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Attorney Docket No. 5063.02US05

DIVISIONAL APPLICATION TRANSMITTAL

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

Sir:

This is a request for filing a

[ ] Continuation [X] Divisional

application, under 37 C.F.R. § 1.53(b), of pending prior Application No. 14/858,612, filed September 18, 2015 for: RADIATION BASED PATTERNING 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.

[X] Preliminary Remarks - 2 pages.

[X] Power of Attorney and Declarations - copies from prior application.

[ ] Electronic Sequence Listing.

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	19 - 20	=0	~~x 40 = $~~	OR	**x 80 = $**
Independent Claims	2 - 3	=0	~~x 210 = $~~	OR	**x 420 = $**
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**	**$1600.00**
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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 **$1600.00**. 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. 60-1363.

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 Inrpia Corporation recorded at Reel 025647, Frame 0344.

4. [X] An Information Disclosure Statement and Transmittal Letter is/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:

Christensen, Fonder, 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.

October 16, 2017
Date

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

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US05
	Application Number	
Title of Invention	RADIATION BASED PATTERNING METHODS	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Jason	K.	Stowers	

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

City	State/Province	Country of Residence
Corvallis	OR	US

Mailing Address of Inventor:

Address 1	805 NW Witham Drive
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State/Province	OR
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Country	US

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

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State/Province	OR
Postal Code	97321
Country	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

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US05
	Application Number	
Title of Invention	RADIATION BASED PATTERNING METHODS	

City	Corvallis	State/Province	OR	Country of Residence	US

Mailing Address of Inventor:

Address 1	3927 NW Lorri Place		
Address 2			
City	Corvalis	State/Province	OR
Postal Code	97330	Country	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	US

Mailing Address of Inventor:

Address 1	19215 Fairmount Boulevard		
Address 2			
City	Eugene	State/Province	OR
Postal Code	97403	Country	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	docket@cfd-ip.com	Add Email	Remove Email

Application Information:

Title of the Invention	RADIATION BASED PATTERNING METHODS		
Attorney Docket Number	5063.02US05	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

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Filing By Reference:

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, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim 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" field blank.

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	Division of	14858612	2015-09-18

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US05
	Application Number	
Title of Invention	RADIATION BASED PATTERNING METHODS	

Prior Application Status	Patented	Remove

Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)	Patent Number	Issue Date (YYYY-MM-DD)
14858612	Continuation of	12850867	2010-08-05	9176377	2015-11-03

Prior Application Status	Expired	Remove

Application Number	Continuity Type	Prior Application Number	Filing or 371(c) 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

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. 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(i)(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.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US05
	Application Number	
Title of Invention	RADIATION BASED PATTERNING METHODS	

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is 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 State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US05
	Application Number	
Title of Invention	RADIATION BASED PATTERNING METHODS	

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 For Applicant:			
Address 1	2001 NW Monroe Avenue		
Address 2	Suite 203		
City	Corvallis	**State/Province**	OR
Country	US	Postal Code	97330
Phone Number		Fax Number	
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 substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US05
	Application Number	
Title of Invention	RADIATION BASED PATTERNING METHODS	

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 Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is a **juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	/Peter S. Dardi/			Date (YYYY-MM-DD)	2017-10-16
First Name	Peter	Last Name	Dardi	Registration Number	39,650

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

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	5063.02US05
	Application Number	
Title of Invention	RADIATION BASED PATTERNING 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 CooperationTreaty.

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.

RADIATION BASED PATTERNING METHODS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional of copending U.S. patent application serial number 14/858,612 to Stowers et al., filed on September 18, 2015, entitled "Patterned Inorganic Layers, Radiation Based Patterning Compositions and Corresponding Methods," which is a continuation of U.S. patent application serial number 12/850,867 to Stowers et al. (now U.S. patent 9,176,377), filed August 5, 2010, entitled "Patterned Inorganic Layers, Radiation Based Patterning Compositions and Corresponding Methods," which claims priority to U.S. provisional patent application serial number 61/350,103 to Stowers et al., entitled "Photopatternable Inorganic Hardmask," all 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

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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

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molar concentration ratio of ligands to metal suboxide cations of at least about 2 and wherein the resist composition is stable with respect to phase separation for at least about 2 hours without additional mixing.

In a further aspect, the invention pertains to a method for formation of a radiation sensitive inorganic coating precursor solution, the method comprising combining a first 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 45ºC 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

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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 600ºC. 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}, $HfOOH^{+}$, $Hf(OH)_2^{+2}$,

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$Hf(OH)_3^+$ 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 225ºC to about 275ºC 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

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,

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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

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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 225ºC and 275ºC 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 50ºC. After exposure at approximately 80mJ/cm^2, a post-exposure bake of 75ºC 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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What we claim is:

1. 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.

2. The method of claim 1 wherein the irradiation is performed with EUV at a dose of no more than about 90 mJ/cm^2.

3. The method of claim 1 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.

4. The method of claim 1 wherein the developing composition comprises tetramethyl ammonium hydroxide.

5. The method of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous base.

6. The method of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent.

7. The method of claim 1 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.

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8. The method of claim 1 further comprising heating the substrate with the patterned coating material to a temperature from about 150ºC to about 600ºC for from one minute to 25 minutes to form a post-patterning condensed structure.

9. The method of claim 8 further comprising performing a second patterning using the post-patterning condensed structure to form a double patterned structure.

10. The method of claim 1 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.

11. The method of claim 10 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.

12. The method of claim 10 wherein the radiation sensitive ligands comprise peroxide ligands, and wherein the coating material further comprises metal suboxide cations.

13. The method of claim 12 wherein the coating material further inorganic polyatomic anions and wherein the peroxide ligand to metal ion ratio is at least about 2

14. 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

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

15. The method of claim 14 further comprising contacting the coated substrate after heating with a developing composition to remove un-irradiated coating material to form the patterned inorganic material.

16. The method of claim 15 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.

17. The method of claim 14 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.

18. The method of claim 14 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.

19. The method of claim 14 wherein the coating has an average thickness of about 5 nm to about 30 nm.

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ABSTRACT

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

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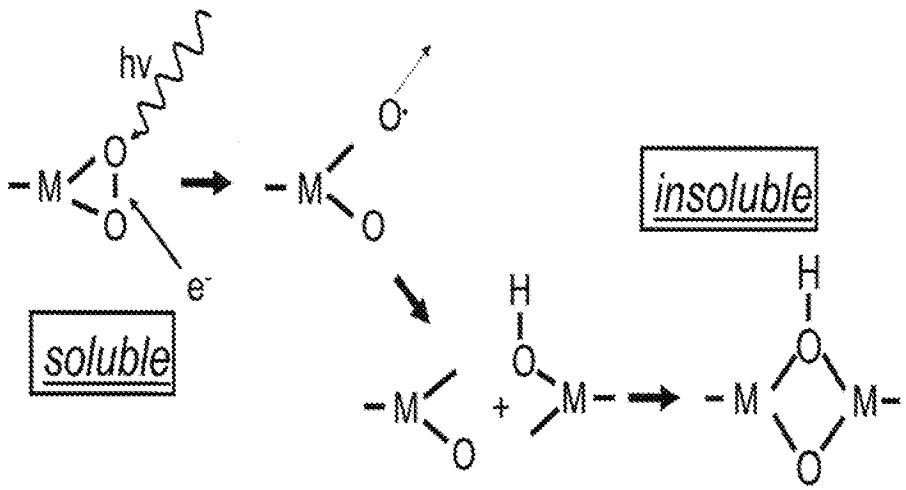

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Fig. 1

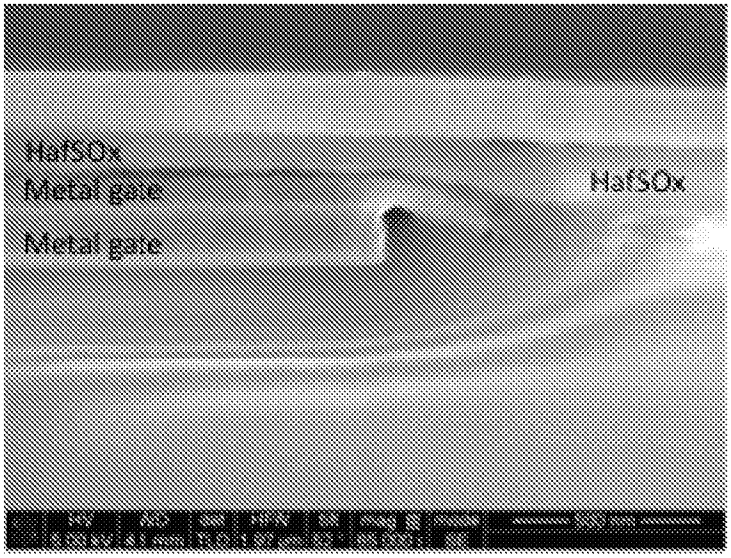

HafSOx
Metal gate
Metal gate
HafSOx

Fig. 9

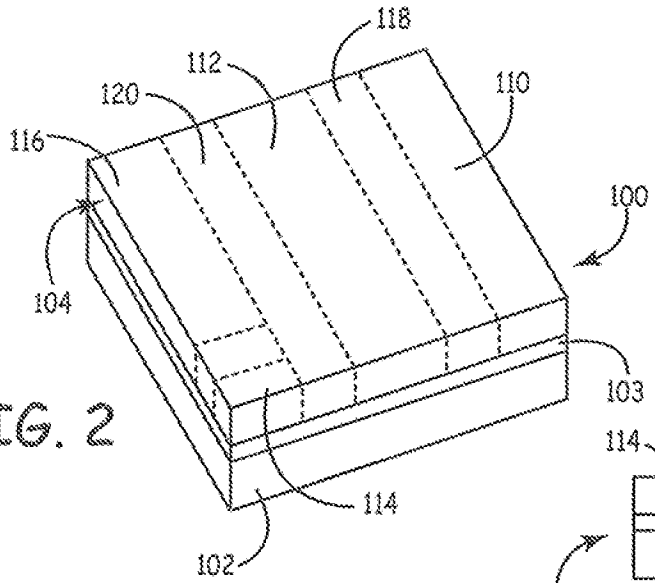


FIG. 2

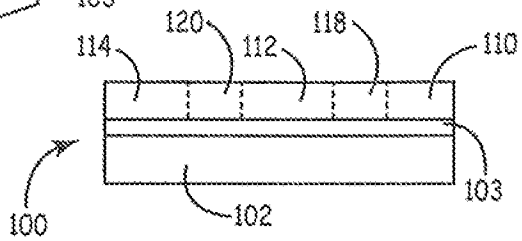


FIG. 3

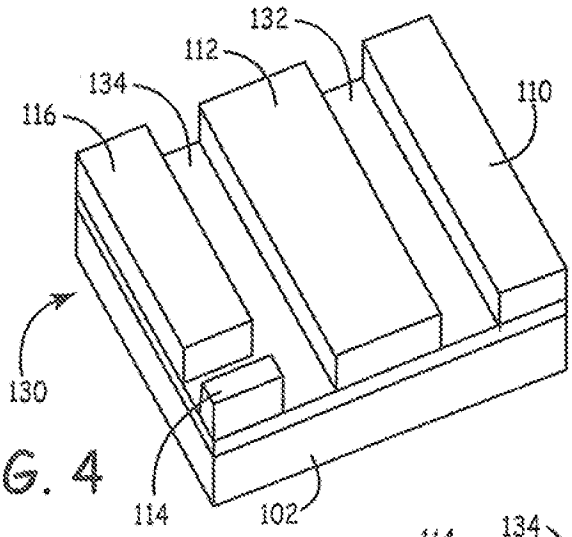


FIG. 4

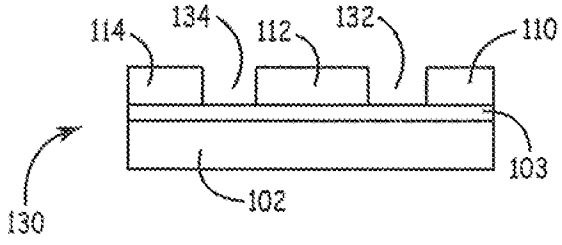


FIG. 5

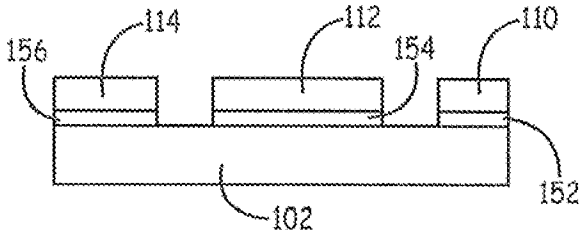


FIG. 6

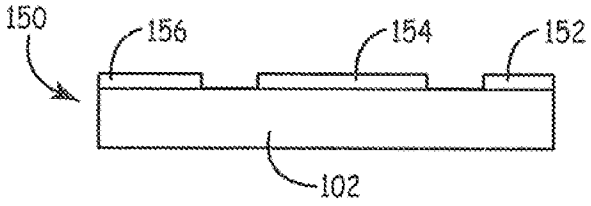


FIG. 7

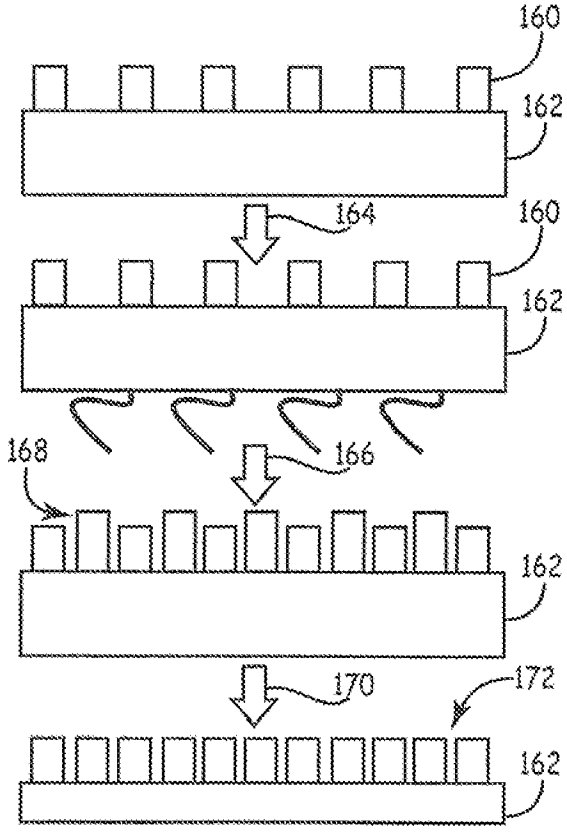


FIG. 8

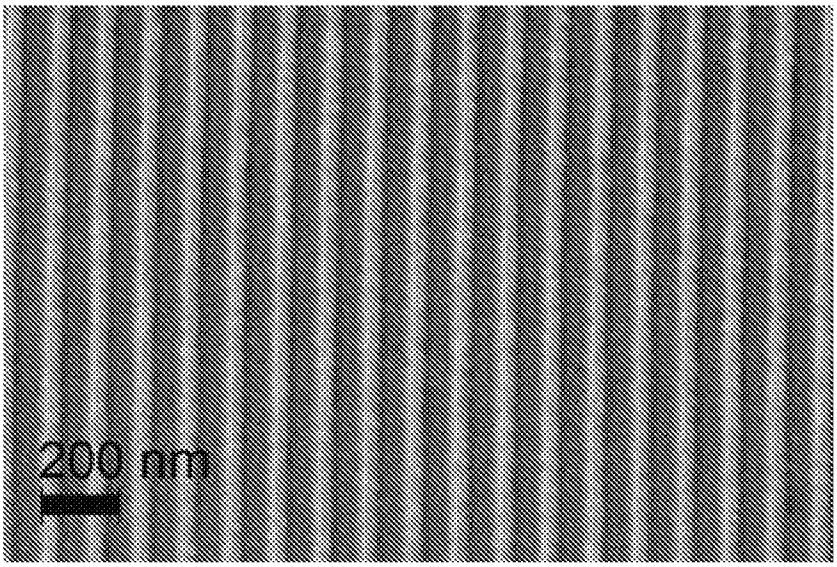


Fig. 10

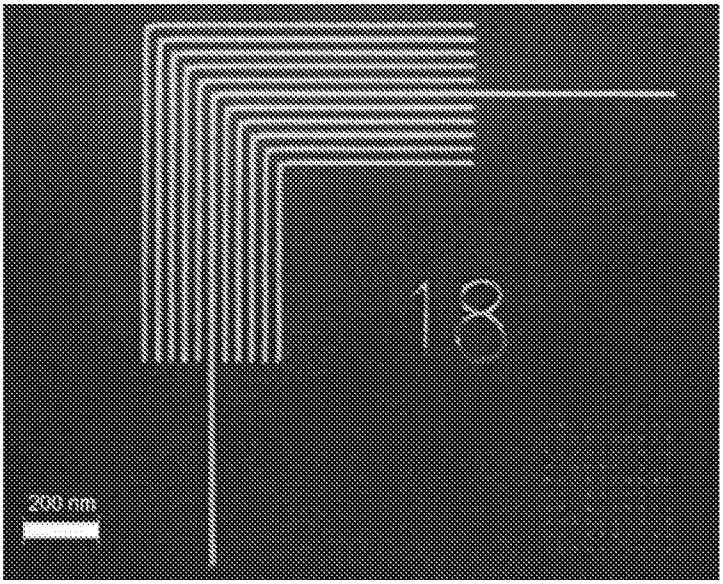


Fig. 11

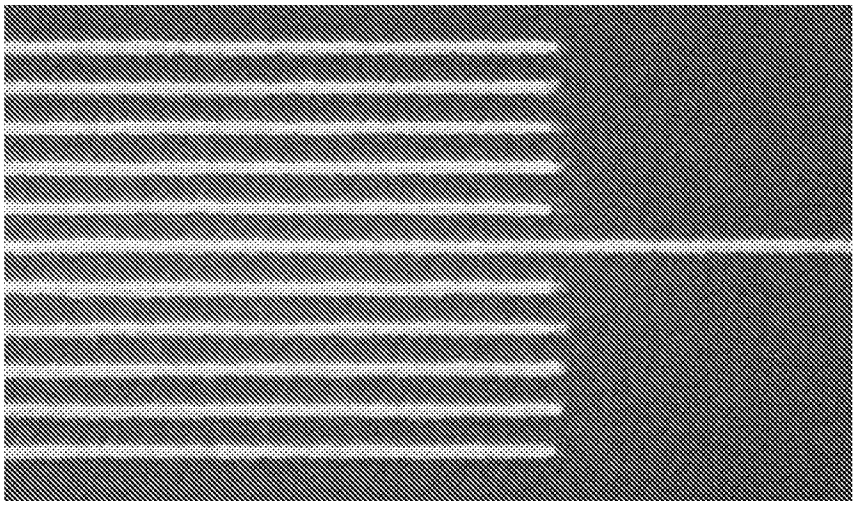


Fig. 12

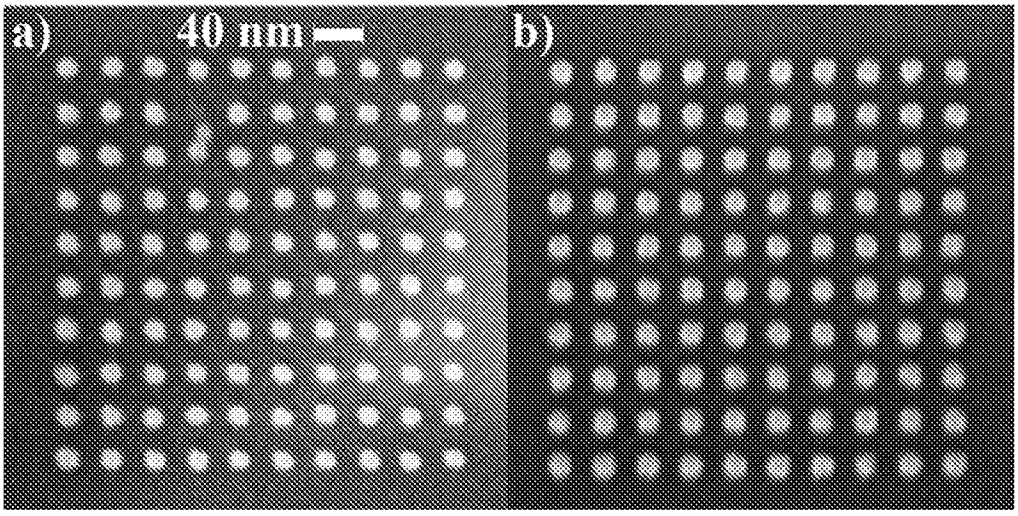


Fig. 13A

Fig. 13B

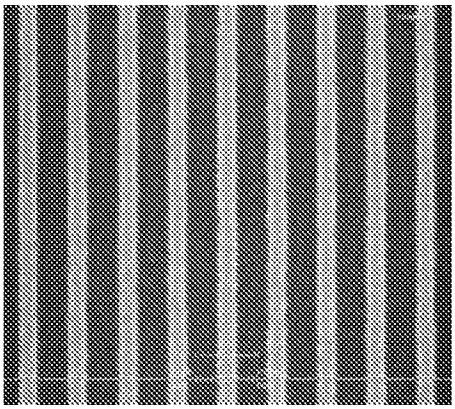


Fig. 14

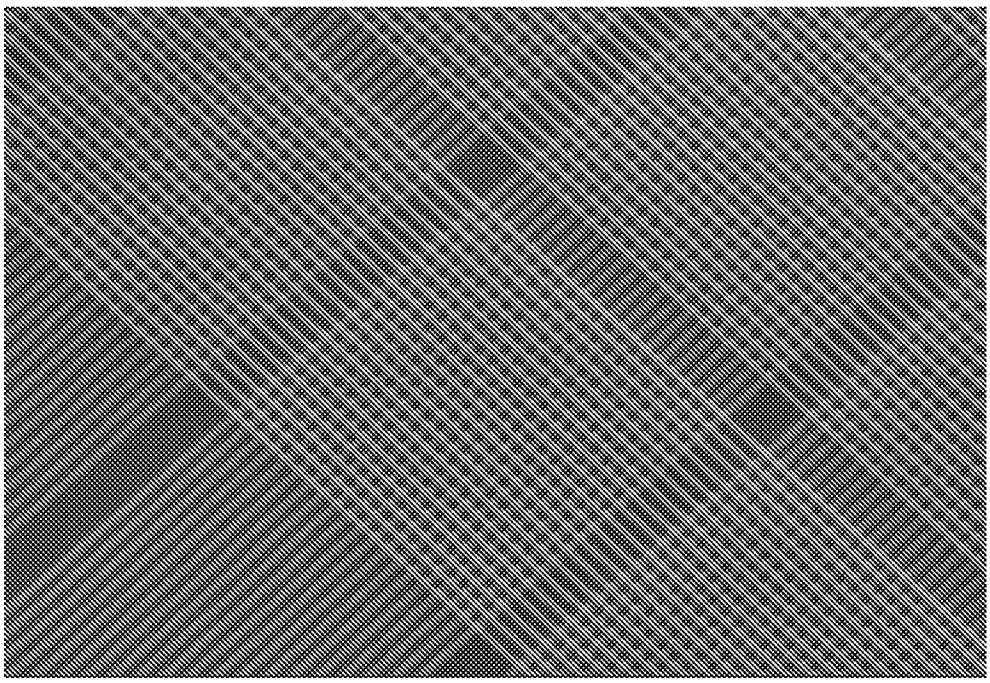


Fig. 15

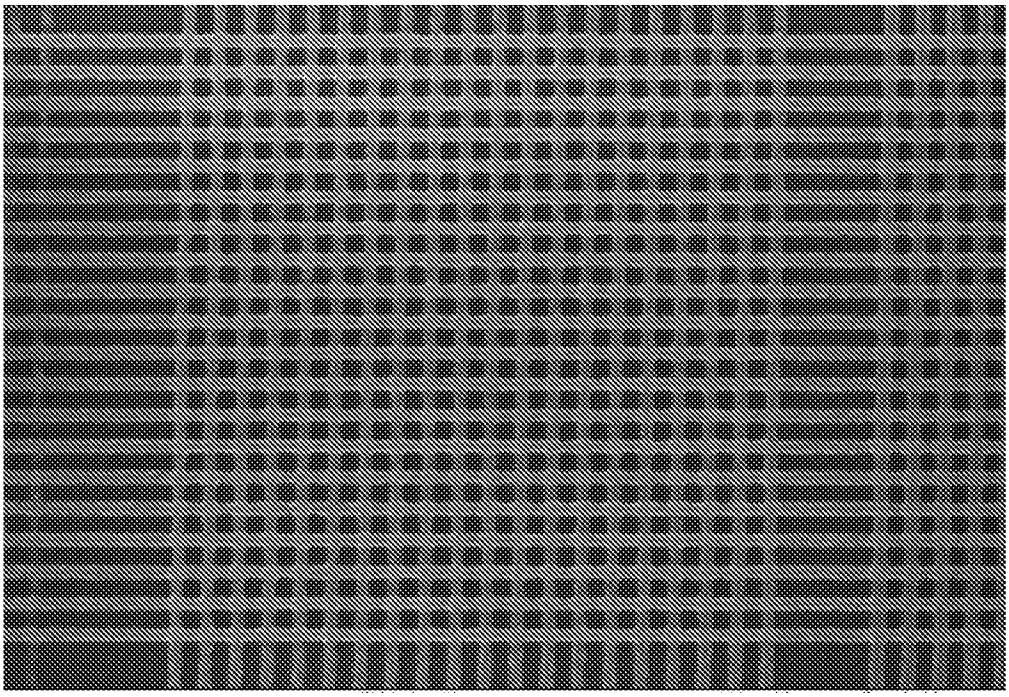


Fig. 16

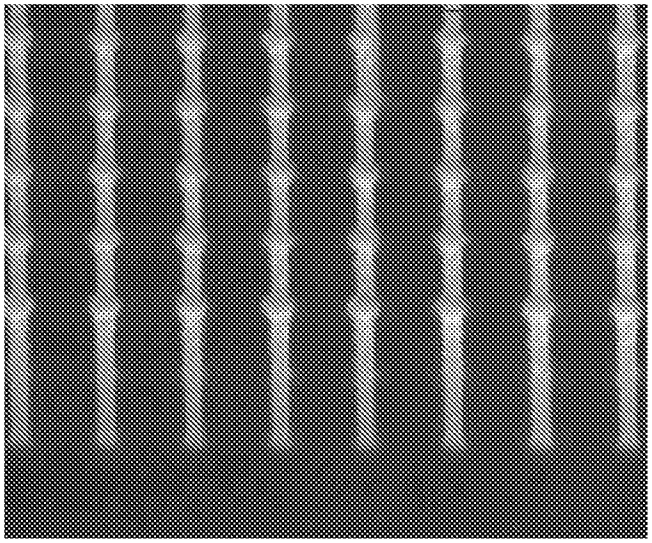


Fig. 17

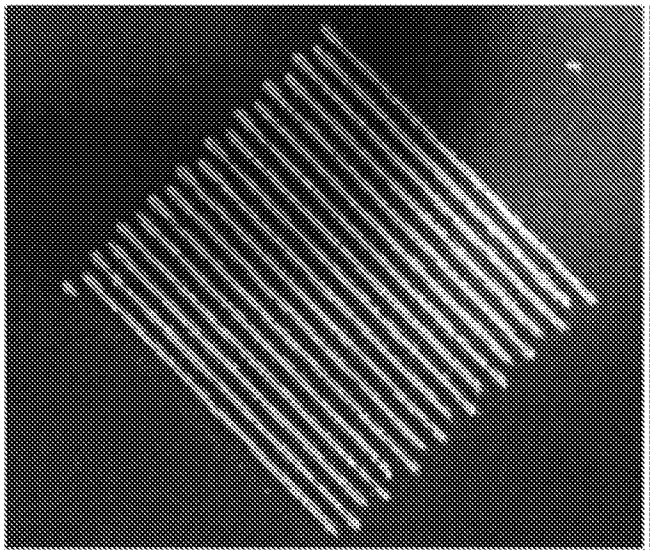


Fig. 18A

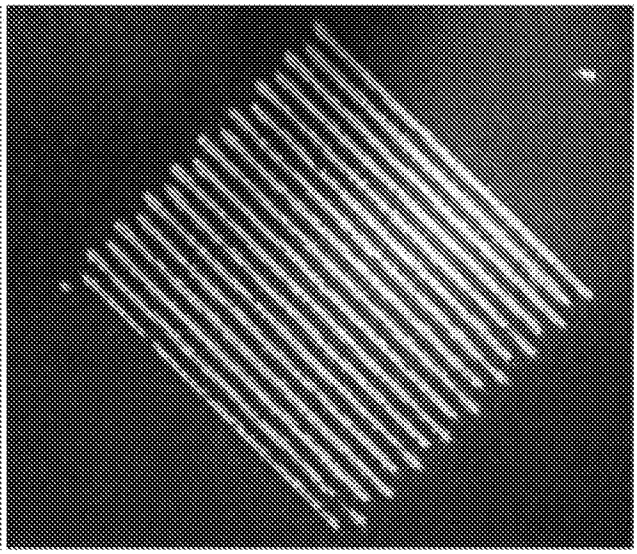


Fig. 18B

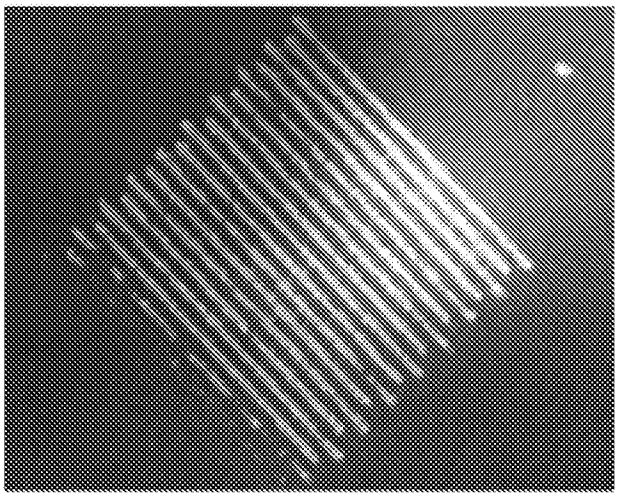


Fig. 18C

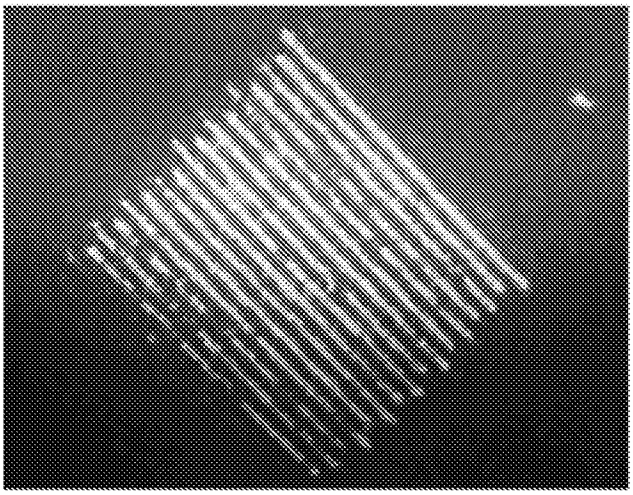


Fig. 18D

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US05

Stowers et al. Confirmation No.: TBA

Application No.: *Divisional of 14/858,612* Examiner: *Not Yet Assigned*

Filed: Herewith

For: RADIATION BASED PATTERNING 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 references were cited by or submitted to the Office in Patent Application No. 14/858,612, filed September 18, 2015, 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).

Respectfully submitted,

/Peter S. Dardi/

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

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

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

October 16, 2017
Date

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

Lam Research Ex. 1009 - Page 60 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

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

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US05

Stowers et al. Confirmation No.: TBA

Application No.: *Divisional of 14/858,612* Examiner: *Not Yet Assigned*

Filed: Herewith

For: RADIATION BASED PATTERNING METHODS

PRELIMINARY REMARKS

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

Sir:

INTRODUCTORY COMMENTS

Prior to examination, please amend the above-identified application as follows:

The present amendment comprises the following sections:

A. 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.

October 16, 2017 /Peter S. Dardi/
Date Peter S. Dardi, Ph.D., Reg. #39,650

REMARKS

Claims 1-19 are pending. Claims 1-4, 7, 10, and 14-17 correspond, respectively, with claims 8-13 and 15-18 of parent application 14/858,612 that were cancelled due to a restriction requirement. Claims 11, 18 and 19 are supported by original parent (14/858,612) claims 14, 10, and 8, respectively. The specification supports claim 5, for example, at page 25, lines 15-22. The specification supports claim 6, for example, at page 30, lines 14-18. The specification supports claim 8, for example, at page 27, lines 21-28. The specification supports claim 9, for example, at page 30, lines 26-31. The specification supports claim 12, for example, at page 2, lines 29-31. The specification supports claim 13, for example, at page 2, line 30 to page 3, line 3. The specification is updated with respect to the cross reference to related applications. No new matter is introduced.

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

Respectfully submitted,

/Peter S. Dardi/

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Lam Research Ex. 1009 - Page 63 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Peter S. Dardi/Michelle Douglas
Attorney Docket Number:	5063.02US05

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:				
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**1600**

Electronic Acknowledgement Receipt

EFS ID:	30660215
Application Number:	15784258
International Application Number:	
Confirmation Number:	9576
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US05
Receipt Date:	16-OCT-2017
Filing Date:	
Time Stamp:	10:41:02
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$1600
RAM confirmation Number	101617INTEFSW10421900
Deposit Account	601363
Authorized User	Peter Dardi

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

37 CFR 1.16 (National application filing, search, and examination fees)

37 CFR 1.17 (Patent application and reexamination processing fees)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal of New Application	DivisionalAppTransmittal.pdf	25166 658b22e27f1bfbea1dacfb2a94813aca7c129636	no	2
Warnings:					
Information:					
2	Application Data Sheet	ApplicationDataSheet-Signed.pdf	1823603 27a8bbddbc79a087db7a4e4a5bef668281b91728	no	9
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Warnings:					
Information:					
4	Claims	Claims.pdf	27516 43d67954071749391428e5f1f9bbb2f2faef223e	no	3
Warnings:					
Information:					
5	Abstract	Abstract.pdf	10355 74b454c5494b06f4c4966154927eb1888a5d12e1	no	1
Warnings:					
Information:					
6	Drawings-only black and white line drawings	Drawings.pdf	2244143 7396ed039cc4dd70dd9d58c351e6b8301d255bca	no	8
Warnings:					
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7	Transmittal Letter	IDSTransmittal.pdf	23688 fe3b07ef5ed677354bbb2acb0ae35737c65f990c	no	2
Warnings:					
Information:					
8	Information Disclosure Statement (IDS) Form (SB08)	IDS_Form_SB_08a-Signed.pdf	1037916 3af7aa9e92ca48e62b3c7ee472e3403ed249c31b	no	10
Warnings:					
Information:					
9	Oath or Declaration filed	Declarations.pdf	602487 4dc316c77065bb54838a3699cfe1b07aa6dcb0fd	no	4
Warnings:					
Information:					
10	Power of Attorney	PowerOfAttorney.pdf	226777 7413da5ea4939e187cf381dcceeae621070a16ac	no	1
Warnings:					
Information:					
11	Preliminary Amendment	PreliminaryRemarks.pdf	26721 7e362af2323606ea3c76018335c965f5f3bf272f	no	2
Warnings:					
Information:					
12	Fee Worksheet (SB06)	fee-info.pdf	34985 8a40c6545eb5cd9e404997f6ac5120afe3117e13	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	6291672	

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New Applications Under 35 U.S.C. 111

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

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

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

New International Application Filed with the USPTO as a Receiving Office

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

PTO/SB/08a (03-15)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	
Filing Date	
First Named Inventor	Jason K. Stowers
Art Unit	
Examiner Name	Not Yet Assigned
Attorney Docket Number	5063.02US05

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	3385915		1968-05-28	Hamling	
	2	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.	

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	Examiner Name	Not Yet Assigned
	Attorney Docket Number	5063.02US05

	9	6020269		2000-02-01	Wang et al.	
	10	6060380		2000-05-09	Subramanian et al.	
	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		2001-07-31	Kennedy et al.	
	15	6287951		2001-09-11	Lucas et al.	
	16	6420088		2002-07-16	Angelopoulos et al.	
	17	6583071		2003-06-24	Weidman et al.	
	18	6730454		2004-05-04	Pfeiffer et al.	
	19	6844604		2005-01-18	Lee et al.	

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	First Named Inventor	Jason K. Stowers
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	Attorney Docket Number	5063.02US05

	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.	
	24	7256129		2007-08-14	Nam et al.	
	25	8053370		2011-11-08	Yang et al.	
	26	8092703		2012-01-10	Ishibashi et al.	
	27	8415000		2013-04-09	Stowers et al.	
	28	8951917		2015-02-10	Ogihara et al.	

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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

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
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	Filing Date	
	First Named Inventor	Jason K. Stowers
	Art Unit	
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	5063.02US05

	1	20020076495		2002-06-20	Maloney et al.	
	2	20040067444		2004-04-08	Wakabayahsi et al.	
	3	20050242330		2005-11-03	Herman et al.	
	4	20060088962		2006-04-27	Herman et al.	
	5	20060234138		2006-10-19	Fehlhaber et al.	
	6	20080055597		2008-03-06	Sun et al.	
	7	20080286683		2008-11-20	Brodsky et al.	
	8	20090174036		2009-07-09	Fuller et al.	
	9	20100044698		2010-02-25	Herman et al.	
	10	20100184259		2010-07-22	Radigan et al.	
	11	20110045406		2011-02-24	Keszler et al.	

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	Examiner Name	Not Yet Assigned
	Attorney Docket Number	5063.02US05

	12	20110293888		2011-12-01	Stowers et al.	
	13	20120223418		2012-09-06	Stowers et al.	
	14	20130224652		2013-08-29	Bass et al.	

