to peroxide (ligand) is 1:0.5 . 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).

Further regards to claims, Stowers et al. teach a method of making a structure by exposing, spin coating and heating the coating material. However, Meyers et al. teach it is well-known to one of ordinary skill in the art to heat the coating material to a temperature about 50 to about 200℃ (see claim 18), which encompasses the instant claimed range from about 45 to about 150℃. Also, Meyers et al. teach the structure us exposed at an electron beam at a dose level of from greater than 0 $\mu C/cm^2$ to at least 400 $\mu C/cm^2$ to define a pattern in the structure (claim 20), which encompasses the instant claimed range of no more than about 100 mJ/cm^2 .

Response to Arguments

8. Applicant's arguments filed 09/30/2016 have been fully considered but they are not persuasive. Applicant’s principle arguments are the following:

A) Applicants argue that MPEP states the claims at issue must be patentably distinct from the first patent. The claims must be viewed on the whole. There is a difference between thickness and other dimensions. Claims 1-17 of '000 does not teach or discuss thickness of the coating. Withdrawal of the non-statutory obviousness type double patenting rejection is respectfully requested.

A) Examiner respectfully disagrees. The coating material of the instant claims and the coating material of patent '000 are identical or substantially identical in structure or composition, or are produced by identical or substantially identical processes, a prima facie case of either anticipation or obviousness has been established. In re Best, 562 F.2d 1252, 1255, 195 USPQ 430, 433 (CCPA 1977). However, it is the position of the examiner that those characteristics of the average thickness of the layer of the coating material are inherent, given that the coating material disclosed by patent ‘000 and the instant claims are the same. A reference that is silent about a claimed invention’s features is inherently anticipatory if the missing feature is necessarily present in that which is described in the reference. Inherency is not established by probabilities or possibilities. *In re Robertson*, 49 USPQ2d 1949 (1999). Therefore, it would have been obvious at the of the invention to include that average thickness of the coating material of patent ‘000 from about 5 nm to about 30 nm as instantly claimed.

B) Applicants argue claims 1-19 of ‘207 are directed toward a system of a hardmask and a resist layer. The presently claimed invention is not directed toward a similar system. Therefore, claims 1-19 of '207 do not render the present invention

patentably indistinct. Withdrawal of the non-statutory obviousness type double patenting rejection is requested.

B) Examiner respectfully disagrees. Patent ‘207 recites a layered structure in claim 1, which corresponds to the structure of claim 1 of the instant claims. Both structures comprises (open claim language) a substrate (see claim 1 of patent ‘207 and claim 1 of instant claims) and hardmask composition layer of patent '207 (corresponds to coating material of the instant claims) having a thickness from about 1 nm to about 50 nm, which encompasses the instant claimed range of average thickness from about 5 nm to about 30 nm. Examiner disagrees with applicants that presently claimed invention is not directed toward a similar system. Both the instant claims and patent ‘207 recite open claim language; therefore, other components and layers may be comprised in their respective invention (structures). Both the instant claims and patent '207 are directed to a structure, which are very similar to each other. Therefore, the rejection is maintained.

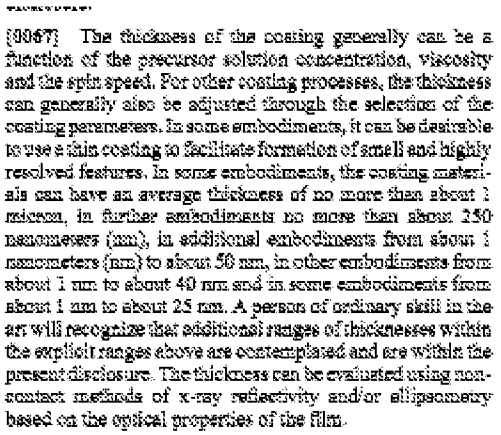
C) Applicants argue that it is very respectfully submitted that the term "about" is a well-settled term of approximation. Well-established case law shows that a suitable construction is to identify if a particular reference or accused device falls within the claimed range with the upper limit of the range being the stated value as modified by the term "about" Such broadening usages as "about" must be given reasonable scope; they must be viewed by the decision maker as they would be understood by persons experienced in the field of the invention. The meaning of the term “ about" is dependent on the facts of a case , the nature of the invention , and the knowledge imparted by the

totality of the earlier disclosure to those skilled in the art. Applicants believes that the claims are presently clear.

C) Examiner respectfully disagrees that in the instant disclosure that the term, “about” is clear and not indefinite. First, the instant disclosure fails to define the meaning of the term, “about” in the claims or specification. The term "about" is not defined by the claim, the specification does not provide a standard for ascertaining the requisite degree, and one of ordinary skill in the art would not be reasonably apprised of the scope of the invention. The courts have stated in determining the range encompassed by the term "about", one must consider the context of the term as it is used in the specification and claims of the application. Ortho-McNeil Pharm., Inc. v. Caraco Pharm. Labs., Ltd., 476 F.3d 1321, 1326, 81 USPQ2d 1427, 1432 (Fed. Cir. 2007). The instant disclosure recites the following on page 33, lines 13-15:

> 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

Also, the USPGUB states in paragraphs [0067]:



[0067] 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 term “about” is ambiguous. However, one of ordinary skill in the art may define the term “about” to be ±5nm, which may be understood by persons experienced in the field of the invention. Lastly, there is no mention of an embodiment from about 5 nm to about 30 nm. Again, the term "about" is not defined by the claims, the specification does not provide a standard for ascertaining the requisite degree. Nonetheless, the claim language of instant claims 21 and 23, regarding “at least about 2" and “no more than about 100 mJ/cm2" are ambiguous and relative terminology. The court held that claims reciting “at least about” were invalid for indefiniteness where there was close prior art and there was nothing in the specification, prosecution history, or the prior art to provide any indication as to what range of specific activity is covered by the term “about.” Amgen, Inc. v. Chugai Pharmaceutical Co., 927 F.2d 1200, 18 USPQ2d 1016 (Fed. Cir. 1991). Therefore, the rejections are maintained.

D) Applicants argue that Stowers does not disclose all the features of claim 1. It requires that one compare the claim’s subject matter as a whole’ with the prior art' to which said subject matter pertains. Stowers does not teach or suggest each and every element. Stowers teaches a line width a line-width roughness of 2 nm. A person of skill

in the art would understand a line-width roughness to describe the sharpness of a developed line. The thickness of the film in Stowers is 35 nm. See paragraphs [0730] and [0731]. Claim 1 discusses the average thickness of the coating material. In claim 1 this thickness is about 5 nm to about 30 nm. Stowers does not teach or suggest each and every element of claim 1. Stowers therefore does not render claim 1 prima facie obvious.

D) Examiner respectfully disagrees. It is noted that the average thickness of the coating material of from about 5 nm to about 30 nm is not clearly defined by the claims and/or instant disclosure. However, one of ordinary skill in the art may define the term “about” to be ±5nm, which may be understood by persons experienced in the field of the invention. In the instant case, Stowers teach the thickness of the film is 35 nm, which meets the limitation of “about 30 nm”. See paragraphs [0730] and [0731]. Therefore, the rejection is maintained.

Conclusion

9. Applicant's amendment of adding new claims 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

Notice of References Cited	Application/Control No. 14/858,612	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	CPC Classification	US Classification
	A	US-				
	B	US-				
	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	CPC Classification
	N	WO 2008082448 A1	07-2008	US	MEYERS STEPHEN T	H01L29/4908
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	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.

PTO/SB/08a (03-15)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14858612
Filing Date	2015-09-18
First Named Inventor	Stowers
Art Unit	1722
Examiner Name	Robinson, Chanceity N.
Attorney Docket Number	5063.02US04

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
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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					

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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	2001154366	JP	A	2001-06-08	Fujitsu Ltd	English Abstract	
	2	2010508560	JP	A	2010-03-18	Oregon State University	Corresponds to WO 2008082448A1	
	3	2011524627	JP	A	2011-09-01	Oregon State University	Corresponds to WO 2009120169A1	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./

Receipt date: 09/30/2016

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	14858612 GAU: 1722
Filing Date	2015-09-18
First Named Inventor	Stowers
Art Unit	1722
Examiner Name	Robinson, Chanceity N.
Attorney Docket Number	5063.02US04

	4	2008082448	WO	A1	2008-07-10	Oregon State University	Corresponds to JP 2010508560A	
	5	2009120169	WO	A1	2009-10-01	Oregon State University	Corresponds to JP 2011524627A	

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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	Office Action from copending Japanese Application No. 2015-207978 dated August 23, 2016 (6 pages).	X

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.R./

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	10/16/2016

*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.