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	1	H03-148659	JP	A	1991-06-25	Fujitsu Ltd.		
	2	2001-154366	JP	A	2001-06-08	Fujitsu Ltd.		
	3	2006-284947	JP		2006-10-19	Fuji Photo Film Co. Ltd.		
	4	2007-514182	JP		2008-05-31	Hewlett-Packard	Corresponds to WO2005-043246	
	5	2005-043246	WO		2005-05-12	Hewlett-Packard		
	6	2008-082448	WO		2008-10-07	Oregon State		

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	Art Unit	
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	5063.02US05

	7	2009-120169	WO		2009-10-01	Oregon State		

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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).	
	2	International Standard ISO 21348 "Space Environment (Natural and Artificial) - Process For Determining Solar Irradiances", First Edition 2007, Reference number: ISO 21348:2007(E).	
	3	MEYERS ET AL., "Solution-Processed Aluminum Oxide Phosphate Thin-Film Dielectrics" Chem. Mater., 2007, 19, 4023-4029. Abstract Only.	
	4	NAKATTA ET AL., "Improvement Of InGaZnO4 Thin Film Transistors Characteristics Utilizing Excimer Laser Annealing" The Japan Society Of Applied Physics, 2009.	
	5	NEEF ET AL., "Effects Of Carbon/Hardmask Interactions On Hardmask Performance", Proceedings of SPIE, 7273, 727311-1 - 727311-7 (2009).	
	6	OWEN ET AL., "1/8 μm Optical Lithography," J. Vac. Sci. Technol. B 10, 3032 (1992).	
	7	STOWERS, "Direct Patterning of Solution Deposited Metal Oxides", A Dissertation to Oregon State University, August 14, 2008.	
	8	STOWERS ET AL., "High Resolution, High Sensitivity Inorganic Resists", Microelectronic Engineering, 86:730-733 (2009).	

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	Examiner Name	Not Yet Assigned
	Attorney Docket Number	5063.02US05

	9	STOWERS ET AL., "Directly Patterned Inorganic Hardmask For EUV Lothography," Proc. SPIE 7969, 796915 (2011); http://dx.doi.org/10.1117/12.879542.
	10	WANG ET AL.,"TiO2 Micro-Devices Fabricated By Laser Direct Writing" Optics Express, 19(18):17390-17935 (August 29, 2011).
	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.
	14	Office Action From Co-pending Korean Application No. 10-2011-0052919 dated March 14, 2013.
	15	Office Action From Co-pending Japanese Application No. 2011-120402 dated June 11, 2013.
	16	Office Action From Co-pending Taiwan Application No. 100116897 dated July 29, 2013 (with translation).
	17	Office Action From Co-pending Japanese Application No. 2015-207978 dated August 23, 2016.

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EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
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	Filing Date	
	First Named Inventor	Jason K. Stowers
	Art Unit	
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	5063.02US05

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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	Filing Date	
	First Named Inventor	Jason K. Stowers
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	Examiner Name	Not Yet Assigned
	Attorney Docket Number	5063.02US05

CERTIFICATION STATEMENT

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

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

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	/Peter S. Dardi/	Date (YYYY-MM-DD)	2017-10-16
Name/Print	Peter S. Dardi, Ph.D.	Registration Number	39,650

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

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 record s.

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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.

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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.

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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)

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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)

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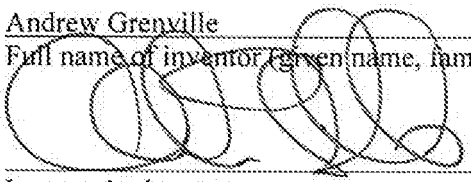
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Andrew Grenville
Full name of inventor (given name, family name)



Inventor's signature

9/28/15
Date

Attorney Docket No. 5063.02US04

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

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

Douglas A Keszler
Inventor's signature

30 September 2015
Date

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Application Number: 15784258 Document Date: 10/16/2017

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PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 15/784,258

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))	19 minus 20 =	*			OR	x 80 =	0.00
INDEPENDENT CLAIMS (37 CFR 1.16(h))	2 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	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
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.

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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
15/784,258	10/16/2017	1721	1600	5063.02US05	19	2

CONFIRMATION NO. 9576

FILING RECEIPT

62274
CHRISTENSEN, FONDER, DARDI & HERBERT PLLC
33 South Sixth Street
Suite 3950
Minneapolis, MN 55402

OC000000095076815

Date Mailed: 10/30/2017

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, Corvallis, OR;

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

Domestic Priority data as claimed by applicant

This application is a DIV of 14/858,612 09/18/2015
which is a CON of 12/850,867 08/05/2010 PAT 9176377
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.

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

If Required, Foreign Filing License Granted: 10/27/2017

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 15/784,258**

Projected Publication Date: 02/08/2018

Non-Publication Request: No

Early Publication Request: No

Title

RADIATION BASED PATTERNING 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).

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Lam Research Ex. 1009 - Page 88 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
15/784,258	10/16/2017	Jason K. Stowers	5063.02US05

CONFIRMATION NO. 9576

PUBLICATION NOTICE

62274
CHRISTENSEN, FONDER, DARDI & HERBERT PLLC
33 South Sixth Street
Suite 3950
Minneapolis, MN 55402

OC000000097280581

Title:RADIATION BASED PATTERNING METHODS

Publication No.US-2018-0039172-A1
Publication Date:02/08/2018

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 Public Records Division. The Public Records Division can be reached by telephone at (571) 272-3150 or (800) 972-6382, by facsimile at (571) 273-3250, by mail addressed to the United States Patent and Trademark Office, Public Records Division, 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 https://portal.uspto.gov/pair/PublicPair. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

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

Lam Research Ex. 1009 - Page 89 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

PTO/SB/08a (03-15)
Approved for use through 07/31/2016. OMB 0651-0031
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

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	1	20150221519	A1	2015-08-06	Marks et al.	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15784258
	Filing Date	2017-10-16
	First Named Inventor	Jason K. Stowers
	Art Unit	1722
	Examiner Name	Chanceity N. Robinson
	Attorney Docket Number	5063.02US05

	1	Anonymous: "International Technology Roadmap for Semiconductors 2009 Edition Executive Summary", 1 January 2009, XP055464243, Retrived from the Internet: URL:https://www.semiconductors.prg/clientuploads/ Research_Technology/ITRS/2009/1_Executive%20Summary.pdf	
	2	LEE ET AL., "Effect of line-edge roughness (LER) and line-width roughness (LWR) on sub-100-nm device performance", Microlithography 2004, vol. 5376, 14 May 2004, page 426, XP055464997, DOI: 10.1117/12.534926.	
	3	MORECROFT ET AL., "Sub-15nm nanoimprint Molds and Pattern Transfer", Journal of Vacuum Science and Technology: Part B, AVS / AIP, Melville, New York, NY, vol 27, no. 6, 3 December 2009, pgs. 2837-2840, XP012129582, ISSN:1071-1023 DOI: 10.1116/1.3264670	
	4	Office Action from Co-pending European Application No. 15178638.1 dated April 16, 2018.	

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EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

CERTIFICATION STATEMENT

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

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

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	/Peter S. Dardi/	Date (YYYY-MM-DD)	2018-05-25
Name/Print	Peter S. Dardi, Ph.D.	Registration Number	39,650

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.

Electronic Acknowledgement Receipt

EFS ID:	32728126
Application Number:	15784258
International Application Number:	
Confirmation Number:	9576
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US05
Receipt Date:	25-MAY-2018
Filing Date:	16-OCT-2017
Time Stamp:	13:59:44
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	IDS_Form_SB_08a-Signed.pdf	1035598 2cc668d9506b14b184d5df0d0927054fd2648ddf	no	4

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Information:					
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Warnings:					
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4	Non Patent Literature	Morecroft_et_al_2009.pdf	513502 281367697e2e6f7ff81f668507fce2da99ee1350	no	4
Warnings:					
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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.

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

New International Application Filed with the USPTO as a Receiving Office

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/784,258	10/16/2017	Jason K. Stowers	5063.02US05	9576

62274 7590 01/07/2019

CHRISTENSEN, FONDER, DARDI & HERBERT PLLC
33 South Sixth Street
Suite 4540
Minneapolis, MN 55402

EXAMINER
ROBINSON, CHANCEITY N

ART UNIT	PAPER NUMBER
1722	

MAIL DATE	DELIVERY MODE
01/07/2019	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. 15/784,258	Applicant(s) Stowers et al.	
	Examiner CHANCEITY N ROBINSON	Art Unit 1722	AIA 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 _____.

☐ 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) 1-19 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) 1-19 is/are rejected.

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

9) ☐ Claim(s) _____ are subject to restriction and/or election requirement

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to **PPHfeedback@uspto.gov.**

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☑ Notice of References Cited (PTO-892)

2) ☑ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date 10/16/2017 & 05/25/2018.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date _____.

4) ☐ Other: _____.

DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. The present application is being examined under the pre-AIA first to invent provisions.

Double Patenting

2. 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.

3. Claims 1-19 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-27 of U.S. Patent No.9, 176, 377. Although the claims at issue are not identical, they are not patentably distinct from each other because both the instant claims and patent '377 recite the same method of forming a patterned inorganic material on a substrate which are equivalent and obvious variant of each other methods.

It is further noted that the **restriction requirement was withdrawn as to any claim that required all the limitations of the allowable claims in US 9,176,377.** Specifically, the restriction requirement of 09/16/2013 was partially withdrawn. Claims 14-30, directed to method no longer withdrawn from consideration because the claim(s) requires all the limitations of an allowable claim. However, claims 31-38, directed to structure withdrawn and canceled from consideration because they do not all require all the limitations of an allowable claim.

In view of the above noted withdrawal of the restriction requirement, applicant was advised that if any claim presented in a continuation or divisional application is

anticipated by, or includes all the limitations of, a claim that is allowable in the present application, such claim may be subject to provisional statutory and/or nonstatutory double patenting rejections over the claims of the instant application. Once a restriction requirement is withdrawn, the provisions of 35 U.S.C. 121 are no longer applicable. See In re Ziegler, 443 F.2d 1211, 1215, 170 USPQ 129, 131-32 (CCPA 1971). See also MPEP § 804.01.

4. Claims 1-19 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 '377 recite the same method of forming a patterned inorganic material on a substrate which are equivalent and obvious variant of each other methods.

Claim Rejections - 35 USC § 112

5. 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.

6. Claims 1-19 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 1-19 recite the term, "about". The term "about" in claims 1-3, 7-8, 13-14, 16, 18 and 19 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

7. 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.

8. 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 though the invention is not identically disclosed or described as set forth in section 102, 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.

9. 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.

10. Claims 1-19 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Stowers, Jason, "Direct patterning of solution deposited metal oxides", (2008) in view of Jason Stowers, Douglas A. Keszler, "High resolution, high sensitivity inorganic resists", (2009), and further in view of Meyers et al. (WO 2008/082448 A1).

Regarding claims 1-19, Stowers teaches a method for forming a patterned structure (inorganic material) on substrate (chapter 4, page 65-page 86; in particular pages 71-72 and 78, line 3-4), the method comprises the step of forming a layer of a radiation patternable coating material (a layer of coating material; last three line of page 71) comprising a solvent (water, metal suboxide cations (ZrO^{2+} and HfO^{2+}),ligands comprising a peroxide group (H_2O_2) and inorganic polyatomic anions (SO_4^{2-}) to form a coated substrate; heating the coated substrate to remove a portion of the solvent (implicit or conventional; page 70, last paragraph); irradiating the coated substrate to a pattern of radiation to condense the coating at the irradiated locations (with 30keV electron beam); heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the coating with a developer (page 78,lines 3-4); and exposing (irradiating) the coating substrate with a developing composition to at least partially remove the coating composition at un-irradiated locations.

Stowers do not explicitly recited the thickness or differential dissolution as instantly claimed. However, Stowers et al. disclose a patterned structure comprising a substrate and a coating material an aqueous precursor solutions comprising $ZrOCI_2 \cdot 8H_20$, $HfOCI_2 \cdot H_20$, 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 in view of Stowers et al. teach a method of making a structure by exposing, spin coating and heating the coating material. Neither Stowers nor Stowers at al. teach the radiation dosage as instantly claimed.

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°C (see claim 18), which encompasses the instant claimed range from about 45 to about 150°C. 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, 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 in view of Sowers 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).

11. The prior art made of record and not relied upon is considered pertinent to applicant's disclosure. See Misumi et al. (US 2010/0119939 A1).

Conclusion

12. Any inquiry concerning this communication or earlier communications from the examiner should be directed to CHANCEITY N ROBINSON whose telephone number is (571)270-3786. The examiner can normally be reached on Monday-Friday (5:30 am-10:00 pm; IFP; PHP).

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 N ROBINSON/
Primary Examiner, Art Unit 1722

Notice of References Cited	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.	
	Examiner CHANCEITY N 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-20100119939-A1	05-2010	Misumi; Koichi	G03F7/022	429/212
	B					
	C					
	D					
	E					
	F					
	G					
	H					
	I					
	J					
	K					
	L					
	M					

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
*	N	WO-2008082448-A1	07-2008	WO	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	Stowers, Jason K.: "Direct patterning of solution deposited metal oxides", Oregon State University - ProQuest Dissertations and These , 14 August 2008 (2008-08-14), XP002675373, ISBN: 9780549913726 Retrieved from the Internet: (Year: 2008)
*	V	STOWERS J ET AL: "High resolution, high sensitivity inorganic resists", MICROELECTRONIC ENGINEERING, ELSEVIER PUBLISHERS BV„ AMSTERDAM, NL, vol. 86, no. 4-6, 1 April 2009 (2009-04-01), pages 730-733, (Year: 2009)
	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.

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/784,258	Stowers et al.
	Examiner	Art Unit
	CHANCEITY N ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	01/05/2019								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
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	13	✓								
	14	✓								
	15	✓								
	16	✓								
	17	✓								
	18	✓								
	19	✓								

Lam Research Ex. 1009 - Page 108 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/784,258	Stowers et al.
	Examiner	Art Unit
	CHANCEITY N ROBINSON	1722

CPC - Searched*		
Symbol	Date	Examiner
G03F 7/00	01/05/2019	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 and IDS Search	01/05/2019	CR

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner

/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722	

Bibliographic Data

Application No: 15/784,258

Foreign Priority claimed: ○ Yes ◉ No

35 USC 119 (a-d) conditions met: ☐ Yes ☐ No ☐ Met After Allowance

Verified and Acknowledged: /CHANCEITY N ROBINSON/ (Examiner's Signature) | CR (Initials)

Title: RADIATION BASED PATTERNING METHODS

FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
10/16/2017	430	1722	5063.02US05
RULE			

APPLICANTS

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Douglas A. Keszler Corvallis, OR, UNITED STATES

Andrew Grenville Eugene, OR, UNITED STATES

CONTINUING DATA

This application is a DIV of 14858612 09/18/2015 PAT 9823564

14858612 is a CON of 12850867 08/05/2010 PAT 9176377

12850867 has PRO of 61350103 06/01/2010

FOREIGN APPLICATIONS

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EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L2	3847446	(method or process) with (substrate or support)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:44
L3	367748	(EUV or UV or ultraviolet) with radiation	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
L4	155899	heat$3 with (coat$3) with (support or substrate)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
L5	5772464	irraditat$4 or expos$4	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
L6	24187	(EUV or UV or ultraviolet) with (dosage or dose)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
L7	1271	2 and 3 and 4 and 5 and 6	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
L8	1189	7 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:46
L9	691	8 and (developer or developing)	US-PGPUB;	OR	ON	2019/01/05

			USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			18:46
L10	54733	(TMAH or (tetramethylammonium adj hydroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
L11	528	9 and 10	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
L12	527	11 and pattern$3	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
L13	20	12 and ligands and (metal adj (ion or cation))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
L14	20	13 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/325 OR G03F7/327 OR G03F7/022 OR G03F7/032 OR G03F7/033 OR G03F7/0382 OR G03F7/0385 OR G03F7/0392 OR G03F7/0397 OR G03F7/32 OR G03F7/322 OR G03F7/09 OR G03F7/2002 OR G03F7/2037 OR G03F7/30 OR G03F7/2004 OR G03F7/162 OR G03F7/168 OR G03F7/40 OR Y10T428/24355 OR H01M10/0525 OR H01M2004/021 OR H01M2004/025 OR H01M2004/027 OR H01M4/045 OR H01M4/049 OR H01M4/134 OR H01M4/1391 OR H01M4/1395 OR H01M4/48 OR H01M4/60 OR H01M4/66 OR H01M4/665 OR H01M4/667 OR H01M4/668 OR Y02E60/122 OR Y02P70/54 OR Y02T10/7011).CPC.)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:48
S1	7	"12850867"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/01/05 16:41

EAST Search History (Interference)

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1/ 5/ 2019 6:56:29 PM
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Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	
Filing Date	
First Named Inventor	Jason K. Stowers
Art Unit	
Examiner Name	Not Yet Assigned
Attorney Docket Number	5063.02US05

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	3385915		1968-05-28	Hamling	
	2	4102683		1978-07-25	DiPiazza	
	3	4370405		1983-01-25	O`Toole et al.	
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	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.N.R/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Jason K. Stowers
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	Examiner Name	Not Yet Assigned
	Attorney Docket Number	5063.02US05

	9	6020269		2000-02-01	Wang et al.	
	10	6060380		2000-05-09	Subramanian et al.	
	11	6183716		2001-02-06	Sleight et al.	
	12	6194323		2001-02-27	Downey et al.	
	13	6197896		2001-03-06	Aviram et al.	
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EFS Web 2.1.17 ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.N.R/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

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Application Number	
Filing Date	
First Named Inventor	Jason K. Stowers
Art Unit	
Examiner Name	Not Yet Assigned
Attorney Docket Number	5063.02US05

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	21	6946677		2005-09-20	Ostergard	
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	27	8415000		2013-04-09	Stowers et al.	
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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear

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First Named Inventor	Jason K. Stowers
Art Unit	
Examiner Name	Not Yet Assigned
Attorney Docket Number	5063.02US05

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	8	20090174036		2009-07-09	Fuller et al.	
	9	20100044698		2010-02-25	Herman et al.	
	10	20100184259		2010-07-22	Radigan et al.	
	11	20110045406		2011-02-24	Keszler et al.	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	
Filing Date	
First Named Inventor	Jason K. Stowers
Art Unit	
Examiner Name	Not Yet Assigned
Attorney Docket Number	5063.02US05

	12	20110293888		2011-12-01	Stowers et al.	
	13	20120223418		2012-09-06	Stowers et al.	
	14	20130224652		2013-08-29	Bass et al.	

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	1	H03-148659	JP	A	1991-06-25	Fujitsu Ltd.		
	2	2001-154366	JP	A	2001-06-08	Fujitsu Ltd.		
	3	2006-284947	JP		2006-10-19	Fuji Photo Film Co. Ltd.		
	4	2007-514182	JP		2008-05-31	Hewlett-Packard	Corresponds to WO2005-043246	
	5	2005-043246	WO		2005-05-12	Hewlett-Packard		
	6	2008-082448	WO		2008-10-07	Oregon State		

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Application Number	
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First Named Inventor	Jason K. Stowers
Art Unit	
Examiner Name	Not Yet Assigned
Attorney Docket Number	5063.02US05

	7	2009-120169 ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.N.R/	WO		2009-10-01	Oregon State	

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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T5
	1	AHMED ET AL., "Synthesis And Characterization Of Zirconium And Hafnium Sulfates, Hydroxide Sulfates And Oxide Sulfates", Acta Chemica Scandinavica, 53:24-33 (1999).	
	2	International Standard ISO 21348 "Space Environment (Natural and Artificial) - Process For Determining Solar Irradiances", First Edition 2007, Reference number: ISO 21348:2007(E).	
	3	MEYERS ET AL., "Solution-Processed Aluminum Oxide Phosphate Thin-Film Dielectrics" Chem. Mater., 2007, 19, 4023-4029. Abstract Only.	
	4	NAKATTA ET AL., "Improvement Of InGaZnO4 Thin Film Transistors Characteristics Utilizing Excimer Laser Annealing" The Japan Society Of Applied Physics, 2009.	
	5	NEEF ET AL., "Effects Of Carbon/Hardmask Interactions On Hardmask Performance", Proceedings of SPIE, 7273, 727311-1 - 727311-7 (2009).	
	6	OWEN ET AL., "1/8 μm Optical Lithography," J. Vac. Sci. Technol. B 10, 3032 (1992).	
	7	STOWERS, "Direct Patterning of Solution Deposited Metal Oxides", A Dissertation to Oregon State University, August 14, 2008.	
	8	STOWERS ET AL., "High Resolution, High Sensitivity Inorganic Resists", Microelectronic Engineering, 86:730-733 (2009).	

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First Named Inventor	Jason K. Stowers
Art Unit	
Examiner Name	Not Yet Assigned
Attorney Docket Number	5063.02US05

	9	STOWERS ET AL., "Directly Patterned Inorganic Hardmask For EUV Lothography," Proc. SPIE 7969, 796915 (2011); http://dx.doi.org/10.1117/12.879542.	
	10	WANG ET AL.,"TiO2 Micro-Devices Fabricated By Laser Direct Writing" Optics Express, 19(18):17390-17935 (August 29, 2011).	
	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.	
	14	Office Action From Co-pending Korean Application No. 10-2011-0052919 dated March 14, 2013.	
	15	Office Action From Co-pending Japanese Application No. 2011-120402 dated June 11, 2013.	
	16	Office Action From Co-pending Taiwan Application No. 100116897 dated July 29, 2013 (with translation).	
	17	Office Action From Co-pending Japanese Application No. 2015-207978 dated August 23, 2016. ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.N.R/	

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Examiner Signature	/CHANCELTY N ROBINSON/	Date Considered	01/05/2019

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First Named Inventor	Jason K. Stowers
Art Unit	
Examiner Name	Not Yet Assigned
Attorney Docket Number	5063.02US05

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(Not for submission under 37 CFR 1.99)

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Filing Date	
First Named Inventor	Jason K. Stowers
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Examiner Name	Not Yet Assigned
Attorney Docket Number	5063.02US05

CERTIFICATION STATEMENT

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

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

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See attached certification statement.

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	/Peter S. Dardi/	Date (YYYY-MM-DD)	2017-10-16
Name/Print	Peter S. Dardi, Ph.D.	Registration Number	39,650

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

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	1	20150221519	A1	2015-08-06	Marks et al.	

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2]	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]
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Art Unit	1722
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	1	Anonymous: "International Technology Roadmap for Semiconductors 2009 Edition Executive Summary", 1 January 2009, XP055464243, Retrived from the Internet: URL:https://www.semiconductors.prg/clientuploads/Research_Technology/ITRS/2009/1_Executive%20Summary.pdf
	2	LEE ET AL., "Effect of line-edge roughness (LER) and line-width roughness (LWR) on sub-100-nm device performance", Microlithography 2004, vol. 5376, 14 May 2004, page 426, XP055464997, DOI: 10.1117/12.534926.
	3	MORECROFT ET AL., "Sub-15nm nanoimprint Molds and Pattern Transfer", Journal of Vacuum Science and Technology: Part B, AVS / AIP, Melville, New York, NY, vol 27, no. 6, 3 December 2009, pgs. 2837-2840, XP012129582, ISSN:1071-1023 DOI: 10.1116/1.3264670
	4	Office Action from Co-pending European Application No. 15178638.1 dated April 16, 2018. ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.N.R/

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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 15/784,258	Filing Date 10/16/2017	☐ 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 $80 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $420 =	
☐ 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)			
AMENDMENT	04/08/2019	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 19	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 2	Minus	*** 3	= 0		x $460 =	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)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ 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.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/AMANDA N FORD/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US05
Stowers et al.	Confirmation No.: 9576
Application No.: 15/784,258	Examiner: Chanceity N. Robinson
Filed: October 16, 2017	Group Art Unit: 1722

For: RADIATION BASED PATTERNING 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 of January 7, 2019, 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. 60-1363.

CERTIFICATE OF ELECTRONIC TRANSMISSION

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April 8, 2019
Date

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

Lam Research Ex. 1009 - Page 129 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

REMARKS

Claims 1-19 are pending. By this Amendment, claims 1 and 3 are amended to more particularly point out the claimed invention, and claim 13 is amended to add a missing period. Specifically, claim 1 is amended to remove the reference to electron beam patterning and for clarity. Claim 3 is amended to remove the reference to electron beam patterning and to insert a reference to the pattern. The specification supports the amendment of claim 3, for example, at .page 28, lines 11-17. No new matter is introduced.

Rejection for Obviousness-Type Double Patenting Over U.S. Patent 9,176,377

The Examiner rejected claims 1-19 under nonstatutory obviousness-type double patenting as being unpatentable over claims 1-27 of U.S. patent 9,176,377 (hereinafter the '377 patent). Claims 2-13 depend from claim 1 and claims 15-19 depend from claim 14. Applicant will consider filing a terminal disclaimer when the claims are found otherwise allowable.

Rejection for Obviousness-Type Double Patenting Over U.S. Patent 8,415,000

The Examiner rejected claims 1-19 under nonstatutory obviousness-type double patenting as being unpatentable over U.S. patent 8,415,000 (hereinafter the '000 patent). With all due respect, there seems to be some misunderstanding. The rejection states that "they [the claims] are not patentably distinct from each other because both the instant claims and patent '377 [claims of the '000 patent?] recite the same method of forming a patterned inorganic material on a substrate." The claims of the '000 patent are not directed to any method. Respectfully, there would seem to be no basis for this rejection. Applicant respectfully requests withdrawal of the rejection of claims 1-19 under nonstatutory obviousness-type double patenting as being unpatentable over the '000 patent.

Rejections Under 35 U.S.C. § 112

The Examiner rejected claims 1-19 under 35 U.S.C. 112(b) or pre-AIA 35 U.S.C. 112, second paragraph as being indefinite. In particular, the Examiner asserts that the recitation of the term "about" in claims 1-3, 7-8, 13-14, 16, 18 and 19 renders the claims indefinite. Applicant notes that claims are interpreted from the view point of a person of ordinary skill in the art. The

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present application would be directed to a person of skill with an advanced degree in Chemistry or Material Science or an undergraduate degree with many years of experience in the related art. With all due respect, the parameters noted are continuous variable that are not amenable to precise evaluation. A person of ordinary skill in the art would recognize that such parameters are determined within measurement precision that is appropriate for the specified processes. Thus, the recitation of "about" would be well understood to a person of ordinary skill in the art.

In view of the comments above, Applicant respectfully maintains that the claims are clear and definite and requests the withdrawal of the rejection of claims 1-19 under 35 U.S.C. 112(b) or pre-AIA 35 U.S.C. 112, second paragraph as being indefinite.

Rejection Under 35 U.S.C. § 103

The Examiner rejected claims 1-19 under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Stowers Thesis (2008) (hereinafter Thesis) in view of Stowers and Keszler 2009 article (hereinafter Stowers) and further in view of published PCT application WO 2008/082448 to Meyers et al (hereinafter Meyers). Claims 2-13 depend from claim 1, and claims 15-19 depend form claim 14. To advance prosecution, Applicant has amended claim 1 to more particularly point out Applicant's claimed invention. Applicant respectfully maintains that the cited references do not teach all of the features of Applicant's claimed invention. Thus, the cited references do not render Applicant's claimed invention *prima facie* obvious. Applicant respectfully requests reconsideration of the rejections based on the following comments.

Claim 1

Claim 1 has been amended to remove the reference to e-beam patterning. The Examiner acknowledges on page 7 of the Office Action that "[n]either Stowers nor Stowers et al. teach the radiation dosage as instantly claimed." For completeness, Applicant notes that Stowers teaches e-beam dosage in Fig. 1. The Examiner cited Meyers for teaching the claimed electron beam dosage levels. Respectfully, Applicant notes that the Office Action seems to mix electron beam dosage levels in $\mu C/cm^2$ with EUV dosages in mJ/cm^2, although these are distinct. The present claim only refers to EUV dosage levels, and none of the references recite or teach the claimed EUV dosage levels to achieve a selected patterning result.

Since the references do not teach all of the features of amended claim 1, the combined teachings of Thesis, Stowers and Meyers do not render claim 1 *prima facie* obvious.

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Claim 14

On page 7 of the Office Action, the Examiner admitted that "Stowers in view of Stowers et al." do not teach a metal ion to ligand ration of at least about 2. Stowers teaches a stoichiometric ratio of 1 metal ion to 0.5 ligands. The Examiner argues that it is obvious to optimize compositional number ratios unless there are certain grounds. On the present facts, Stowers does not suggest alternative ratios. The 0.5 ratio of Stowers and Meyers is a stoichiometric value with one ligand (peroxide) bridging between two metal ions. There is not suggestion providing any reason to alter this value of peroxide ligands, let alone adjusting this value to improve the results. Applicant has demonstrated that exceptional results can be achieved by unexpectedly increasing the peroxide ligand concentrations by at least a factor of four. This is a patentable improvement not suggested by the cited art. Therefore, respectfully, the cited art does not render claim 14 *prima facie* obvious.

Summary

For the reasons discussed above the combined teachings of Thesis, Stowers and Meyers do not render Applicant's claimed invention *prima facie* obvious. Applicant respectfully requests withdrawal of the rejection of claims 1-19 under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Thesis in view of Stowers and further in view of Meyers. While Applicant does not acquiesce with respect to specific assertions in the rejection directed to the features of the dependent claims, Applicant does not comment further on these in view of the comments and amendments above relating to the independent claims that are dispositive.

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CONCLUSION

In view of the foregoing, it is submitted that this application is in condition for allowance. Favorable consideration and prompt allowance of the application are respectfully requested.

The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,

/Peter S. Dardi/

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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 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 according to the selected pattern.

2. (Original) The method of claim 1 wherein the irradiation is performed with EUV at a dose of no more than about 90 mJ/cm^2.

3. (Currently Amended) The method of claim 1 wherein the selected pattern has a pitch of no more than about 60 nm ~~irradiation is performed with e-beam radiation with a dose equivalent to no more than about 250 μC/cm^2 at 30 kV~~.

4. (Original) The method of claim 1 wherein the developing composition comprises tetramethyl ammonium hydroxide.

5. (Original) The method of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous base.

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6. (Original) The method of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent.

7. (Original) The method of claim 1 further comprising heating the coated substrate after irradiation to a temperature of at least about 45ºC prior to contacting the irradiated layer with the developing composition.

8. (Original) The method of claim 1 further comprising heating the substrate with the patterned coating material to a temperature from about 150ºC to about 600ºC for from one minute to 25 minutes to form a post-patterning condensed structure.

9. (Original) The method of claim 8 further comprising performing a second patterning using the post-patterning condensed structure to form a double patterned structure.

10. (Original) The method of claim 1 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.

11. (Original) The method of claim 10 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.

12. (Original) The method of claim 10 wherein the radiation sensitive ligands comprise peroxide ligands, and wherein the coating material further comprises metal suboxide cations.

13. (Currently Amended) The method of claim 12 wherein the coating material further inorganic polyatomic anions and wherein the peroxide ligand to metal ion ratio is at least about 2.

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14. (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 45ºC prior to contacting the coating with a developing composition.

15. (Original) The method of claim 14 further comprising contacting the coated substrate after heating with a developing composition to remove un-irradiated coating material to form the patterned inorganic material.

16. (Original) The method of claim 15 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.

17. (Original) The method of claim 14 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.

18. (Original) The method of claim 14 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.

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19. (Original) The method of claim 14 wherein the coating has an average thickness of about 5 nm to about 30 nm.

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.00US05

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	2	4144222	A	1979-03-13	Shinmi et al.	
	3	4174346	A	1979-11-13	Collins et al.	
	4	4380559	A	1983-04-19	Mandai et al.	

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	1	20020160298	A1	2002-10-31	Minami et al.	
	2	20100099908	A1	2010-04-22	Yoshitomo et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
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	First Named Inventor	Jason K. Stowers
	Art Unit	1722
	Examiner Name	Chanceity N. Robinson
	Attorney Docket Number	5063.00US05

	3	20100279228	A1	2010-11-04	Davis et al.	
	4	20130078796	A1	2013-03-28	Ganesan et al.	

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	1	102027603	CN	A	2011-04-20	Eastman Kodak Co.	English Abstract Only	
	2	1326136	EP	A1	2003-07-09	Samsung Electronics Co., Ltd.		

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	Application Number	15784258
	Filing Date	2017-10-16
	First Named Inventor	Jason K. Stowers
	Art Unit	1722
	Examiner Name	Chanceity N. Robinson
	Attorney Docket Number	5063.00US05

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.00US05

CERTIFICATION STATEMENT

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

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

☒ 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	/Peter S. Dardi/	Date (YYYY-MM-DD)	2019-04-08
Name/Print	Peter S. Dardi, Ph.D.	Registration Number	39,650

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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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.

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Bibliographic data: CN102027603 (A) — 2011-04-20

Process for depositing organic materials

Inventor(s): CAROL FREEMAN DIANE; HOWARD LEVY DAVID; JEROME COWDERY-CORVAN PETER ± (FREEMAN DIANE CAROL, ; LEVY DAVID HOWARD, ; COWDERY-CORVAN PETER JEROME)

Applicant(s): EASTMAN KODAK CO ± (EASTMAN KODAK CO)

Classification: **- international:** ***B05D7/24; C23C16/30; C23C16/455; H01L31/18; H01L51/50***
- cooperative: **C23C16/30**; **C23C16/45551**; **C23C16/45553**; **C23C16/545**; B05D1/60; B05D2252/02

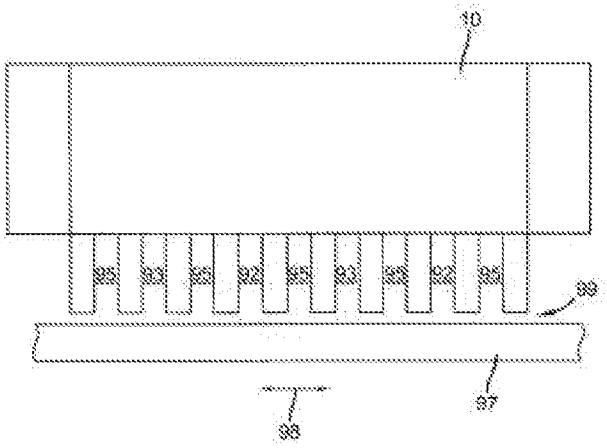
Application number: CN20088108812 20080917

Priority number(s): WO2008US10801 20080917 ; US20070861618 20070926

Also published as: CN102027603 (B) EP2210270 (A2) EP2210270 (B1) JP2011506758 (A) US2009081883 (A1) more

Abstract of CN102027603 (A)

A process of making an organic thin film on a substrate by atomic layer deposition is disclosed, the process comprising simultaneously directing a series of gas flows along substantially parallel elongated channels, and wherein the series of gas flows comprises, in order, at least a first reactive gaseous material, an inert purge gas, and a second reactive gaseous material, optionally repeated a plurality of times, wherein the first reactive gaseous material is capable of reacting with a substrate surface treated with the second reactive gaseous material wherein the first reactive gaseous material, the second reactive gaseous material or both is a volatile organic compound. The process is carried out substantially at or above



atmospheric pressure and at a temperature under 250 DEG C, during deposition of the organic thin film.

(19)中华人民共和国国家知识产权局

(12)发明专利申请

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代理人 赵苏林 李连涛

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C23C 16/455(2006.01)
C23C 16/30(2006.01)

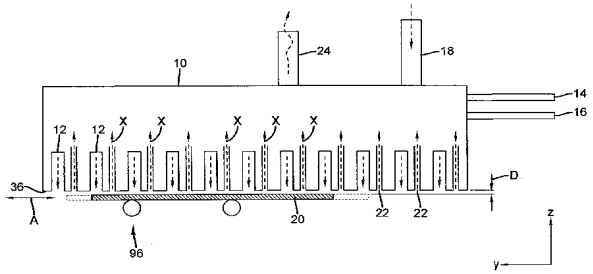
权利要求书 2 页 说明书 19 页 附图 11 页

(54)发明名称

沉积有机材料的方法

(57)摘要

一种通过原子层沉积在基板上制备有机薄膜的方法，所述方法包括同时引导一系列气流沿着基本上平行的伸长的通道通过，其中该系列气流包括依次的至少第一反应性气态材料、惰性吹扫气体和第二反应性气态材料，任选重复多次，其中所述第一反应性气态材料能够与用第二反应性气态材料处理过的基质反应，其中所述第一反应性气态材料、第二反应性气态材料或者二者为挥发性有机化合物。在有机薄膜的沉积过程中，所述方法基本上在大气压下或高于大气压下进行，其中沉积过程的基质温度低于250℃。



CN 102027603 A

1. 一种通过原子层沉积在基板上制备有机薄膜的方法，包括同时引导一系列气流沿着基本上平行的伸长的通道方向，其中该系列气流依次包括至少第一反应性气态材料、惰性吹扫气体和第二反应性气态材料，任选重复多次，其中所述第一反应性气态材料能够与用第二反应性气态材料处理过的基板表面反应，并且第二反应性气态材料能够与被第一反应性气态材料处理过的表面反应，以形成薄膜，其中所述第一反应性气态材料、第二反应性气态材料或者二者为挥发性有机化合物，

其中所述方法基本上在大气压下或高于大气压下进行，其中沉积过程中的基板温度低于 250℃，并且其中沉积的有机薄膜包括至少 20 个原子重量百分数的碳。

2. 权利要求 1 的方法，其中所述第一反应性气态材料包含金属或类金属原子。

3. 权利要求 2 的方法，其中所述第一反应性气态材料包含与碳、氮、氧或氢键合的金属或类金属原子。

4. 权利要求 2 的方法，其中所述金属或类金属原子选自铝、锌、钛和硅。

5. 权利要求 2 的方法，其中所述金属或类金属原子与 β - 二酮化合物缔合。

6. 权利要求 1 的方法，其中所述第二反应性气态材料包含一个或多个选自羟基、硫醇基和胺基的官能团。

7. 权利要求 1 的方法，其中所述第二反应性化合物选自二醇、二硫醇、二胺和喹啉化物。

8. 权利要求 1 的方法，其中所述有机薄膜为无机 - 有机杂化薄膜。

9. 权利要求 1 的方法，其中由沉积装置提供所述系列的气流，其中所述沉积装置在俯视图中面对基板的方向上，包括一系列基本上平行的敞开的伸长的输出开口，所述输出开口设置基板上与之接近处，且在所述沉积装置的输出面内，所述输出面与经历沉积的基板表面间隔在 1mm 内，其中任选地在用于第一反应性气态材料和第二反应性气态材料的伸长的输出通道之间没有排气通道。

10. 权利要求 1 的方法，其中所述方法在沉积体系中进行，所述沉积体系包含 ：

(a) 分别用于多个气态材料的多个源，其中所述气态材料至少包括分别用于第一、第二和第三气态材料的第一、第二和第三源 ；

(b) 至少一个输送头，其用于将多个气态材料输送至接受薄膜沉积的基板，所述输送头包括 ：

(i) 包括至少第一、第二和第三入口的多个入口，其中所述第一、第二和第三入口分别用于所述第一、第二和第三气态材料 ；

(ii) 输出面，其与基板间隔一定距离并且包括多个基本上平行的伸长的输出开口，其中所述输出开口用于第一、第二和第三气态材料中各个气态材料，其中所述输送头设计为从输出面上的伸长的输出开口同时输送所述第一、第二和第三气态材料。

11. 权利要求 10 的方法，其中由于一种或多种气态材料由输送头流动至用于薄膜沉积的基板表面上，因而产生了至少部分力，所述力在薄膜沉积过程中使输送头的输出面与基板表面保持分离，和其中所述沉积装置进一步包括位于伸长的基本上平行的输出开口之间的排气通道，其中所述输出口用于所述的至少第一和第二反应性气态材料。

12. 权利要求 1 的方法，其中将基板的给定区域暴露于通道内的气流下，历时小于 100 毫秒，其中所述基板与沉积装置的相对运动的速度至少为 0.1cm/ 秒。

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13. 权利要求 1 的方法，其中所述挥发性化合物在大气压下，低于 300℃的温度下能够蒸发。

14. 权利要求 1 的方法，其中用于薄膜材料沉积的基板的总表面积超过沉积装置的输出面的总表面积。

15. 权利要求 1 的方法，其中所述基板或用于基板的支持体包含移动网。

16. 权利要求 1 的方法，其中所述方法与环境大气处于未密封的关系。

17. 权利要求 1 的方法，其中所述方法用于制备电子器件的绝缘层，其中所述电子器件含有放置在至少两个导电电极之间的所述绝缘层。

18. 权利要求 1 的方法，其中所述方法用于制备保护电子器件免受其周围环境损害的屏蔽层。

19. 权利要求 1 的方法，其进一步包括基板支持体，所述基板支持体使基板表面与沉积装置的输出面保持 0.3mm 以内的间隔距离。

20. 权利要求 18 的方法，其中所述电子器件选自集成电路、有源矩阵显示器、太阳能电池、有源矩阵照排机、传感器和射频价签、识别标签或存货标签。

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沉积有机材料的方法

发明领域

[0001] 本发明总的涉及薄的有机膜，更尤其地，涉及一种使用原子或分子层沉积法在基质上沉积有机薄膜的方法。 尤其，本发明涉及一种制备有机薄膜，包括无机 - 有机杂化薄膜的膜的方法，所述薄膜可以用在电子或光学器件中。

[0002] 发明背景

[0003] 现代电子仪器需要多构图层的电或光学活性材料，其通常沉积在相对大的基板之上。 电子器件，例如射频识别 (RFID) 标签、光伏器件、光学和化学传感器都需要在其电子线路中有一些程度的构图 (patterning)。 平板显示器，例如液晶显示器或电致发光显示器（不包括 OLED）依赖于精密构图顺序的层，以形成背板的薄膜元件。 这些元件包括电容器、晶体管和电源总线。 为了增强性能并降低成本，工业上一直在寻找材料沉积和层构图的新方法。

[0004] 有机膜，包括有机 - 无机杂化膜，对于许多应用，包括绝缘层和保护层而言可能都非常有用。 虽然溶液浇铸法可以沉积许多有机或杂化有机膜，但是人们仍旧关注通过分子沉积法获得质量非常好的有机膜，该方法承诺可以提供更高质量的膜或者膜的沉积可能不经历容易的溶液处理途径。

[0005] 在化学气相沉积 (CVD) 技术中，两种反应性气体混合形成希望的膜材料，该方法对于实现高质量的膜增长而言可能是有用的途径。 原子层沉积（″ ALD″）是又一种可选的膜沉积技术，与其上一代 CVD 技术相比，其能够提供改善的厚度分辨率和保形能力。 ALD 法将传统 CVD 的传统薄膜沉积法分成单个的原子层沉积步骤。

[0006] ALD 可以用作制造步骤，用以形成多种类型的薄膜电子器件，包括半导体器件和支撑电子元件，例如电阻器和电容器、绝缘体、总线和其它导电结构。 可以用 ALD 沉积的一般类型的功能材料包括导体、电介质或绝缘体和半导体。

[0007] 采用 ALD 沉积的功能层可以制备许多器件结构。 电容器是通过在两个导体之间放置电介质而形成。 二极管是通过在两个导电电极之间配置两个互补载体类型的半导体而形成。 在互补载体类型的半导体之间还可以置放内在的半导体区域，指示出该区域的自由电荷载体数目低。还可以在两个导体之间配置单个半导体来构建二极管，其中导体 / 半导体界面之一产生肖特基 (Schottky) 势垒，其从一个方向对电流产生强阻止。 晶体管是通过在导体（门）上配置绝缘层，再在绝缘层上配置半导体层而形成。 如果两个或多个附加的导体电极（源和漏极）配置成间隔开地与顶部半导体层接触，则可形成晶体管。只要出现临界界面，则上述器件中的任何一种均可做成各种不同的结构。

[0008] 有利地， ALD 步骤是自终止的，并且当进行到或超过自终止暴露时间时，能够在一层原子层上形成精确沉积。 原子层一般为 0.1 到 0.5 个分子单层，其典型的尺寸数量级不超过数埃。 在 ALD 中，原子层的沉积是由反应性分子前体与基板之间的化学反应所致。 在每个单独的 ALD 反应 - 沉积步骤中，通过净反应形成期望的原子层并将原本包含在分子前体中的“多余”原子充分除去。 在 ALD 的最纯形式中，ALD 包括在完全没有其它前体或反应前体存在下对每个前体的吸收和反应。 实践中，在任何一个方法中都难

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以避免不同前体之间的一些直接反应，从而发生少量的化学气相沉积反应。 任何一种声称进行 ALD 的方法的目标都是为了获得与 ALD 方法相当的器件性能和品质，同时认可对少量的 CVD 反应的容许。

[0009] 在 ALD 应用中，通常在单独步骤中引入两种分子前体进入 ALD 反应器。例如，金属前体分子，ML_x，包含金属元素，即与原子或分子配体 L 连接的 M。 例如，M 可以是但不限于：Al、W、Ta、Si、Zn 等。 当制备出基板表面而可以直接与分子前体进行反应时，金属前体与基板发生反应。 例如，基板表面通常制成包含可与金属前体进行反应的含氢配体 AH 等。 硫 (S)、氧 (O) 和氮 (N) 是一些典型的 A 物质。 气态前体分子有效地与基板表面上的所有配体进行反应，从而在金属的单一原子层上形成沉积：

[0010] 基板 -AH+ML_x →基板 -AML_{x-1}+HL (1)

[0011] 其中 HL 是反应副产物。 反应过程中，最初的表面配体 AH 被消耗，而表面被 AML_{x-1} 配体所覆盖，该 AML_{x-1} 配体将不会与金属前体 ML_x 发生进一步反应。 因此，当表面上所有最初的 AH 配体都被 AML_{x-1} 代替后，反应将自终止。 在该反应阶段之后通常是惰性气体吹扫阶段，其将过量的金属前体和 HL 副产物在单独引入另一种前体之前清除出室。

[0012] 然后，使用第二分子前体来恢复基板对金属前体的表面反应性。 这可通过例如，除去 L 配体并重新沉积 AH 配体来实现。 在这种情况中，该第二前体通常含有期望的（通常为非金属的）元素（即 O、N、S）和氢（即 H_2O、NH_3、H_2S）。 下一步的反应如下：

[0013] 基板 -A-ML+AHY →基板 -A-M-AH+HL (2)

[0014] 这将表面变回为其 AH 覆盖的状态。（这里，为了简便起见，化学反应不是配平的。）希望有的附加元素 A 被引入到膜中，而不希望有的配体 L 则作为挥发性副产物被去除。 该反应再次消耗反应位（此次为 L 终止位），并且当基板上的反应位被完全消耗时反应自终止。 然后，通过在第二吹扫阶段中通入惰性吹扫气体，该第二分子前体将从沉积室内清除。

[0015] 总之，此后的 ALD 方法需要交替流至基板的化学物质的顺序。 如上面所讨论的，代表性的 ALD 方法是一个具有四个不同操作阶段的循环：

[0016] 1.ML_x 反应；

[0017] 2.ML_x 吹扫；

[0018] 3.AH_y 反应；和

[0019] 4.AH_y 吹扫，然后返回到阶段 1。

[0020] ALD 更通常用于沉积其中的金属前体为卤化物、烷氧化物、二酮化物螯合物的无机化合物，或者有机金属化合物。 当分别沉积氧化物、氮化物或硫化物时，所述第二前体更通常为氧、氮或硫源。 虽然研究得相对少一些，但是 ALD 在沉积有机化合物或有机 / 无机杂化层中仍然有用。 在这些情况下，仍旧可以使自限制反应具有交替的次序，除了由这种方法制备的限制层可能为与原子层相对的分子层。 这样，这种技术还可以称作分子层沉积 (MLD)，尽管基本概念和沉积设备与 ALD 法和设备都相似。 有机膜的原子层沉积或分子层沉积的例子可以在 Matti Putkonen 等，“ATOMIC LAYER DEPOSITION OF POLYIMIDE THIN FILMS”， theJournal of Materials Chemistry 中，2007，17，

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664-669 中找到。 除非上下文中另有指示，否则如本文中所用的，术语 “原子层沉积” 指 ALD 和 MLD。

[0021] 常用的 ALD 沉积周期为重复下述顺序 ：交替进行表面反应和通过除去前体将基板表面恢复至初始反应状态，以及中间插入吹扫步骤。 ALD 操作的关键特征是将基板恢复至其初始表面化学状况。 使用该组重复步骤可以以相同量度的层将膜层叠在基板上，其中所述层的化学动力学、每周期的沉积量、组成和厚度全部相同。

[0022] 自饱和表面反应使得 ALD 对运输非 - 均匀性不敏感。 而如果对这种运输非 - 均匀性敏感，出于工程耐受度和流动过程的局限或相关的表面拓扑（即沉积到三维中，高的长宽比结构）的原因，则可能会损害表面均匀性。 作为一般性原则，在反应过程中化学物质的非均匀流动通常会导致在不同区域出现不同的完成时间。 然而，使用 ALD 使得各个反应在整个基板表面均能完成。 因此，完成动力学上的差异并不会有损均匀性。 这是由于首先完成反应的区域将自终止反应 ；而其它区域能够继续反应直至所有处理的表面均进行完目标反应为止。

[0023] 通常来说，ALD 方法在单一 ALD 周期（包括前面列出的步骤 1- 步骤 4）中沉积 0.1-0.2nm 的膜。为了提供在 3nm 到 300nm 范围内的均匀膜厚以用于许多或绝大部分的半导体应用，甚至提供更厚的膜用于其它应用，必须获得有用且经济上可行的循环时间。工业生产量标准规定，对基板的加工时间为 2 分钟到 3 分钟，这意味着 ALD 循环时间必须在 0.6 秒到 6 秒的范围。

[0024] ALD 方法必须能够有效地执行这样的序列并能可靠地进行多次循环，从而能够对多种基板进行有成本效益的涂覆。 为了使在任何给定反应温度下 ALD 反应达到自终止所需的时间达到最短，一种方法是通过使用所谓的 “脉冲” 方法，而使流入 ALD 反应器中的化学物质流量最大。 在脉冲的 ALD 方法中，基板安置在室内，通过使第一气体进入室，然后通过泵循环除去这种气体，再引入第二气体进入室，然后通过泵循环除去该第二气体，从而暴露于上述气体序列。 这种序列可以在任何频率，以及改变气体类型和 / 或浓度下重复。 净效果是整个室随着时间经历着气体组成的改变，因此这种类型的 ALD 可称作是时间依赖型 ALD。 绝大多数现有的 ALD 方法是时间依赖型 ALD。

[0025] 为了使进入 ALD 反应器中的化学物质流量最大化，最好是在高压和最低稀释的惰性气体条件下向 ALD 反应器中引入分子前体。 然而，这些措施与需要获得短的循环时间和快速从 ALD 反应器中除去这些分子前体相抵触。 快速除去反过来要求气体在 ALD 反应器中的停留时间最小化。

[0026] 现有的 ALD 方法一方面已经在缩短反应时间的需要和改善化学利用效率之间进行折衷，另一方面在最小化吹扫气体残留的需要和化学物质除去时间之间进行了折衷。一种克服时间依赖型 ALD 系统的内在限制的方法是连续地提供每种反应气，并移动使基板接连通过每种气体。 在这些系统中，存在相对恒定的气体组成，但它们处于处理系统中的特定区域或空间。 因此，这些系统称为空间依赖型 ALD 系统。

[0027] 例 如， Yudovsky 的 题 为 “GAS DISTRIBUTION SYSTEM FORCYCLICAL LAYER DEPOSITION” 的美国专利 6,821,563 描述了一种真空下的空间依赖型 ALD 处理系统，该系统具有用于前体和吹扫气体的独立气口，每个气口之间以真空泵口间隔。 气流沿每个气口垂直向下导入基板。 壁与隔板将气流分开，用真空泵抽空每个气流两侧的

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气体。 每个隔板的下部延伸靠近基板，例如离开基板表面 0.5nm 或更远。 这种情况下，隔板的下部与基板表面分离的距离足够使气流在与基板表面反应后沿隔板的下部流向真空口。

[0028] 提供旋转转盘式或其它运输装置用来装载一个或多个基板晶片。 采用这种排列，基板穿梭往返于不同气流之下，从而实现 ALD 沉积。 在一种实施方案中，基板以线性路径移动通过室，在该室中基板往复通过数次。

[0029] 另一种使用连续气流空间依赖型 ALD 的方法在 Suntola 等人的题为 “METHOD FOR PERFORMING GROWTH OF COMPOUND THINFILMS” 的美国专利 4,413,022 中有描述。 气流阵列具有交替的源气体开口、载气开口和真空排气开口。 基板在阵列上的往复运动也在无需脉冲操作下即实现 ALD 沉积。 特别是在图 13 和 14 的实施方案中，通过基板在固定的源开口阵列上的往复运动形成在基板表面和反应气体之间的顺序互动。 在排气开口之间，由载气开口形成扩散屏障。 Suntola 等人声称，具有这样实施方案的操作即使在大气压下也可进行，尽管对方法提及甚少或者没有细节或实例的描述。

[0030] 尽管在 Yudovsky 的′ 563 专利和在 Suntola 等人的′ 022 专利中描述的这些方法可以避免脉冲气体方法中固有的难题，但这些方法存在其它的缺点。 例如，难以在阵列中的不同点保持均匀的真空和在互补压力下保持同步的气流和真空，因此要牺牲提供给基板表面的气流均匀度。 无论是 Yudovsky 的′ 563 专利中的气流输送单元还是 Suntola 等人的′ 022 专利中的气流阵列均不能用在与基板距离小于 0.5mm 的更接近处。

[0031] Selitser 的美国专利申请公开 2005/0084610 揭露了一种大气压原子层化学气相沉积法。 Selitser 指出，在反应速率上的显著增加是通过将操作压力变为大气压获得的，这样将涉及增加反应物的浓度数量级，结果导致表面反应物速率的增加。 尽管图 10 示出的实施方案中的室壁均被除去了，但 Selitser 的实施方案包括分离的用于方法各步骤的室。在旋转的圆形的基板夹持带的周围设置了一系列分离的注射器。 每个注射器包括独立操作的反应物，吹扫，和排气歧管；在沉积方法中当每个基板通过这里时，这些注射器控制并完成一个完整的单层沉积和反应物吹扫周期。 Selitser 的申请中对气体注射器和歧管描述很少或没有具体描述，尽管在 Selitser 的申请中指出通过对注射器的间隔进行选择，从而通过置于每个注射器中的吹扫气流和废气歧管来防止来自临近注射器的交叉污染。

[0032] A.A.Dameron 在递交至 AVS 54th International Symposium 的论文，论文 TF-M0A8（将在 2007 年 10 月 15 日演讲）的摘要中公开了使用三甲基铝和各种二醇将 alucone 聚合物膜分子层沉积在硅基板上。 如 Jang 等人在 US 公开专利 No.2007/0190247 中所公开的 Alq_3， Znq_3 和 Tiq_3（其中 q 为 8- 羟基喹啉）薄膜的原子层沉积也是已知的。Appl.Phys.Lett.，59 卷，4 期，1991 年 7 月中公开了通过分子层沉积由单层生长步骤形成的聚合物膜。 Yitzchaik 的 US 专利 No.6,808,803 中公开了一种使所选的多环芳香族化合物形成分子薄膜的方法，其中所述多环芳香族化合物例如为能够形成在轴的末端有二酰胺链接的多环四羧基 - 二酐化合物等。

[0033] 仍旧需要提供通过原子层沉积来沉积有机材料的材料和方法，其能够克服现有技术的问题和缺点。

[0034] 发明概述

[0035] 本发明提供一种与空间依赖型 ALD 相容的有机材料沉积方法。 尤其地，本发明

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涉及一种通过原子层沉积在基板上制备有机薄膜的方法，包括同时引导一系列气流沿着基本上平行的伸长的通道通过，其中该系列气流包括依次的至少第一反应性气态材料、惰性吹扫气体和第二反应性气态材料，任选重复多次，其中所述第一反应性气态材料能够与用第二反应性气态材料处理的基板表面反应，并且第二反应性气态材料能够与被第一反应性气态材料处理过的表面反应形成薄膜，其中所述第一反应性气态材料、第二反应性气态材料或者二者为挥发性有机化合物，其中所述方法基本上在大气压或高于大气压下进行，其中沉积过程的基板温度低于 250℃，并且其中所述沉积的有机薄膜包括至少 20 个原子重量百分比的碳。

[0036] 在所述方法中，所述基板或气态材料沉积装置，或者二者能够在沉积装置的输出面和基板之间提供相对运动，同时还保持紧密的接近度。

[0037] 在优选的实施方案中，所述方法可以通过使经历薄膜沉积的基板连续运动来进行操作，其中所述方法能够将支持体输送至沉积装置上或者将支持体作为网输送过沉积装置，优选在基本上为大气压下的未密封的周围环境中进行。

[0038] 本发明的再进一步的优点是能够适用于在网或其它移动基板上进行沉积，包括在大面积的基板上进行沉积。

[0039] 本发明的进一步的优点是在优选的实施方案中其可以使操作在大气压条件下进行。

[0040] 本发明更进一步的优点是其可以用于大气压下的低温方法中，该方法可以在敞开至环境大气的未密封的环境下进行。

[0041] 本发明还涉及一种通过本方法制备的优选在柔性基板上的晶体管，其包含有机或无机 - 有机杂化材料。

[0042] 当下列详细描述与显示和描述本发明的说明性实施方案的附图结合时，所属领域那些熟练技术人员阅读之后将显而易见地了解本发明的目的、特征和优越性。

[0043] 附图简述

[0044] 虽然说明书和权利要求书特别地得出结论，指出并且清楚地要求了本发明的技术方案，但是人们相信通过下列说明并结合所附的附图，本发明将会被更好地理解，其中：

[0045] 图 1 为在本发明的一个实施方案中，用于原子层沉积的输送头的横断面侧视图；

[0046] 图 2 是描述在本发明中使用的 ALD 方法的各步骤的流程图；

[0047] 图 3 是可用于本发明方法中的原子层沉积的沉积装置的一种实施方案的横断面侧视图；

[0048] 图 4 是将气态材料分布于待进行薄膜沉积的基板的一种气态材料的典型系统的实施方案的横断面侧视图；

[0049] 图 5A 和 5B 是气态材料系统分配的一种实施方案的横断面侧视图，图中示意地示出伴随的沉积操作；

[0050] 图 6 是沉积装置的一种实施方案的一部分的输出面侧的透视视图，图中示出输出通道相对于基板的取向和，往复运动示出气体流动在沉积装置中的一种典型的布局；

[0051] 图 7A 和 7B 是与前面图 4-6B 的横断面正交的横断面视图，示出了在各种实施方

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案中的输出通道的气流方向；

[0052] 图 8 是示出往复和正交运动的交替运动模式的示意图；

[0053] 图 9 是使用本法方法的沉积系统的一种实施方案的框图；

[0054] 图 10 是显示另一个带有固定沉积装置的沉积体系实施方案的框图，其中所述沉积体系用在本发明的方法中的移动网中；

[0055] 图 11 是本发明的方法中所用的沉积装置的横断面侧视图，其显示了供给基板的气态材料的排列，其中所述基板要经历实施例中的薄膜沉积法；和

[0056] 图 12 是本发明的方法中所用的沉积装置的横断面侧视图，其显示了供给基板的气态材料的排列，其中所述基板要经历实施例中的薄膜沉积法。

[0057] 发明详述

[0058] 如上所述，本发明涉及一种通过原子层沉积而在基板上制备有机薄膜的方法，其包括同时引导一系列气体沿着基本上平行的伸长的通道流动，并流出伸长的输出开口，以形成有机薄膜，其中第一反应性气态材料、第二反应性气态材料，或者二者为挥发性有机化合物。沉积的有机薄膜包括至少 20％原子重量的碳。所述有机薄膜可以为无机 - 有机杂化薄膜。

[0059] 在本发明的方法中，该系列气流包括至少第一反应性气态材料、惰性吹扫气和第二反应性材料，其任选重复多次，其中所述第一反应性气态材料能够与经第二反应性气态材料处理过的基板表面反应和第二反应性气态材料能够与经第一反应性气态材料处理过的表面反应，而形成薄膜。

[0060] 在一个实施方案中，所述第一反应性气态材料、第二反应性气态材料，或者二者为挥发性有机化合物，并且所述第一反应性气态材料包含金属或类金属原子，例如与碳、氮、氧或氢键合的金属或类金属原子。所述金属或类金属原子例如为铝、锌、钛或硅。所述金属或类金属原子可以与 β - 二酮化物化合物缔合。

[0061] 在一个实施方案中，所述第二反应性气态材料包含一个或多个羟基、硫醇基或胺基。例如，所述第二反应性化合物可以为二醇、二硫醇、二胺或喹啉化物。

[0062] 制备本发明的含有机物的薄膜的整个方法可以在低于最大支持体温度，300℃以下进行，更优选低于 250℃，或者甚至在大约室温 (25℃ -70℃) 的温度下进行。对温度的选择通常取决于所属领域已知的支持体和工艺参数，而只要具有本文中所包括的本发明的知识即可。这些温度大大低于传统的集成电路和半导体加工温度，其使得能应用各种相对廉价的支持体中的任何一种，例如柔性聚合物支持体。因此，本发明使制备具有显著改善的性能的相对廉价的含有薄膜晶体管的电路成为可能。

[0063] 在下面的描述中，术语“气体”或“气态材料”采用广义含义，包括任何范围的蒸发的或气态元素、化合物或材料。这里使用的其它术语例如：反应物、前体、真空、惰性气体均使用它们被材料沉积领域的技术人员所理解的传统含义。文中提供的附图不是按比例绘制的，但旨在示出本发明的一些实施方案的整体功能和结构布置。

[0064] 相对于制备含有有机材料的薄膜的常规方法而言，本发明的方法提供了显著的转变，其采用将气态材料输送至基板表面的体系，其中所述体系能够适应在更大的和基于网的基板上进行沉积，并且能够以改善的产出速度实现高度均匀的薄膜沉积。本发明的方法采用连续的空间依赖型 ALD(与脉冲 ALD 或时间依赖型 ALD 相反) 气态材料分

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配。 本发明的方法可以在大气压或近 - 大气压下操作并且能够在未密封或者开放环境下操作。

[0065] 参见图 1，示出了根据本发明在基板 20 上进行原子层沉积用的输送头 10 的一种实施方案的横断面侧视图。 输送头 10 具有作为接受第一气态材料的进口的气体入口导管 14，作为接受第二气态材料的进口的气体入口导管 16，以及作为接受第三气态材料的进口的气体入口导管 18。 这些气体在输出界面 36 处通过输出通道 12 发射，输出通道 12 的结构布局可包括如下面所述的扩散器。 图 1 中的虚线箭头代表从输送头 10 向基板 20 输送气体。 图 1 中，点线箭头 X 也指明气体排气的路径（在本图中表示为向上的方向）和排气通道 22，其与提供排气口的排气导管 24 连通。 由于排出的气体仍可能含有一定量的未反应前体，因此不希望使主要含一种反应物质的排出气流与主要含另一种反应物质的排出气流混合。 因此认识到输送头 10 可含有数个独立的排气口。

[0066] 在一种实施方案中，气体入口导管 14 和 16 适于接受在基板表面上顺序反应的第一和第二气体来进行 ALD 沉积，而气体入口导管 18 接受相对于第一和第二气体为惰性的吹扫气体。 输送头 10 与基板 20 间隔距离 D，而基板可位于基板支持体之上，对此下面将有更详细的描述。 通过基板 20 的运动，输送头 10 的运动，或基板 20 和输送头 10 两者的运动，可在基板 20 和输送头 10 之间产生往复运动。 在图 1 中所示的特定实施方案中，基板 20 通过基板支持体 96 以往复方式跨过输出界面 36 运动，如箭头 A 和基板左右边的虚框所示。 应当注意的是，使用输送头 10 的薄膜沉积并不总是要求往复运动。 也可以提供在基板 20 和输送头 10 之间的其它类型的相对运动，例如基板 20 或输送头 10 在一个或多个方向的运动。

[0067] 图 2 为用于制备薄膜的 ALD 法的优选实施方案的通用步骤图，其中使用了两种反应性气体，即第一分子前体和第二分子前体。 气体由气体源提供并通过如沉积装置输送到基板。 可使用测量和阀门装置来将气态材料提供给沉积装置。

[0068] 如步骤 1 中所示，为了在基板上沉积出材料的薄膜，系统中提供了连续供应的气态材料。 随后，进行序列 15 中的各个步骤。 在步骤 2 中，对应于基板的给定区域（称为通道区域），使第一分子前体或反应物气态材料导向流入基板的通道区域上的第一通道，并且与之反应。 在步骤 3 中，基板和多通道流在系统中发生相对运动，为步骤 4 打好基础，在步骤 4 中，采用惰性气体的第二通道（吹扫）流出现在给定的通道区域上。然后，在步骤 5 中，基板与多通道流的相对运动为步骤 6 打好基础，在步骤 6 中，给定通道区域发生原子层沉积，其中第二分子前体目前（在这一特定实施方案中，横向或基本上平行于基板表面）在基板的给定通道区域上并与基板上之前的层发生反应来产生（理论上）单层的期望材料。 第一分子前体是气态形式，例如有机化合物或有机金属化合物，如二乙基锌或三甲基铝。 在这种实施方案中，所述第二分子前体也为气态形式并且可以为例如有机化合物，其与有机金属化合物反应形成杂化的无机 - 有机或可选的不同的有机金属化合物。

[0069] 在步骤 7 中，基板和多通道流的相对运动为步骤 8 打好基础，在步骤 8 中，再次使用到惰性气体，这次是吹扫之前的步骤 6 中给定通道区域的过量的第二分子前体。 在步骤 9 中，基板和多通道流再次发生相对运动，为重复序列打好基础，回到步骤 2。 多次重复该周期直到获得理想的膜为止。 在该方法的这种实施方案中，对相应于被流动通道

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覆盖的区域的基板给定通道区域重复这些步骤。 其间，在步骤 1 中向各个通道提供必要的气态材料。 与图 1 中框 15 的序列进行的同时，其它临近通道区域也进行操作，得到如整体步骤 11 中所示的平行的多通道流。 如上所述平行流可与沉积装置的输出面基本成正交或基本成平行。

[0070] 第二分子前体的主要作用是使基板表面调节回具有与第一分子前体反应的反应性。 所述第二分子前体还提供来自分子气体的材料，使其与表面上的第一材料结合，形成具有新鲜沉积的第一前体的化合物。

[0071] 该特定实施方案无需使用真空吹扫，以在将分子前体施用于基板后将其除去。在 ALD 法中，大部分研究人员能够预期吹扫步骤是最显著的限制生产能力的步骤。

[0072] 假设使用 AX 和 BY 作为图 3 中的两种反应气体。 当提供反应气体 AX 流并流经给定的基板区域时，反应气体 AX 的原子被化学吸附到基板上，得到一层 A 和配体 X 的表面（缔合化学吸附）（步骤 2）。 然后，用惰性气体吹扫剩余的反应气 AX（步骤 4）。 接着，流入反应气体 BY，在 AX（表面）和 BY（气体）之间发生化学反应，在基板上得到 AB 的分子层（离解化学吸附）（步骤 6）。 对剩余的气体 BY 和反应副产物进行吹扫（步骤 8）。 通过重复方法循环（步骤 2-9）多次，可增加薄膜厚度。

[0073] 由于所述膜一次能沉积一个单层，因此其倾向于具有相同的形状并且具有均匀的厚度。

[0074] 使用本发明的方法能够制备的材料包括但不限于：alucone、 borocone、酚醛树脂 (Bakelite) 和聚氨酯。

[0075] 所属领域熟练技术人员显而易见可知，可以沉积两种、三种或多种材料的合金，化合物可以沉积为两种、三种或多种成份，同样可以制备分级的膜和纳米层合物等物质。

[0076] 这些变型是在交替的周期中使用本发明的具体实施方案而得的简单变型。 在本发明的精神和范围之内有许多其它变型，因此本发明仅仅通过随后的权利要求来限定。

[0077] 对于可用于 ALD 薄膜方法中的各种挥发性的含锌前体，前体的组合以及反应物，请参考 Glocker 和 Shah 编辑的《(薄膜加工技术手册》(Handbook of Thin Film Process Technology)，第 1 卷， B 1.5：1 到 B1.5：16 页，物理学会 (Institute of Physics(IOP)) 发行，费城，1995，在此引入本文供参考；由 Nalwa 编辑的《薄膜材料手册》(Handbook of ThinFilm Materials)，第 1 卷，103-159 页。

[0078] 虽然氧化物基板提供了用于 ALD 沉积的组 (groups)，但是还可以使用进行适当的表面处理的塑料基板。

[0079] 现在参考图 3，其显示了输送头装置 10 的一个实施方案的横断面侧视图，所述输送头装置 10 可以在本发明的方法中，用于根据本发明在基板 20 上进行原子层沉积。输送头 10 具有用于接受第一气态材料的气体入口 14，用于接受第二气态材料的气体入口 16，和用于接受第三气态材料的气体入口 18。 这些气体通过输出通道 12 在输出面 36 处发射，其中所述输出通道 12 具有随后描述的结构设置。 图 3 和随后的图 5A 和 5B 中的箭头指从输出通道接收的气态材料的扩散运输，而非流动。 在该具体实施方案中，如下面进一步描述的，所述流动基本上指向图的页面外。

[0080] 在一个实施方案中，使气体入口 14 和 16 适合于接受第一和第二气体，所述气体

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在基板表面上依次反应以实现 ALD 沉积，气体入口 18 接收相对于第一和第二气体而言为惰性的吹扫气。 如随后更详细地描述的，输送头 10 距离基板支持体之上的基板 20 间隔距离 D。 可以通过基板 20 的运动、输送头 10 的运动或者基板 20 和输送头 10 的共同运动而在基板 20 和输送头 10 之间提供往复运动。 在图 3 所示的具体实施方案中，如在图 1 中的箭头 A 和指向基板 20 右侧和左侧的虚框所指示的，基板 20 以往复方式跨过输出面 36 移动。 应该注意，对于使用输送头 10 的薄膜沉积而言，并不总是需要往复运动。 如随后更详细地描述的，还可以在基板 20 和输送头 10 之间提供其它类型的相对运动，例如基板 20 或输送头 10 在一个或多个方向上的运动。

[0081] 图 4 的横断面图显示在输送头 10 的一部分输出面 36 上发射出的气流。 在该特定设置中，由隔板 13 分隔的每个输出通道 12 与图 3 中所见的气体入口 14、16 或 18 中的一个气态流体连通。 每个输出通道 12 通常输送第一有机氧化性反应物气态材料 O1，或者第二有机金属或有机反应物气态材料 O2，或者第三惰性气态材料 I。

[0082] 图 4 显示了相对基本或简单的气体设置。 根据预计，在薄膜的单次沉积中，可以在不同端口处依次输送多个第二沉积前体（类似于材料 O1）或多个第一前体材料（类似于材料 O2）。 可选地，当制备复合薄膜材料，例如具有交替的材料层或者在材料中混有较少量的掺杂物时，可以在单一的输出通道处施用反应气体混合物，例如金属前体材料混合物或金属与非金属前体的混合物。 标记为 I 的中间物流将任何其中的气体可能彼此反应的反应物通道分开。

[0083] 第一和第二反应物气态材料 O1 和 O2 彼此反应而实现 ALD 沉积，但是反应物气态材料 O1 和 O2 都不与惰性气态材料 I 反应。 惰性气态材料 I 可以为氮、氩、氦或 ALD 法中常用做吹扫气的其它气体。 惰性气态材料 I 相对于第一或第二反应物气态材料 O1 和 O2 而言是惰性的。 第一和第二反应物气态材料之间的反应会形成有机金属化合物或其它二元化合物，例如在一个实施方案中为 alucone。 多于两个反应物气态材料之间的反应可能形成其它材料，例如三元化合物。

[0084] 图 5A 和 5B 的横断面图以简化的图解形式显示，当输送反应物气态材料 O1 和 O2 时，基板 20 沿输送头 10 的输出面 36 通过时所进行的 ALD 涂覆操作。 在图 5A 中，基板 20 的表面首先暴露于来自输出通道 12 的 O1，所述输出通道旨在输送第一反应物气态材料 O1。 此时基板表面含有部分反应形式的材料 O1，此时将其指示为表面物质 S1，其易于与材料 O2 反应。 然后，当基板 20 进入到第二反应物气态材料 O2 的反应性化合物路径中时，发生与 O2 反应，形成产物材料 P 的薄膜，其可以由两种反应物气态材料形成。

[0085] 如图 5A 和 5B 所示，向第一和第二反应物气态材料 O1 和 O2 的气流之间的每个交替输出通道 12 中提供惰性气态材料 I。 连续的输出通道 12 是相邻的，即享有由所示实施方案中的隔板 22 形成的共同的边界。 这里，输出通道 12 通过隔板 22 限定并相互分开，该隔板 22 相对于基板 20 的表面垂直延伸。

[0086] 图 6 示出了从输出面 36 观察的（即从图 3-5B 的底面）输送头 10 的一种实施方案的透视图，这种输送头可用于本方法。 在本实施方案中限定并分开相邻输出通道 12 的隔板 13 在这里看来被部分切去，这是为了更好地看到气流从气体出口端口 24 流入。 图 6 还示出了用于本公开的图物中使用的参考 x，y，z 坐标轴分配。 输出通道 12 基本上是平

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行的并在对应于 x 坐标轴的长度方向延伸。 使用这样的坐标分配，基板 20 的往复运动，或相对于基板 20 的运动时在 y 轴方向。

[0087] 图 6 显示为了采用该实施方案从输送头 10 输送各种气态材料，用于所述气态材料的气流 F_1、 F_O 和 F_M。 气流 F_1、 F_O 和 F_M 在 x- 方向上，即沿着伸长的输出通道 12 的长度方向。

[0088] 图 7A 和 7B 的横断面视图是与图 3-5B 的横断面正交的方向截断的，在该视图中，显示气流在一个方向流动。 在每个输出通道 12 内，相应的气态材料从气体输出口 24 流出，如图 7A 和 7B 视图中的虚影所示。 在图 7A 的实施方案中，气流 F_1 引导气态材料沿输出通道 12 的长度方向流动并跨过基板 20，正如在图 6 中所描述的那样。 在该布局中，气流 F1 继续流经输送头 10 的边缘，向外流入周围环境中，或者根据需要流到气体收集歧管（未示出）中。 图 8B 示出了用于气流 F2 的另一种替代实施方案，其中输出通道 12 也提供了排气口 26 用于再引导和引出气流。 尽管流动最好是单向的，但可以发生一定程度的混合，甚至在一定程度上是有利的，这取决于气流速率和特定应用中涉及的其它情况。

[0089] 可在特定的输送头 10 中使用的输出通道 12 是使用任何一种气流配置或其组合来配置的，这些气流配置可以是图 7A 的 F1 流，图 7B 的 F2 流，或一些其它的变型，其中气态材料沿输出通道 12 流动跨过基板 20，优选通过可控混合使流动基本上是层流的或平滑的形式。 在一种实施方案中，向输送反应物气态材料的每个输出通道 12 提供一个或多个排气口 26。 例如，参考图 7，标记为 O 和 M 的第一和第二反应物气态材料的输出通道 12 配置了排气口 26，用来按照 F2 流型排出或引出反应物物质（图 8B）。 这就使得材料得到一定程度的循环，并防止了在接近歧管末端处发生不期望的混合和反应。 用于标记为 I 的惰性气态材料的输出通道 12 不使用排气口 26，因此按照 F1 流的模式（图 7A）。 尽管在一些实施方案中层流是优选的，但可以发生一定程度的混合，甚至在一定程度上可能是有利的，这取决于气流速率和特定应用中涉及的其它情况。

[0090] 通常意义下的排气口 26 不是真空端口，而仅仅是用于引出相应的输出通道 12 中的气流，因此有利于在通道内形成均匀的气体流型。 负抽出，即仅比气体输出口 24 处的气压对应的略低，可有助于形成有序的气流。 负抽出例如在 0.9 和 1.0 个大气压之间操作，而典型的真空例如是低于 0.1 个大气压。 如在图 8B 中用点线勾画出的任选的挡板 58 可提供用于再引导流型进入排气口 26。

[0091] 由于不需要环绕隔板 13 至真空排气处存在气流，因此输出面 36 可以位于与基板表面非常接近处，可在 1mil（约 0.025mm）之内。 相比之下，之前的方法，例如在前面引用过的 Yudovsky 的美国专利 6,821,563 中描述的那样，需要气流环绕于通道侧壁边缘，因此就限制了与基板表面的距离为 0.5mm 或更大。 本发明中优选使输送头 10 位于基板表面的更近处。 在一种优选的实施方案中，从基板表面的距离 D 可以是距定位装置的输出面或提供流动通道的导向壁的底部 0.4mm 或更小，优选在 0.3mm 内，更优选在 0.25mm 内。

[0092] 为了沿输出通道 12 的长度方向提供平滑的流动，气体输出口 24 可以与法线倾斜某一角度，如在图 7A 和 7B 中所示。 任选地也可采用一些类型的气流再导向结构来将来自气体输出口 24 的向下气流重新导向，从而形成基本上与输出面 36 平行的气流。 如在图 5A 和 5B 中具体描述的那样，输送头 10 需要与基板 20 的表面发生相对运动来实现它

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的沉积功能。 这种相对运动可以以多种途径获得，包括输送头 10 和基板 20 中任一者的运动或两者的运动，例如提供基板支持体的方法的运动。

[0093] 根据所需要的沉积周期数，运动可以是震荡式的或往复式的或连续式的。 尽管连续方法是优选的，但也可以采用基板旋转，特别是在间歇方法中。

[0094] 通常，ALD 需要多个沉积周期，在每次周期中构建可控的膜深度。 根据前面给出的气态材料类型的命名，单周期，例如在简单设计中，提供第一反应物气态材料 O1 的一次涂布和第二反应物气态材料 O2 的一次涂布。