REMARKS

Claims 1-7 and 21-25 are pending. By this Amendment, claims 1, 6, 21, 22 and 25 are amended to remove the word about. No new matter is added.

35 U.S.C. § 112

Claims 1-7 and 21-25 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. In particular, the Examiner raised specific issues with respect to the term "about". While Applicant respectfully maintains that the claims were clear to a person of ordinary skill in the art as written, Applicant has amended the claims to advance prosecution. Applicant has removed the term "about" from the claims. With respect to the relevant parameters, a person of ordinary skill in the art would interpret "about" in the present context as corresponding to experimental error in the measurements of continuous variable of the present type. From that perspective, the amended claims have effectively the same scope following amendment to remove the term "about" since the values would be interpreted in view of the accuracy of the measurements. In view of the amendment, Applicant respectfully requests withdrawal of the rejection of claims 1-7 and 21-25 under 35 U.S.C. §112 (pre-AIA), second paragraph, as being indefinite.

Double Patenting

Non-Statutory Double Patenting over U.S. Pat. No. 8,415,000

Claims 1-7 and 21-25 are rejected on the ground of non-statutory double patenting as being unpatentable over claims 1-17 of U.S. Pat. No. 8,415,000 to Stowers et al. (Pat. '000). In particular, the Examiner has argued that both the instant claims and the claims of Pat. '000 are drawn to a structure comprising a substrate and a coating material on the surface comprising metal ions with radiation sensitive ligands. Because these claims use open claims language, Examiner argues that

Lam Research Ex. 1007 - Page 504 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

the each of the claims can comprise the same elements. Respectfully, however, this is an incorrect interpretation of the law regarding non-statutory double patenting.

"Generally, an obviousness-type double patenting analysis entails two steps. First, as a matter of law, a court construes the claim in the earlier patent and the claim in the later patent and determines the differences. Second, the court determines whether the differences in subject matter between the two claims render the claims patentably distinct. A later claim that is not patentably distinct from an earlier claim in a commonly owned patent is invalid for obvious-type double patenting. A later patent claim is not patentably distinct from an earlier patent claim if the later claim is obvious over, or anticipated by, the earlier claim." *Eli Lilly & Co. v. Barr Labs., Inc.*, 251 F.3d 955, 968 (Fed. Cir. 2001) (internal citations omitted). Obviousness is determined by preforming an analysis similar to that preformed for obviousness under 35 U.S.C. § 103. *Otsuka Pharm. Co. v. Sandoz, Inc.*, 678 F.3d 1280, 1298 (Fed. Cir. 2012). The written description of the early claims is "considered only to the extent necessary to construe its claims" *Eli Lilly & Co. v. Teva Parenteral Medicines, Inc.*, 689 F.3d 1368, 1378–79 (Fed. Cir. 2012).

With all due respect, the Examiner seems to be using the disclosure of the '000 patent rather than the claims. This is a clear error of law. In the present case, the '000 patent shares a common parent with the present application that are related as continuations. Being a continuation does not automatically require an obviousness-type double patenting rejection. A parent specification always teaches the subject matter of the claims of a continuation application because this is required for the priority claim. With all due respect, when the law is properly followed, the CLAIMS of the '000 patent do not render the present claims *prima facie* obvious. Claims 1-17 of '000 does not teach or discuss thickness of the coating. Rather, claims 1-17 of '000 discuss the line-width roughness and pitch of particular features. Therefore, claims 1-17 of '000 do not render the present invention patentably indistinct. Withdrawal of the non-statutory obviousness type double patenting rejection is respectfully requested.

Lam Research Ex. 1007 - Page 505 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Non-Statutory Double Patenting over U.S. Pat. No. 9,281,207

Claims 1-7 are rejected on the ground of non-statutory obviousness type double patenting as unpatentable over claims 1-19 of U.S. Pat. No. 9,281,207 ('207). With all due respect, claims 1-19 of '207 are directed toward a system of a hardmask and a resist layer. With all due respect, Applicant respectfully notes that the present rejection is based on clear error of law. The Examiner has not established *prima facie* obviousness based on the claims of the '207 patent. Applicant respectfully requests reconsideration of the rejection based on the following comments.

Applicant may have inadvertently led the issues astray. With all due respect, an obviousness analysis is not determined based on similarity So there is no legal relevance on whether or not the systems are similar with respect to the present claims and the claims of the '207 patent. With respect to the claims of the '207 patent, these claims do not teach radiation sensitive ligands. Furthermore, the hard mask layer would not be expected to be radiation patternable since the hard mask layer is expected to remain intact following radiation patterning. Since this feature is missing from the claims of the '207 patent and not suggested, the present claims respectfully are not *prima facie* obvious over the claims of the '207 patent.

Therefore, claims 1-19 of '207 do not render the present invention patentably indistinct. Withdrawal of the non-statutory obviousness type double patenting rejection is respectfully requested.

Lam Research Ex. 1007 - Page 506 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

35 U.S.C. § 103

Claim Rejections over Stowers and Meyers

The Examiner rejected claims 1-7 and 21-25 under 35 U.S.C. 103(a) as obvious over Jason Stowers, Douglas A. Keszler, "High resolution, high sensitivity inorganic resists" (2009) (Stowers) in view of WO 2008/082448 to Meyers et al. (Meyers). Claims 2-7 and 21-25 directly depend on claim 1. Since the combination of Stowers and Meyers 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.

"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.'".

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).

With regard to claim 1, the combination of Stowers and Meyers does not teach or suggest a thickness of between about 5 nm and about 30 nm. Rather, Stowers teaches a thickness of 35 nm or greater. Examiner has argued that 35 nm is within the range "about 30 nm". While Applicant maintains the argument that "about 30 nm" is not obvious over Stowers, claim 1 has been amended to remove the term "about" in order to advance prosecution. Therefore, the ranges do not overlap and they are not close enough that one would expect them to have the same properties. As indicated by the Examiner, Meyers does not teach or suggest a thickness between 5 nm and 30 nm. Stowers in view of Meyers does not teach or suggest each and every element of claim 1. The combination of Stowers and Meyers therefore does not render claim 1 *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 1-7 and 21-25 under 35 U.S.C. § 103(a) as obvious over Stowers in view of Meyers. 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.

Lam Research Ex. 1007 - Page 508 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

/Peter S. Dardi/

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Lam Research Ex. 1007 - Page 509 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Acknowledgement Receipt

EFS ID:	27827190
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
Receipt Date:	19-DEC-2016
Filing Date:	18-SEP-2015
Time Stamp:	11:57:35
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_After_Final.pdf	53351 16971ce69b9c07c090e57b4d8f9068136799a4d0	yes	9

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Response After Final Action	1	1
	Claims	2	3
	Applicant Arguments/Remarks Made in an Amendment	4	9
Warnings:			
Information:			
	Total Files Size (in bytes):	53351	

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.

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) A structure comprising a substrate and a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands and wherein the coating material has an average thickness from [[about]] 5 nm to [[about]] 30 nm, wherein exposure of the coating material to UV, EUV and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material.

2. (Original) The structure of claim 1 wherein the metal ions comprise metal suboxide ions.

3. (Original) The structure of claim 1 wherein the metal of the metal ions comprises 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.

4. (Original) The structure of claim 1 wherein the radiation sensitive ligands comprise peroxide ligands.

5. (Original) The structure of claim 1 wherein the coating material further comprises polyatomic anions.

6. (Currently Amended) The structure of claim 1 wherein the average thickness is from [[about]] 5 nm to [[about]] 25 nm.

7. (Original) The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists.

8-20. (Cancelled)

21. (Currently Amended) The structure of claim 1 having a metal ion to radiosensitive ligand ratio of at least [[about]] 2.

22. (Currently Amended) The structure of claim 1 wherein the coating material has been heated to temperatures from [[about]] 45°C to [[about]] 150°C.

23. (Previously Presented) The structure of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous solvent.

24. (Previously Presented) The structure of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent.

25. (Currently Amended) The structure of claim 1 wherein the coating material can be effectively patterned with UV radiation or EUV radiation at a dose of no more than [[about]] 100 mJ/cm^2.

Lam Research Ex. 1007 - Page 513 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.: 5063.02US04

Stowers et al. Confirmation No.: 1074

Application No.: 14/858,612 Examiner: Robinson, Chanceity N.

Filed: September 18, 2015 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 October 18, 2016, 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.