[0095] 用于 O1 和 O2 反应物气态材料的输出通道之间的距离决定了用于往复移动所需的距离，以完成每个周期。 例如，对于每个输出通道 12 的宽度 W 来说，输送头 10 具有以宽度 W 计的 0.034 英寸的标称通道宽度，这将需要至少 0.20 英寸的往复运动（沿着本文中所用的 y 轴）。 对于该例子而言，基板 20 的区域暴露于第一反应物气态材料 O1 和第二反应物气态材料 O2 下，并且移动过该段距离。 在一些情况下，出于均匀性的考虑，每个周期中可能需要随机测量往复运动的量，例如用以减少边缘效应或者依据往复移动的极限值来堆积。

[0096] 输送头 10 可以仅具有足够的输出通道 12 以提供单独一个周期。 可选地，输送头 10 可以设置有多个周期，使其覆盖更大的沉积面积或者使其往复移动一定距离，使得可以在往返移动距离的一个往返运动中进行两个或多个沉积周期。

[0097] 在一种实施方案中，基板的给定区域暴露于通道内气流的时间少于 500 毫秒，优选少于 100 毫秒。 在震荡中，基板与通道的相对运动的速度至少为 0.1cm/sec，而气流在通道中的速率至少为 1cm/sec。 优选地，沉积方法中基板的温度为 300℃以下，更优选地为 250℃以下。

[0098] 对于本方法的一个实施方案中所用的输送头 10 而言，其中使用的往复运动的优越性在于可以在面积超出输出面 36 的基板 20 上进行沉积。 图 8 示意显示了如何实现该更宽的覆盖面积：如箭头 R 显示的，采用沿 y 轴的往复运动，以及相对于 x 轴的、与往复运动正交或横切的运动。 应该再次强调，如图 9 所示，在 x 或 y 方向上的运动可以通过输送头 10 的运动，或由提供运动的基板支持体 74 所提供的基板 20 的运动，或者输送头 10 和基板 20 的共同运动来实现。

[0099] 在图 8 中，输送头和基板的相对运动是相互垂直的。 但也可以让这种相对运动为平行的。 在这种情况下，相对运动需要具有非零的频率分量来代表震荡和为零的频率分量来代表基板 20 的位移。 这种组合可通过如下方式实现：震荡与输送头 10 在固定基板 20 上的位移的结合；震荡与基板 20 相对于固定的基板 20 沉积装置的位移的结合；或者任意结合，其中震荡和固定运动由基板 20 和输送头 10 两者的运动提供。

[0100] 在优选的实施方案中，ALD 可在大气压或接近大气压下以及在范围广泛的环境温度和基板温度进行，优选在 300℃以下进行。 优选地，为了将污染的可能最小化而需要相对干净的环境；然而，当选用本发明的方法的优选实施方案时，为了得到良好的表现，不必是完全的“清洁室”条件或填充惰性气体的密封环境。

[0101] 图 9 显示用于制备有机薄膜的原子层沉积 (ALD)60 系统，其具有室 50，用于提供控制相对较好并且无污染的环境。 气体供应 28a、28b 和 28c 通过输送管线 32 向输送头 10 提供第一、第二和第三气态材料。 任选使用的柔性供给管线 32 有助于使输送头 10

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易于移动。 为了简便起见，图 10 中未示出任选的真空蒸发回收过程和其它支撑元件，但是其也是可以使用的。 输送子系统 54 提供基板支持体，沿输送头 10 的输出面 36 传送基板 20，按照本公开中采用的坐标轴系，提供在 x 方向的运动。 运动控制以及对阀和其它支撑部件的整体控制例如可由控制逻辑处理器 56，例如计算机或专用微处理器组件来提供。 在图 10 的布置中，控制逻辑处理器 56 控制螺线管 30 以向输送头 10 提供往复运动，以及控制输送子系统 54 的输送马达 52。

[0102] 图 10 示出了使用静止输送头 10 的用于在网状配置中沉积薄膜的原子层沉积 (ALD) 系统 70，其中流型与图 10 的构型正交取向。 在这种配置下，网输送机 62 自身的运动提供 ALD 沉积所需的移动。 往复运动也可用于这种环境下，例如通过重复反转网辊的旋转方向来使网基板 66 相对于输送头 10 作向前和向后的运动。 往复运动也可通过使输送头 10 的往复运动沿一弧形得到，该弧形的轴与辊的轴重叠，同时网基板 66 以恒定动作而移动。 在另一种实施方案中，输送头 10 的至少一部分具有的输出面 36 有一定程度的曲率（未示出），这对于某些网涂布应用是有利的。 曲率可以是凸的或凹的。

[0103] 任选地，本发明的方法可以采用其它装置或体系来实现，所述装置或系统在共同受让的 US 公开号 2007/0238311、US 公开号 2007/0228470、US 申请系列号 11/620,744 和 US 申请系列号 11/620,740 专利中进行了更详细地描述。 这些体系试图克服空间型 ALD 体系的一个困难方面，即连续流动的多种反应性气体的不希望的混合。 尤其，美国公开号 2007/0238311 采用新的横向流型防止混合，而 US 系列 No.11/620,744 和 US 系列 No.11/620,740 的专利申请采用下述方式实现改善的气体分离：借助方法中的反应性气体的压力产生部分漂浮的涂覆压头。 所有上面确定的申请都以引用方式全文引入进来。

[0104] 在后三个申请的实施方案中，在基板上进行薄膜材料沉积时，输送装置具有用于向其提供气态材料的输出面，该基板在三组伸长的发射通道中的至少一组伸长的发射通道内包含伸长的发射通道（即，至少一组为：(i) 一个或多个第一伸长的发射通道，(ii) 一个或多个第二伸长的通道，和 (iii) 多个第三伸长的通道），所述发射通道能够分别引导第一气态材料、第二气态材料和第三气态材料中的至少一个按照相对于输送装置的输出面基本正交方向上流动，位于至少一组与基板表面基本正交的伸长的发射通道内的各个伸长的发射通道可以直接或间接地提供气态材料的这种流动。

[0105] 如本文中所用的，术语“伸长的发射通道”或“伸长的输出通道”各自与沉积输送头的输出面内的伸长的输出开口相连。 所述伸长的输出开口可以在伸长的发射通道的气流出口内形成，或者可以通过例如扩散器或在伸长的输出口之前的实现气体流动的其它手段来间接连接。

[0106] 在一个实施方案中，孔板设置为基本上平行于输出面，并且至少一个孔板上的孔形成第一、第二和第三伸长的发射通道。 在可选的实施方案中，孔板相对于输出面基本上垂直设置。

[0107] 在一种这样的实施方案中，沉积装置包括排气通道，例如用于在基板上薄膜材料沉积的输送装置，包括：(a) 包括分别能够接受第一反应物气态材料、第二反应物气态材料和第三（惰性吹扫）气态材料的共同供应的至少第一进口、第二进口和第三进口的多个进口；(b) 能够接受来自薄膜材料沉积的排放气体的至少一个排气口和至少两个伸长的排气通道，每个伸长的排气通道均能够与至少一个排气口形成气态流体联通；和 (c)

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至少三组多个伸长的输出通道，(i) 第一组多个第一伸长的输出通道，(ii) 第二组多个第二伸长的输出通道，和 (iii) 第三组多个第三伸长的输出通道，第一、第二和第三伸长的输出通道中的每一组能够分别与对应的第一进口、第二进口和第三进口中之一形成气态流体连通；其中第一、第二和第三伸长的输出通道中的每一个和每一个伸长的排气通道在长度方向的基本上平行延伸；其中每个第一伸长的输出通道在它的至少一个伸长侧通过相对较近的伸长的排气通道和相对次近的第三伸长的输出通道与最近的第二伸长的输出通道间隔开；并且，其中每个第一伸长的发射通道和每个第二伸长的发射通道位于相对较近的伸长的排气通道之间和相对次近的伸长的输出通道之间。

[0108] 进一步的实施方案包括气体扩散器，其与三组伸长的发射通道中的至少一组相关联，使得在将薄膜材料沉积到基板上的方法中，第一，第二和第三气态材料中的至少一种分别能够在从输送装置到达基板之前通过气体扩散器，并且其中气体扩散器保持从至少一组伸长的发射通道中的每个伸长的发射通道向下流出的第一，第二和第三气态材料中的至少一种的流动分离。

[0109] 在一个实施方案中，这种气体扩散器能够为通过该处的气态材料提供大于 1×10^2 的摩擦系数，从而提供背压并且促进所述至少一种第一、第二和第三气态材料流出输送装置时的压力均衡。在一个实施方案中，所述气体扩散器包括多孔材料，所述第一、第二和第三气态材料中的至少一种通过该多孔材料。在本发明的第二实施方案中，所述气体扩散器包括机械形成的组件，所述组件包括至少两个包括互连的通道的元件，例如，其中喷管与由位于两个元件内的平行表面之间的薄空间所提供的流路连接。

[0110] 在一种实施方案中，来自沉积装置的一种或多种气流提供的压力对将基板的表面与输送头的表面分开有贡献，从而提供了“悬浮头”或“空气轴承”型的沉积头，这可有助于稳定气流并限制气流的混合。

[0111] 本发明的方法的优点在于它能够在广泛的温度范围下在基板上进行沉积，在一些实施方案中，包括室温或接近室温。本发明的方法可在真空环境中操作，但特别适用于在大气压下或接近大气压下操作。

[0112] 通过技术人员已知的常规技术可以完成由 ALD 沉积材料制备薄膜电子器件。在一个实施方案中提供基板，可以将上面描述的材料的膜或层施用于所述基板，并且与所述层进行电接触。精确的过程顺序由希望的电子器件的结构来决定。制造这些结构的技术包括选择性沉积、顺序掩模、光刻法，激光法和 / 或技术人员已知的其它方式。

[0113] 在制造、试验和 / 或使用过程中用于支撑电子器件或层的支持体包括有机或无机材料。例如，所述支持体可以包括无机玻璃、陶瓷箔、聚合材料、填充的聚合材料、涂覆的金属箔、丙烯酸树脂、环氧树脂、聚酰胺、聚碳酸酯、聚酰亚胺、聚酮、聚（氧 -1，4- 亚苯氧基 -1，4- 亚苯基羰基 -1，4- 亚苯基）（有时称作聚（醚醚酮）或 PEEK）、聚降冰片烯、聚苯醚、聚（萘二酸乙二醇酯）(PEN)、聚（对苯二甲酸乙二醇酯）(PET)、聚（醚砜）(PES)、聚（苯硫醚）(PPS)，和纤维 - 增强的塑料 (FRP)。柔性基板还可以为薄的金属箔，例如不锈钢，只要其涂覆了绝缘层从而与薄膜晶体管电分离即可。在本发明的一些实施方案中，柔性支持体使辊加工成为可能，所述辊加工可以是连续的，从而提供规模经济并且由于在平的和 / 或刚性支持体上进行制造而产生的经济性。所选的柔性支持体优选采用类似徒手的小的力即能够包住直径小于 50cm，更优

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选小于 25cm，最优选小于 10cm 的圆柱的周边，而不会发生扭曲或破裂。 优选的柔性支撑可以为在其上进行滚压。 但是，如果不考虑柔软性，则所述基板可以为由包括玻璃和硅的材料制成的晶片或片。 所述基板的厚度可以变化，根据特定的例子，其可以为 100 μ m-1cm。

[0114] 如上所述，使用本发明的方法可以制备的有机材料包括但不限于，聚合物，例如 alucone、 borocone、绝缘电木和聚氨酯。 Alucone 和类似的聚合物在薄膜中包括三维网络。

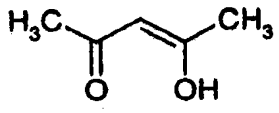
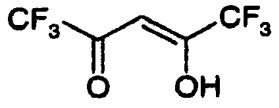
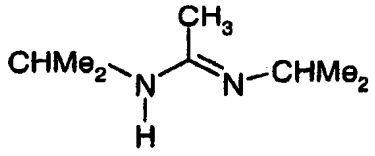
[0115] Alucone，例如为醇铝聚合物，如 C.Niamh McMahon 等在 Chem.Mater.1999，11，3181-3188 中所描述的。 McMahon 等描述了通过乙二醇与 $Al(tBu)_3$ 前体之间的反应获得 $[Al(tBu)_{2x}(OCH_2CH_2O)_{1.5-x}]_n$ $(0.3\leq 2x\leq 0.8)$，其中“tBu”指叔丁基，从而制得叔丁基 alucone。 还可以制备乙氧基 alucone。

[0116] 可以将任何数量的有机和有机金属前体用于本方法的各种实施方案中，条件是当适当处理的表面暴露于第一前体时，进行反应而在表面上留下对第二反应前体具有反应性的部分。 此外，第二前体的反应应当使表面恢复至又易于与第一前体发生反应的状态。 因此，可以持续进行 ALD 序列。

[0117] 如果将含有金属的前体用作反应物之一，则常用化合物包括金属化合物，例如三甲基铝、三乙基铝、二甲基锌、三甲基锌、四氯化钛、四乙氧基钛、硅烷、四乙氧基硅烷，以及可以快速反应的任何其它金属源。

[0118] 可选地，可以使金属作为与各种化合物的配合或反应形式来输送，其中特别有用的一类是 β - 二酮。 下表显示一些代表性的 β - 二酮和适于制备含金属的前体的其它化合物。

[0119]

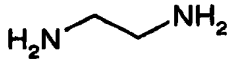
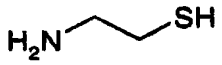
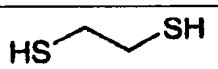
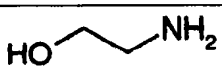
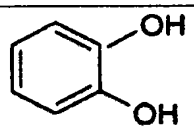
乙酰丙酮化物	
六氟乙酰丙酮	
N,N'-二异丙基乙酰胺化物	

[0120]

[0121] 纯有机前体（例如，含有非金属的分子，其具有至少两个碳原子并且仅由一个共价键组成）可以用在本方法中，其需要至少两个活性位以进行反应，并且可以随后保留表面反应性。 这种化合物的例子为二醇，例如乙二醇、二胺和二硫醇，如下表中与其它适当的化合物一起所列出的。 所属领域技术人员会认识到，这些材料和其它类的材料可以适用于本发明的实践中：

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[0122]

1,2-二氨基乙烷	
1-氨基-2-巯基乙烷	
1,2-乙二硫醇	
乙醇胺	
儿茶酚	

[0123] 实施例

[0124] 对涂覆装置的描述

[0125] 本实施例中所用的涂覆装置基于图 1-7 中所示的设计。 下列所有薄膜实施例使用图 11 中指示的流动装备。 向所述流动装备供给氮气流 81，所述氮气流已经经过纯化，将氧气和水杂质除至低于 1ppm。 所述气体经歧管而转向至若干流量计，其控制吹扫气体流和转至鼓泡器的气体流，以选择反应性前体。 除了氮气供给之外，还将空气流 90 输送至装置中。 用分子筛对所述空气进行预处理以除去水分。

[0126] 将下列气流输送至 ALD 涂覆装置中：含有被氮气稀释的反应物 O1 的气流 92；含有被氮气稀释的反应物 O2 的气流 93；仅由惰性气体组成的氮气吹扫气流 95。 按照下述方式控制这些物流的组成和气流。

[0127] 气体鼓泡器 82 含有前体 O2。 流量计 85 将纯的氮气流输送至鼓泡器 82 中。 此时鼓泡器的输出中含有被前体材料饱和了的氮气。 这些输出物流与由流量计 87 输送来的氮气稀释流混合，得到金属前体流 92 的总气流。

[0128] 气体鼓泡器 84 含有前体 O1。 流量计 88 将纯的氮气流输送至气体鼓泡器 84 中，其输出代表被 O1 蒸汽饱和的氮气物流。 空气流 90 受流量计 91 控制。 气体鼓泡器 84 的输出和氮气物流与来自流量计 89 的稀释物流混合，产生含有气流 93 的 O2 前体的总流。

[0129] 流量计 94 控制待输送至涂覆装置的纯氮气的流动。

[0130] 然后按照图 12 中的指示将物流或气流 92、93 和 95 输送至常压涂覆头，在此引导它们离开通道或微室槽。 在伸长的通道和基板 97 之间存在约 30 微米的间隙 99。 所述微室大约 2.5mm 高，0.86mm 宽，并且通过所述涂覆头的长度，该长度为 76mm。 将该构造中的反应物材料输送至所述槽的中间并使其从前后流出。

[0131] 为了进行沉积，将所述涂覆头设置在一部分基板之上，之后如箭头 98 所表示的，使其在基板之上以往复方式移动。 往复周期的长度为 32mm。 往复周期的运动速率为 30mm/ 秒。

[0132] 用傅立叶转换红外光谱（FTIR）分析沉积膜的组成。

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[0133] 所用的材料：

[0134] (1) 抛光的硅基板

[0135] (2) Me_3Al（可商购自 Aldrich Chemical Co.）

[0136] (3) 乙二醇（试剂等级，可商购自 Aldrich Chemical Co.）

[0137] 实施例 1

[0138] Alucone，一种含有机物的薄膜的制备

[0139] 该实施例描述了 alucone，一种含有显著量的有机材料的薄膜的制备。对于该沉积而言，鼓泡器 82 含有作为 O2 前体的三甲基铝，鼓泡器 84 含有作为 O1 前体的乙二醇。

[0140] 将 2.5×2.5 平方英寸 (62.5 平方 mm) 的硅晶片设置在该装置的压盘 (platen) 上，借助真空度将其保持在适当位置并将其加热至 200℃。将所述带基板的压盘设置在引导反应性气体流的涂覆头之下。使用测微计将硅基板和涂覆头之间的间距调节至 30 微米。

[0141] 将所述涂覆头维持在 40℃。单一气体的流速示于下表 1 中，使涂覆头按照指定的周期数跨过基板振动，从而开始涂覆过程。

[0142] 表 1

[0143]

试样	流量计 85	流量计 88	流量计 87	流量计 89	流量计 94	周期	基板温度，℃
1	12	100	130	130	750	1000	200

[0144] * 流量值为 sccm（每分钟的标准立方厘米）

[0145] 用 FTIR 分析沉积的膜。涂层的红外谱图（图 19）指示，存在以近 2870cm^{-1} 的 v(-CH_2-) 烃吸收为基础的有机材料。在纯乙二醇液体中还观察到位于 1088 和 1040cm^{-1} 处的峰，其归于 v(-CH_2-O-) 键。在近 900-700cm^{-1} 处的宽吸收指示了 v(Al-O) 振动模式。在波数 700 及以下观察到了非常强烈的吸收带，这是由于存在硅晶片基板。通过与标准乙二醇 IR 参考谱图（在线的 Aldrich Chemical 图书馆）比较可以确信，观察到的吸收峰并不对应于剩余量的乙二醇，这是由于在乙二醇中不存在位于 3360cm^{-1} 处的非常强的 v(O-H) 伸缩谱带。

[0146] 实施例 2

[0147] Borocone 的制备

[0148] 可以使用 ALD 或分子层晶体取向附生形成 Borocone。该假设的实施例描述了 borocone，一种含有显著量有机材料的薄膜的制备。对于该沉积而言，鼓泡器 82 含有作为 O2 前体的硼酸三甲酯，$B(OMe)_3$，鼓泡器 84 含有作为 O1 前体的乙二醇。

[0149] 用于制备 borocone 的装置与实施例 1 中描述的装置相同。将 2.5×2.5 平方英寸 (62.5 平方 mm) 的硅晶片设置在该装置的压盘上，借助真空将其保持在适当位置并加热至 200℃。将所述带基板的压盘设置在引导反应性气流的涂覆头之下。使用测微计将硅基板和涂覆头之间的间距调节至 30 微米。

[0150] 将所述涂覆头维持在 40℃。将所述基板维持在 30℃ -250℃。通过控制涂覆头

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的振动周期数，或在基板看来的 ALD 周期数，或基板温度可以获得希望的 borocone 厚度。 表 2 含有涂覆方法中所用的单一气体的流速，其中所述涂覆方法用于由三甲基硼酸盐和乙二醇制备 borocone。

[0151] 表 2

[0152]

流量计 85	流量计 88	流量计 87	流量计 89	流量计 94
2	100	130	130	750

[0153] * 流量值为 sccm（每分钟的标准立方厘米）

[0154] 实施例 3

[0155] 聚氨酯的制备

[0156] 在本发明的另一个假设实施例中，可以使用 ALD 或分子层晶体取向附生形成聚氨酯薄膜。 该实施例描述聚氨酯膜，一种含有显著量有机材料的薄膜的制备。 对于该沉积而言，鼓泡器 82 含有作为 O2 前体的 1，4- 丁二醇，鼓泡器 84 含有作为 O1 前体的 1，4- 二异氰酸根丁烷。

[0157] 用于制备聚氨酯薄膜的装置与实施例 1 中描述的装置相同。 将 2.5×2.5 平方英寸 (62.5 平方 mm) 的硅板设置在该装置的压盘上，借助真空将其保持在适当位置并加热至 200℃。 将所述带基板的压盘设置在用于引导反应性气流的涂覆头之下。 使用测微计将硅基板和涂覆头之间的间距调节至 30 微米。

[0158] 将所述涂覆头的温度维持在 40℃。 将所述基板维持在 30℃ -250℃。 通过控制涂覆头的振动周期数，或在基板看来的 ALD 周期数，或基板温度可以获得希望的聚氨酯厚度。 表 2 含有涂覆方法中所用的单一气体的流速，其中所述涂覆方法用于由 1，4- 丁烷和 1，4- 二异氰酸根丁烷制备聚氨酯。

[0159] 表 3

[0160]

流量计 85	流量计 88	流量计 87	流量计 89	流量计 94
100	100	130	130	750

[0161] * 流量值为 sccm（每分钟的标准立方米）

[0162] 部件列表

[0163] 1 向系统连续供应气态材料

[0164] 2 在基板的通道区域上的第一分子前体的第一通道流

[0165] 3 基板和多通道流的相对运动

[0166] 4 在通道区域上的惰性气体的第二通道流

[0167] 5 基板和多通道流的相对运动

[0168] 6 在通道区域上的第二分子前体的第三通道流

[0169] 7 基板和多通道流的相对运动

[0170] 8 在通道区域上的惰性气体的第四通道流

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[0171] 9 基板和多通道流的相对运动

[0172] 10 输送头

[0173] 11 平行的多通道流

[0174] 12 输出通道

[0175] 13 排气通道

[0176] 14，16，18 气体进口

[0177] 15 序列

[0178] 20 基板

[0179] 22 隔板

[0180] 24 气体输出口

[0181] 26 排气口

[0182] 28a，28b，28c 气体供应

[0183] 30 螺线管

[0184] 32 供应线

[0185] 36 输出面

[0186] 50 室

[0187] 52 输送马达

[0188] 54 输送子系统

[0189] 56 控制逻辑处理器

[0190] 58 挡板

[0191] 60 原子层沉积（ALD）法

[0192] 62 网状输送机

[0193] 66 网状基板

[0194] 70 原子层沉积（ALD）系统

[0195] 74 基板支持体

[0196] 81 氮气流

[0197] 82，84 气体起泡器

[0198] 85，87，88 流量计

[0199] 89，91，94 流量计

[0200] 90 空气流

[0201] 92 金属前体流

[0202] 93 含氧化剂流

[0203] 95 氮气吹扫流

[0204] 96 基板支持体

[0205] 97 示例基板

[0206] 98 箭头

[0207] 99 间隙

[0208] 120 ALD

[0209] A 箭头

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[0210] D 距离

[0211] F1，F2 气流

[0212] F_1，F_O，F_M 气流

[0213] H 高度

[0214] I 惰性气态材料

[0215] L 通道长度

[0216] M 第二反应物气态材料

[0217] O1 第一反应物气态材料

[0218] O2 第二有机氧化性反应物气态材料

[0219] P 产物材料

[0220] R 箭头

[0221] S1 表面物质

[0222] W 通道宽度

[0223] X 箭头

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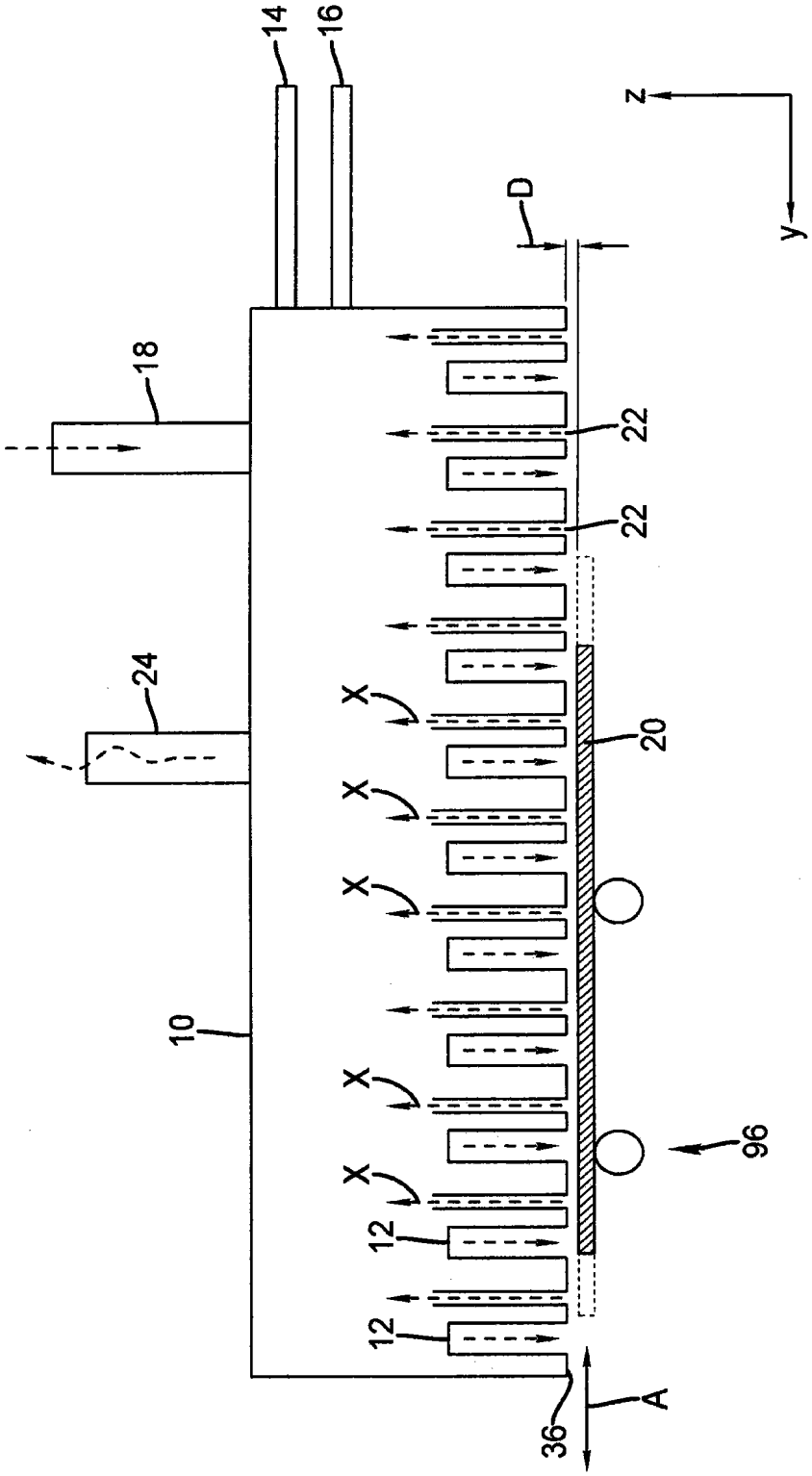


图 1

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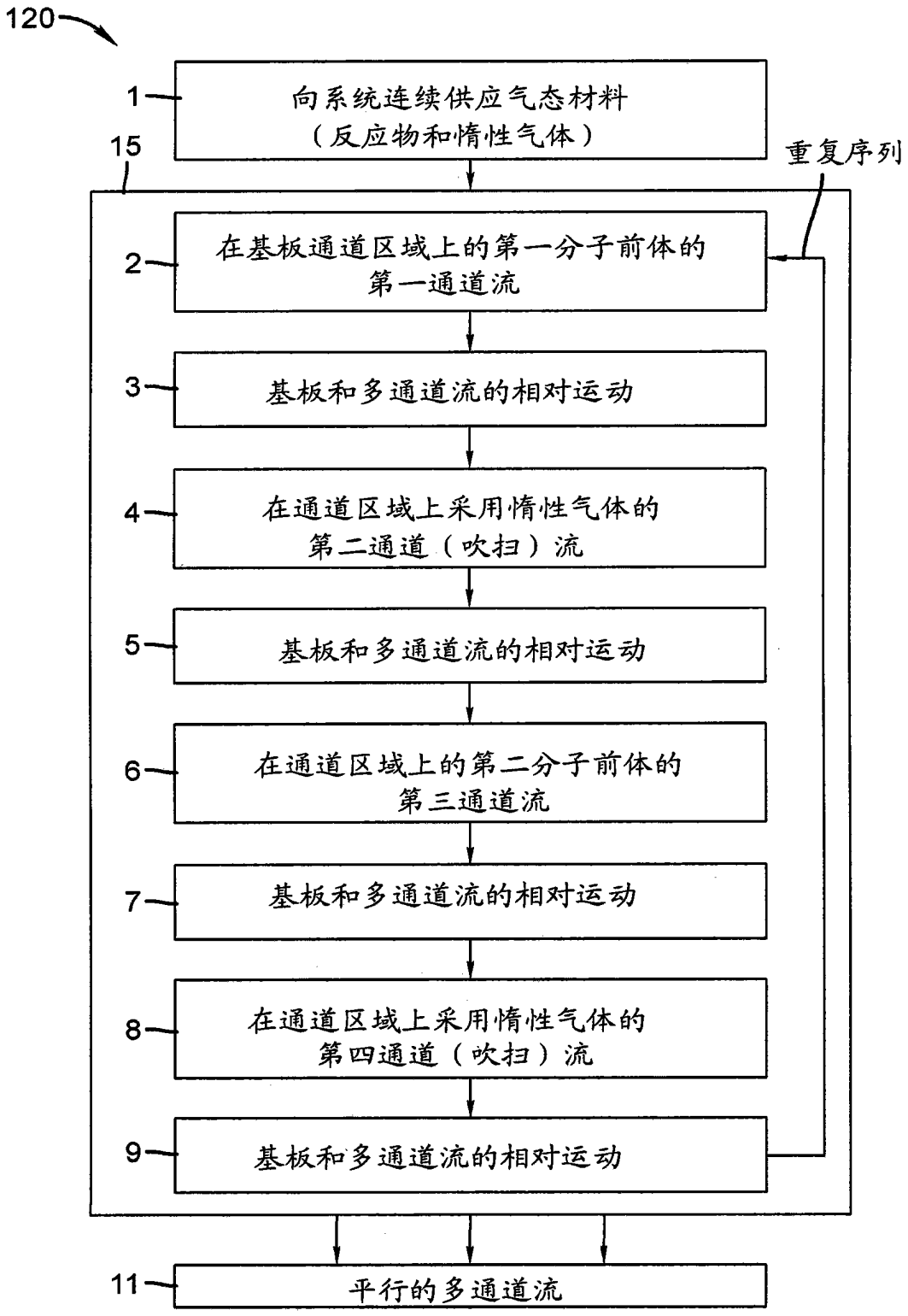


图 2

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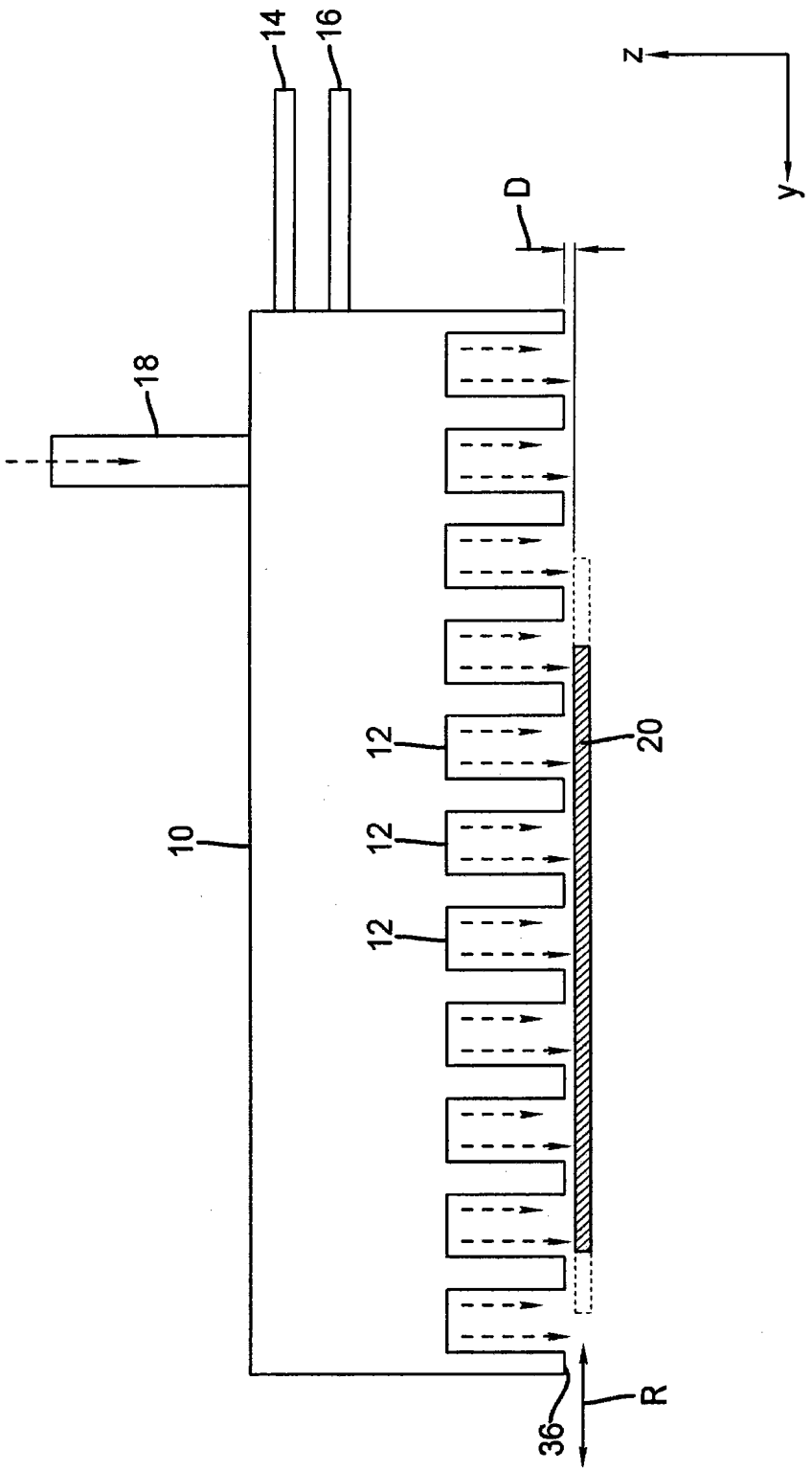


图 3

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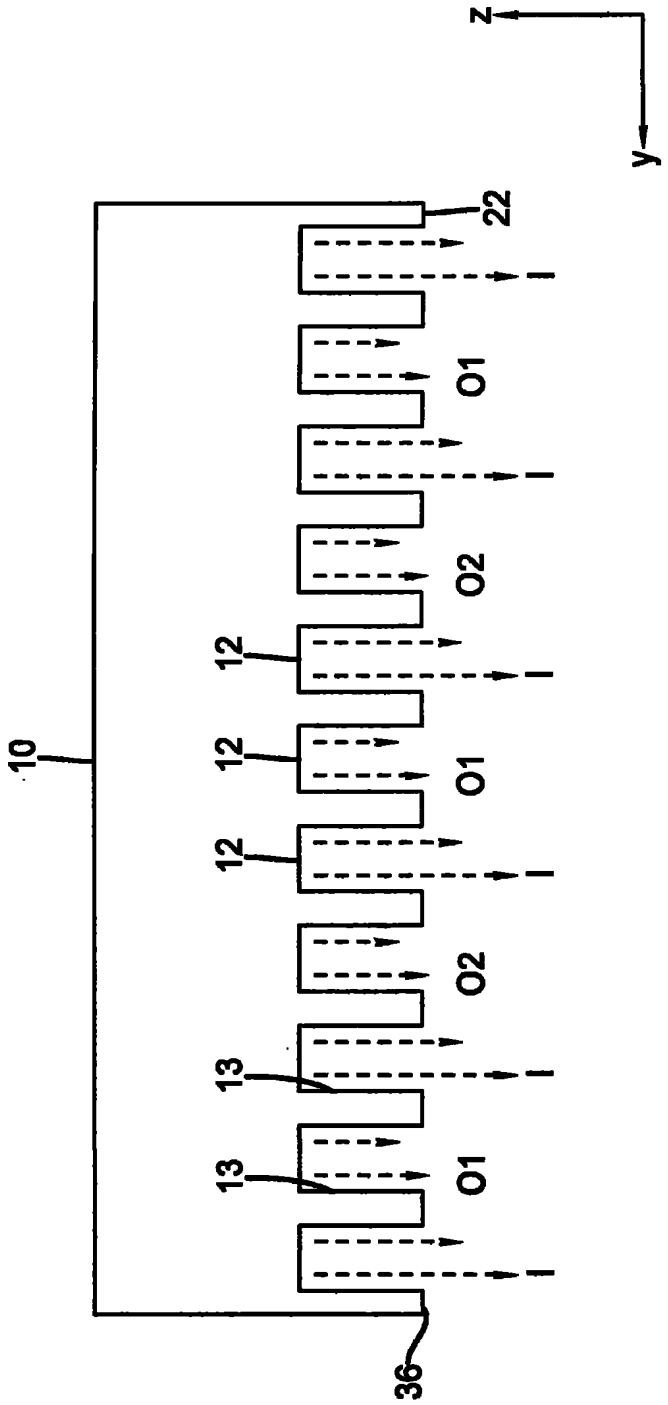


图 4

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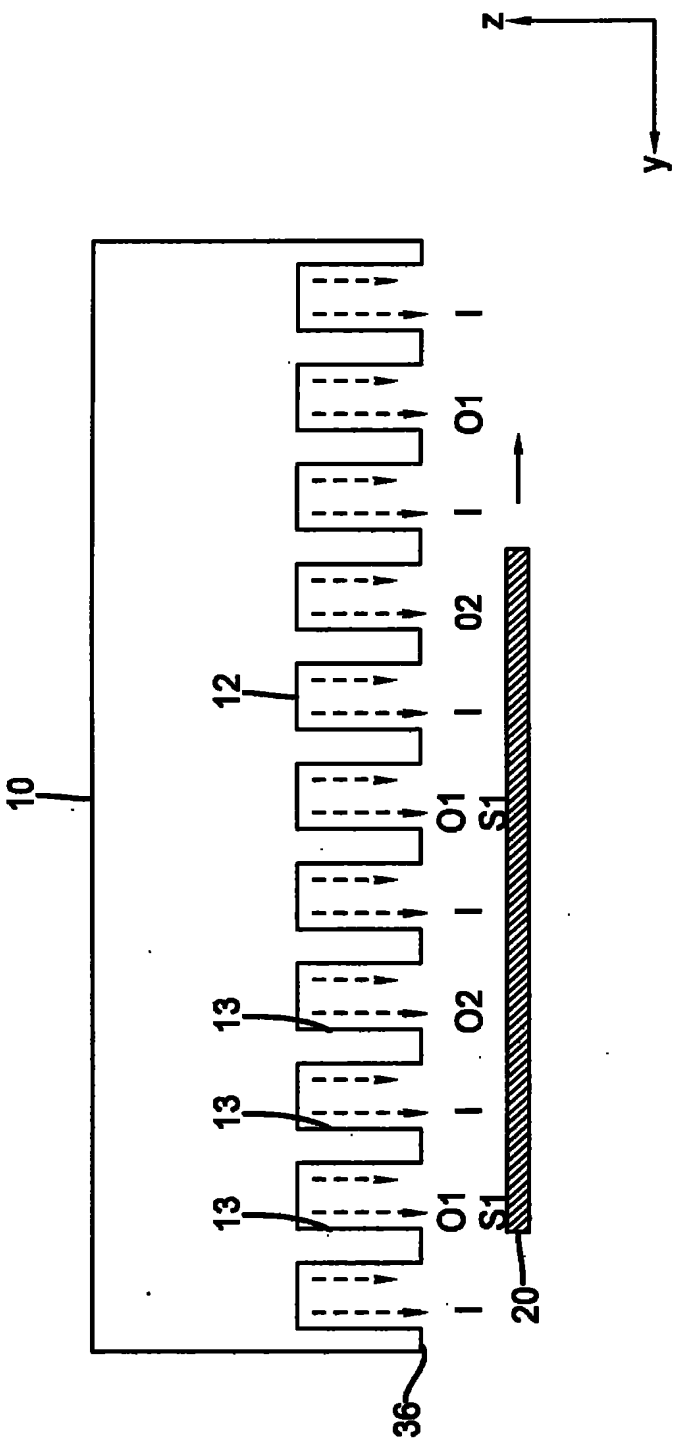


图 5A

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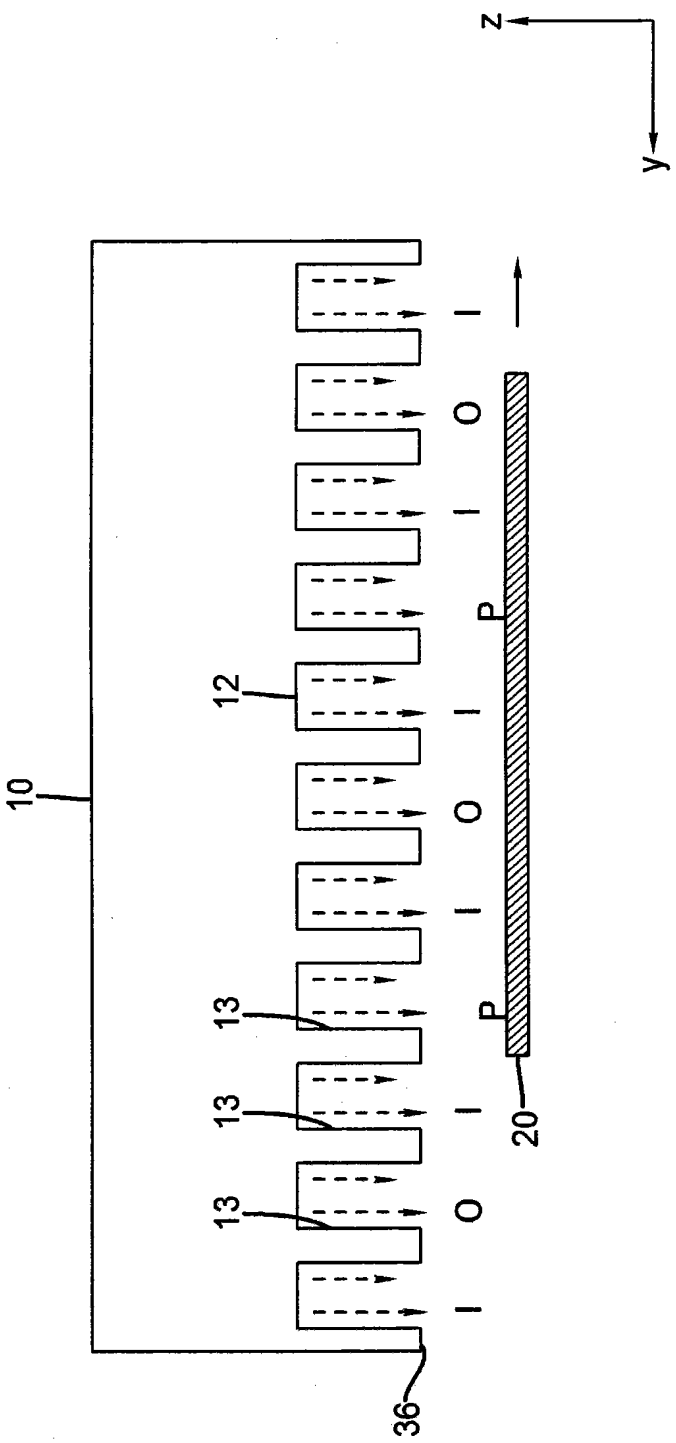


图 5B

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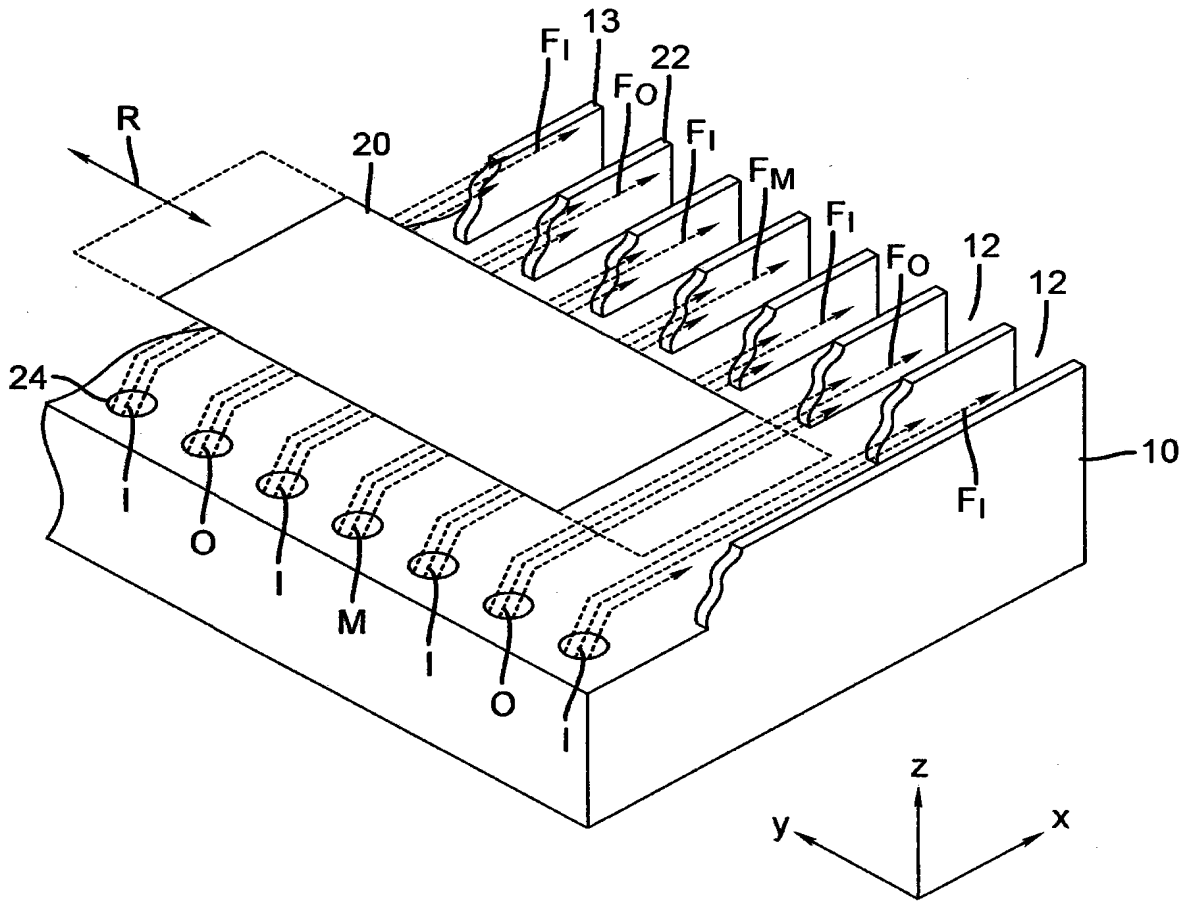


图 6

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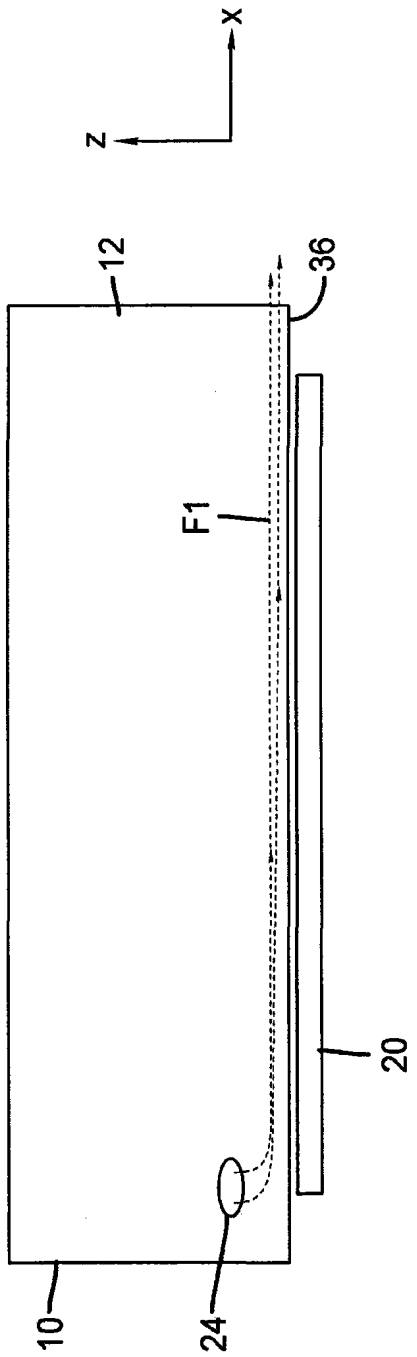


图 7A

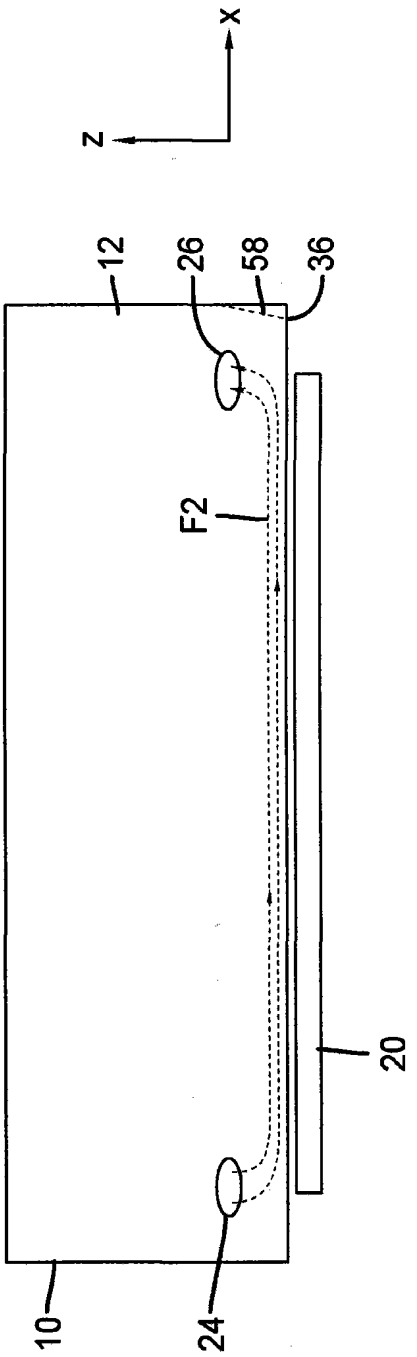


图 7B

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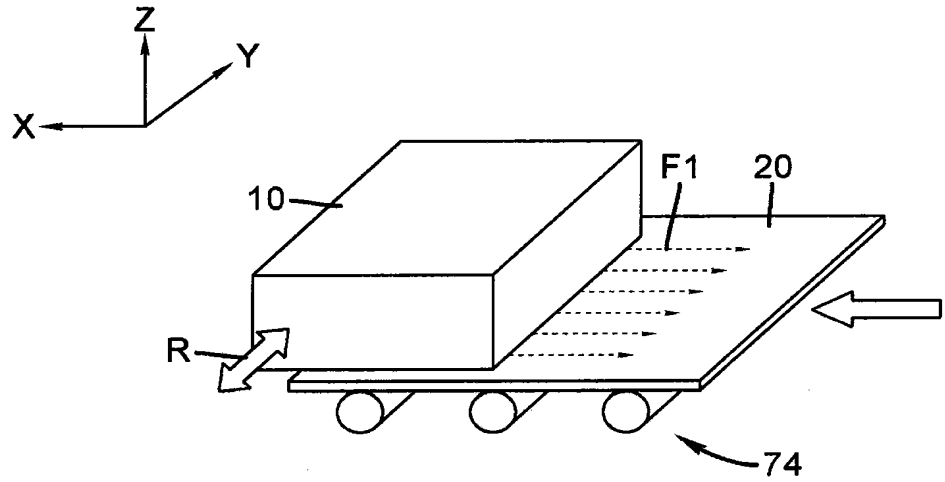


图 8

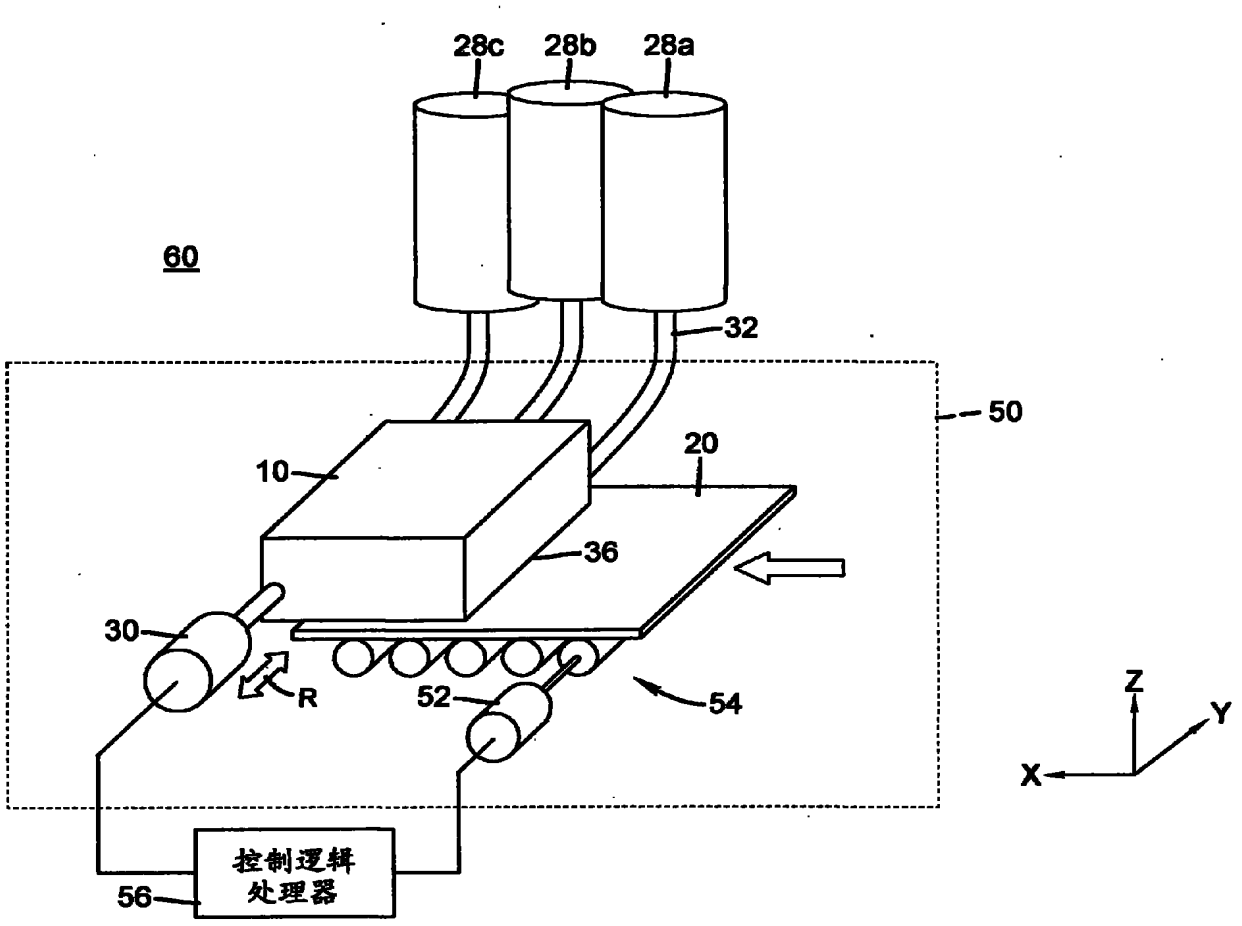


图 9

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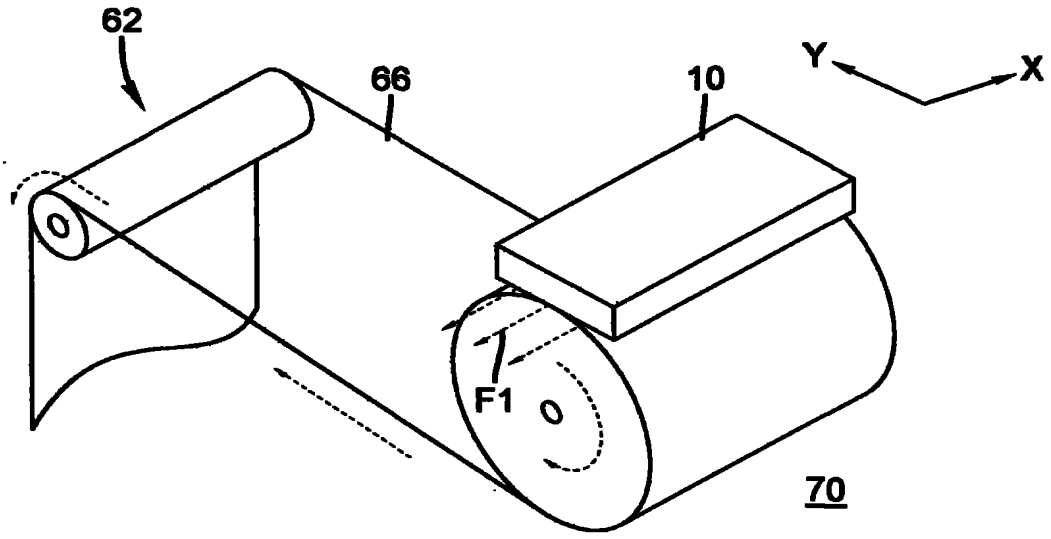


图 10

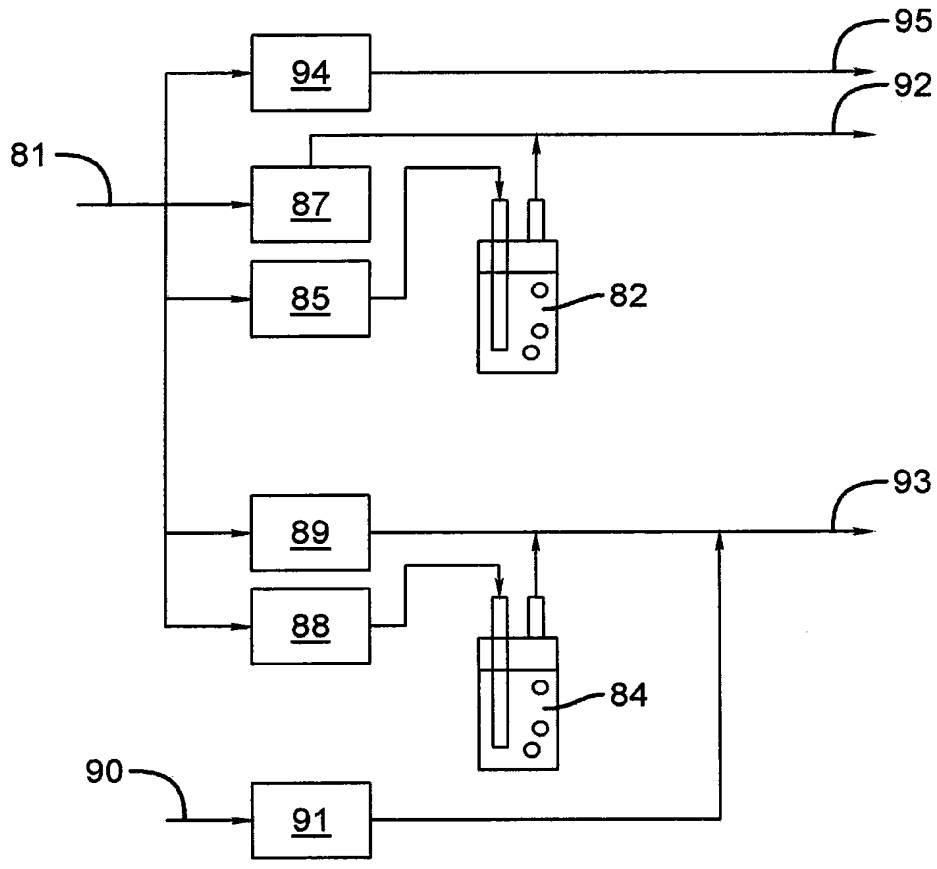


图 11

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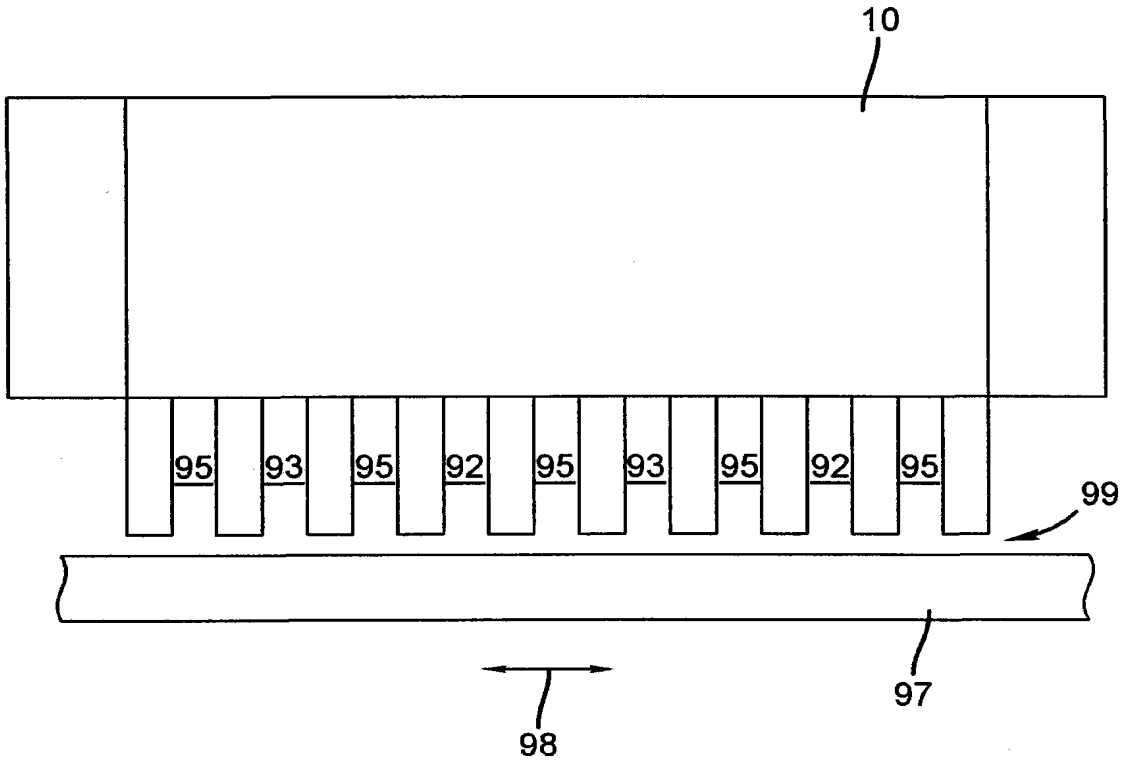


图 12

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(54) Process of forming a micro-pattern of a metal or a metal oxide

(57) Disclosed herein is a rapid and efficient process of forming a metal-containing pattern by causing a difference of solubility between exposed and unexposed areas of a thin film consisting of a metal complex through a photoreaction, and developing the film to produce a patterned film, followed by oxidation or reduction so as to provide a pure metal or metal oxide pattern. By virtue of the present invention, it has been realized to form electroconductive patterned films of a metal without using photosensitive resins.

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Description

[0001] The present invention relates, in general, to a process of forming a micro-pattern of a metal or a metal oxide, in particular, to a process of forming a micro-pattern of a metal or a metal oxide, wherein a metal complex is used which exhibits a difference of solubility depending on the degree of exposure to light having a particular wavelength.

[0002] As well known to those skilled in the art, a patterned thin film formed on a substrate using materials having different electrical properties has been applied to various electronic devices. In an electronic device production process, a metal thin film is generally coated on a substrate such as a crystallized silicone wafer and then patterned.

[0003] A conventional method of forming a metal pattern comprises the steps of applying an organometallic compound on a surface of a silicone or glass substrate according to a chemical vapor deposition process or an atomic layer deposition process to form a thin film on the substrate; coating a photoresist on the resulting organometallic film according to a spin coating process; patterning the resulting photoresist film according to a photolithography process; and etching the patterned photoresist film. Another conventional method of forming a metal pattern comprises the steps of depositing a metal film on a substrate according to a plasma deposition process, a sputtering process, or an electric plating process; coating a photoresist on the resulting metal film; patterning the photoresist film using light; and etching the patterned photoresist film to reveal a desired metal pattern. Unfortunately, these conventional methods require setting of a high temperature and vacuum condition, and essentially involve a patterning step using a photoresist and an etching step for removing the photoresist, thus having a disadvantage of a high production cost due to such complicated process. Other disadvantages of these conventional methods are that resolution of the resulting pattern is inevitably reduced because the patterning and etching steps are typically repeated several times, and that a surface of a deposited metal film is not smooth, causing these conventional methods to additionally accompany a flatting step.

[0004] Meanwhile, various methods of forming a metal pattern without using a photoreaction have been suggested. For example, Japanese Patent Publication No. 62-263973 discloses a method of forming a metal pattern, in which an electronic beam is irradiated to a thin film of a metal complex without inducing any photoreaction. In addition, U.S. Pat. No. 5,064,685 discloses a method of forming a metal thin film using a thermal decomposition reaction, comprising the steps of applying a metal complex-containing ink on a substrate; and heating the resulting substrate with the use of a laser beam. According to this patent, the substrate is exposed to a high temperature, and materials other than metals are prevented from being deposited on the substrate.

[0005] On the other hand, US Patent No. 5,534,312 describes that a metal pattern can be made through coating a substrate with a metal complex prepared by bonding one or more photosensitive organic ligands to one or more metal atoms, and exposing the coated substrate directly to electromagnetic radiation without applying a photosensitive resin on the coating film of the metal complex. The metal complex essentially consists of at least one ligand selected from the group consisting of: acetylacetonates(both substituted and unsubstituted); dialkyldithiocarbamates; carboxylate; pyridines; amines; diamines; arsines; diarsenes; phosphines; diphosphenes; arenes; alkoxy ligands; alkyl ligands; and aryl ligands. Particularly, in the case that the complex comprises more than one ligand, at least one of the ligand is selected from the group consisting of: oxalato; halogens; hydrogen; hydroxy; cyano; carbonyl; nitro; nitrito; nitrate; nitrosyl; ethylenes; acetylenes; thiocyanato; isothyocyanato; aquo; azides; carbonato; amines; and, thiocarbonyl. When exposed to electromagnetic radiation, the metal complex goes through a photochemical reaction resulting in dissociation of the organic ligands from the central metal atoms, to produce a new metal-containing material adherent to the substrate. However, this patent is disadvantageous in that the rate of such transformation is relatively low, and consequently many hours are required to complete the patterning process. Other disadvantages are that ligand contamination is likely to occur because the separation of the ligands from the metal completely depends on photoreaction, and that, if the final film consists of a metal oxide, the oxide film should be reduced and annealed under a mixed gas of hydrogen with nitrogen at 200°C or higher for 30 minutes to several hours so as to improve conductivity of the film. Additionally, the organic ligands constituting the metal complex have so large steric hindrance, and consequently occupy so large space as to result in a large percentage of contraction in the thickness of the resulting metal film upon their decomposition by exposure to light.

[0006] The present invention relates to a rapid and efficient process of forming a metal-containing pattern by causing a difference of solubility between exposed and unexposed areas of a thin film consisting of a metal complex through a photoreaction, and developing the film to produce a patterned film, followed by oxidation or reduction so as to provide a pure metal or metal oxide pattern.

[0007] The present invention provides a method of forming a metal or metal oxide pattern on a substrate comprising the steps of:

(a) depositing a thin film of a metal complex on a surface of the substrate;
(b) exposing the film to alight source by the use of a photomask having a desired pattern to cause the metal complex in exposed areas of the film to be decomposed resulting in a difference of solubility between exposed areas and unexposed areas;

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(c) developing the film with an organic solvent capable of dissolving the metal complex to remove the metal complex in unexposed areas leaving only a metal-containing patterned film; and
(d) reducing or oxidizing the metal-containing patterned film to provide a pure metal or metal oxide pattern on the substrate.

[0008] All of the above features and other features of the present invention will be successfully achieved from the present invention described in the following.

[0009] The metal complexes used in the present invention are represented by the formula (I) :

$$M_mL_nX_p \quad (I)$$

wherein,

M is a metal atom selected from transition elements, lanthanoids, and main group elements;
L is an organic ligand comprising at least one donor atom and 20 or less carbon atoms, and, if m is 2 or more, L may interconnect M's;
X is a mono-, di- or tri-valent anion;
m is an integer ranging from 1 to 10, provided that
M's may be different each other when m is 2 or more;
n is an integer ranging from 0 to 60, provided that
L's may be different each other when n is 2 or more;
p is an integer ranging from 0 to 60, provided that
X's may be different each other when p is 2 or more; and
n plus p is not equal to 0.

[0010] In the metal complex of the formula (I), the number of the ligand L to be coordinated to one metal atom depends on the kind and oxidation number of the metal, and up to 6 ligands can be bonded to one metal atom. Similarly, up to 6 anions can be bonded to one metal atom.

[0011] The metal M is preferably a post-transition element of IX-XII family including Co, Ag, Au, Cu, Pd, Ni, Pt, Zn, and Cd, or a main group element including Al.

[0012] The ligand L is an organic compound essentially consisting of both at least one donor atom such as N, P, As, O, S, Se, and Te and 20 or less carbon atoms. Non-limiting examples of such ligand include anionic ligands such as acetylacetonates, acetate, β-ketoiminates, β-diiminates, β-ketoesters, dialkyldithiocarbamates, carboxylate, oxalato, halogens, hydrogen, hydroxy, cyno, nitro, nitrate, nitroxyl, azides, carbonato, thiocyanato, isothiocyanato, alkoxy ligands, and derivatives thereof; and neutral ligands such as pyridines, amines, diamines, arsines, diarsines, phosphines, diphosphines, arenes, carbonyl, imidazolylidene, ethylene, acetylene, H_2O, thiocarbonyl, thioether, and derivatives thereof.

[0013] The anion X functions to adjust net charge of the metal complex to zero, and may or may not make a coordinate bond with the metal atom. Preferable anions can be exemplified by halogeno, hydroxide, cyanide(CN^-), nitrite(NO_2^-), nitrate(NO_3^-), nitroxyl(NO^-), azide(N_3^-), thiocyanato, isothiocyanato, tetraalkylborate(BR_4^-, wherein R = Me, Et, or Ph), tetrahaloborate(BX_4^-, wherein X = F, or Br), hexafluorophosphate(PF_6^-), triflate ($CF_3SO_3^-$), tosylate(Ts^-), sulfate(SO_4^{2-}), and carbonate (CO_3^{2-}).

[0014] According to the present invention, the metal complex is first dissolved in an organic solvent to provide a coating solution that is suitable for the application to a surface of a substrate. Then, the application of the coating solution can be accomplished by, for example, spin coating, roll coating, dip coating, spray coating, flow coating, or screen printing, while spin coating is most preferred. Preferable examples of the organic solvent used in the preparation of the coating solution include, but are not limited to, nitriles such as acetonitrile, propionitrile, pentanenitrile, hexanenitrile, heptanenitrile, and isobutylnitrile; aliphatic hydrocarbons such as hexane, heptane, octane, and dodecane; aromatic hydrocarbons such as anisole, mesitylene, and xylene; ketones such as methyl isobutyl ketone, 1-methyl-2-pyrrolidinone, cyclohexanone, and acetone; ethers such as tetrahydrofuran, diisobutyl ether, and isopropyl ether; acetates such as ethyl acetate, butyl acetate, and propylene glycol methyl ether acetate; alcohols such as isopropyl alcohol, butyl alcohol, hexyl alcohol, and octyl alcohol; and silicon-based solvent. More than two of these organic solvents can be also used in combination.

[0015] Meanwhile, the substrate used in the present invention includes, without limitation, substrates made of inorganic materials such as silicon and glass, as well as substrates made of organic materials such as plastic. Besides, substrates made of a composite of organic materials with inorganic materials can be also used.

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[0016] A coating film formed on the substrate as described above is exposed to electromagnetic radiation with a photomask placed thereon. During the exposure, the subject metal complex in exposed areas undergoes a photochemical reaction and is converted into a new metal-containing compound, which has sufficiently low solubility in any of the developer described below as compared with the original metal complex. Thus, the electromagnetic radiation causes the coordinate bonds between the organic ligands and the metal atoms to be destabilized and broken, resulting in partial dissociation of the ligands from the metal atoms. Once such dissociation is triggered, decomposition of the remaining part of the metal complex progresses rapidly, leaving a metal or a metal oxide on the substrate depending on the atmosphere where the exposure was performed. While a mechanism by which such photochemical reaction occurs will vary in accordance with the metal and the ligand involved in the reaction, the following four mechanisms seem to mainly contribute to the unstabilization and breakdown of the coordinate bonds between the organic ligands and the metal atoms: i) metal-to-ligand charge transfer; ii) ligand-to-metal charge transfer; iii) d-d excitation; and iv) intra-molecular charge transfer. As a light source for the electromagnetic radiation is preferred UV light.

[0017] An important advantage of the present invention is that the coating film containing the subject metal complex is exposed to the electromagnetic radiation only for a relatively short time required for making the metal complex in exposed areas insoluble in an organic solvent to be used in the subsequent developing step. That is, the coating film of the metal complex needs not to be exposed for such a long time that the metal complex may be entirely converted to a metal or a metal oxide, and thus the exposure time can be decreased to a minimum. Considering that the decrease of exposure time results in the increase of productivity, shorter exposure time is generally favored.

[0018] While optimal exposure time will vary depending on the ligands constituting the subject metal complex, it usually requires about 30 minutes or more for most ligands to be dissociated from the metal atom. However, only about 10 minutes is sufficient to make the complex in exposed areas of the coating film much less soluble in the same solution than the complex in unexposed areas, and so exposed areas remain adherent on the substrate after subsequent developing step, thereby providing a metal-containing patterned film.

[0019] Following the exposure, unexposed areas of the coating film are washed off with a suitable developer. Then, only exposed areas of the coating film remain on the substrate to provide a desired pattern. The developer may be the same as or different from the solvent used in the preparation of the coating solution, and may be also an inorganic solvent(e.g., tetramethylamoniumhydroxide, "TMAH") used in a conventional semiconductor process.

[0020] In the present invention, the steps of exposing and developing may be conducted under a vacuum condition or in an atmosphere of air, or O_2, H_2, N_2, Ar or a mixed gas thereof. During these steps, the temperature should be adjusted to room temperature or in a temperature range where the subject metal complex is safe from thermal decomposition.

[0021] After developing, the patterned film is subjected to reduction or oxidation. If a patterned film of a metal is desired, reduction is conducted in an atmosphere of vacuum, or H_2, N_2, Ar or a mixed gas thereof, and if necessary, by using a suitable reductant. The reductants used in the present invention can be exemplified by organic reductants including hydrazines, silanes, amines, and derivatives thereof, as well as by inorganic reductants including metal hydrides such as $NaBH_4$ and $LiAlH_4$. These reductants can be used as a solution in a suitable solvent or as itself, depending on whether the reduction is performed in a gas-phase or a liquid-phase.

[0022] On the other hand, if a patterned film is desired to be composed of a metal oxide, oxidation is conducted in an atmosphere of air, or O_2 optionally by using a suitable oxidant. Useful oxidants can be exemplified by organic oxidants including N-oxides such as trimethylamine N-oxide and pyridine N-oxide, peroxides such as bis(trimethylsilyl) peroxide, perbenzoic acid, O_3 and O_2, as well as by inorganic oxidants including H_2O_2, H_2SO_4, and HNO_3.