December 19, 2016
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. # 69,343

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 14/858,612	Filing Date 09/18/2015	☐ To be Mailed

ENTITY: ☒ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

	(Column 1)	(Column 2)		
FOR	NUMBER FILED	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

		(Column 1)		(Column 2)	(Column 3)		
	12/19/2016	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
AMENDMENT	Total (37 CFR 1.16(i))	* 12	Minus	** 20	= 0	X $80 =	0
	Independent (37 CFR 1.16(h))	* 1	Minus	***3	= 0	X $420 =	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**

		(Column 1)		(Column 2)	(Column 3)		
		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
AMENDMENT	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
JAMES TUNSTALL

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
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Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/858,612	09/18/2015	Jason K. Stowers	5063.02US04	1074

62274 7590 01/03/2017

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
01/03/2017	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.** 14/858,612	**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 19 December 2016 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:
The proposed amendments filed after a final rejection, but prior to the date of filing a brief, will not be entered because they raise new issues that would require further consideration and/or search.

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: 1-7 and 21-25.
Claim(s) withdrawn from consideration:

/CHANCEITY ROBINSON/
Primary Examiner, Art Unit 1722

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US04

Stowers et al. Confirmation No.: 1074

Application No.: 14/858,612 Examiner: Robinson, Chanceity N.

Filed: September 18, 2015 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

DO NOT ENTER: /C.N.R/

12/28/2016

Sir:

INTRODUCTORY COMMENTS

In response to the Office Action dated October 18, 2016, 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.

December 19, 2016
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. # 69,343

Electronic Patent Application Fee Transmittal

Application Number:	14858612
Filing Date:	18-Sep-2015
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/Allison Goette
Attorney Docket Number:	5063.02US04

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:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
RCE- 1st Request	1801	1	1200	1200
		Total in USD ($)		**1200**

Customer No. 62274
Christensen, Fonder, Dardi & Herbert PLLC
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Facsimile: (763) 571-5157

Attorney Docket No. 5063.02US04

REQUEST FOR CONTINUED EXAMINATION (RCE) TRANSMITTAL

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

Sir:

This is a Request for Continued Examination (RCE) under 37 C.F.R. § 1.114 of Application No. 14/858,612, filed September 18, 2015 for: PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS, by: Jason K. Stowers, Alan J. Telecky, Douglas A. Keszler and Andrew Grenville.

1. Submission required under 37 C.F.R. § 1.114
   a. [X] Previously submitted
      [X] Please enter in the present application the unentered Amendment under 37 C.F.R. § 1.116, with any attachments, filed on December 19, 2016 in said prior application.
      [ ] Consider the arguments in the Appeal Brief or reply Brief previously filed on _____
      [ ] Other _____

   b. [ ] Enclosed
      [ ] An Amendment is enclosed. Claims added by this Amendment are properly numbered consecutively beginning with the number next following the highest numbered claim in the prior application.
      [ ] Affidavit(s)/Declaration(s)
      [ ] Information Disclosure Statement (IDS)
      [ ] Other _____

2. [X] The filing fee is calculated below:

	Claims Remaining After Amendment	Highest No. Previously Paid For	Present Extra (Equals)	Small Entity Rate	Add'l Fee	OR	Large Entity Rate	Add'l Fee
Total	12	- 20	= 0	x 40	$		x 80	$
Indep.	1	- 3	= 0	x 210	$		x 420	$
RCE fee				+ 600	$		+ 1200	$1200
Mult. Dep.			=	[+ 390]	$		[+ 780]	$
				TOTAL	$	OR	TOTAL	$1200

[ ] First Presentation of Multiple Dependent Claim [MDC]

* 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, write "20" in this space.
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, write "3" in this space.
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found from the equivalent box in Column 1 of a prior Amendment or the number of claims originally filed.

3. [ ] Applicants are entitled to small entity status in accordance with 37 CFR 1.27.

4. [X] The Commissioner is authorized to charge a credit card in the amount of $1,200.00 (The RCE fee under 37 C.F.R. § 1.17(e) is required by 37 C.F.R. § 1.114 when the RCE is filed). 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. 60-1363.

Respectfully submitted,

Kayla J. Fossen
Registration No. 69,343

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 60-1363.

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 11, 2017
Date

Kayla J. Fossen, Reg. #69,343

Lam Research Ex. 1007 - Page 522 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Acknowledgement Receipt

EFS ID:	28038118
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
Receipt Date:	11-JAN-2017
Filing Date:	18-SEP-2015
Time Stamp:	17:07:15
Application Type:	Utility under 35 USC 111(a)

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Payment was successfully received in RAM	$1200
RAM confirmation Number	011217INTEFSW17092600
Deposit Account	601363
Authorized User	Kayla Fossen

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

37 CFR 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	Request for Continued Examination (RCE)	RCE_Transmittal.pdf	151858 147316abe462aa9728a5e7d511940a11cf286c93	no	2
Warnings:					
This is not a USPTO supplied RCE SB30 form.					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30528 128bbac8d2f27a4900d7fa1869d0c0fd7596fd50	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	182386		

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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.

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	1	(14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/16 13:02
S2	66252	(metal adj ions) and (ligands)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:02
S3	29121	(UV or ultraviolet or electron-beam or EUV) and S2	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:03
S4	6581	S3 and ((alter$1 or change$1) with chemical)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S5	5760	S4 and substrate	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S6	1990	S5 and peroxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S7	85	S5 and (peroxide with ligand)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S8	65	S7 and anion	US-PGPUB;	OR	ON	2016/06/16

			USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			13:04
S9	14	S8 and polyatomic and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S10	14	S9 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/327 OR G03F7/0002 OR G03F7/11 OR G03F7/09 OR G03F7/2002 OR G03F7/2037 OR G03F7/30 OR G03F7/2004 OR G03F7/32 OR H01L29/7869 OR H01L27/1225 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 B32B2457/14 OR B32B9/005 OR B82Y10/00 OR B82Y40/00 OR C01G1/10 OR C01G25/006 OR C01G25/06 OR C01G27/006 OR C01G27/06).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:07
S11	3	((14/858612) or (12/850867)).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 13:58
S12	5	((14/858612) or (12/850867) or (13/284531)).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 14:05
S13	123950	substrate and (metal adj ion)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
S14	19	radiation adj sensitive adj ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
S15	14	S13 and S14	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	ON	2016/06/27 14:18

			DERWENT; IBM_TDB			
S16	13	S15 and (UV or EUV or electron-beam or ultraviolet)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
S17	6	S16 and differential	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:19
S18	4	S17 and peroxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:19
S19	1	(14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 14:21
S20	1	S19 and about	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:22
S21	1	S20 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/327).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:23
S22	6	("2009120169").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 14:48
S23	0	S22 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 15:10
S24	0	S22 and nm	US-PGPUB; USPAT; USOCR;	OR	ON	2016/06/27 15:10

			FPRS; EPO; JPO; DERWENT; IBM_TDB			
S25	5	(("8415000") or ("9281207")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 15:28
S26	1	(14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:05
S27	1	S26 and (thickness)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:05
S28	5	(("2001154366") or ("2010508560") or ("2011524627")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:47
S29	15	(("2001154366") or ("2010508560") or ("2011524627") or ("2008082448") or ("2009120169")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:49
S30	2	S29 and (aqueous and organic)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/10/16 17:36
S31	1	S29 and (ratio)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/10/16 18:00
S32	1	S30 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/10/16 18:00
S33	16049913	(substrate or support)	US-PGPUB;	OR	ON	2017/02/25

			USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			20:29
S34	592304	ligands	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:29
S35	343499	metal adj ion	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:29
S36	54996	S33 and S34 and S35	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:31
S37	2065753	(photosensitive or coating or layer or composition) with thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:32
S38	62857	(photosensitive or coating or layer or composition) with (metal adj ion)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:32
S39	19292	S37 and S38	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:32
S40	2660	S36 and S39	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:32
S41	996314	(UV or EUV or (electron-beam adj radiation))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT;	OR	ON	2017/02/25 20:33

			IBM_TDB			
S42	1585681	(UV or EUV or ultraviolet or (electron-beam adj radiation))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:33
S43	1725	S40 and S42	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:33
S44	7	suboxide adj ion	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:33
S45	2	(13/284531).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2017/02/25 20:51
S46	348698	ion with (Cu or Al or V or Cr or Ho or Lu)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 21:13
S47	7	(peroxide adj ligand) and S46	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 21:14
S48	26072	(peroxide) and S46	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 21:14
S49	231	S43 and S48	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 21:14
S50	3	("20040081611").PN.	US-PGPUB; USPAT; USOCR; FPRS;	OR	OFF	2017/02/25 21:27