[0023] For the purpose of enhancing the adhesive strength of the patterned film to the substrate, the patterned film can be optionally subjected to an additional annealing step at a temperature of 30-1,000°C following the reduction or the oxidation. In the prior techniques where annealing step is essentially required for conversion of a metal precursor to a metal, a plastic substrate should-not be used due to its poor thermal-resistance. On the other hand, the annealing step involved in the present invention does not aim to accomplish such thermal decomposition of a metal complex, and therefore the annealing temperature can be adequately controlled to prevent deformation of even a plastic substrate.

[0024] The present invention can be more clearly understood with referring to the following examples. It should be understood that the following examples are not intended to restrict the scope of the present invention in any manner. All synthetic procedures in the following examples were conducted in an N_2 atmosphere deprived of O_2 and moisture according to Schlenk technique or Glove box technique well known to those skilled in the art.

Preparation Example 1: Synthesis of $Ag(NH_2Pr)_n(NO_3)$ compound (n=1, 2, 3 and 4)

[0025] To a 50ml round-bottom Schlenk flask were added 3.4g(20.0mmol) of silver nitrate ($AgNO_3$) together with 15ml of acetonitrile(CH_3CN) and stirred to dissolve completely. To the flask was dropwise added 3.6g(60.9mmol) of propylamine by means of a syringe and allowed to react for 1 hour with stirring at room temperature. The reaction

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mixture was filtered through a 0.2um membrane filter, and excess propylamine and acetonitrile were completely evaporated from the filtrate under a reduced pressure, to afford colorless oil.

[0026] Mass spectrometry verified that different metal complexes each comprising 1-4 propylamine ligands are present in the oil, and molar ratio of silver atom:propylamie ligand was proven to be 1:1.2 by atomic analysis. These results indicate that major product of this example is a compound where molar ratio of silver atom:propylamine ligand is 1:1, but this complex is unstable. Expectedly, change of the molar ratio between the two starting materials(i.e., silver nitrate and propylamine) did not alter the ^{1}H-NMR spectrum for the final product, where all protons resonated upfiled compared to those of pure propylamine as follows:

^{1}H-NMR(CD_3CN, ppm): 2.68 [t, 2H, N-$\underline{CH_2}$], 1.49 [m, 2H, $C\underline{H_2}CH_3$], 0.90 [t, 3H, $CH_2C\underline{H_3}$]

Examples 1-3: Effect of coating solvent

[0027] Dependence of photosensitivity and reducibility of the metal complexes of Preparation Example 1 on coating solvent was determined. The $Ag(NH_2Pr)_n(NO_3)$ compound (n=1, 2, 3 and 4) of Preparation Example 1 was dissolved in a nitrile solvent including acetonitrile(CH_3CN) and propionitrile(CH_3CH_2CN) and an alcohol solvent including isopropylalcohol(IPA), respectively, and then applied to a surface of a glass substrate by spin coating. The resulting coating film with a photomask positioned thereon was exposed to broadband UV light by means of Oriel 60200(Oriel, USA), followed by developing with the same solvent as used in the coating step. Photosensitivity of the metal complex was measured by exposure time required for making exposed areas of the coating film insoluble in the developer(defined as "photoreaction time" in Table 1). The higher is the photosensitivity, the shorter is the photoreaction time. As shown in Table 1, significant variance of photosensitivity according to the coating solvent was not observed, indicating that both nitrile solvent and alcohol solvent are suitable for stability and coating property of the metal complex of the present invention.

[0028] After the developing step, the exposed areas of the coating film were reduced with 0.1M hydrazine solution in acetonitrile at room temperature under atmospheric pressure for 30 seconds, to provide a patterned film of pure silver. Reducibility was also hardly affected by which solvent was used in the coating step. Similar results were obtained from reduction in a gas phase(data not shown).

Table 1

Exam.	Metal complex*	Solvent	Photoreaction time (min)	Reductant (M/sec)	Specific resistance**(μΩcm)
1	$Ag(NH_2Pr)_n(NO_3)$	CH_3CN	5	Hydrazine (0.1/30)	15-20
2	$Ag(NH_2Pr)_n(NO_3)$	CH_3CH_2CN	5	Hydrazine (0.1/30)	20-30
3	$Ag(NH_2Pr)_n(NO_3)$	IPA	5	Hydrazine (0.1/30)	15-20

* Pr = propyl

**Specific resistance was measured by four-point probe.

Examples 4-11: Effect of ligand

[0029] Other metal complexes, which were prepared in a similar manner as in the Preparation Example 1 except that various ligands were substituted for propylamine, were examined for photosensitivity and reducibility. All metal complexes, except $Ag\{NH(C_2H_4OH)_2\}_2(NO_3)$, were dissolved in acetonitrile, respectively, and then applied to a surface of a glass substrate by spin coating. Photosensitivity and reducibility of the resulting coating film were then determined in a similar manner as in the Example 1. The results are summarized in Table 2, which indicate that photosensitivity and reducibility of a metal complex are deteriorated by a ligand that has many carbon atoms and is bulky. Similar results were obtained from reduction in a gas phase(data not shown).

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Table 2

Exam.	Metal complex*	Solvent	Photoreaction time (min)	Reductant (M/sec)	Specific resistance (μΩcm)
4	$Ag(NH_2Bu)_n(NO_3)$	CH_3CN	5	Hydrazine (0.1/30)	15-20
5	$Ag\{C_2H_5CH(NH_2)CH_3\}_2(NO_3)$	CH_3CN	10	Hydrazine (0.1/30)	40-200
6	$Ag(aniline)_2(NO_3)$	CH_3CN	10	Hydrazine (0.1/30)	~2000
7	$Ag(TMEDA)_2(NO_3)$	CH_3CN	1	Hydrazine (0.1/30)	~100
8	$Ag(t\text{-}BuNH_2)_2(NO_3)$	CH_3CN	5	Hydrazine (0.1/30)	20-30
9	$Ag(Py_2)(NO_3)$	CH_3CN	10	Hydrazine (0.1/30)	~300
10	$Ag(NH_2C_3H_6OH)_2(NO_3)$	CH_3CN	10	Hydrazine (0.1/30)	~100
11	$Ag\{NH(C_2H_4OH)_2\}_2(NO_3)$	C_2H_5OH	5	Hydrazine (0.1/30)	20-30

* Bu = Butyl; TMEDA = tetramethylethylenediamine; Py =pyridine

Preparation Example 2: Synthesis of $Ag(NH_2Pr)_n(NO_2)$ compound (n=1, 2, 3 and 4)

[0030] To a 50ml round-bottom Schlenk flask were added 3.08g(20.0mmol) of silver nitrite($AgNO_2$) together with 15ml of acetonitrile(CH_3CN) and stirred to dissolve completely. To the flask was dropwise added 3.6g(60.9mmol) of propylamine by means of a syringe and allowed to react for 1 hour with stirring at room temperature. The reaction mixture was filtered through a 0.2um membrane filter, and excess propylamine and acetonitrile were completely evaporated from the filtrate under a reduced pressure, to afford transparent yellowish oil. Similar ^{1}H-NMR spectrum was obtained as in the Preparation Example 1.

^{1}H-NMR(CD_3CN, ppm): 2.68 [t, 2H, N-$\underline{CH_2}$], 1.49 [m, 2H, $\underline{CH_2}CH_3$], 0.90 [t, 3H, $CH_2\underline{CH_3}$]

Examples 12-14: Effect of coating solvent

[0031] Dependence of photosensitivity and reducibility of the metal complexes of Preparation Example 2 on coating solvent was determined. The $Ag(NH_2Pr)_n(NO_2)$ compound (n=1, 2, 3 and 4) of Preparation Example 2 was dissolved in a nitrile solvent including acetonitrile(CH_3CN) and propionitrile(CH_3CH_2CN) and an alcohol solvent including isopropylalcohol(IPA), respectively, and then applied to a surface of a glass substrate by spin coating. The resulting coating film with a photomask positioned thereon was exposed to broadband UV light by means of Oriel 60200(Oriel, USA), followed by developing with the same solvent as used in the coating step. Subsequently, the exposed areas of the coating film were reduced with 0.01M hydrazine solution in acetonitrile at room temperature under atmospheric pressure, to provide a patterned film of pure silver. As shown in Table 3, excellent photosensitivity was observed regardless of the kind of the coating solvent, and reducibility was so improved that the relatively low concentration of reductant(i.e., 0.01M) was sufficient to provide a pure silver pattern.

Table 3

Exam.	Metal complex*	Solvent	Photoreaction time (min)	Reductant (M/sec)	Specific resistance (μΩcm)
12	$Ag(NH_2Pr)_n(NO_2)$	CH_3CN	3	Hydrazine (0.01/10)	15-20

* Pr = propyl

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Table 3 (continued)

Exam.	Metal complex*	Solvent	Photoreaction time (min)	Reductant (M/sec)	Specific resistance (μΩcm)
13	$Ag(NH_2Pr)_n(NO_2)$	CH_3CH_2CN	3	Hydrazine (0.01/10)	20-30
14	$Ag(NH_2Pr)_n(NO_2)$	IPA	3	Hydrazine (0.01/10)	15-20

* Pr = propyl

[0032] Meanwhile, the metal complexes of the Preparation Example 2 were proven to be superior to those of the Preparation Example 1 in light of solubility in the developer as well as photosensitivity.

Examples 15-20: Effect of ligand and anion

[0033] Other metal complexes, which were prepared in a similar manner as in the Preparation Example 1 except that the ligand(i.e., propylamine) and/or the anion(i.e., nitrite) was varied, were examined for photosensitivity and reducibility. Each metal complex was dissolved in acetonitrile, and then applied to a surface of a glass substrate by spin coating. Photosensitivity and reducibility of the resulting coating film were then determined in a similar manner as in the Example 1. The results are summarized in Table 4.

Table 4

Examp.	Metal complex*	Solvent	Photoreaction time (min)	Reductant (M/sec)	Specific resistance** (μΩcm)
15	$Ag(NH_2Bu)_n(NO_2)$	CH_3CN	3	Hydrazine (0.01/30)	15-20
16	$Ag(NH_2Pr)_n(BF_4)$	CH_3CN	10	Hydrazine (0.01/30)	~3000
17	$Ag(NH_2Pr)$ (Acac)	CH_3CN	30	Hydrazine (0.01/30)	N.D.
18	$Ag(NH_2Pr)$ (DBM)	CH_3CN	30	Hydrazine (0.01/30)	N.D.
19	$Ag(NH_2Pr)$ (Ac)	CH_3CN	30	Hydrazine (0.01/30)	N.D.
20	$Ag(NH_2Pr)$ (N_3)	CH_3CN	30	Hydrazine (0.01/30)	N.D.

* Bu = Butyl; Pr = Propyl; Acac = acetylacetonate; DBM = dibenzoylmethane; Ac = acetate

** N.D. = not determined

[0034] As shown in the Table 4, photosensitivity and reducibility were significantly affected by the change of ligand or anion. For the metal complex used in Example 16, where BF^{4-} is substituted for nitrite, exhibited slightly. decreased photosensitivity, while adhesiveness to a glass substrate was highly improved. The metal complexes used in Example 17-20 exhibited much lower photosensitivity than that of $Ag(NH_2Pr)_n(NO_2)$ and even $Ag(NH_2Pr)_n(NO_3)$. Further, though electroconductive metal pattern was obtained in Examples 16-20, specific resistance thereof was so elevated to reach a MΩ level.

Examples 21-23: Effect of reductant

[0035] Reducibility of the $Ag(NH_2Pr)_n(NO_3)$ compound and the $Ag(NH_2Pr)_n(NO_2)$ compound was examined, respectively, by using $LiAlH_4$ or trimethoxy silane as a reductant. Deposition of a coating film on a surface of a glass substrate followed by patterning and reduction was conducted according to the same manner as in the above Example 1. As shown in Table 5, reduction was successfully accomplished though $LiAlH_4$ and trimethoxy silane were somewhat inferior to hydrazine in their reducing power.

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Table 5

Exam.	Metal complex*	Solvent	Photoreaction time (min)	Reductant (M/sec)	Specific resistance** (μΩcm)
21	$Ag(NH_2Pr)_n(NO_3)$	CH_3CN	5	$LiAlH_4$/THF (0.1/30)	30-40
22	$Ag(NH_2Pr)_n(NO_2)$	CH_3CN	3	$LiAlH_4$/THF (0.1/30)	20-30
23	$Ag(NH_2Pr)_n(NO_2)$	CH_3CN	3	$(MeO)_3SiH$ (0.5/30)	200-220

* Pr = Propyl

** N.D. = not determined

Examples 24-27: Effect of metal

[0036] Metal complexes having a different metal component other than silver, which were prepared in a similar manner as in the Preparation Example 1, were examined for photosensitivity and reducibility, respectively. Deposition of a coating film on a surface of a glass substrate followed by patterning and reduction was conducted according to the same manner as in the above Example 1. As shown in Table 6, metal complexes containing copper or cobalt exhibited relatively low photosensitivity and fairly high specific resistance amounting to about 3-4 MΩcm, but they succeeded in providing an electroconductive patterned film. Particularly, $Au(NH_2Pr)_nCN$ was readily reduced by hydrazine like the Ag complexes and exhibited very low specific resistance ranging from 20 to 30 μΩcm.

Table 6

Exam.	Metal complex*	Solvent	Photoreaction time (min)	Reductant (M/sec)	Specific resistance** (μΩcm)
24	$Cu(NH_2Pr)_n(NO_3)_2$	CH_3CN	30	Hydrazine (0.1/30)	N.D.
25	$Au(NH_2Pr)_n(CN)$	CH_3CN	30	Hydrazine (0.01/30)	20-30
26	$Au(NH_2Pr)_n(Cl)$	CH_3CN	30	Hydrazine (0.01/30)	N.D.
27	$Co(Acac)_2$	CH_3CN	30	Hydrazine (0.01/30)	N.D.

*Pr = Propyl; Acac = acetylacetonate

** N.D. = not determined

[0037] As stated above, by virtue of the present invention, it has been realized to form electroconductive patterned films of a metal through easy coating process and simple chemical reactions, without using photosensitive resins.

Claims

1. A method of forming a metal or metal oxide pattern on a substrate comprising the steps of:

(a) depositing a thin film of a metal complex on a surface of the substrate;
(b) exposing the film to a light source by the use of a photomask having a desired pattern to cause the metal complex in exposed areas of the film to be decomposed resulting in a difference of solubility between exposed areas and unexposed areas;
(c) developing the film with an organic solvent capable of dissolving the metal complex to remove the metal complex in unexposed areas leaving only a metal-containing patterned film; and
(d) reducing or oxidizing the metal-containing patterned film to provide a pure metal or metal oxide pattern on the substrate.

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2. The method according to claim 1, wherein the metal complex is represented by the formula (I):

$$M_mL_nX_p \quad (I)$$

wherein,

M is a metal atom selected from transition elements, lanthanoids, and main group elements;
L is an organic ligand comprising at least one donor atom and 20 or less carbon atoms, and, if m is 2 or more, L may interconnect M's;
X is a mono-, di- or tri-valent anion;
m is an integer ranging from 1 to 10, provided that M's may be different each other when m is 2 or more;
n is an integer ranging from 0 to 60, provided that L's may be different each other when n is 2 or more;
p is an integer ranging from 0 to 60, provided that X's may be different each other when p is 2 or more; and
n plus p is not equal to 0.

3. The method according to claim 1 or 2, wherein the metal complex is dissolved in a nitrile-based solvent, an aliphatic hydrocarbon-based solvent, an aromatic hydrocarbon-based solvent, a ketone-based solvent, an ether-based solvent, an acetate-based solvent, an alcohol-based solvent, a silicon-based solvent, or a mixture thereof prior to the step (a).

4. The method according to any of claims 1 to 3, wherein the substrate is made of an inorganic material, an organic material, or a composite thereof.

5. The method according to any of claims 1 to 4, wherein the depositing of step (a) is carried out through spin coating, roll coating, dip coating, spray coating, flow coating, or screen printing.

6. The method according to any of claims 1 to 5, wherein the exposing of step (b) is carried out in an atmosphere of vacuum, air, or O_2, H_2, N_2, Ar or a mixed gas thereof.

7. The method according to claims 1 to 6, wherein the exposing of step (b) is carried out at room temperature or in at a temperature where thermal decomposition of the metal complex does not occur.

8. The method according to any of claims 1 to 7, wherein the exposing of step (b) is carried out by the use of UV light as a light source.

9. The method according to any of claims 1 to 8, wherein the developing of step (c) is carried out by the use of a nitrile-based solvent, an aliphatic hydrocarbon-based solvent, an aromatic hydrocarbon-based solvent, a ketone-based solvent, an ether-based solvent, an acetate-based solvent, an alcohol-based solvent, a silicon-based solvent, or a mixture thereof.

10. The method according to any of claims 1 to 9, wherein the reducing or oxidizing of step (d) is carried out in a liquid- or gas-phase.

11. The method according to any of claims 1 to 10,
wherein the reducing of step (d) is carried out by the use of a reductant selected from the group consisting of hydrazines, silanes, amines, and metal hydrides.

12. The method according to any of claims 1 to 10,
wherein the oxidizing of step (d) is carried out by the use of an oxidant selected from N-oxides, peroxides, perbenzoic acid, O_3, O_2, hydrogen peroxide, sulfuric acid, and nitric acid.

13. The method according to any of claims 1 to 11,
wherein the reducing of step (d) is carried out in an atmosphere of vacuum, or H_2, N_2, Ar or a mixed gas thereof.

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14. The method according to any of claims 1 to 10 and 12, wherein the oxidizing of step (d) is carried out in an atmosphere of air, or O_2.

15. The method according to any of claims 1 to 14, further comprising annealing at a temperature of 30-1,000° C after step (d) .

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 25 8983

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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A,D	WO 96 15289 A (SIMON FRASER UNIVERSITY) 23 May 1996 (1996-05-23) * page 14, line 15 - line 21 * * claims *	1-15	
A	US 3 492 151 A (L.A. CESCON) 27 January 1970 (1970-01-27) * column 2, line 62 - line 65 * * column 3, line 48 - line 50 * * column 6; example 8 *	1-15	
A	US 5 849 465 A (H. UCHIDA ET AL.) 15 December 1998 (1998-12-15) * figure 9 * * claims *	1-15	
A	US 5 824 456 A (K. OGI ET AL.) 20 October 1998 (1998-10-20) * claims 1,13 *	1-15	TECHNICAL FIELDS SEARCHED (Int.Cl.7) G03F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 April 2003	Dupart, J.-M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 02 25 8983

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14-04-2003

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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Electronic Patent Application Fee Transmittal

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Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Peter S. Dardi/Michelle Douglas
Attorney Docket Number:	5063.02US05

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($)
Miscellaneous:				
SUBMISSION- INFORMATION DISCLOSURE STMT	1806	1	240	240
		Total in USD ($)		**240**

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First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
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37 CFR 1.16 (National application filing, search, and examination fees)

37 CFR 1.17 (Patent application and reexamination processing fees)

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		Amendment.pdf	55980 8a505585d85c3271aaa693dad04ea757a20c53f5	yes	9
	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	
	Amendment/Req. Reconsideration-After Non-Final Reject		1	1	
	Claims		2	4	
	Applicant Arguments/Remarks Made in an Amendment		5	9	
Warnings:					
Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	IDS_Form_SB_08a-signed.pdf	1035521 3894e301c163bf6b2cfc026dbfb3e63800438d76	no	5
Warnings:					
Information:					
3	Foreign Reference	CN102027603A_EAO.pdf	1804025 95960637f4ede39003305e1c03e2886b95b09f08	no	35
Warnings:					
Information:					
4	Foreign Reference	EP1326136A1.pdf	631064 ea5bc4395c71c48ca0ed1d7f9c5970b686ca7da2	no	12
Warnings:					
Information:					
5	Fee Worksheet (SB06)	fee-info.pdf	30436 8e0c7c1101f9fc9b425599ff09ae4f3f04694dd4	no	2

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

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/784,258	10/16/2017	Jason K. Stowers	5063.02US05	9576

62274 7590 06/11/2019

CHRISTENSEN, FONDER, DARDI & HERBERT PLLC
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EXAMINER	
ROBINSON, CHANCEITY N	

ART UNIT	PAPER NUMBER
1722	

MAIL DATE	DELIVERY MODE
06/11/2019	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. 15/784,258	Applicant(s) Stowers et al.	
	Examiner CHANCEITY N ROBINSON	Art Unit 1722	AIA (FITF) 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 04/08/2019.

☐ 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) 1-19 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) 1-19 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 04/08/2019.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date _____.

4) ☐ Other: _____.

Notice of Pre-AIA or AIA Status

1. The present application is being examined under the pre-AIA first to invent provisions.

2. The Applicant's request for reconsideration filed on April 08, 2019 was received. Claims 1, 3 and 13 have been amended.

3. The text of those sections of Title 35, U.S.C. code not included in this action can be found in the prior Office Action issued on January 07, 2019.

Claim Rejections - 35 USC § 112

4. The following is a quotation of 35 U.S.C. 112(b):

> (b) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.

> The following is a quotation of 35 U.S.C. 112 (pre-AIA), second paragraph:
> The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

5. Claim 10 is rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention. Claim 10 recites "…wherein interactions 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." There is insufficient antecedent basis for the coating material with e-beam radiation in the claim. The claim as written is indefinite and unclear. Appropriate correction is required.

6. Claims 1-19 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 1-19 recite the term, "about". The term "about" in claims 1-3, 7-8, 13-

14, 16, 18 and 19 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

7. Claims 1-19 are rejected on the ground of nonstatutory double patenting as being unpatentable over claims 1-27 of U.S. Patent No.9, 176, 377. Although the claims at issue are not identical, they are not patentably distinct from each other because both the instant claims and patent '377 recite the same method of forming a patterned inorganic material on a substrate which are equivalent and obvious variant of each other methods.

It is further noted that the **restriction requirement was withdrawn as to any claim that required all the limitations of the allowable claims in US 9,176,377.** Specifically, the restriction requirement of 09/16/2013 was partially withdrawn. Claims 14-30, directed to method no longer withdrawn from consideration because the claim(s) requires all the limitations of an allowable claim. However, claims 31-38, directed to structure withdrawn and canceled from consideration because they do not all require all the limitations of an allowable claim.

In view of the above noted withdrawal of the restriction requirement, applicant was advised that if any claim presented in a continuation or divisional application is anticipated by, or includes all the limitations of, a claim that is allowable in the present application, such claim may be subject to provisional statutory and/or nonstatutory double patenting rejections over the claims of the instant application. Once a restriction requirement is withdrawn, the provisions of 35 U.S.C. 121 are no longer applicable. See

In re Ziegler, 443 F.2d 1211, 1215, 170 USPQ 129, 131-32 (CCPA 1971). See also MPEP § 804.01.

8. Claims 1-19 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 recite the same method of forming a patterned inorganic material on a substrate which are equivalent and obvious variant of each other methods.

9. Claims 1-19 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Stowers, Jason, "Direct patterning of solution deposited metal oxides", (2008) in view of Jason Stowers, Douglas A. Keszler, "High resolution, high sensitivity inorganic resists", (2009), and further in view of Meyers et al. (WO 2008/082448 A1).

Regarding claims 1-19, Stowers teaches a method for forming a patterned structure (inorganic material) on substrate (chapter 4, page 65-page 86; in particular pages 71-72 and 78, line 3-4), the method comprises the step of forming a layer of a radiation patternable coating material (a layer of coating material; last three line of page 71) comprising a solvent (water, metal suboxide cations (ZrO^{2+} and HfO^{2+}),ligands comprising a peroxide group (H_2O_2) and inorganic polyatomic anions (SO_4^{2-}) to form a coated substrate; heating the coated substrate to remove a portion of the solvent (implicit or conventional; page 70, last paragraph); irradiating the coated substrate to a pattern of radiation to condense the coating at the irradiated locations (with 30keV electron beam; which meets the limitation of instant claim 13); heating the coated substrate after irradiation to a temperature of at least about 45°C prior to contacting the coating with a developer (page 78,lines 3-4); and exposing (irradiating) the coating substrate with a

developing composition to at least partially remove the coating composition at un-irradiated locations.

Stowers do not explicitly recited the thickness or differential dissolution as instantly claimed. However, Stowers et al. disclose a patterned 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 in view of Stowers et al. teach a method of making a structure by exposing, spin coating and heating the coating material. Neither Stowers nor Stowers at al. teach the radiation dosage as instantly claimed.

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°C (see claim 18), which encompasses the instant claimed range from about 45 to about 150°C. 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, 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 in view of Sowers 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).

Response to Arguments

10. Applicant's arguments filed 04/08/2019 have been fully considered but they are not persuasive. Applicant's principle arguments are the following:

A) Applicants argue that claims of the '000 patent are directed to any method. Respectfully, there would seem to be no basis for this rejection. Applicant respectfully requests withdrawal of the rejection of claims 1-19 under nonstatutory obviousness-type double patenting as being unpatentable over the '000 patent.

A) Examiner respectfully disagrees. Patent '000 claim 5 explicitly recites method for forming the patterned structure of claim (see below):

> 5. A method for forming the patterned structure of claim 1, the method comprising:
> irradiating a layer of coating material with extreme ultraviolet light at a dose of no more than about 100 mJ/cm^2 or with an electron beam at a dose equivalent to no more than about 300 μC/cm^2 at 30 kV; and
> contacting the irradiated layer with a developing composition to dissolve an irradiated material to form the patterned inorganic material.

The method and the coating material of the instant claims and the coating material and the method 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). Therefore, the rejection will be maintained.

B) Applicants will consider filing a terminal disclaimer over claims 1-27 of U.S. Patent 9,176,377 when the claims are found otherwise allowable.

B) Examiner will therefore maintained the rejection.

C) Applicants argue that claims are interpreted from the view point of a person of ordinary skill in the art. A person of ordinary skill in the art would recognize that such parameters are determined within measurement precision that is appropriate for specified processes. Thus, the recitation of “about” would be understood to a person of ordinary skill in the art. Applicant respectfully maintains that the claims are clear and definite and request withdrawal of the rejection.

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 [0066]:

> [0066] 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 recited by the instant claims 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. Applicant notes that Stowers teaches e-beam dosage in Fig. 1. Applicant notes that the Office Action seems to mix electron beam dosage levels with EUV dosages, although these are distinct. Since the references do not teach all of the features of amended claim 1, the combined teachings of Thesis, Stowers and Meyers do not render claim 1 prima facie obvious.

D) Examiner respectfully disagrees. Instant claim 12, which depends from claim 1 recites the irradiating the coated substrate using electron beam radiation, Stowers continue to teach the limitations recited by the instant claims. See citations above. Therefore, the rejection is maintained.

E) Applicants argue that Stowers does not suggest alternative ratios. The 0.5 ratio of Stowers and Meyers is a stoichiometric value with one ligand (peroxide) bridging between two metal ions. Applicants has demonstrated that exceptional results can be achieved by unexpectedly increasing the peroxide ligand concentrations by at least a factor of four. This is a patentable improvement not suggested by the cited art. Therefore, the cited art does not render claim 14 prima facie obvious.

E) Examiner respectfully disagrees. The instant disclosure does not show unexpected results of increasing the peroxide ligand concentrations by at least a factor of four as argued. The disclosure recites "the peroxide ligand to metal ion ratio is at least about 2", which is 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). Stowers et al. recognize that metal ion to peroxide (ligand) is 1:0.5. It is well-understood by one of ordinary skill in the art that 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, the rejection is maintained.

Conclusion

Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event,

however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CHANCEITY N ROBINSON whose telephone number is (571)270-3786. The examiner can normally be reached on Monday-Friday (5:30 am-10:00 pm; IFP; PHP).

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 N ROBINSON/
Primary Examiner, Art Unit 1722

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/784,258	Stowers et al.
	Examiner	Art Unit
	CHANCEITY N ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	06/09/2019								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
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	16	✓								
	17	✓								
	18	✓								
	19	✓								

Lam Research Ex. 1009 - Page 209 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/784,258	Stowers et al.
	Examiner	Art Unit
	CHANCEITY N ROBINSON	1722

CPC - Searched*		
Symbol	Date	Examiner
G03F 7/00	01/05/2019	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 and IDS Search	01/05/2019	CR
East Search Updated	06/09/2019	CR

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner

/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722	

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	1	("8415000").PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/06/09 21:42
L2	2	"15784258"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/06/09 21:50
S1	7	"12850867"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/01/05 16:41
S2	3847446	(method or process) with (substrate or support)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:44
S3	367748	(EUV or UV or ultraviolet) with radiation	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S4	155899	heat$3 with (coat$3) with (support or substrate)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S5	5772464	irraditat$4 or expos$4	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S6	24187	(EUV or UV or ultraviolet) with (dosage or dose)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	ON	2019/01/05 18:45

			DERWENT; IBM_TDB			
S7	1271	S2 and S3 and S4 and S5 and S6	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S8	1189	S7 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:46
S9	691	S8 and (developer or developing)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:46
S10	54733	(TMAH or (tetramethylammonium adj hydroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S11	528	S9 and S10	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S12	527	S11 and pattern$3	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S13	20	S12 and ligands and (metal adj (ion or cation))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S14	20	S13 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/325 OR G03F7/327 OR G03F7/022 OR G03F7/032 OR G03F7/033 OR G03F7/0382 OR G03F7/0385 OR G03F7/0392 OR G03F7/0397 OR G03F7/32 OR G03F7/322 OR G03F7/09 OR G03F7/2002 OR G03F7/2037 OR G03F7/30 OR G03F7/2004 OR	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:48

		G03F7/162 OR G03F7/168 OR G03F7/40 OR Y10T428/24355 OR H01M10/0525 OR H01M2004/021 OR H01M2004/025 OR H01M2004/027 OR H01M4/045 OR H01M4/049 OR H01M4/134 OR H01M4/1391 OR H01M4/1395 OR H01M4/48 OR H01M4/60 OR H01M4/66 OR H01M4/665 OR H01M4/667 OR H01M4/668 OR Y02E60/122 OR Y02P70/54 OR Y02T10/7011).CPC.)				

EAST Search History (Interference)

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6/ 9/ 2019 10:08:53 PM
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Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (03-15)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.00US05

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	4014858	A	1977-03-29	Chipman et al.	
	2	4144222	A	1979-03-13	Shinmi et al.	
	3	4174346	A	1979-11-13	Collins et al.	
	4	4380559	A	1983-04-19	Mandai et al.	

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	1	20020160298	A1	2002-10-31	Minami et al.	
	2	20100099908	A1	2010-04-22	Yoshitomo et al.	

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	3	20100279228	A1	2010-11-04	Davis et al.	
	4	20130078796	A1	2013-03-28	Ganesan et al.	
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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2]	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	102027603	CN	A	2011-04-20	Eastman Kodak Co.	English Abstract Only	
	2	1326136	EP	A1	2003-07-09	Samsung Electronics Co., Ltd.		
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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1		

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EXAMINER SIGNATURE

Examiner Signature	/CHANCEITY N ROBINSON/	Date Considered	06/03/2019

*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.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15784258
	Filing Date	2017-10-16
	First Named Inventor	Jason K. Stowers
	Art Unit	1722
	Examiner Name	Chanceity N. Robinson
	Attorney Docket Number	5063.00US05

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.00US05

CERTIFICATION STATEMENT

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

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

☒ 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	/Peter S. Dardi/	Date (YYYY-MM-DD)	2019-04-08
Name/Print	Peter S. Dardi, Ph.D.	Registration Number	39,650

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 15/784,258	Filing Date 10/16/2017	☐ 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 $80 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $420 =	
☐ 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)			
AMENDMENT	08/09/2019	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 19	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 2	Minus	*** 3	= 0		x $460 =	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)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ 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.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/SHAREILL A COLES/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

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

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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US05
Stowers et al.	Confirmation No.: 9576
Application No.: 15/784,258	Examiner: Chanceity N. Robinson
Filed: October 16, 2017	Group Art Unit: 1722

For: RADIATION BASED PATTERNING 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 Final Office Action of June 11, 2019, 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. 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 9, 2019
Date

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

Lam Research Ex. 1009 - Page 220 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

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. (Previously Presented) 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; and

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

2. (Original) The method of claim 1 wherein the irradiation is performed with EUV at a dose of no more than about 90 mJ/cm^2.

3. (Previously Presented) The method of claim 1 wherein the selected pattern has a pitch of no more than about 60 nm.

4. (Original) The method of claim 1 wherein the developing composition comprises tetramethyl ammonium hydroxide.

5. (Original) The method of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous base.

6. (Original) The method of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent.

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7. (Original) The method of claim 1 further comprising heating the coated substrate after irradiation to a temperature of at least about 45ºC prior to contacting the irradiated layer with the developing composition.

8. (Original) The method of claim 1 further comprising heating the substrate with the patterned coating material to a temperature from about 150ºC to about 600ºC for from one minute to 25 minutes to form a post-patterning condensed structure.

9. (Original) The method of claim 8 further comprising performing a second patterning using the post-patterning condensed structure to form a double patterned structure.

10. (Currently Amended) The method of claim 1 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.

11. (Original) The method of claim 10 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.

12. (Original) The method of claim 10 wherein the radiation sensitive ligands comprise peroxide ligands, and wherein the coating material further comprises metal suboxide cations.

13. (Currently Amended) The method of claim 12 wherein the coating material further comprises inorganic polyatomic anions and wherein the peroxide ligand to metal ion ratio is at least about 2.

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

Lam Research Ex. 1009 - Page 222 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

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 45ºC prior to contacting the coating with a developing composition.

15. (Original) The method of claim 14 further comprising contacting the coated substrate after heating with a developing composition to remove un-irradiated coating material to form the patterned inorganic material.

16. (Original) The method of claim 15 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.

17. (Original) The method of claim 14 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.

18. (Original) The method of claim 14 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.

19. (Original) The method of claim 14 wherein the coating has an average thickness of about 5 nm to about 30 nm.

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REMARKS

Claims 1-19 are pending. By this Amendment, claim 10 is amended to more particularly point out the claimed invention. Claim 13 is amended to correct a typographical error. Specifically, claim 10 is amended to remove the references to electron beam radiation. Claim 13 is amended to correct a typographical error by adding the word "comprises" after the word "further". No new matter is introduced.

Rejections Under 35 U.S.C. 112

The Examiner rejected claim 10 under 35 U.S.C. 112(b) or pre-AIA 35 U.S.C. 112, second paragraph, as being indefinite. In particular, the Examiner asserts that there is insufficient antecedent basis for the coating material with e-beam radiation in the claim. Applicant amends claim 10 to remove the reference to e-beam radiation. In view of the amendment, it is believed that the claim is clear.

The Examiner rejected claims 1-19 under 35 U.S.C. 112(b) or pre-AIA 35 U.S.C. 112, second paragraph, as being indefinite. In particular, the Examiner asserts that the recitation of the term "about" in claims 1-3, 7-8, 13-14, 16, 18, and 19 renders the claims indefinite. Applicant notes that the application is a continuation of U.S. patent application serial number 12/850,867 (now U.S. patent 9,176,377). In this parent patent, claims 1, 2, 6, 7, 9-11, and 13 were found to be allowable. These claims provided clarity for one of ordinary skill in the art through the term "about."

As a demonstration of this established standard for clarity, the below excerpts of examples in the instant application (underlining added) serve to remind one of ordinary skill in the art of the existence of fluctuations to target values which are the nature of this art. The term "about" therefore serves as a necessary boundary for clearly defining the scope of the invention.

[0102] 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.times.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.

Lam Research Ex. 1009 - Page 224 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

[0105] The EUV images were obtained using projection lithography with a numerical aperture of 0.25 operating at 13 nm. The resist was applied with a thickness of 20 nm by spin coating on a silicon wafer, followed by a post-apply bake of 50.degree. C. After exposure at approximately 80 mJ/cm.sup.2, a post-exposure bake of 75.degree. C. was used prior to development in 25% TMAH. The developed patterns are shown in FIGS. 18A-D. The patterns shown in FIG. 18 have pitches of A) 32-nm, B) 30-nm, C) 28-nm and D) 26-nm.

On the present facts, there is no close prior art. In the context of the present measurements, a person of ordinary skill in the art is appropriately apprised of the scope of the presently claimed invention. Thus, Applicant respectfully maintains that the Examiner has not established *prima facie* lack of clarity. Applicant requests withdrawal of the rejection of claims 1-19 under 35 U.S.C. 112(b) or pre-AIA 35 U.S.C. 112, second paragraph, as being indefinite.

Rejection for Obvious –Type Double Patenting Over U.S. Patent 9,176,377

The Examiner rejected claims 1-19 under nonstatuatory obviousness-type double patenting as being unpatentable over claims 1-27 of U.S. patent 9,176,377 (hereinafter the '377 patent). Examiner states that the instant claims and patent Applicant has filed a terminal disclaimer with this amendment to obviate the rejection. In view of the terminal disclaimer, Applicant respectfully requests withdrawal of the rejection of claims 1-19 under nonstatuatory obviousness-type double patenting as being unpatentable over the '377 patent.

Rejection for Obvious –Type Double Patenting Over U.S. Patent 8,415,000

The Examiner rejected claims 1-19 under nonstatuatory obviousness-type double patenting as being unpatentable over claims 1-17 of U.S. patent 8,415,000 (hereinafter the '000 patent). Examiner stated that the instant claims and patent '000 recite the same method of forming a patterned inorganic material on a substrate. Claims 2-4 and 6-17 of '000 depend from claim 1, which is directed to a patterned structure, not a method. As noted by the Examiner, claim 5 of '000 is a method for forming a patterned structure. However, with respect to the present claim 1, claim 5 of '000 does not teach or suggest a method that is operational with a coating material of thickness about 5 nm to 30 nm, and the structural claims (1-4 and 6-17) do not suggest this feature. The coating thickness enables a considerable improvement by virtue of enabling sharp patterning of adjacent structures with a very small pitch. With respect to the present claim 14, claim 5 of '000

Lam Research Ex. 1009 - Page 225 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

does not teach or suggest a post-irradiation, pre-development heating step. Since the claims of the '000 patent do not teach or suggest all of the features of the presently claimed invention, the claims do not render the present claims *prima facie* obvious. Applicant respectfully requests withdrawal of the rejection of claims 1-19 under nonstatuatory obviousness-type double patenting as being unpatentable over the '000 patent.

Rejection Under pre-AIA 35 U.S.C. 103(a)

The Examiner rejected claims 1-19 under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Stowers, Jason, "Direct patterning of solution deposited metal oxides", (2008) (hereinafter Stowers) in view of Jason Stowers, Douglas A. Keszler, "High resolution high sensitivity inorganic resists", (2009) (hereinafter Stowers et al.), and further in view of Meyers et al, (WO 2008/082448 A1) (hereinafter Meyers). Claims 2-13 depend from claim 1, and claims 15-19 depend from claim 14. Examiner stated that Stowers teaches a method for forming a patterned structure on a substrate, the method involving the irradiation with an electron beam. Stowers et al. also teaches on the use of electron beam irradiation, as summarized in the abstract "New inorganic electron-beam resists have been developed…". Additionally, Meyers teaches the use of an electron beam. The instant claims, as currently amended, are not directed to the use of an electron beam. Applicant respectfully maintains that the cited art does not render Applicant's claimed invention *prima facie* obvious. Applicant requests reconsideration of the rejection based on the following comments.

With respect to claim 1, the Examiner asserted that "[i]nstant claim 12, which depends from claim 1 recites the irradiating the coated substrate using electron beam irradiation." Applicant believes that the Examiner was referring to claim 10. Claim 10 is a dependent claim characterizing the material used in the method. The stipulation that the material is altered by an e-beam does not change the indication in claim 1 that the patterning is performed with UV or EUV radiation, but claim 10 has been amended nevertheless to remove a reference to e-beam. In any case, the cited references do not teach the UV/EUV dose for patterning.

As has been discussed previously, Stowers et al. does not teach UV patterning. Meyers is focused also on e-beam patterning, although Example 7 of Meyers has four sentences and two figures directed to patterning with light from an unfiltered deuterium lamp. With respect to the EUV doses, Applicant refers to Stowers Chapter 3, where some preliminary work involving EUV pattering is described. Stowers Chapters 2 and 4 discuss e-beam patterning, in contrast to Chapter

Lam Research Ex. 1009 - Page 226 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

3, which discusses EUV patterning. Stowers Chapter 2 overlaps significantly with Stowers et al. None of the cited references teaches patterning with the claimed dosage range for UV/EUV light. Since the references do not teach all of the features of Applicant's claim 1, the combined teachings of Stowers, Stowers et al., and Meyers do not render claim 1 *prima facie* obvious.

With respect to claim 14, Examiner states that Stowers et al. disclose that peroxide inhibits condensation of metal oxides, and it is obvious for those skilled in the art to predict function effects of stability with respect to phase separation in the invention of this application by increasing concentration ratio of peroxide. Stowers et al. teaches a stoichiometric ratio of 1 metal ion to 0.5 ligands of peroxide. With all due respect, Stowers et al. does not teach that the peroxide ratio is a results effective variable. The Examiner responds to this by asserting that Applicant has not shown "exceptional results." If *prima facie* obviousness has not been shown, then Applicant has no need to rebut the rejection. Significantly, *prima facie* obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. *In re Ochiai*, 37 USPQ 1127, 1131 (Fed. Cir. 1995). "When the references cited by the examiner fail to establish a *prima facie* case of obviousness, the rejection is improper and will be overturned." *In re Ochiai*, 71 F.3d 1565, 1569 (Fed. Cir. 1995). The Examiner's failure to establish *prima facie* obviousness is a reversible error of law.

Furthermore, the Applicant has demonstrated that exceptional and unexpected radiation-induced selective desorption of the coating material can be achieved by increasing the peroxide ligand concentrations by at least a factor of four. The innovative use of the peroxide ligand in the present application requires a stoichiometric ratio of 1 metal ion to at least about 2 ligands of peroxide. This is a patentable improvement not suggested by the cited art. This improved processing has enabled the previously unachievable patterning results that are claimed in the '000 as well as KR 1364953. Since Stowers et al. does not teach that the peroxide ratio is a results effective variable and does not suggest the claimed range, *prima facie* obviousness has not been established, and any showing of *prima facie* obviousness has been rebutted with a showing of unexpected results.

For the reasons discussed above the combined teachings of Stowers, Stowers et al, and Meyers do not render Applicant's claimed invention *prima facie* obvious. Applicant respectfully requests withdrawal of the rejection of the claims 1-19 under pre-AIA 35 U.S.C. 103 (a) as being unpatentable over Stowers, in view of Stowers et al. and further in view of Meyers. While

Lam Research Ex. 1009 - Page 227 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Applicant does not acquiesce with respect to specific assertions in the rejection directed to the features of the dependent claims, Applicant does not comment further on these in view of the comments and amendments above relating to the independent claims that are dispositive.

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,

/Peter S. Dardi/

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

Customer No. 62274
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Lam Research Ex. 1009 - Page 228 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

Electronic Acknowledgement Receipt

EFS ID:	36834544
Application Number:	15784258
International Application Number:	
Confirmation Number:	9576
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US05
Receipt Date:	09-AUG-2019
Filing Date:	16-OCT-2017
Time Stamp:	15:25:43
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		AmendmentAF.pdf	63655 130a39d7f28320f8bcb369893aa01a46fdc07b49	yes	9

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Response After Final Action	1	1
	Claims	2	4
	Applicant Arguments/Remarks Made in an Amendment	5	9
Warnings:			
Information:			
	Total Files Size (in bytes):	63655	

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.

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.
15/784,258	10/16/2017	Jason K. Stowers	5063.02US05	9576

62274 7590 08/16/2019

CHRISTENSEN, FONDER, DARDI & HERBERT PLLC
33 South Sixth Street
Suite 4540
Minneapolis, MN 55402

EXAMINER	
ROBINSON, CHANCEITY N	

ART UNIT	PAPER NUMBER
1722	

MAIL DATE	DELIVERY MODE
08/16/2019	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.** 15/784,258	**Applicant(s)** Stowers et al.	
	Examiner CHANCEITY N ROBINSON	**Art Unit** 1722	**AIA (FITF) Status** No

--The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

THE REPLY FILED 09 August 2019 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 APPLICANTS 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 37CFR 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 Continuation Sheet (See 37CFR 1.116 and 41.33(a)).
4. ☐ The amendments are not in compliance with 37CFR 1.121. See attached Notice of Non-Compliant Amendment (PTOL-324).
5. ☐ Applicants reply has overcome the following rejection(s): _____
6. ☐ Newly proposed or amended claim(s) _____ would be allowable if submitted in a separate, timely filed amendment canceling the non-allowable claim(s).
7. ☑ For purposes of appeal, the proposed amendment(s):(a) ☑ will not be entered, or (b) ☐ will be entered, and an explanation of how the new or amended claims would be rejected is provided below or appended.

AFFIDAVIT OR OTHER EVIDENCE

8. ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____
9. ☐ The affidavit or other evidence filed after final action, but before or on the date of filing a Notice of Appeal will not be entered because applicant failed to provide a showing of good and sufficient reasons why the affidavit or other evidence is necessary and was not earlier presented. See 37 CFR 1.116(e).
10. ☐ The affidavit or other evidence filed after the date of filing the Notice of Appeal, but prior to the date of filing a brief, will not be entered because the affidavit or other evidence failed to overcome all rejections under appeal and/or appellant fails to provide a showing of good and sufficient reasons why it is necessary and was not earlier presented. See 37 CFR 41.33(d)(1).
11. ☐ The affidavit or other evidence is entered. An explanation of the status of the claims after entry is below or attached.

REQUEST FOR RECONSIDERATION/OTHER

12. ☑ The request for reconsideration has been considered but does NOT place the application in condition for allowance because: See Continuation Sheet.
13. ☐ Note the attached Information *Disclosure Statement*(s). (PTO/SB/08) Paper No(s). _____
14. ☐ Other: _____.

STATUS OF CLAIMS

15. The status of the claim(s) is (or will be) as follows:
    Claim(s) allowed:_____.
    Claim(s) objected to:_____.
    Claim(s) rejected:1-19.
    Claim(s) withdrawn from consideration:_____.

/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722	

Continuation of 3. NOTE: 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.

Continuation of REQUEST FOR RECONSIDERATION/OTHER 12. Applicants stated that a terminal disclaimer has been filed with this amendment to obviate the ODP rejection over US Patent 9,176,377; however, there is no terminal disclaimer on record . Therefore, the rejection is maintained.

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 5063.02US05

Stowers et al. Confirmation No.: 9576

Application No.: 15/784,258 Examiner: Chanceity N. Robinson

Filed: October 16, 2017 Group Art Unit: 1722

For: RADIATION BASED PATTERNING METHODS

AMENDMENT AFTER FINAL

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

DO NOT ENTER: /C.N.R/

08/15/2019

Sir:

INTRODUCTORY COMMENTS

In response to the Final Office Action of June 11, 2019, 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. 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 9, 2019 /Peter S. Dardi/

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

Lam Research Ex. 1009 - Page 234 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

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	15784258
Filing Date	16-Oct-2017
First Named Inventor	Jason Stowers
Attorney Docket Number	5063.02US05
Title of Invention	RADIATION BASED PATTERNING 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)

9176377

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 39650 ○ 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	/Peter S. Dardi/
Name	Peter S. Dardi

*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.

Electronic Patent Application Fee Transmittal

Application Number:	15784258
Filing Date:	16-Oct-2017
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Peter S. Dardi
Attorney Docket Number:	5063.02US05

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**

Doc Code: DISQ.E.FILE
Document Description: Electronic Terminal Disclaimer – Approved

Application No.: 15784258

Filing Date: 16-Oct-2017

Applicant/Patent under Reexamination: Stowers

Electronic Terminal Disclaimer filed on August 20, 2019

☒ 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

Electronic Acknowledgement Receipt

EFS ID:	36921560
Application Number:	15784258
International Application Number:	
Confirmation Number:	9576
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US05
Receipt Date:	20-AUG-2019
Filing Date:	16-OCT-2017
Time Stamp:	13:02:47
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	E20198JD02454203
Deposit Account	601363
Authorized User	Peter Dardi

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

37 CFR 1.16 (National application filing, search, and examination fees)

37 CFR 1.17 (Patent application and reexamination processing fees)

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	Terminal Disclaimer-Filed (Electronic)	eTerminal-Disclaimer.pdf	33327 431a4575814713d2e5b65842257b898c64557569	no	2
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30296 23e1b8e3fb424287169334b1d8dc24440b38790e	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	63623		

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New Applications Under 35 U.S.C. 111

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

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

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

New International Application Filed with the USPTO as a Receiving Office

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

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US05
Stowers et al.	Confirmation No.: 9576
Application No.: 15/784,258	Examiner: Chanceity N. Robinson
Filed: October 16, 2017	Group Art Unit: 1722

For: RADIATION BASED PATTERNING METHODS

NOTICE OF APPEAL

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

Sir:

In accordance with 37 C.F.R. § 1.191, Applicant hereby appeals to the Patent Trial and Appeal Board from the Final Office Action mailed June 11, 2019, finally rejecting claims 1-19 in the above-identified patent application. The Commissioner is authorized to charge a credit card payment in the amount of **$800.00** to cover the fee is submitted herewith.

Respectfully submitted,

/Peter S. Dardi/

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

Customer No. 62274
Christensen, Fonder, Dardi & Herbert PLLC
33 South Sixth Street
Suite 4540
Minneapolis, Minnesota 55402
Telephone: (404) 949-5730

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.

September 11, 2019	/Peter S. Dardi/
Date	Peter S. Dardi, Ph.D., Reg. #39,650

Electronic Patent Application Fee Transmittal

Application Number:	15784258
Filing Date:	16-Oct-2017
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Peter S. Dardi/Michelle Douglas
Attorney Docket Number:	5063.02US05

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:				
NOTICE OF APPEAL	1401	1	800	800
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**800**

Electronic Acknowledgement Receipt

EFS ID:	37134904
Application Number:	15784258
International Application Number:	
Confirmation Number:	9576
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US05
Receipt Date:	11-SEP-2019
Filing Date:	16-OCT-2017
Time Stamp:	15:56:34
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$800
RAM confirmation Number	E20199AF57118320
Deposit Account	601363
Authorized User	Peter Dardi

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

37 CFR 1.16 (National application filing, search, and examination fees)

37 CFR 1.17 (Patent application and reexamination processing fees)

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	Notice of Appeal Filed	NoticeOfAppeal.pdf	20268 51cc31e7b68cbf980ccaeeb51cc29d9d22f9dc5b	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30440 3064afb748a22b2a6e771047e9ecd9ce8aaa4e4c	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	50708		

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New Applications Under 35 U.S.C. 111

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

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

New International Application Filed with the USPTO as a Receiving Office

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

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US05
Stowers et al.	Confirmation No.: 9576
Application No.: 15/784,258	Examiner: Chanceity N. Robinson
Filed: October 16, 2017	Group Art Unit: 1722

For: RADIATION BASED PATTERNING METHODS

BEFORE THE BOARD OF PATENT TRIAL AND APPEALS BOARD

BRIEF FOR APPELLANT

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For: RADIATION BASED PATTERNING METHODS

BEFORE THE BOARD OF PATENT TRIALS AND APPEALS BOARD
APPEAL BRIEF

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

Sir:

INTRODUCTORY COMMENTS

This is an appeal of the final rejection of claims 1-19. A Final Rejection was mailed June 11, 2019. A Notice of Appeal was filed on September 11, 2019. This Appeal Brief is timely filed.

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.

November 15, 2019
Date

/Diane Bennett/
Diane E. Bennett, Ph.D., Reg. #63,240

REAL PARTY IN INTEREST

The real party in interest in the present appeal is the current assignee, Inpria Corporation.

RELATED APPEALS AND INTERFERENCES

The assignee, Inpria Corporation, has no pending appeals that are related to, would directly affect or be directly affected by, or have a bearing on the Board's decision in the present appeal.

STATUS OF CLAIMS

Claims 1-19 are pending and stand rejected.

STATUS OF AMENDMENTS

As indicated in the Advisory Action of August 16, 2019, the Amendment After Final of August 9, 2019 was not entered with the filing of the present appeal. The amended claims were directed to clarifications, and it is believed that the amendments would have simplified issues for Appeal. Specifically, the Amendment in question removed the references to electron beam radiation in claim 10 that are inconsistent with the present language of claim 1. The Amendment also corrected a typographical error by adding the word "comprises" after the word "further".

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SUMMARY OF CLAIMED SUBJECT MATTER

The presently claimed invention is directed to radiation based patterning methods. Claims 1 and 14 are independent claims on appeal. Claims 9, 13, and 16 are dependent claims that are argued on appeal. The following summary focuses on these five claims. Citations in this section are directed to the application as filed.

Claim 1 is directed to a "method for forming a patterned structure comprising a substrate and a patterned coating material on a surface of the substrate". See Specification page 3, lines 25-27. The method comprises "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". See Specification page 21, lines 20-24; page 3, lines 27-28; and Example 3, page 33, lines 12-15; and Example 4, page 34, lines 29-30. The method also comprises "contacting the irradiated layer with a developing composition to dissolve un-irradiated material to form a patterned coating material according to the selected pattern." See Specification page 3, lines 25-31.

Claim 9 is directed to the method of claim 1 and further comprises "performing a second patterning using the post-patterning condensed structure to form a double patterned structure". See Specification Example 4, page 34, lines 18-20.

Claim 13 is directed to the method of claims 1 and 10. The method further comprises the "radiation sensitive ligands comprise peroxide ligands". See Specification page 3, lines 10-16. The coating material in the method further comprises "metal suboxide cations" and "inorganic polyatomic anions". See Specification Example 3, page 33, lines 10-25 and page 5, lines 18-19, respectively. The method also comprises "the peroxide ligand to metal ion ratio is at least about 2". See Specification page 2, line 29 to page 3, line 1.

Claim 14 is directed to a "method for forming a patterned inorganic material on a substrate". See Specification page 3, lines 10-18. The method comprises a "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". See Specification page 3, lines 4-18. The irradiation creates a differential dissolution rate between irradiated and un-irradiated locations. See Specification page 3, lines 16-17; page 8, lines 9-20; page 11, lines 5-14; and page 24, lines 26-

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28. The coating material is formed by removing solvent from a deposited precursor solution. See Specification, page 10, line 20 to page 11, line 4 and page 14, lines 16-18. The peroxide ligand to metal ion ratio is at least about 2. See Specification, page 3, lines 4-9 and page 8, lines 14-17. The method also comprises heating the coated substrate after irradiation to a temperature of at least about 45ºC prior to contacting the coating with a developing composition. See Specification page 24, line 28 to page 25, line 11.

Claim 16 is directed to the method of claim 14 and further comprises "contacting the coated substrate after heating with a developing composition to remove un-irradiated coating material to form the patterned inorganic material". See Specification page 3, lines 16-18 and 29-31. The method further comprises 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". See Specification page 3, lines 19-24.

GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

1. The rejection of claim 10 under 35 U.S.C. 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.

2. The rejection of claims 1-19 under 35 U.S.C. 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.

3. The rejection of claims 1-19 on the ground of nonstatutory double patenting as being unpatentable over claims 1-27 of U.S. Patent No. 9,176,377 to Stowers et al.

4. The rejection of claims 1-19 on the ground of nonstatutory double patenting as being unpatentable over claims 1-17 of U.S. Patent No. 8,415,000 to Stowers et al.

5. The rejection of claims 1-19 under pre-AIA 35 U.S.C. § 103(a) as being unpatentable over Stowers, "Direct patterning of solution deposited metal oxides", (2008) in view of Stowers et al., “High Resolution, High Sensitivity Inorganic Resists”, (2009) and further view of Meyers et al.,

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WO 2008/082448 A1. Note that WO 2008/082448 is actually to Keszler et al., and Dr. Meyers is listed as the last of five inventors. For consistency with the usage during prosecution, this reference will still be referred to as Meyers.

ARGUMENT

SUMMARY OF LEGAL PRINCIPLES

A. Legal Authority

The Court of Appeals for the Federal Circuit has exclusive appellate jurisdiction for cases arising under the patent law under 28 U.S.C. § 1295 (a)(1). Federal Circuit patent law is subject to review by the U.S. Supreme Court, and the Supreme Court occasionally rules on patent cases that provide ultimate authority for interpreting the patent statutes. "The PTO lacks substantive rulemaking authority." *Koninklijke Philips Electronics N.V. v. Cardiac Science,* 590 F.3d 1326, 1337 (Fed.Cir.2010) "Judicial precedent is as binding on administrative agencies as are statutes. We remind the district court and the [USPTO] Board that they must follow judicial precedent...."). *Id.* at 1137.

B. Indefiniteness

The patent statute at 35 U.S.C. § 112(b) (previously 35 U.S.C. § 112, second paragraph) requires that 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 his invention." "The ultimate conclusion of indefiniteness is one of law, which we are free to review anew on appeal." *In re Warmerdam*, 33 F.3d 1354, 1361 (Fed. Cir. 1994). "The question becomes whether one of ordinary skill in the art would understand what is claimed when the claim is read in light of the specification." *BJ Services Co. v. Halliburton Energy Services, Inc.*, 338 F.3d 1368, 1372 (Fed. Cir. 2003); rehearing and rehearing *en banc* denied October 17, 2003.

"Cognizant of the competing concerns, we read § 112, ¶ 2 [predecessor to section 112(b)] to require that a patent's claims, viewed in light of the specification and prosecution history, inform those skilled in the art about the scope of the invention with reasonable certainty. The definiteness requirement, so understood, mandates clarity, while recognizing that absolute precision is

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unattainable. The standard we adopt accords with opinions of this Court stating that 'the certainty which the law requires in patents is not greater than is reasonable, having regard to their subject-matter.'" *Nautilus, Inc. v Biosig Instruments, Inc.*, 572 U.S. 898, 911, 134 S.Ct. 2120, 2129 (2014).

"The § 112 ¶ 2 requirement strikes a 'delicate balance' between 'the inherent limitations of language' and providing 'clear notice of what is claimed.' *Sonix Technology Co., Ltd. v. Publications International, Ltd.* 844 F.3d 1370, 1377 (Fed. Cir. 2017) citing *Nautilus*, 134 S.Ct. at 2129. "Thus, 'a patentee need not define his invention with mathematical precision in order to comply with the definiteness requirement.'" *Id.* citing *Invitrogen Corp. v. Biocrest Mfg., L.P.*, 424 F.3d 1374, 1384 (Fed. Cir. 2005). "Rather, how much clarity is required necessarily invokes some standard of reasonable precision in the use of language in the context of the circumstances." *In re Packard*, 751 F.3d 1307, 1313 (Fed. Cir. 2014). "The USPTO, in examining an application, is obliged to test the claims for reasonable precision according to these principles." *Id.*

C. Claim Construction

It is well settled that, during patent examination, claims must be given "their broadest reasonable construction 'in light of the specification as it would be interpreted by one of ordinary skill in the art.'" *Phillips v. AWH Corp.*, 415 F.3d 1303, 1317 (Fed. Cir. 2005) quoting *In re Am. Acad. of Sci. Tech. Ctr.*, 367 F.3d 1359, 1364 (Fed. Cir. 2004). "The PTO broadly interprets claims during examination of a patent application since the applicant may 'amend his claims to obtain protection commensurate with his actual contribution to the art.' This approach serves the public interest by reducing the possibility that claims, finally allowed, will be given broader scope than is justified. Applicants' interests are not impaired since they are not foreclosed from obtaining appropriate coverage for their invention with express claim language." *In re Yamamoto*, 740 F.2d 1569, 1571-72 (Fed. Cir. 1984) (internal citations omitted).

However, "[t]he protocol of giving claims their broadest reasonable interpretation during examination does not include giving claims a legally incorrect interpretation." *In re Skvorecz*, 580 F.3d 1262, 1267 (Fed. Cir. 2009). "This [broadest reasonable interpretation] protocol is solely an examination expedient, not a rule of claim construction. Its purpose is to facilitate exploring the metes and bounds to which the applicant may be entitled, and thus to aid in sharpening and clarifying the claims during the application stage, when claims are readily changed." *Id.* "[T]he

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broadest-construction rubric coupled with the term 'comprising' does not give the PTO an unfettered license to interpret claims to embrace anything remotely related to the claimed invention. Rather, claims should always be read in light of the specification and teachings in the underlying patent." *In re Suitco Surface, Inc.*, 603 F.3d 1255, 1260 (Fed. Cir. 2010) (emphasis added). "[T]his court has instructed that any such [broadest reasonable] construction be '*consistent with the specification*, ... and that claim language should be read in light of the specification as it would be interpreted by on of ordinary skill in the art.'" *Id.* citing *In re Bond*, 910 F.2d 831, 833, 15 USPQ2d 1566, 1567 (Fed. Cir. 1990) (quoting *In re Sneed*, 710 F.2d 1544, 1548 (Fed. Cir. 1983)) (emphasis added by *In re Suitco Surface, Inc.*).

D. Obviousness

1. Burden of Proof

"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.'" *In re Ochiai*,71 F.3d 1565, 1569 (Fed. Cir. 1995). "[T]he ultimate determination of patentability is made on the entire record." *In re Oetiker,* 977 F.2d 1443, 1445 (Fed. Cir. 1992). "After evidence or argument is submitted by the applicant in response, patentability is determined on the totality of the record, by a preponderance of evidence with due consideration to persuasiveness of argument." *Id.* "Obviousness is a mixed question of fact and law. Although the Board's ultimate conclusion that the claims are not obvious is a legal determination subject to de novo review, the subsidiary factual findings are reviewed for substantial evidence." *Intelligent Bio-Systems, Inc. v. Ullunina Cambridge Ltd.*, 821 F.3d 1359, 1366 (Fed. Cir. 2016)(*inter partes review*).

The objective analysis for applying 35 U.S.C. § 103 requires: (1) determination of the scope and content of the prior art are; (2) ascertaining the differences between the prior art and claims at issue; (3) resolving the level of ordinary skill in the art and (4) against the previous background, determining the obviousness or nonobviousness of the subject matter." *KSR Intern. Co. v. Teleflex Inc.*, 550 U.S. 398, 400 (2007) citing *Graham v. John Deere Co. of Kansas City*, 383 U.S. 1, 17–18, 86 S.Ct. 684, 15 L.Ed.2d 545.

2. *Prima Facie* Obviousness

"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). "When the references cited by the examiner fail to establish a *prima facie* case of obviousness, the rejection is improper and will be overturned." *In re Ochiai*, 71 F.3d 1565, 1569 (Fed. Cir. 1995).

Significantly, *prima facie* obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. *In re Ochiai*, 37 USPQ 1127, 1131 (Fed. Cir. 1995). Also, the prior art reference (or references when combined) must teach or suggest the particular combination or modification. The teaching or suggestion to make the claimed combination and reasonable expectation of success must both be found in the prior art, and not based on applicant's disclosure. In re Vaeck, 947 F.2d 488, 20 USPQ2d 1438 (Fed. Cir. 1991). "It is impermissible, however, to simply engage in a hindsight reconstruction of the claimed invention, using applicant's structure as a template and selecting elements from references to fill the gaps." In re Gorman, 18 USPQ2d 1885, 1888 (Fed. Cir. 1991).

"An applicant may rebut a *prima facie* case of obviousness by providing a 'showing of facts supporting the opposite conclusion.' Such a showing dissipates the *prima facie* holding and requires the examiner to 'consider all of the evidence anew.'" *In re Kumar*, 418 F.3d 1361, 1368 (Fed. Cir. 2005), quoting *In re Piasecki*, 745 F.2d 1468, 1472 (Fed. Cir. 1984) and *In re Rinehart*, 531 F.2d 1048, 1052 (CCPA 1976). "Rebuttal evidence may show, for example, that the claimed invention achieved unexpected results relative to the prior art, *In re Geisler*, 116 F.3d 1465, 1469-70 (Fed. Cir. 1997); that the prior art teaches away from the claimed invention, *Id.* at 1471; that objective evidence (e.g., commercial success) supports the conclusion that the invention would not have been obvious to a skilled artisan, *Piasecki*, 745 F.2d at 1475; or that the prior art did not enable one skilled in the art to produce the now-claimed invention, *In re Payne*, 606 F.2d 303, 314-15 (CCPA 1979)." *In re Kumar*, 418 F.3d at 1368.

3. Claims Must be Read as a Whole

When determining the scope of the claims for the purpose of 35 U.S.C. § 103, "[e]ach claimed invention must be considered as a whole." *W.L. Gore & Associates, Inc. v. Garlock, Inc.*,

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721 F.2d 1540, 1548 (Fed. Cir. 1983). The question presented in 35 U.S.C. § 103 is whether the inventions set forth in the individual claims "each as a whole, would have been obvious to one of ordinary skill in the art when they were made," *Stratoflex, Inc. v. Aeroquip Corp.*, 713 F.2d 1530, 1537 (Fed. Cir. 1983). "A patent may not be obtained ... if the differences between the [claimed invention] and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person of ordinary skill in the art." *Ecolochem, Inc. v. Southern California Edison Company*, 227 F.3d 1361, 1371 (Fed. Cir. 2000), citing 35 U.S.C. § 103(a).

4. There Must Be Some Teaching or Suggestion in the Art to Modify the Teachings of the Cited References

"Obviousness is tested by what the combined teachings of the references would have suggested to those of ordinary skill in the art." *In re Fine*, 837 F.2d 1071, 1076 (Fed. Cir. 1988) (internal quotation marks omitted) citing *In re Keller*, 642 F.2d 413, 425 (CCPA 1981). The Supreme Court has clarified that the examination of the teachings of the prior art should not be performed rigidly. Specifically, "a court must ask whether the improvement is more than the predictable use of prior art elements according to their established functions." *KSR Int'l Co.*, 550 U.S. at 402. "Often, it will be necessary for a court to look to interrelated teachings of multiple patents; the effects of demands known to the design community or present in the marketplace; and the background knowledge possessed by a person of ordinary skill in the art, all in order to determine whether there was an apparent reason to combine the known elements in the fashion claimed by the patent at issue." *Id.* at 402. The Court noted that "it can be important to identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does. This is so because inventions in most, if not all, instances rely upon building blocks long since uncovered, and claimed discoveries almost of necessity will be combinations of what, in some sense, is already known." *Id.*, at 402. "Under the correct analysis, any need or problem known in the field of endeavor at the time of invention and addressed by the patent can provide a reason for combining the elements in the manner claimed." *Id.*, at 403.

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ANALYSIS

1. The rejection of claim 10 under 35 U.S.C. under 35 U.S.C. §112(b) or 35 U.S.C. § 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention.

Claim 10 was rejected under 35 U.S.C. §112(b) or 35 U.S.C. 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. Appellant maintains that claim 10 is appropriately clear under the law and requests reversal of the rejection based on the following comments.

Applicant notes that the un-entered Amendment After Final of June 11, 2019 attempted to amend claim 10 to remove the reference to e-beam radiation. While Appellant respectfully believes that this amendment would have simplified issues for appeal, the Examiner did not enter this amendment for the purposes of appeal. Nevertheless, Appellant respectfully maintains that the claim is sufficiently clear such that a person of ordinary skill in the art would understand the claim. Of course, entry of the amendment would have rendered such issues moot.

The Examiner asserted a lack of antecedent basis. But with all due respect, there is no antecedent reference for the property noted by the Examiner. The claim merely states a property of the coating under irradiation with e-beam radiation. Claim 10 does not refer to "the" e-beam radiation. Since there is no antecedent reference at all, respectfully there cannot be a lack of antecedent basis.

Thus, Appellant respectfully maintain that claim 10 is clear to a person of ordinary skill in the art. Since there is no antecedent reference, there cannot be an insufficient antecedent basis. Respectfully, the rejection seems to have been based on a misunderstanding. Appellant respectfully requests reversal of the rejection of claims 10 under 35 U.S.C. § 112 as being indefinite.

2. The rejection of claims 1-19 under 35 U.S.C. 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

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distinctly claim the subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention.

Claims 1-19 were rejected under 35 U.S.C. §112(b) or 35 U.S.C. 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. Appellant maintains that claims 1-19 are appropriately clear under the law and requests reversal of the rejection based on the following comments.

The Examiners asserted that the term about is a "relative term which renders the claim indefinite" and also "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".

Indefiniteness is a question of law that is reviewed without deference. *Cardiac Pacemakers, Inc. v. St. Jude Medical, Inc.*, 296 F.3d 1106, 1113 (Fed. Cir. 2002). "The definiteness inquiry focuses on whether those skilled in the art would understand the scope of the claim when the claim is read in light of the rest of the specification." *Union Pac. Res. Co. v. Chesapeake Energy Corp.,* 236 F.3d 684, 692 (Fed.Cir.2001), internal citations omitted. "Definiteness problems often arise when words of degree are used in a claim. That some claim language may not be precise, however, does not automatically render a claim invalid." *Seattle Box Co., Inc. v. Indus. Crating & Packing, Inc.,* 731 F.2d 818, 826 (Fed.Cir.1984).

In the context of real (non-integer) numbers, any values necessarily reflect imprecision in the evaluation of such values, and such condition would be recognized by a person of ordinary skill in the art. This reality has been acknowledged in the case law. "BJ Services argues that the term "about" is intended to encompass the range of experimental error that occurs in any measurement and that one of skill in the art would readily understand the range that "about 0.06" was intended to include." *BJ Services Co. v. Halliburton Energy Services, Inc.*, 338 F.3d 1368, 1372 (Fed. Cir. 2003). In the *BJ Services* case, both sides presented evidence regarding the ranges of experimental error. Based on this evidence, the court held that the jury could reasonably find that the expression "about 0.06" was clear and definite.

"Rather, how much clarity is required necessarily invokes some standard of reasonable precision in the use of language in the context of the circumstances." *In re Packard*, 751 F.3d

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1307, 1313 (Fed. Cir. 2014). "The USPTO, in examining an application, is obliged to test the claims for reasonable precision according to these principles." *Id.* "It makes good sense, for definiteness and clarity as for other validity requirements, for the USPTO initially to reject claims based on a well-founded prima facie case of lack of clarity (in its several forms) based on the perspective of one of ordinary skill in the art in view of the entire written description and developing prosecution history" *Id.* at 1312.

In the relevant context, a person of ordinary skill in the art would have an advanced chemistry or related degree or a lesser degree and significant years of experience. Appellant notes that the present application is a continuation of U.S. patent application serial number 12/850,867 (now U.S. patent 9,176,377). Many of the issued claims provide clarity for one of ordinary skill in the art through the term "about." Significantly, the present application is connected to U.S. patent 9,176,377 through a terminal disclaimer that was filed on August 20, 2019.

Issued claims for U.S. patent 9,176,377 include the following recitations of the term "about" (underlining added):

- molar concentration ratio of ligands to metal suboxide cations of at least about 2 (claim 1)
- for at least about 24 hours (claim 1)
- metal suboxide cation concentration from about 0.01 M to about 1.4 M (claim 1)
- metal suboxide cation concentration from about 0.1 M to about 1.0 M (claim 2)
- molar concentration ratio of ligands to metal suboxide cations of at least about 5 (claim 6)
- molar concentration ratio of ligands to metal suboxide cations of at least about 7 (claim 7)
- molar concentration ratio of ligands to metal suboxide cations is at least about 2 (claim 9)
- at least about 5 minutes (claim 9)
- at least about 15 minutes (claim 10)
- at least about 45°C (claim 11)
- wavelength of about 193 nm (claim 13)
- molar concentration ratio of ligands to metal suboxide cations of at least about 5 (claim 17)
- average thickness from about 1 nm to about 40 nm (claim 19)
- no more than about 75 seconds (claim 23)
- concentration of tetramethyl ammonium hydroxide of about 2.38 weight percent (claim 25)

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Considering the matter further and as a demonstration of this established standard for clarity, the below excerpts of examples in the instant application (underlining added) serve to remind one of ordinary skill in the art of the existence of fluctuations to target values which are the nature of this art. The term "about" therefore serves as a necessary boundary for clearly defining the scope of the invention.

[0102] 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.times.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.

On the present facts, there is no close prior art. In the context of the present measurements, a person of ordinary skill in the art is appropriately apprised of the scope of the presently claimed invention. "('When prima facie obviousness is established and evidence is submitted in rebuttal, the decision-maker must start over.... An earlier decision should not, as it was here, be considered as set in concrete, and applicant's rebuttal evidence then be evaluated only on its knockdown ability.... [A] final finding of obviousness may of course be reached, but such finding will rest upon evaluation of all facts in evidence, uninfluenced by any earlier conclusion reached....')); *see also In re Jung,* 637 F.3d 1356, 1362 (Fed.Cir.2011)." *In re Packard*, 751 F.3d at 1312, quoting *In re Rinehart,* 531 F.2d 1048, 1052 (CCPA 1976). "The same approach to making the examination process work is an appropriate one for addressing the question of indefiniteness." *In re Packard* at 1312. "Rebuttal is merely "a showing of facts supporting the opposite conclusion", *In re Heldt,* 433 F.2d 808, 811, 167 USPQ 676, 678 (CCPA 1970)" *In re Piasecki*, 745 F.2d 1468, 1472 (Fed. Cir. 1984).

The Examiner provided rebuttal arguments on pages 8-10 of the final office Action. The Examiner refers to Example 3 of the present application to support her arguments. In Example 3 it is stated that the "coating material was deposited at a thickness form '[sic, from] 10-50 nm." The Examiner also points to statements in paragraph [0066] of the specification. In paragraph [0066], it is stated that the "thickness can be evaluated using non-contact methods of x-ray reflectivity

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and/or elipsometry based on optical properties of the film." This paragraph also provides general ranges of thicknesses. In the context of Example 3, a person of ordinary skill in the art will understand that the reference to 10-50 nm thickness refers either to multiple samples that were formed for testing or to the fact that the thicknesses were only estimated based on the amount of material used without a direct measurement of the thicknesses, and not to the uncertainty of performing one measurement. Referring to conventional ellipsometry instrumentation, FilmTek 2000 PAR-SE has a stated accuracy for resist of 0.02% (https://sci-soft.com/product/filmtek-2000-par-se/). So for a 50 nm thick resist, the measurement error would be around 1 nm. A person of ordinary skill in the art would readily understand this order of magnitude error being reflected in such a measurement.

With all due respect, it is believed that the rejection is based at least in part on a misunderstanding of the discussion in Example 3. Appellant believes that the facts support the position that a person of ordinary skill in the art would readily understand the scope and meaning of the claims. Thus, Appellant respectfully maintain that claims 1-19 are clear to a person of ordinary skill in the art. Based on the indication of the scope of the language in the specification, the rejection is based on clear reversible error. Appellant respectfully requests reversal of the rejection of claims 1-19 under 35 U.S.C. § 112 as being indefinite.

3. The rejection of claims 1-19 on the ground of nonstatutory double patenting as being unpatentable over claims 1-27 of U.S. Patent No. 9,176,377 to Stowers et al.

The Examiner rejected claims 1-19 on the ground of nonstatutory double patenting over claims 1-27 of U.S. Patent No. 9,176,377. A terminal disclaimer has been filled, obviating the rejection. Withdrawal of the rejection is respectfully submitted.

4. The rejection of claims 1-19 on the ground of nonstatutory double patenting as being unpatentable over claims 1-17 of U.S. Patent No. 8,415,000 to Stowers et al.

The Examiner rejected claims 1-19 on the ground of nonstatutory double patenting over claims 1-17 of U.S. Patent No. 8,415,000. The Examiner stated that the instant claims and patent

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‘000 recite the same method of forming a patterned inorganic material on a substrate. While Appellant respectfully disagrees with the Examiner's assertion of obviousness over the claims of the '000 patent, a terminal disclaimer is filed with this Appeal Brief to advance prosecution. Appellant believes that this rejection is then presently moot. Appellant respectfully requests withdrawal of the rejection of claims 1-19 under nonstatutory obviousness-type double patenting as being unpatentable over the ‘000 patent.

5. The rejection of claims 1-19 under pre-AIA 35 U.S.C. § 103(a) as being unpatentable over Stowers, "Direct patterning of solution deposited metal oxides", (2008) (hereinafter Stowers) in view of Stowers et al., “High Resolution, High Sensitivity Inorganic Resists”, (2009) (hereinafter Stowers et al.) and further view of Meyers et al., WO 2008/082448 A1 (hereinafter Meyers).

With all due respect, the combined teachings of Stowers, Stowers et al., and Meyers do not render Appellant’s claimed invention *prima facie* unpatentable since they do not teach or suggest all of the features of Appellant’s claimed invention. The Examiner's position is based on clear reversible errors, as explained in the following. With all due respect, on the record as a whole, the Examiner has failed to establish obviousness by a preponderance of the evidence, and the analysis follows.

Claims 2-13 depend from independent claim 1, and claims 15-19 depend from independent claim 14. The two separate claim groups are argued separately. Furthermore, while claims 2-13 are patentable for the reasons to be presented for claim 1, additional separate arguments are also presented for claims 9 and 13. Similarly, while claims 15-19 are patentable for the reasons presented for claim 14, additional separate arguments are presented for claim 16.

Claims 1-13

With respect to claim 1, Appellant’s claimed method is directed to patterning with UV or EUV radiation. Also, while electron beam irradiation was removed form claim 1, the rejection continues to refer to electron-beam irradiation. Seemingly, the explanation for this was the reference to electron-beam irradiation in dependent claim 10. But as explained above under the 112 issues, claim 10 is directed to properties of the coating and not to indicating that the claimed

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method is performed with electron-beam irradiation. Also, Appellant attempted to remove the electron-beam language from claim 10 to avoid any misunderstanding, but the amendment was not entered even though it would have simplified issues for appeal.