			EPO; JPO; DERWENT; IBM_TDB			
S51	6	(("9281207") or ("8415000")).PN. or (14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2017/02/27 07:27

EAST Search History (Interference)

< This search history is empty>

2/ 27/ 2017 8:56:26 AM
C:\ Users\ crobinson4\ Documents\ EAST\ Workspaces\ 14858612.wsp

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14858612	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

CPC- SEARCHED		
Symbol	Date	Examiner
G03F 7/20	06/27/2016	CR

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

SEARCH NOTES		
Search Notes	Date	Examiner
East, Assignee and Inventorship Search	06/27/2016	CR
East and IDS Search Updated	10/16/2016	CR
East Search Updated	02/27/2017	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
	14858612	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	02/27/2017								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
	8	-								
	9	-								
	10	-								
	11	-								
	12	-								
	13	-								
	14	-								
	15	-								
	16	-								
	17	-								
	18	-								
	19	-								
	20	-								
	21	✓								
	22	✓								
	23	✓								
	24	✓								
	25	✓								

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/858,612	09/18/2015	Jason K. Stowers	5063.02US04	1074

62274 7590 03/01/2017

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Fridley, MN 55432

EXAMINER	
ROBINSON, CHANCEITY N	

ART UNIT	PAPER NUMBER
1722	

MAIL DATE	DELIVERY MODE
03/01/2017	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. 14/858,612	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 *01/11/2017*.

☐ 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) *1-7 and 21-25* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-7 and 21-25* 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

Continued Examination Under 37 CFR 1.114

2. A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission filed on 01/11/2017 has been entered.

3. Claims 1-7 and 21-25 are currently pending.

Double Patenting

4. 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 conflicting claims 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); *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 nonstatutory double patenting provided the reference application or patent either is shown to be commonly owned with the examined application, or claims an invention made as a result of activities undertaken within the scope of a joint research agreement. See MPEP § 717.02 for applications subject to examination under the first inventor to file provisions of the AIA as explained in MPEP § 2159. See MPEP §§ 706.02(l) (1) - 706.02(l)(3) for applications not subject to examination under the first inventor to file provisions of the AIA. A terminal disclaimer must be signed in compliance with 37 CFR 1.321(b).

The USPTO Internet website contains terminal disclaimer forms which may be used. Please visit www.uspto.gov/patent/patents-forms. The filing date of the application in which the form is filed determines what form (e.g., PTO/SB/25, PTO/SB/26, PTO/AIA/25, or PTO/AIA/26) 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 www.uspto.gov/patents/process/file/efs/guidance/eTD-info-I.jsp.

5. Claims 1-7 and 21-25 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-17 of U.S. Patent No. 8,415,000 B2.

Although the claims at issue are not identical, they are not patentably distinct from each other because both the instant claims and patent ‘000 have claims drawn to a structure (patterned structure of patent ‘000; claim 1) comprising a substrate(substrate of patent ‘000; claim 1) and a coating material (a layer of coating material of patent ‘000; claim 5) on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands (patterned inorganic material of patent ‘000; claims 1-17). Although patent ‘000 does not explicitly recite the coating material has an average thickness from 5 nm to 30 nm as instantly claimed, the coating material of the instant claims and the coating material of patent '000 are identical or substantially identical in structure or composition, or are produced by identical or substantially identical processes, a prima facie case of either anticipation or obviousness has been established. In re Best, 562 F.2d 1252, 1255, 195 USPQ 430, 433 (CCPA 1977). However, it is the position of the examiner that those characteristics of the average thickness of the layer of the coating material are inherent, given that the coating material disclosed by patent ‘000 and the instant claims are the same. A reference that is silent about a claimed invention’s features is inherently anticipatory if the missing feature is necessarily present in that which is described in the reference. Inherency is not established by probabilities or possibilities. *In re Robertson*, 49 USPQ2d 1949 (1999). Therefore, it would have been obvious at the time of the invention to include that average thickness of the coating material of patent ‘000 from 5 nm to 30 nm as instantly claimed. Furthermore, both the instant claims and patent ‘000 recite open claim language; therefore, other components may be comprised in their respective invention.

Response to Arguments

6. Applicant's arguments filed 09/30/2016 have been fully considered but they are not persuasive. Applicant's principle arguments are the following:

A) Applicants argue that the examiner incorrectly interpretation of the law regarding non-statutory double patenting. With all due respect, the Examiner seems to be using the disclosure of the '000 patent rather than the claims. This is a clear error of law. In the present case, the '000 patent shares a common parent with the present application that are related as continuation. The claims of the '000 patent of not render the present claims prima facie obvious. Claims 1-17 of '000 does not teach or discuss thickness of the coating. Therefore, claims 1-17 of '000 do not render the present invention patent invention patentably indistinct. Withdrawal of the non-statutory obviousness type double patenting rejection is respectfully requested.

A) Examiner respectfully disagrees. The instant claims and patent '000 have claims drawn to a structure (patterned structure of patent '000; claim 1) comprising a substrate (substrate of patent '000; claim 1) and a coating material (a layer of coating material of patent '000; claim 5) on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands (patterned inorganic material of patent '000; claims 1-17). The metal ion of the instant claim 3 is Hf, Zr or combination, which is recited in claim 2 of patent '000. Although patent '000 does not explicitly recite the coating material has an average thickness from 5 nm to 30 nm as instantly claimed, the coating material of the instant claims and the coating material of patent '000 are identical or substantially identical in structure or composition, or are

produced by identical or substantially identical processes, a prima facie case of either anticipation or obviousness has been established. In re Best, 562 F.2d 1252, 1255, 195 USPQ 430, 433 (CCPA 1977). However, it is the position of the examiner that those characteristics of the average thickness of the layer of the coating material are inherent, given that the coating material disclosed by patent '000 and the instant claims are the same. A reference that is silent about a claimed invention's features is inherently anticipatory if the missing feature is necessarily present in that which is described in the reference. Inherency is not established by probabilities or possibilities. *In re Robertson*, 49 USPQ2d 1949 (1999). Therefore, it would have been obvious at the time of the invention to include that average thickness of the coating material of patent '000 from 5 nm to 30 nm as instantly claimed. Furthermore, both the instant claims and patent '000 recite open claim language; therefore, other components may be comprised in their respective invention.

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.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

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

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 14/858,612	Filing Date 09/18/2015	☐ 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 **05/31/2017**

	(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))	* 12	Minus	** 20	= 0	X $80 =	0
Independent (37 CFR 1.16(h))	* 1	Minus	***3	= 0	X $420 =	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
YUVANNA CHAPHIV

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.

REMARKS

Claims 1-7 and 21-25 are pending. The claims stand rejected. Applicant respectfully requests reconsideration of the rejection based on the following analysis.

Non-Statutory Double Patenting over U.S. Pat. No. 8,415,000

Claims 1-7 and 21-25 are rejected on the ground of non-statutory double patenting as being unpatentable over claims 1-17 of U.S. Pat. No. 8,415,000 to Stowers et al. (hereinafter '000 patent). In particular, the Examiner has argued that both the instant claims and the claims of Pat. '000 are drawn to a structure comprising a substrate and a coating material on the surface comprising metal ions with radiation sensitive ligands. With all due respect, there seems to be a misunderstanding. Respectfully, the present claims are not *prima facie* obvious over the claims of the '000 patent. Applicant respectfully requests reconsideration of the rejection based on the following comments.

The Office Action asserts that "patent '000 have claims drawn to a structure ... wherein the coating material comprises metal ions with radiation sensitive ligands ..." With all due respect, the claims of the '000 patent do not refer to radiation sensitive ligands. Claim 1 of '000 patent reads:

1. (Currently Amended) A patterned 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 for features with an average pitch of no more than about 60 nm or with an average line-width roughness from about 1.2 nm to about 1.6 nm for individual features having an average width of no more than about 30 nm.

This claim of the '000 patent is referring to a patterned structure, which would generally be formed **after** irradiation and development. Respectfully, there are no radiation sensitive ligands recited in the patterned structure in the independent or dependent claims of the '000 patent. The present claims are directed to the structure used in processing that is formed **prior** to irradiation

Lam Research Ex. 1007 - Page 543 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

and development and do not recite as being patterned, although the nature of the radiation sensitivity is explained. With all due respect, these different claim sets are not directed to similar structures one with radiation sensitive ligands and one without recitation of radiation sensitive ligands. Applicant apologizes for not having been clear on this point previously. But due to these differences, the claims of the '000 patent respectfully do not render the present claims *prima facie* obvious. Therefore, Applicant respectfully requests withdrawal of the rejection of claims 1-7 and 21-25 are rejected on the ground of non-statutory double patenting as being unpatentable over claims 1-17 of the '000 patent.

CONCLUSIONS

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. 1007 - Page 544 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Acknowledgement Receipt

EFS ID:	29350735
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
Receipt Date:	31-MAY-2017
Filing Date:	18-SEP-2015
Time Stamp:	15:52:02
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.pdf	35490 358c0c4215d93da6b5762d7f5f88f9700a2aab91	yes	5

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Amendment/Req. Reconsideration-After Non-Final Reject	1	1
	Claims	2	3
	Applicant Arguments/Remarks Made in an Amendment	4	5
Warnings:			
Information:			
	Total Files Size (in bytes):	35490	

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.

LIST 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) A structure comprising a substrate and a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands and wherein the coating material has an average thickness from 5 nm to 30 nm, wherein exposure of the coating material to UV, EUV and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material.

2. (Original) The structure of claim 1 wherein the metal ions comprise metal suboxide ions.

3. (Original) The structure of claim 1 wherein the metal of the metal ions comprises 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.

4. (Original) The structure of claim 1 wherein the radiation sensitive ligands comprise peroxide ligands.

5. (Original) The structure of claim 1 wherein the coating material further comprises polyatomic anions.

6. (Previously Presented) The structure of claim 1 wherein the average thickness is from 5 nm to 25 nm.

7. (Original) The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists.

8-20. (Cancelled)

21. (Previously Presented) The structure of claim 1 having a metal ion to radiosensitive ligand ratio of at least 2.

22. (Previously Presented) The structure of claim 1 wherein the coating material has been heated to temperatures from 45°C to 150°C.

23. (Previously Presented) The structure of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous solvent.

24. (Previously Presented) The structure of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent.

25. (Previously Presented) The structure of claim 1 wherein the coating material can be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm^2.

Lam Research Ex. 1007 - Page 548 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.: 5063.02US04
Stowers et al.	Confirmation No.: 1074
Application No.: 14/858,612	Examiner: Chanceity N. Robinson
Filed: September 18, 2015	Group Art Unit: 1722

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

RESPONSE

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

Sir:

INTRODUCTORY COMMENTS

In response to the Office Action of March 1, 2017, please consider the following remarks. This document includes the following sections.

A. List of the Claims

B. Remarks

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 60-1363.

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 31, 2017
Date

/Kayla J. Fossen/
Kayla J. Fossen, Reg. #69,343

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14858612	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

CPC- SEARCHED		
Symbol	Date	Examiner
G03F 7/20	06/27/2016	CR

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

SEARCH NOTES		
Search Notes	Date	Examiner
East, Assignee and Inventorship Search	06/27/2016	CR
East and IDS Search Updated	10/16/2016	CR
East Search Updated	02/27/2017	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
	14858612	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	06/07/2017								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
	8	-								
	9	-								
	10	-								
	11	-								
	12	-								
	13	-								
	14	-								
	15	-								
	16	-								
	17	-								
	18	-								
	19	-								
	20	-								
	21	✓								
	22	✓								
	23	✓								
	24	✓								
	25	✓								

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.
14/858,612	09/18/2015	Jason K. Stowers	5063.02US04	1074

62274 7590 06/08/2017

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
06/08/2017	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. 14/858,612	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 *05/31/2017*.

☐ 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) *1-7 and 21-25* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *1-7 and 21-25* 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. The Applicant's request for reconsideration filed on May 31 2017 was received. Claims 8-20 have been canceled.

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 March 01, 2017.

Double Patenting

4. Claims 1-7 and 21-25 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-17 of U.S. Patent No. 8,415,000 B2. Although the claims at issue are not identical, they are not patentably distinct from each other because both the instant claims and patent '000 have claims drawn to a structure (patterned structure of patent '000; claim 1) comprising a substrate(substrate of patent '000; claim 1) and a coating material (a layer of coating material of patent '000; claim 5) on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands (patterned inorganic material of patent '000; claims 1-17). Although patent '000 does not explicitly recite the coating material has an average thickness from 5 nm to 30 nm as instantly claimed, the coating material of the instant claims and the coating material of patent '000 are identical or substantially identical in structure or composition, or are produced by identical or substantially identical processes, a prima facie case of either anticipation or obviousness has been

established. In re Best, 562 F.2d 1252, 1255, 195 USPQ 430, 433 (CCPA 1977). However, it is the position of the examiner that those characteristics of the average thickness of the layer of the coating material are inherent, given that the coating material disclosed by patent ‘000 and the instant claims are the same. A reference that is silent about a claimed invention’s features is inherently anticipatory if the missing feature is necessarily present in that which is described in the reference. Inherency is not established by probabilities or possibilities. *In re Robertson*, 49 USPQ2d 1949 (1999). Therefore, it would have been obvious at the time of the invention to include that average thickness of the coating material of patent ‘000 from 5 nm to 30 nm as instantly claimed. Furthermore, both the instant claims and patent ‘000 recite open claim language; therefore, other components may be comprised in their respective invention.

Response to Arguments

5. Applicant's arguments filed 05/31/2017 have been fully considered but they are not persuasive. Applicant’s principle arguments are the following:

A) Applicants argue that the present claims are not prima facie obvious over the claims of the ‘000 patent. The claims of the ‘000 patent do not refer to radiation sensitive ligands. The claim of the ‘000 patent is referring to a patterned structure, which would generally be formed after irradiation and development. Respectfully, there are no radiation sensitive ligands recited in the patterned structure in the independent or ,dependent claims of the '000 patent. The present claims are directed to the structure used ion processing that is formed prior to irradiation and development and do not recited as being patterned , although the nature of the radiation sensitivity is explained..

Therefore, claims 1-17 of '000 do not render the present invention patent invention patentably indistinct. Withdrawal of the non-statutory obviousness type double patenting rejection is respectfully requested.

A) Examiner respectfully disagrees. Applicants are reminded that the instant claims are drawn to a product (structure) as well as patent ‘000 (patterned structure), and neither the instant claims nor patent '000 are drawn to method or process steps, such as “ formed after irradiation and development” or processing that is formed prior to irradiation and development” . In response to applicant's argument that the references fail to show certain features of applicant’s invention, it is noted that the features upon which applicant relies (i.e., “formed after irradiation and development” or processing that is formed prior to irradiation and development) are not recited in the rejected claim(s). Although the claims are interpreted in light of the specification, limitations from the specification are not read into the claims. See *In re Van Geuns*, 988 F.2d 1181, 26 USPQ2d 1057 (Fed. Cir. 1993). Nonetheless, the instant claims and patent ‘000 have claims drawn to a structure (patterned structure of patent ‘000; claim 1) comprising a substrate (substrate of patent ‘000; claim 1) and a coating material (a layer of coating material of patent ‘000; claim 5) on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands (patterned inorganic material of patent ‘000; claims 1-17). The metal ion of the instant claim 3 is Hf, Zr or combination, which is recited in claim 2 of patent ‘000. Although patent ‘000 does not explicitly recite the coating material has an average thickness from 5 nm to 30 nm as instantly claimed, the coating material of the instant claims and the coating material of

patent '000 are identical or substantially identical in structure or composition, or are produced by identical or substantially identical processes, a prima facie case of either anticipation or obviousness has been established. In re Best, 562 F.2d 1252, 1255, 195 USPQ 430, 433 (CCPA 1977). Furthermore, both the instant claims and patent ‘000 recite open claim language; therefore, other components may be comprised in their respective invention. Therefore, the rejection is maintained.

Conclusion

6. THIS ACTION IS MADE FINAL. 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 mailing 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.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

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

Electronic Patent Application Fee Transmittal

Application Number:	14858612
Filing Date:	18-Sep-2015
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
Attorney Docket Number:	5063.02US04

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
STATUTORY OR TERMINAL DISCLAIMER	1814	1	160	160
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**160**

REMARKS

Claims 1-7 and 21-25 are pending. By this Response, no claims are amended or added.

Double Patenting Rejection

The Examiner has indicated that claims are rejected on the ground of non-statutory double patenting as being unpatentable over claims 1-17 of U.S. Patent No. 8,415,000 B2 ('000). While the applicant does not acquiesce to the argument that the thickness of the film is inherent to the claims of '000, a terminal disclaimer has been filed to advance prosecution. In view of the terminal disclaimer, Applicant respectfully requests withdrawal of the non-statutory double patenting rejection over '000.

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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Lam Research Ex. 1007 - Page 561 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Acknowledgement Receipt

EFS ID:	30015079
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
Receipt Date:	08-AUG-2017
Filing Date:	18-SEP-2015
Time Stamp:	14:03:23
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		ResponseAF.pdf	28156 bf3cd6e6707b6fd27a96ef42a7228e11ae84616b	yes	4

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Applicant Arguments/Remarks Made in an Amendment	4	4
	Claims	2	3
	Response After Final Action	1	1
Warnings:			
Information:			
	Total Files Size (in bytes):	28156	

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.

Electronic Acknowledgement Receipt

EFS ID:	30015019
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
Receipt Date:	08-AUG-2017
Filing Date:	18-SEP-2015
Time Stamp:	14:30:25
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$160
RAM confirmation Number	080917INTEFSW14302200
Deposit Account	
Authorized User	

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

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Terminal Disclaimer-Filed (Electronic)	eTerminal-Disclaimer.pdf	33430 8ad50179cda43048f63a657825ceda10f9fd2db1	no	2
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30396 eea1f1d9cf7576fdfb9b2a29b6c5ff18dd520334	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	63826		

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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.

Doc Code: DIST.E.FILE **Document Description: Electronic Terminal Disclaimer - Filed**	PTO/SB/26 U.S. Patent and Trademark Office Department of Commerce

Electronic Petition Request	**TERMINAL DISCLAIMER TO OBVIATE A DOUBLE PATENTING REJECTION OVER A "PRIOR" PATENT**
Application Number	14858612
Filing Date	18-Sep-2015
First Named Inventor	Jason Stowers
Attorney Docket Number	5063.02US04
Title of Invention	PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

☒ Filing of terminal disclaimer does not obviate requirement for response under 37 CFR 1.111 to outstanding Office Action

☒ This electronic Terminal Disclaimer is not being used for a Joint Research Agreement.

Owner	Percent Interest
Inpria Corporation	100%

The owner(s) with percent interest listed above in the instant application hereby disclaims, except as provided below, the terminal part of the statutory term of any patent granted on the instant application which would extend beyond the expiration date of the full statutory term of prior patent number(s)

8415000

as the term of said prior patent is presently shortened by any terminal disclaimer. The owner hereby agrees that any patent so granted on the instant application shall be enforceable only for and during such period that it and the prior patent are commonly owned. This agreement runs with any patent granted on the instant application and is binding upon the grantee, its successors or assigns.

In making the above disclaimer, the owner does not disclaim the terminal part of the term of any patent granted on the instant application that would extend to the expiration date of the full statutory term of the prior patent, "as the term of said prior patent is presently shortened by any terminal disclaimer," in the event that said prior patent later:
- expires for failure to pay a maintenance fee;
- is held unenforceable;
- is found invalid by a court of competent jurisdiction;
- is statutorily disclaimed in whole or terminally disclaimed under 37 CFR 1.321;
- has all claims canceled by a reexamination certificate;
- is reissued; or
- is in any manner terminated prior to the expiration of its full statutory term as presently shortened by any terminal disclaimer.

◉ Terminal disclaimer fee under 37 CFR 1.20(d) is included with Electronic Terminal Disclaimer request.

○	I certify, in accordance with 37 CFR 1.4(d)(4), that the terminal disclaimer fee under 37 CFR 1.20(d) required for this terminal disclaimer has already been paid in the above-identified application.

Applicant claims the following fee status:

○ Small Entity

○ Micro Entity

◉ Regular Undiscounted

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.

THIS PORTION MUST BE COMPLETED BY THE SIGNATORY OR SIGNATORIES

I certify, in accordance with 37 CFR 1.4(d)(4) that I am:

◉ An attorney or agent registered to practice before the Patent and Trademark Office who is of record in this application

Registration Number 69343

○ A sole inventor

○ A joint inventor; I certify that I am authorized to sign this submission on behalf of all of the inventors as evidenced by the power of attorney in the application

○ A joint inventor; all of whom are signing this request

Signature	/Kayla J. Fossen/
Name	Kayla J. Fossen

*Statement under 37 CFR 3.73(b) is required if terminal disclaimer is signed by the assignee (owner).
Form PTO/SB/96 may be used for making this certification. See MPEP § 324.

Doc Code: DISQ.E.FILE
Document Description: Electronic Terminal Disclaimer – Approved

Application No.: 14858612

Filing Date: 18-Sep-2015

Applicant/Patent under Reexamination: Stowers

Electronic Terminal Disclaimer filed on August 8, 2017

☒ APPROVED

This patent is subject to a terminal disclaimer

☐ DISAPPROVED

Approved/Disapproved by: Electronic Terminal Disclaimer automatically approved by EFS-Web

U.S. Patent and Trademark Office

LIST 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) A structure comprising a substrate and a coating material on a surface of the substrate, wherein the coating material comprises metal ions with radiation sensitive ligands and wherein the coating material has an average thickness from 5 nm to 30 nm, wherein exposure of the coating material to UV, EUV and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material.

2. (Original) The structure of claim 1 wherein the metal ions comprise metal suboxide ions.

3. (Original) The structure of claim 1 wherein the metal of the metal ions comprises 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.

4. (Original) The structure of claim 1 wherein the radiation sensitive ligands comprise peroxide ligands.

5. (Original) The structure of claim 1 wherein the coating material further comprises polyatomic anions.

6. (Previously Presented) The structure of claim 1 wherein the average thickness is from 5 nm to 25 nm.

7. (Original) The structure of claim 1 wherein the coating material has high absorption of EUV radiation relative to conventional radiation-based resists.

8-20. (Cancelled)

21. (Previously Presented) The structure of claim 1 having a metal ion to radiosensitive ligand ratio of at least 2.

22. (Previously Presented) The structure of claim 1 wherein the coating material has been heated to temperatures from 45°C to 150°C.

23. (Previously Presented) The structure of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous solvent.

24. (Previously Presented) The structure of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent.

25. (Previously Presented) The structure of claim 1 wherein the coating material can be effectively patterned with UV radiation or EUV radiation at a dose of no more than 100 mJ/cm^2.

Lam Research Ex. 1007 - Page 570 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.: 5063.02US04
Stowers et al.	Confirmation No.: 1074
Application No.: 14/858,612	Examiner: Chanceity N. Robinson
Filed: September 18, 2015	Group Art Unit: 1722

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

RESPONSE 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 of June 8, 2017, please consider the following remarks. This document has the following sections.

A. List of the Claims

B. Remarks

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 60-1363.

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.

August 8, 2017
Date

/Kayla J. Fossen /
Kayla J. Fossen, Reg. #69,343

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 14/858,612	Filing Date 09/18/2015	☐ To be Mailed

ENTITY: ☒ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

	(Column 1)	(Column 2)		
FOR	NUMBER FILED	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

		(Column 1)		(Column 2)	(Column 3)		
	08/08/2017	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
AMENDMENT	Total (37 CFR 1.16(i))	* 12	Minus	** 20	= 0	X $80 =	0
	Independent (37 CFR 1.16(h))	* 1	Minus	***3	= 0	X $420 =	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**

		(Column 1)		(Column 2)	(Column 3)		
		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
AMENDMENT	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
eugenia v. hardy

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.

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	1	(14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/16 13:02
S2	66252	(metal adj ions) and (ligands)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:02
S3	29121	(UV or ultraviolet or electron-beam or EUV) and S2	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:03
S4	6581	S3 and ((alter$1 or change$1) with chemical)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S5	5760	S4 and substrate	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S6	1990	S5 and peroxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S7	85	S5 and (peroxide with ligand)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S8	65	S7 and anion	US-PGPUB;	OR	ON	2016/06/16

			USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			13:04
S9	14	S8 and polyatomic and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:04
S10	14	S9 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/327 OR G03F7/0002 OR G03F7/11 OR G03F7/09 OR G03F7/2002 OR G03F7/2037 OR G03F7/30 OR G03F7/2004 OR G03F7/32 OR H01L29/7869 OR H01L27/1225 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 B32B2457/14 OR B32B9/005 OR B82Y10/00 OR B82Y40/00 OR C01G1/10 OR C01G25/006 OR C01G25/06 OR C01G27/006 OR C01G27/06).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/16 13:07
S11	3	((14/858612) or (12/850867)).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 13:58
S12	5	((14/858612) or (12/850867) or (13/284531)).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 14:05
S13	123950	substrate and (metal adj ion)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
S14	19	radiation adj sensitive adj ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
S15	14	S13 and S14	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	ON	2016/06/27 14:18

			DERWENT; IBM_TDB			
S16	13	S15 and (UV or EUV or electron-beam or ultraviolet)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:18
S17	6	S16 and differential	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:19
S18	4	S17 and peroxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:19
S19	1	(14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 14:21
S20	1	S19 and about	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:22
S21	1	S20 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/327).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 14:23
S22	6	("2009120169").PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/06/27 14:48
S23	0	S22 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/06/27 15:10
S24	0	S22 and nm	US-PGPUB; USPAT; USOCR;	OR	ON	2016/06/27 15:10

			FPRS; EPO; JPO; DERWENT; IBM_TDB			
S25	5	(("8415000") or ("9281207")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 15:28
S26	1	(14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:05
S27	1	S26 and (thickness)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:05
S28	5	(("2001154366") or ("2010508560") or ("2011524627")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:47
S29	15	(("2001154366") or ("2010508560") or ("2011524627") or ("2008082448") or ("2009120169")).PN.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2016/10/16 16:49
S30	2	S29 and (aqueous and organic)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/10/16 17:36
S31	1	S29 and (ratio)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/10/16 18:00
S32	1	S30 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2016/10/16 18:00
S33	16049913	(substrate or support)	US-PGPUB;	OR	ON	2017/02/25

			USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			20:29
S34	592304	ligands	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:29
S35	343499	metal adj ion	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:29
S36	54996	S33 and S34 and S35	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:31
S37	2065753	(photosensitive or coating or layer or composition) with thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:32
S38	62857	(photosensitive or coating or layer or composition) with (metal adj ion)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:32
S39	19292	S37 and S38	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:32
S40	2660	S36 and S39	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:32
S41	996314	(UV or EUV or (electron-beam adj radiation))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT;	OR	ON	2017/02/25 20:33

			IBM_TDB			
S42	1585681	(UV or EUV or ultraviolet or (electron-beam adj radiation))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:33
S43	1725	S40 and S42	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:33
S44	7	suboxide adj ion	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 20:33
S45	2	(13/284531).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2017/02/25 20:51
S46	348698	ion with (Cu or Al or V or Cr or Ho or Lu)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 21:13
S47	7	(peroxide adj ligand) and S46	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 21:14
S48	26072	(peroxide) and S46	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 21:14
S49	231	S43 and S48	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2017/02/25 21:14
S50	3	("20040081611").PN.	US-PGPUB; USPAT; USOCR; FPRS;	OR	OFF	2017/02/25 21:27

			EPO; JPO; DERWENT; IBM_TDB			
S51	6	(("9281207") or ("8415000")).PN. or (14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2017/02/27 07:27
S52	4	("8415000").PN. or (14/858612).APP.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2017/06/07 11:58

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	1764070	(structure or plate) with (substrate or support)	US-PGPUB; USPAT	OR	ON	2017/08/11 08:44
L2	13934	ligand with (metal adj ion)	US-PGPUB; USPAT	OR	ON	2017/08/11 08:45
L3	4097	1 and 2	US-PGPUB; USPAT	OR	ON	2017/08/11 08:45
L4	1888	3 and radiation	US-PGPUB; USPAT	OR	ON	2017/08/11 08:45
L5	1454	4 and (UV or EUV or ultraviolet or electron-beam)	US-PGPUB; USPAT	OR	ON	2017/08/11 08:45
L6	0	5 and (disolution adj rate)	US-PGPUB; USPAT	OR	ON	2017/08/11 08:46
L7	8	5 and (dissolution adj rate)	US-PGPUB; USPAT	OR	ON	2017/08/11 08:46
L8	8	7 AND ((A61L27/18 OR A61L2300/25 OR A61L2300/252 OR A61L2300/256 OR A61L2300/412 OR A61L2300/414 OR A61L2300/426 OR A61L2300/45 OR A61L27/38 OR A61L27/50 OR A61L27/54 OR C07D471/04 OR C07D473/34 OR C07D487/04 OR C07D473/00 OR C08L67/04 OR G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/2004 OR G03F7/32 OR G03F7/322 OR G03F7/325 OR G03F7/327 OR G03F7/40 OR C12M25/14 OR C12N2501/115 OR C12N2501/165 OR C12N2533/40 OR C12N2533/52 OR C12N2533/54 OR C12N5/0068 OR C25D3/38 OR C25D3/58 OR C25D5/10 OR C25D5/18 OR C25D5/34 OR C25D5/50 OR C25D7/123 OR H01J37/32357 OR	US-PGPUB; USPAT	OR	ON	2017/08/11 08:46

		Y10T428/24355).CPC.)				

8/ 11/ 2017 8:50:03 AM
C:\ Users\ crobinson4\ Documents\ EAST\ Workspaces\ 14858612.wsp

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14858612	STOWERS ET AL.
	Examiner	Art Unit
	CHANCEITY ROBINSON	1722

CPC- SEARCHED		
Symbol	Date	Examiner
G03F 7/20	06/27/2016	CR

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

SEARCH NOTES		
Search Notes	Date	Examiner
East, Assignee and Inventorship Search	06/27/2016	CR
East and IDS Search Updated	10/16/2016	CR
East Search Updated	08/11/2017	CR

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner
G03F	7/20	08/11/2017	CR

	/CHANCEITY ROBINSON/ Primary Examiner.Art Unit 1722

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 08/23/2017

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: 08/23/2017

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/858,612	09/18/2015	Jason K. Stowers	5063.02US04	1074

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	UNDISCOUNTED	$960	$0	$0	$960	11/24/2017

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.

Lam Research Ex. 1007 - Page 582 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

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 08/23/2017
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.
14/858,612	09/18/2015	Jason K. Stowers	5063.02US04	1074

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	UNDISCOUNTED	$960	$0	$0	$960	11/24/2017

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. 1007 - Page 583 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
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P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/858,612	09/18/2015	Jason K. Stowers	5063.02US04	1074

62274 7590 08/23/2017

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: 08/23/2017

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.

Lam Research Ex. 1007 - Page 584 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

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. 14/858,612	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 *08/08/2017*.
   ☐ 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 *1-7 and 21-25*. 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

Terminal Disclaimer

2. The terminal disclaimer filed on 08/08/20174 disclaiming the terminal portion of any patent granted on this application has been reviewed and is accepted. The terminal disclaimer has been recorded.

3. The following is an examiner's statement of reasons for allowance: Claims 1-7 and 21-25 are allowed. No other prior art teaches a structure comprising a coating material comprising metal ions with radiation sensitive ligands, wherein the coating material has an average thickness from 5 nm to 30 nm and wherein the exposure of the coating material to UV, EUV, and/or electron-beam radiation alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates between exposed and un-exposed regions of the coating material 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.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

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

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14858612	STOWERS ET AL.
	Examiner	**Art Unit**
	CHANCEITY ROBINSON	1722

CPC								
Symbol							**Type**	**Version**
G03F		7	/	0043			F	2013-01-01
Y10T		428	/	24355			A	2015-01-15
G03F		7	/	0042			I	2013-01-01
G03F		7	/	20			I	2013-01-01
G03F		7	/	327			I	2013-01-01
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CPC Combination Sets									
Symbol							**Type**	**Set**	**Ranking**	**Version**
			/							
			/							

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	12	
/CHANCEITY ROBINSON/ Primary Examiner.Art Unit 1722	08/11/2017	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14858612	STOWERS ET AL.
	Examiner	**Art Unit**
	CHANCEITY ROBINSON	1722

US ORIGINAL CLASSIFICATION		INTERNATIONAL CLASSIFICATION										
CLASS	SUBCLASS	CLAIMED					NON-CLAIMED					
		G	0	3	F	7 / 20 (2006.01.01)						
CROSS REFERENCE(S)												
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)											

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	12	
/CHANCEITY ROBINSON/ Primary Examiner.Art Unit 1722	08/11/2017	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14858612	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		17												
2	2		18												
3	3		19												
4	4		20												
5	5	8	21												
6	6	9	22												
7	7	10	23												
	8	11	24												
	9	12	25												
	10														
	11														
	12														
	13														
	14														
	15														
	16														

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 12	
/CHANCEITY ROBINSON/ Primary Examiner.Art Unit 1722 (Primary Examiner)	08/11/2017 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure 1

U.S. Patent and Trademark Office

Part of Paper No. 20170811

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	14858612	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	08/11/2017								
1	1	=								
2	2	=								
3	3	=								
4	4	=								
5	5	=								
6	6	=								
7	7	=								
	8	-								
	9	-								
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	16	-								
	17	-								
	18	-								
	19	-								
	20	-								
8	21	=								
9	22	=								
10	23	=								
11	24	=								
12	25	=								

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US04
Stowers et al.	Confirmation No.: 1074
Application No.: 14/858,612	Examiner: Chanceity N. Robinson
Filed: September 18, 2015	Group Art Unit: 1722

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

RESPONSE AFTER FINAL

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

OK TO ENTER: /C.N.R/

08/11/2017

Sir:

INTRODUCTORY COMMENTS

In response to the Office Action of June 8, 2017, please consider the following remarks. This document has the following sections.

A. List of the Claims

B. Remarks

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 60-1363.

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.

August 8, 2017
Date

/Kayla J. Fossen /
Kayla J. Fossen, Reg. #69,343

Electronic Patent Application Fee Transmittal

Application Number:	14858612
Filing Date:	18-Sep-2015
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:	5063.02US04

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
UTILITY APPL ISSUE FEE	1501	1	960	960
PUBL. FEE- EARLY, VOLUNTARY, OR NORMAL	1504	1	0	0
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**960**

Electronic Acknowledgement Receipt

EFS ID:	30660048
Application Number:	14858612
International Application Number:	
Confirmation Number:	1074
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:	5063.02US04
Receipt Date:	16-OCT-2017
Filing Date:	18-SEP-2015
Time Stamp:	10:49:13
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$960
RAM confirmation Number	101617INTEFSW10491200
Deposit Account	
Authorized User	
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

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)	Web85b.pdf	46342 6cfda554f49d7fdfb668648a1eb672863a9b34ec	no	2
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	32179 846584168fb2b1e301c70f95055d4ba7b4d61a8a	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	78521		

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.

Document Description: Issue Fee Payment (PTO-85B)

Issue Fee Transmittal Form

Application Number	Filing Date	First Named Inventor	Atty. Docket No.	Confirmation No.
14858612	18-Sep-2015	Jason Stowers	5063.02US04	1074

TITLE OF INVENTION :

PATTERNED INORGANIC LAYERS, RADIATION BASED PATTERNING COMPOSITIONS AND CORRESPONDING METHODS

Entity Status	Application Type	Art Unit	Class - Subclass	EXAMINER
Regular Undiscounted	Utility under 35 USC 111(a)	1722	270100	CHANCEITY ROBINSON

Issue Fee Due	Publication Due	Total Fee(s) Due	Date Due	Prev. Paid Fee
$960	$0	$960	24-Nov-2017	$0

1.Change of Correspondence Address and/or Indication Of Fee Address (37 CFR 1.33 & 1.363)

Current Correspondence Address:	Current Indicated Fee Address :
62274 CHRISTENSEN, FONDER, DARDI & HERBERT PLLC Moore Lake Plaza, Suite 205 1250 East Moore Lake Drive Fridley MN 55432 UNITED STATES 763 412 3820 DARDI@CFD-IP.COM	
☐ Change of correspondence address requested, system generated AIA/122-EFS form attached	☐ Fee Address indication requested, system generated SB/47-EFS form attached

2.Entity Status

Change in Entity Status

○ Applicant certifying micro entity status; system generated Micro Entity certification form attached. See 37 CFR 1.29.
Note: Absent a valid certification of micro entity status, issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment. If this box is checked, you will be prompted to choose a micro entity status on the gross income basis (37 CFR 1.29(a)) or the institution of higher education basis (37 CFR 1.29(d)), and make the applicable certification online.

○ 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.

Doc Code: IFEE PTOL/85B-EFS

Document Description: Issue Fee Payment (PTO-85B)

3.The Following Fee(s) Are Submitted:

☒ Issue Fee

☐ I authorize USPTO to apply my previously paid issue fee to the current fees due

☐ Publication Fee

☐ The Director is hereby authorized to apply my previously paid issue fee to the current fee due and to charge deficient fees to Deposit Account Number _____

☐ Advance Order - # of copies _____

☒ If **in addition to** the payment of the issue fee amount submitted with this form, there are any discrepancies in any amount(s) due, the Director is authorized to charge any deficiency or credit any overpayment, to Deposit Account Number 60-1363 . The **issue fee must be submitted** with this form. **If payment of the issue fee does not accompany this form, checking this box and providing a deposit account number will NOT be effective to satisfy full payment of the fee(s) due.**

4.Firm and/or Attorney Names To Be Printed

NOTE: If no name is listed, no name will be printed
For printing on the patent front page, list to be displayed as entered

1. CHRISTENSEN, FONDER, DARDI & HERBERT PLLC
2. Peter S. Dardi, Ph.D.
3.

5.Assignee Name(s) and Residence Data To Be Printed

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.

Name	City	State	Country	Category
Inpria Corporation	Corvallis	OREGON	united states	corporation

6.Signature

I certify, in accordance with 37 CFR 1.4(d)(4) that I am an attorney or agent registered to practice before the Patent and Trademark Office who has filed and has been granted power of attorney in this application. I also certify that this Fee(s) Transmittal form is being transmitted to the USPTO via EFS-WEB on the date indicated below.

Signature	/Peter S. Dardi/	**Date**	10-16-2017
Name	Peter S. Dardi	**Registration Number**	39650

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	
Filing Date	2015-09-18
First Named Inventor	Stowers
Art Unit	TBA
Examiner Name	To be assigned
Attorney Docket Number	5063.02US04

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		05/1968 ~~1968-05-28~~	Hamling	
Change(s) applied to document, /N.W.S./ 8/31/2017	2	4102683		1978-07-25	DiPiazza	
	3	4370405		1983-01-25	O'Toole et al.	
	4	4732841		1988-03-22	Radigan	
	5	4891303		1990-01-02	Garza et al.	
	6	4910122		1990-03-20	Arnold et al.	
	7	5025094		1991-06-18	King	
	8	5672243		1997-09-30	Hsia et al.	

Notice of References Cited	Application/Control No. 14/858,612	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	CPC Classification	US Classification
	A	US-				
	B	US-				
	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	CPC Classification
	N	WO 2008082448 A1	07-2008	~~US~~ WO	MEYERS STEPHEN T	H01L29/4908
	O					
	P					
	Q					
	R					
	S					
	T					

Change(s) applied to document.
/N.W.S./
8/31/2017

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	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.

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Alexandria, Virginia 22313-1450
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APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
14/858,612	11/21/2017	9823564	5063.02US04	1074

62274 7590 11/02/2017

CHRISTENSEN, FONDER, DARDI & HERBERT PLLC
33 South Sixth Street
Suite 3950
Minneapolis, MN 55402

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 0 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):

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

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AO 120 (Rev. 08/10)

TO:	REPORT ON THE FILING OR DETERMINATION OF AN ACTION REGARDING A PATENT OR TRADEMARK
Mail Stop 8 Director of the U.S. Patent and Trademark Office P.O. Box 1450 Alexandria, VA 22313-1450	

In Compliance with 35 U.S.C. § 290 and/or 15 U.S.C. § 1116 you are hereby advised that a court action has been filed in the U.S. District Court District of Delaware on the following

☐ Trademarks or ☑ Patents. (☐ the patent action involves 35 U.S.C. § 292.):

DOCKET NO.	DATE FILED	U.S. DISTRICT COURT District of Delaware
PLAINTIFF INPRIA CORPORATION		DEFENDANT LAM RESEARCH CORPORATION

	PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1	U.S. 10,732,505	8/4/2020	Inpria Corporation
2	U.S. 9,823,564	11/21/2017	Inpria Corporation
3	U.S. 9,310,684	4/12/2016	Inpria Corporation
4			
5			

In the above---entitled case, the following patent(s)/ trademark(s) have been included:

DATE INCLUDED	INCLUDED BY ☐ Amendment ☐ Answer ☐ Cross Bill ☐ Other Pleading	
PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1		
2		
3		
4		
5		

In the above---entitled case, the following decision has been rendered or judgement issued:

DECISION/JUDGEMENT

CLERK	(BY) DEPUTY CLERK	DATE

Copy 1---Upon initiation of action, mail this copy to Director Copy 3---Upon termination of action, mail this copy to Director
Copy 2---Upon filing document adding patent(s), mail this copy to Director Copy 4---Case file copy