Stowers is a Ph.D. Thesis, and Stowers et al. is basically chapter 2 of the Thesis which had as authors Stowers and Professor Keszler. Claim 1 is directed to patterning with UV or EUV radiation. In the Final Office Action dated 6/11/2019, the Examiner stated on page 4 that Stowers teaches a method for forming a patterned structure on a substrate, the method involving "irradiating the coated substrate to a pattern of irradiation to condense the coating at the irradiated locations (with 30keV electron beam; which meets the limitation of instant claim 13 [sic, claim 10?])." Whether or not Stowers meets the limitation of claim 10, the Examiner respectfully has ignored the claimed method of claim 1.

The Examiner asserted in the response to Appellant's arguments on page 10 of the Office Action that "[i]nstant claim 12, which depends from claim 1 recites irradiating the coated substrate using electron beam irradiation." Appellant believes that the Examiner was referring to claim 10. Claim 10 is a dependent claim characterizing the material used in the method. The stipulation that the material is altered by an e-beam does not change the indication in claim 1 that the patterning is performed with UV or EUV radiation. Whether or not claim 10 is amended to remove the reference to e-beam in claim 10, claim 10 is still a description of a property of the coating material and not directed to how the claimed method is performed. In any case, the cited references also do not teach the UV/EUV dose for patterning.

While respectfully, the Examiner has clearly failed to articulate a *prima facie* case of obviousness which is reversible error, Appellant will direct their analysis to the references in view of the language of claim 1. Stowers et al. teaches on the use of electron beam irradiation, as summarized in the abstract "New inorganic electron-beam resists have been developed…". Additionally, Meyers teaches primarily the use of an electron beam. In Chapter 3, Stowers makes some reference to EUV irradiation, and Meyers makes some reference to the use of a deuterium lamp. Nevertheless, the combined teachings of the references fall far short of suggesting the presently claimed invention as explained in the following, representing additional reversible errors. Appellant requests reconsideration of the rejection based on the following comments.

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As noted above, Stowers et al. does not teach UV patterning. Meyers is focused also on e-beam patterning, although Example 7 of Meyers has four sentences and two figures directed to patterning with light from an unfiltered deuterium lamp and the detailed description has a brief mention of the use of a deuterium lamp. With respect to the EUV doses, Appellant refers to Stowers Chapter 3, where some preliminary work involving EUV pattering is described. Stowers Chapters 2 and 4 discuss e-beam patterning, in contrast to Chapter 3, which discusses EUV patterning. Stowers Chapter 2 overlaps significantly with Stowers et al. Appellant notes that the authors of Stowers and Stowers et al. are present inventors. Stowers and Stowers et al. are evidence of the present invention being a manifestation of the inventors' continued exploration.

The rejection in the final Office Action asserts on page 4 that Stowers teaches irradiation "with 30keV electron beam; which meets the limitation of instant claim 13 [sic, 10?]." With all due respect, claim 13 does not recite e-beam irradiation, and claim 1 is directed to exclusively UV or EUV irradiation. While Stowers provides some teaching of EUV patterning in Chapter 3, Stowers does not teach the claimed dosage ranges in Appellant's claim 1. Stowers et al. is directed to e-beam patterning and also does not provide UV or EUV doses. Meyers also does not teach UV or EUV doses, so this feature of claim 1 is absent from the cited references.

On page 5 of the Office Action, the Examiner admits that "Stowers do not explicitly recite the thickness or differential dissolution as instantly claimed." The Examiner cites Stowers et al. for teaching the thickness. But respectfully this assertion regarding Stowers et al. is incorrect for two reasons. First, the Examiner asserts that 35 nm is about 30 nm, but reference to Fig. 4 of Stowers et al. and the discussion on page 21 of the present application suggests that the thickness can be evaluated on the order of one nm. A person of ordinary skill in the art would not understand a 5 nm different to fall within the scope of about 30 nm. Second, Stowers et al. use their thickness of patterning coating for performing e-beam patterning. The Examiner asserts that Stowers et al. teach that "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)." With all due respect, Stowers et al. does not say that. The only reference to UV based patterning in the Introduction of Stowers et al. is in the context of using masks made by e-beam lithography. "All other forms of lithography, i.e. extreme ultra-violet, deep ultra-violate, and nano-

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imprint lithography, depend on the capabilities of electron-beam lithography to produce masks and templates that are required in their implementation." Stowers et al. does not suggest the use of this radiation sensitive coating for UV patterning.

Meyers teaches a general description of patterning on pages 25-32. On page 28, lines 8-13, Meyers gives a broad discussion of thicknesses as being from 1 nm to 100 nm. In Example 7, Meyers describes thicknesses of a titanium oxide coating (15-50 nm) for processing with a deuterium lamp and $HfO_{2-x}SO_4)_x$, with a thickness from 30-60 nm for e-beam patterning. The thickness ranges in Meyers seem to imply that these were not directly measured, but were estimated from material deposited. Stowers described coatings with thicknesses from 30 to 35 nm in Chapter 3. For an understanding of the present invention, it is significant to understand the correlation between dose and thickness since these parameters are not separately adjustable.

The ability to form a pattern with thinner resist layers involves a sufficient etch contrast. If the etch contrast is insufficient, then the resist is removed by the etching process before a pattern is sufficiently formed. Lowering the radiation dose can lower the etch contrast, which would then correspondingly suggest the use of a thicker resist coating. The innovation of the present invention is the ability to form a coating with a sufficient etch contrast to lower the UV/EUV radiation dose while maintaining the ability to use a thinner coating.

With respect to the claimed radiation dose, the Examiner cites Meyers. This seems to be based on a misunderstanding. Specifically, the Office Action refers to a teaching in Meyers of an electron beam "dose level 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." With all due respect, electron beam doses in microcuries does not directly relate to UV doses in millijoules. Meyers does not teach UV doses. The other cited references similarly do not teach UV or EUV doses in the claimed range. Stowers exemplifies at Fig. 3.7 an EUV dose of 289 mJ/cm^2.

"When the references cited by the examiner fail to establish a *prima facie* case of obviousness, the rejection is improper and will be overturned." *In re Ochiai*, 71 F.3d 1565, 1569 (Fed. Cir. 1995). "A *prima facie* case of obviousness is established when the teachings from the prior art itself would appear to have suggested the claimed subject matter to a person of ordinary skill in the art." *In re Rijckaert*, 9 F.3d 1531, 1533 (Fed. Cir. 1993), internal citations omitted.

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None of the cited references teach patterning with the claimed dosage range for UV/EUV light. Claim 1 further recites etching to form a pattern, which is not independent of the dose or the thickness. The three pieces of the claim are interrelated: the ability to form a pattern, the radiation dose and the thickness.

The teachings of the cited references do not provide a reasonable expectation of success because they do not teach materials with a sufficient etch contrast. The teaching or suggestion to make the claimed combination and reasonable expectation of success must both be found in the prior art, and not based on applicant's disclosure. In re Vaeck, 947 F.2d 488, 20 USPQ2d 1438 (Fed. Cir. 1991). "The reasonable expectation of success requirement refers to the likelihood of success in combining references **to meet the limitations of the claimed invention**." *Cumberland Pharmaceuticals Inc. v. Mylan Institutional LLC*, 846 F.3d 1213, 1222 (Fed. Cir. 2017) (*inter partes review*) (emphasis added), quoting *Intelligent Bio-Systems, Inc. v. Illumina Cambridge Ltd.*, 821 F.3d 1359, 1367 (Fed. Cir. 2016). "[F]ailure to consider the appropriate scope of the patent's *claimed invention* in evaluating the reasonable expectation of success ... constitutes a legal error that [is] review[ed] without deference." *Intelligent Bio-Systems*, 821 F.2d at 1367, quoting *Allergan, Inc. v. Apotex Inc.*, 754 F.3d 952, 966 (Fed. Cir. 2014) (emphasis in original).

With all due respect, substantial evidence on the record does not support a finding of a reasonable expectation of success. "The substantial evidence standard 'involves examination of the record as a whole, taking into account evidence that both justifies and detracts from an agency's decision.' *In re Gartside*, 203 F.3d at 1312." *OSI Pharmaceuticals, LLC v. Apotex, Inc.*, 939 F.3d 1375, 1384 (Fed. Cir. 2019). On page 5 of the final Office Action, the Examiner acknowledges that Stowers does not teach the "differential dissolution as instantly claimed." The Examiner refers to Stowers et al. for this feature, but Stowers et al. is directed to electron beam patterning. When the evidence does not support a finding of a reasonable expectation of success, "[i]t is only with the benefit of hindsight that a person of skill in the art would have had a reasonable expectation of success in view of the asserted references." *Id.* Since the references do not provide a reasonable expectation of success, the rejection is based on clear reversible error.

Since the references do not teach all of the features of Appellant's claim 1 and do not provide a reasonable expectation of success, the combined teachings of Stowers, Stowers et al., and Meyers do not render claim 1 *prima facie* obvious.

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Claim 9

While claim 9 is patentable for the reasons presented for claim 1, Appellant provides these additional and separate arguments for claim 9. Claim 9 further specifies that the claimed method further comprises "performing a second patterning using the post-patterning condensed structure to form a double patterned structure." Appellant could not identify any arguments presented against claim 9 in the final Office Action. The cited references do not seem to teach this feature. Respectfully, there would seem to be no basis for rejection of claim 9 on the record. "When the references cited by the examiner fail to establish a *prima facie* case of obviousness, the rejection is improper and will be overturned." *In re Ochiai*, 71 F.3d 1565, 1569 (Fed. Cir. 1995). The rejection of claim 9 is based on clear reversible error of law.

Claim 13

While claim 13 is patentable for the same reasons as claim 1, Appellant presents these additional and separate arguments for claim 13. Claim 13 depends directly from claim 12, which depends from claim 1. Claim 13 further specifies in combination with claim 12 that "the radiation sensitive ligands comprise peroxide ligands, and wherein the coating material further comprises metal suboxide cations [claim 12]" and that "the coating material further comprises inorganic polyatomic anions and wherein the peroxide ligand to metal ion ratio is at least about 2."

In the final office Action on page 6 it is stated that "Stowers et al. recognize that metal ion to peroxide (ligand) is 1:0.5. 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 [sic]. 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 the existence of non-obviousness except advantageous effects compared with the invention of Reference." With all due respect, this position of the Examiner is based on both legal and factual reversible errors.

With respect to factual errors, Appellant has noted that exceptional and unexpected results have been achieved. See related patent US 8,415,000, in which claim 1 reads as follows:

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1. 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 recognizes previously unobtainable patterning features using any type of patterning resist. This exceptional result has been acknowledged by the USPTO.

Stowers and Stowers et al. refer to the stoichiometric ligand ratio of 1 metal to 0.5 peroxide ligands. Meyers discusses peroxide and other ligands generally, without any specific information provided. There are no teachings in the cited references that would point a person of ordinary skill in the art to the claimed range of peroxide ligands.

Claims 14-19

Claims 15-19 depend from claim 14. With respect to claim 14, Examiner states that Stowers et al. disclose that peroxide inhibits condensation of metal oxides, and it is obvious for those skilled in the art to predict function effects of stability with respect to phase separation in the invention of this application by increasing concentration ratio of peroxide. Stowers et al. teaches a stoichiometric ratio of 1 metal ion to 0.5 ligands of peroxide. With all due respect, Stowers et al. does not teach that the peroxide ratio is a results effective variable. The Examiner responds to this on page 10 of the Final Office Action dated 6/11/2019 by asserting that Appellant has not shown "exceptional results." If *prima facie* obviousness has not been shown, then Appellant has no need to rebut the rejection. "When the references cited by the examiner fail to establish a *prima facie* case of obviousness, the rejection is improper and will be overturned." *In re Ochiai*, 71 F.3d 1565, 1569 (Fed. Cir. 1995). "A patent may not be obtained ... if the differences between the [claimed invention] and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person of ordinary skill in the art." *Ecolochem, Inc. v. Southern California Edison Company*, 227 F.3d 1361, 1371 (Fed. Cir. 2000), citing 35 U.S.C. § 103(a). The Examiner's failure to establish *prima facie* obviousness is a reversible error of law.

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Furthermore, the Appellant has demonstrated that exceptional and unexpected radiation-induced selective desorption of the coating material can be achieved by increasing the peroxide ligand concentrations by at least a factor of four. The innovative use of the peroxide ligand in the present application requires a stoichiometric ratio of 1 metal ion to at least about 2 ligands of peroxide. This is a patentable improvement not suggested by the cited art. This improved processing has enabled the previously unachievable patterned structures that are claimed in Appellant's U.S. Patent 8,415,000 as well as Korean Patent 101364953. In Appellant's current application, claim 14 recites the peroxide ligand to metal ion ratios which are part of the specific method that enables the achievement of the improved results.

"While it may ordinarily be the case that determination of optimum values for parameters of prior art process would be at least prima facie obvious, that conclusion depends upon what prior art discloses with respect to those parameters and, if prior art disclosure suggests the outer limits of the range of suitable variables, and that the optimum resides within that range, and if there are indicates elsewhere that in fact that optimum should be sought within that range, determination of optimum values outside that range may not be obvious." *In re Sebek*, 465 F.2d 904, 907 (CCPA 1972). "While a rejection based on ranges approaching each other might well be appropriate where there is a teaching in the prior art that the end points of the prior art range are approximate, or can be flexibly applied, the PTAB cites to no such evidence. And, Appellees are not able to cite to any evidence of such a teaching before us. Indeed, if anything, Maugans emphasizes limiting the amount of the first polymer, as increasing such amount negatively affects the spinnability and fabric strength." *In re Patel*, 566 Fed. Appx. 1005, 1009-1011 (Fed. Cir. 2014). Unpublished Federal Circuit cases issuing after January 1, 2007 can be cited under Fed. Rule of Appellate Procedure 32.1. See also *In re Applied Materials, Inc.*, 692 F.3d 1289 (Fed. Cir. 2012).

Since Stowers et al. does not teach that the peroxide ratio is a results effective variable and does not suggest the claimed range, *prima facie* obviousness has not been established, and any showing of *prima facie* obviousness has been rebutted with a showing of unexpected results. Appellant respectfully has established that the rejection is based on clear reversible error. There is no teaching, suggestion, or motivation that the claimed ranges of peroxide ligand rations would be of interest. Since the cited art does not motivate the modification of their teachings, the claims are not *prima facie* obvious and maintenance of the rejection is clear error of law. Furthermore,

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the unexpected results shown by Appellant would rebut any showing of obviousness, such that a review of the evidence as a whole does not support obviousness.

"('When prima facie obviousness is established and evidence is submitted in rebuttal, the decision-maker must start over.... An earlier decision should not, as it was here, be considered as set in concrete, and applicant's rebuttal evidence then be evaluated only on its knockdown ability.... [A] final finding of obviousness may of course be reached, but such finding will rest upon evaluation of all facts in evidence, uninfluenced by any earlier conclusion reached....')); *see also In re Jung,* 637 F.3d 1356, 1362 (Fed.Cir.2011)." *In re Packard*, 751 F.3d at 1312, quoting *In re Rinehart,* 531 F.2d 1048, 1052 (CCPA 1976).

Appellant has noted clear reversible error in that the evidence does not establish *prima facie* obviousness and that unexpected improvements have been shown. Appellant respectfully requests reversal of the rejection of claims 14-19.

Claim 16

While claim 16 is patentable for all of the reasons presented above for claim 14 from which it depends, Appellant presents the following additional and separate arguments directed to the specific features of claim 16. Claim 16 further specifies that "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." Appellant could identify no discussion of this claim in the final Office Action. It is respectfully believed that no basis has been provided for rejection of this claim. Since *prima facie* obvious has clearly not been established for this claim, maintenance of this rejection is based on clear reversible error. Appellant respectfully requests an explanation of the rejection of this claim or its allowance.

Summary

For the reasons discussed above the combined teachings of Stowers, Stowers et al, and Meyers do not render Appellant's claimed invention *prima facie* obvious. While not needed on the present evidence, unexpected improved results have also been presented. Based on the evidence of record, Appellant has established clear reversible error with respect to the rejections. Appellant respectfully requests reversal of the rejection of the claims 1-19 under pre-AIA 35

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U.S.C. 103 (a) as being unpatentable over Stowers, in view of Stowers et al. and further in view of Meyers.

REQUEST FOR RELIEF

Appellant believes that the Patent Office has failed to meet its burden of persuasion with respect to unpatentability of any of the claims on the present record. Thus, Appellant respectfully requests the reversal of the rejections of claims and advancement of the application to allowance.

Respectfully submitted,

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CLAIMS APPENDIX

1. (Previously Presented) 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; and

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

2. (Original) The method of claim 1 wherein the irradiation is performed with EUV at a dose of no more than about 90 mJ/cm^2.

3. (Previously Presented) The method of claim 1 wherein the selected pattern has a pitch of no more than about 60 nm.

4. (Original) The method of claim 1 wherein the developing composition comprises tetramethyl ammonium hydroxide.

5. (Original) The method of claim 1 wherein following exposure an exposed coating region is insoluble in an aqueous base.

6. (Original) The method of claim 1 wherein following exposure an exposed coating region is soluble in an organic solvent.

7. (Original) The method of claim 1 further comprising heating the coated substrate after irradiation to a temperature of at least about 45ºC prior to contacting the irradiated layer with the developing composition.

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8. (Original) The method of claim 1 further comprising heating the substrate with the patterned coating material to a temperature from about 150ºC to about 600ºC for from one minute to 25 minutes to form a post-patterning condensed structure.

9. (Original) The method of claim 8 further comprising performing a second patterning using the post-patterning condensed structure to form a double patterned structure.

10. (Previously Presented) The method of claim 1 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.

11. (Original) The method of claim 10 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.

12. (Original) The method of claim 10 wherein the radiation sensitive ligands comprise peroxide ligands, and wherein the coating material further comprises metal suboxide cations.

13. (Previously Presented) The method of claim 12 wherein the coating material further comprises inorganic polyatomic anions and wherein the peroxide ligand to metal ion ratio is at least about 2.

14. (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,

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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 45ºC prior to contacting the coating with a developing composition.

15. (Original) The method of claim 14 further comprising contacting the coated substrate after heating with a developing composition to remove un-irradiated coating material to form the patterned inorganic material.

16. (Original) The method of claim 15 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.

17. (Original) The method of claim 14 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.

18. (Original) The method of claim 14 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.

19. (Original) The method of claim 14 wherein the coating has an average thickness of about 5 nm to about 30 nm.

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RELATED PROCEEDINGS APPENDIX

None.

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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US05
Stowers et al.	Confirmation No.: 9576
Application No.: 15/784,258	Examiner: Chanceity N. Robinson
Filed: October 16, 2017	Group Art Unit: 1722
For: RADIATION BASED PATTERNING METHODS	

PETITION FOR EXTENSION OF PERIOD FOR RESPONSE
UNDER 37 C.F.R. § 1.136(a)

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

Sir:

Pursuant to 37 C.F.R. § 1.136(a), an extension of time of one (1) month (from November 11, 2019 to December 11, 2019) within which to respond to the Notice of Appeal dated September 11, 2019 is requested. The Commissioner is authorized to charge to a credit card in the amount of **$200.00** for the extension fee. The Commissioner is authorized to charge Deposit Account No. 60-1363 for any underpayments, overpayments or additionally required fees.

Respectfully submitted,

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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.

November 15, 2019	/Diane Bennett/
Date	Diane E. Bennett, Ph.D., Reg. #63,240

Electronic Patent Application Fee Transmittal

Application Number:	15784258
Filing Date:	16-Oct-2017
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Diane Elizabeth Bennett/Michelle Douglas
Attorney Docket Number:	5063.02US05

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($)
Extension - 1 month with $0 paid	1251	1	200	200
Miscellaneous:				
			Total in USD ($)	**200**

Electronic Acknowledgement Receipt

EFS ID:	37760397
Application Number:	15784258
International Application Number:	
Confirmation Number:	9576
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Diane Elizabeth Bennett
Filer Authorized By:	
Attorney Docket Number:	5063.02US05
Receipt Date:	15-NOV-2019
Filing Date:	16-OCT-2017
Time Stamp:	10:15:27
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$200
RAM confirmation Number	E2019AEA17287074
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	Appeal Brief Filed	AppealBrief.pdf	174367 7f2bec0d4c21b0dc0d58931874f895bc49e1beff	no	29
Warnings:					
Information:					
2	Extension of Time	ExtensionOfTime-1.pdf	20622 96d80794267e4491082df752ba016e39d3e1d13f	no	1
Warnings:					
Information:					
3	Fee Worksheet (SB06)	fee-info.pdf	30922 2fdbb4dbeee34d63aee4405d490accc67c4a35fd	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	225911		

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.

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	15784258
Filing Date	16-Oct-2017
First Named Inventor	Jason Stowers
Attorney Docket Number	5063.02US05
Title of Invention	RADIATION BASED PATTERNING 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 39650 ○ 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	/Peter S. Dardi/
Name	Peter S. Dardi

*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.

Electronic Patent Application Fee Transmittal

Application Number:	15784258
Filing Date:	16-Oct-2017
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Filer:	Peter S. Dardi
Attorney Docket Number:	5063.02US05

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**

Doc Code: DISQ.E.FILE
Document Description: Electronic Terminal Disclaimer – Approved

Application No.: 15784258

Filing Date: 16-Oct-2017

Applicant/Patent under Reexamination: Stowers

Electronic Terminal Disclaimer filed on January 23, 2020

☒ 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

Electronic Acknowledgement Receipt

EFS ID:	38379492
Application Number:	15784258
International Application Number:	
Confirmation Number:	9576
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Peter S. Dardi
Filer Authorized By:	
Attorney Docket Number:	5063.02US05
Receipt Date:	23-JAN-2020
Filing Date:	16-OCT-2017
Time Stamp:	14:42:48
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	E20201ME42452673
Deposit Account	601363
Authorized User	Peter Dardi

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

37 CFR 1.16 (National application filing, search, and examination fees)

37 CFR 1.17 (Patent application and reexamination processing fees)

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	Terminal Disclaimer-Filed (Electronic)	eTerminal-Disclaimer.pdf	33335 31a6ea4cade7015db8db1b720d4e0a1942eae2b8	no	2
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30296 d823c9e5129b99dd4f14d465b7775f9500938833	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	63631		

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.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
15/784,258	10/16/2017	Jason K. Stowers	5063.02US05	9576

62274 7590 02/04/2020

CHRISTENSEN, FONDER, DARDI & HERBERT PLLC
33 South Sixth Street
Suite 4540
Minneapolis, MN 55402

EXAMINER
ROBINSON, CHANCEITY N

ART UNIT	PAPER NUMBER
1722	

NOTIFICATION DATE	DELIVERY MODE
02/04/2020	ELECTRONIC

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.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

docket@cfd-ip.com
patents@cfd-ip.com

Office Action Summary	Application No. 15/784,258	Applicant(s) Stowers et al.	
	Examiner CHANCEITY N ROBINSON	Art Unit 1722	AIA (FITF) 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 11/15/2019.

☐ 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) 1-19 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) 1-11 is/are rejected.

8) ☑ Claim(s) 12-19 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: _____.

Notice of Pre-AIA or AIA Status

1. The present application is being examined under the pre-AIA first to invent provisions.

Prosecution Reopened

2. In view of the appeal brief filed on 11/15/2019, PROSECUTION IS HEREBY REOPENED. New ground of rejection are set forth below.

To avoid abandonment of the application, appellant must exercise one of the following two options:

(1) file a reply under 37 CFR 1.111 (if this Office action is non-final) or a reply under 37 CFR 1.113 (if this Office action is final); or,

(2) initiate a new appeal by filing a notice of appeal under 37 CFR 41.31 followed by an appeal brief under 37 CFR 41.37. The previously paid notice of appeal fee and appeal brief fee can be applied to the new appeal. If, however, the appeal fees set forth in 37 CFR 41.20 have been increased since they were previously paid, then appellant must pay the difference between the increased fees and the amount previously paid.

A Supervisory Patent Examiner (SPE) has approved of reopening prosecution by signing below:

/CYNTHIA H KELLY/
Supervisory Patent Examiner, Art Unit 1722

Terminal Disclaimer

3. The terminal disclaimers filed on 08/20/2019 & 01/23/2020 disclaiming the terminal portion of any patent granted on this application have been reviewed and are accepted. The terminal disclaimers have been recorded.

Claim Objections

4. Claims 14, 15 and 16 are objected to because of the following informalities:

Claim 14 recites "wherein the peroxide ligand to metal ion ratio is at least about 2". However, the term "metal ion" should be recited as "the metal suboxides cations". Examiner notes that applicant have support for the amendment based on claim 14, line 4 and claim 17, line 1.

Further, claims 15 and 16 recite "the patterned inorganic material"; however, the term should be replaced with "the patterned coating material". Claim 14 does not recite that radiation patternable coating material only contains "inorganic material". The term "comprising" recited by claim 14 means the coating material may include other inorganic and organic materials.

Claims 17-19 depends on claims 14 and 15; therefore, the claims are also objected to because of the informalities.

Appropriate correction is required.

Claim Rejections - 35 USC § 103

5. 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.

6. The following is a quotation of pre-AIA 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

7. The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under pre-AIA 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.

2. Ascertaining the differences between the prior art and the claims at issue.

3. Resolving the level of ordinary skill in the pertinent art.

4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

8. Claims 1-6, 8, 10 and 11 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (US 8,257,910 B1).

Regarding claim 1, Guerrero et al. disclose a method for forming a pattern structure (abstract, claims, col. 1, lines 56-61 and examples) comprising a substrate (col. 1, lines 65-67) and a patterned coating material (photoresist layer; claim 27) 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 with EUV radiation at a dose of no more than 100 mJ/cm^2 (from about 5 to about 100 mJ/cm^2 ; col. 3, lines 62-67); and contacting the irradiated layer with a developing composition (developer) to dissolve un-irradiated (unexposed) material form a patterned coating material according to the selected pattern (col. 4, lines 32-39).

Further regards to claim 1, Guerrero et al. do not explicitly recite a layer of coating material having an average thickness from about 5 nm to about 30 nm as instantly recited. However, 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 term “about” is ambiguous. However, one of ordinary skill in the art may define the term “about” to be ±10 nm, 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 in the instant disclosure.

Nonetheless, Guerrero et al. explicitly teach the photoresist layer generally from about 40 mm (col. 3, lines 58-59) which meets the limitation of about 30 nm as defined by the claims when “about” is defined by one of ordinary skill in the art to be ±10 nm.

Regarding claim 2, Guerrero et al. explicitly teach the irradiation is performed with EUV at a dose of no more than about 90 mJ/cm^2 (col. 3, lines 62-67).

Regarding claim 3, Guerrero et al. explicitly teach the selected pattern has a pitch of no more than about 60 nm (30-nm or 50-nm; examples i.e. formulations 5, 8 and 9).

Regarding claim 4, Guerrero et al. explicitly teach the developing composition (developer) comprise tetra methyl ammonium hydroxide (TMAH; col. 4, lines 51-55).

Regarding claims 5 and 6, Guerrero et al. do not explicitly recite the exposed coating region in insoluble in an aqueous base as recited by claim 5 and/or soluble in an organic solvent as recited by claim 6. It is noted that the exposed coating regions of the instant claims and Guerrero et al. are the same. Therefore those characteristics are inherent, given that exposed coating regions of the instant claims and Guerrero et al. 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).

Regarding claim 8, Guerrero et al. explicitly teach further heating (post-exposure bake; col. 4, lines 25-31) the substrate with the pattern coating material (examples) to a temperature of about 140°C for from about 30 seconds to about 120 seconds (½ minute to 2 minutes), which meets the limitation of about 150°C nm as defined by the claims when "about" is defined by one of ordinary skill in the art to be ±10 degrees C.

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 term "about" is ambiguous. However, one of ordinary skill in the art may define the term "about" to be ±10 degrees C, which may be understood by persons experienced in the field of the invention.

Regarding claim 10, Guerrero et al. explicitly teach the coating material prior to irradiation comprises metal ions with radiation sensitive ligands (col. 5, lines 59-61).and an interaction of the coating material with EUV (Examples and col. 3, lines 62-67).

Further regards to claim 10, the limitation "wherein interaction of the coating material with EUV alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates" is intended use language. *In re Leshin*, 125 USPQ 416, 417-418; 277 F2d 197 (CCPA 1960).

Regarding claim 11, Guerrero et al. explicitly teach the metal of the metal ions comprises Ti, Zr and Hf (col. 5, lines 56-61).

9. Claim 9 is rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (US 8,257,910 B1) as applied to claims 1-6, 8, 10 and 11 above, and further in view of Ando (US 2010/0167217 A1).

Regarding claim 9, Guerrero et al. do not explicitly recite the method further comprises performing a second patterning using a post-patterning condensed structure to form a double patterned structure as instantly claimed. It is noted that Guerrero et al. teach the method comprising heating the substrate with the coated material (photoresist) to form a post-patterning structure (see claims and examples). However, Ando teaches it is well-known to one of ordinary skill in the art to utilizes a double patterning process to a method of forming a resist pattern (patterned structure; [0003 and 0013-0014] figures and examples) in order to provide double patterned structure capable of forming an isolated space pattern or hole pattern at a high level of resolution (figures and [0029-0031]). Guerrero et al. and Ando are analogous art in the resist patterning field. Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to include the double patterning process step to method of forming a pattern structure of Guerrero et al. in view of being capable of forming an isolated space pattern or hole pattern at a high level of resolution.

10. Claims 1-6 and 8-11 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (US 8,257,910 B1) in view of Cheng et al. (US 2009/0214823 A1).

Regarding claim 1, Guerrero et al. disclose a method for forming a pattern structure (abstract, claims, col. 1, lines 56-61 and examples) comprising a substrate (col. 1, lines 65-67) and a patterned coating material (photoresist layer; claim 27) 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 with EUV radiation at a dose of no more than 100 mJ/cm^2 (from about 5 to about 100 mJ/cm^2 ; col. 3, lines 62-67); and contacting the irradiated layer with a developing composition (developer) to dissolve un-irradiated (unexposed) material form a patterned coating material according to the selected pattern (col. 4, lines 32-39).

Further regards to claim 1, Guerrero et al. do not explicitly recite a layer of coating material having an average thickness from about 5 nm to about 30 nm as instantly recited. However, 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 term “about” is ambiguous. However, one of ordinary skill in the art may define the term “about” to be ±10 nm, 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 in the instant disclosure.

Nonetheless, Cheng et al. teach a method and a pattered structure (abstract, claims, figures and examples) comprising irradiating using EUV radiation [0053] a layer of coating material on the surface of a substrate having a thickness from about 5 nm to about 500 nm [0044 and fig. 5], which encompasses the instant claimed range of a layer of coating material having an average thickness from about 5 nm to about 30 nm. Cheng et al. and Guerrero et al. are analogous art in the patterned structure field. Further, It is well-known by one of ordinary skill in

the art that thickness can be optimizable as it affects chemical affinity. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215. Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify the thickness of the coating material of Guerrero et al. to have a thickness from about 5 nm to about 30 nm as taught by Cheng et al. in view of aiding in the chemical affinity.

Regarding claim 2, Guerrero et al. explicitly teach the irradiation is performed with EUV at a dose of no more than about 90 mJ/cm^2 (col. 3, lines 62-67).

Regarding claim 3, Guerrero et al. explicitly teach the selected pattern has a pitch of no more than about 60 nm (30-nm or 50-nm; examples i.e. formulations 5, 8 and 9).

Regarding claim 4, Guerrero et al. explicitly teach the developing composition (developer) comprise tetra methyl ammonium hydroxide (TMAH; col. 4, lines 51-55).

Regarding claims 5 and 6, Guerrero et al. do not explicitly recite the exposed coating region in insoluble in an aqueous base as recited by claim 5 and/or soluble in an organic solvent as recited by claim 6. It is noted that the exposed coating regions of the instant claims and Guerrero et al. ae the same. However, it is the position of the examiner that those characteristics are inherent, given that exposed coating regions of the instant claims and Guerrero et al. 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).

Regarding claim 8, Guerrero et al. explicitly teach further heating (post-exposure bake; col. 4, lines 25-31) the substrate with the pattern coating material (examples) to a temperature of about 140°C for from about 30 seconds to about 120 seconds (½ minute to 2 minutes), which

meets the limitation of about 150°C nm as defined by the claims when "about" is defined by one of ordinary skill in the art to be ±10 degrees C.

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 term "about" is ambiguous. However, one of ordinary skill in the art may define the term "about" to be ±10 degrees C, which may be understood by persons experienced in the field of the invention.

Regarding claim 9, Guerrero et al. do not explicitly recite the method further comprises performing a second patterning using a post-patterning condensed structure to form a double patterned structure as instantly claimed. It is noted that Guerrero et al. teach the method comprising heating the substrate with the coated material (photoresist) to form a post-patterning structure (see claims and examples). However, Cheng et al. teach it is well-known to one of ordinary skill in the art to utilize a process employing double patterning to advantageously lower process costs an increases throughput [0070]. Guerrero et al. and Cheng et al. are analogous art in the patterned structure field. Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to include the double patterning process step to method of forming a pattern structure of Guerrero et al. in view of advantageously lower process costs an increases throughput.

Regarding claim 10, Guerrero et al. explicitly teach the coating material prior to irradiation comprises metal ions with radiation sensitive ligands (col. 5, lines 59-61).and an interaction of the coating material with EUV (Examples and col. 3, lines 62-67).

Further regards to claim 10, the limitation "wherein interaction of the coating material with EUV alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates" is intended use language. *In re Leshin*, 125 USPQ 416, 417-418; 277 F2d 197 (CCPA 1960).

Regarding claim 11, Guerrero et al. explicitly teach the metal of the metal ions comprises Ti, Zr and Hf (col. 5, lines 56-61).

11. Claim 7 is rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (US 8,257,910 B1) as applied to claims 1-6, 8, 10 and 11 above, and further in view of Cheng et al. (US 8,828,493 B2).

Regarding claim 7, Guerrero et al. do not explicitly recite the method further comprises 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 as instantly claimed. However, Cheng et al. teach method for forming layered structures (patterned structures; abstract, claims and examples) comprising a step thermally treating by heating the initial layer or exposed initial layer at a temperature of 60 to 300 °C prior to development (col. 11, lines 25-48) meeting the limitation of 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. The thermal treatment can be effective in inducing a desirable polarity change (col. 11, lines 41-43). Guerrero et al. and Cheng et al. are analogous art in the patterned structure field. Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to include thermal treatment

step prior to development steps to method of forming a pattern structure of Guerrero et al. in view of inducing a desirable polarity change.

12. Claim 7 is rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (US 8,257,910 B1) in view of Cheng et al. (US 2009/0214823 A1) as applied to claims 1-6, and 8-11 above, and further in view of Cheng, Joy et al. (US 8,828,493 B2).

Regarding claim 7, Guerrero et al. do not explicitly recite the method further comprises 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 as instantly claimed. However, Cheng, Joy et al. teach method for forming layered structures (patterned structures; abstract, claims and examples) comprising a step thermally treating by heating the initial layer or exposed initial layer at a temperature of 60 to 300 °C prior to development (col. 11, lines 25-48) meeting the limitation of 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. The thermal treatment can be effective in inducing a desirable polarity change (col. 11, lines 41-43). Guerrero et al. and Cheng, Joy et al. are analogous art in the patterned structure field. Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to include thermal treatment step prior to development steps to method of forming a pattern structure of Guerrero et al. in view of inducing a desirable polarity change.

13. Claims 1-8 and 10-11 are rejected under pre-AIA 35 U.S.C. 103(a) as being unpatentable over Guerrero et al. (US 8,257,910 B1) in view of Fedynyshyn et al. (US 8,158,338 B2).

Regarding claim 1, Guerrero et al. disclose a method for forming a pattern structure (abstract, claims, col. 1, lines 56-61 and examples) comprising a substrate (col. 1, lines 65-67) and a patterned coating material (photoresist layer; claim 27) 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 with EUV radiation at a dose of no more than 100 mJ/cm^2 (from about 5 to about 100 mJ/cm^2 ; col. 3, lines 62-67); and contacting the irradiated layer with a developing composition (developer) to dissolve un-irradiated (unexposed) material form a patterned coating material according to the selected pattern (col. 4, lines 32-39).

Further regards to claim 1, Guerrero et al. do not explicitly recite a layer of coating material having an average thickness from about 5 nm to about 30 nm as instantly recited. However, 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 term “about” is ambiguous. However, one of ordinary skill in the art may define the term “about” to be ±10 nm, 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 in the instant disclosure.

Nonetheless, Fedynyshyn et al. teach a method and a resist structure (abstract, claims, figures and examples) comprising irradiating using EUV radiation (col. 2, lines 50-54) layer of coating material on the surface of a substrate having less than about 100 nm (col. 19, lines 6-13), which encompasses the instant claimed range of a layer of coating material having an average thickness from about 5 nm to about 30 nm. Fedynyshyn et al. and Guerrero et al. are analogous art in the patterned resist field. Further, it is well-known to one of ordinary skill in the art that the

thickness is optimizable. Discovery of optimum value of result effective variable in known process is ordinarily within skill of art. *In re Boesch*, CCPA 1980, 617 F.2d 272, 205 USPQ215. Therefore, it would have been obvious to one of ordinary skill in the art at the time of the invention to modify the thickness of the coating material of Guerrero et al. to have a thickness less than 100 nm as taught by Fedynyshyn et al. in view of applying a thin resist layer on substrate for performing a particular lithographic step.

Regarding claim 2, Guerrero et al. explicitly teach the irradiation is performed with EUV at a dose of no more than about 90 mJ/cm^2 (col. 3, lines 62-67).

Regarding claim 3, Guerrero et al. explicitly teach the selected pattern has a pitch of no more than about 60 nm (30-nm or 50-nm; examples i.e. formulations 5, 8 and 9).

Regarding claim 4, Guerrero et al. explicitly teach the developing composition (developer) comprise tetra methyl ammonium hydroxide (TMAH; col. 4, lines 51-55).

Regarding claims 5 and 6, Guerrero et al. do not explicitly recite the exposed coating region in insoluble in an aqueous base as recited by claim 5 and/or soluble in an organic solvent as recited by claim 6. It is noted that the exposed coating regions of the instant claims and Guerrero et al. ae the same. However, it is the position of the examiner that those characteristics are inherent, given that exposed coating regions of the instant claims and Guerrero et al. ae 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).

Regarding claim 7, Guerrero et al in view of Fedynyshyn et al. teach method further comprises 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 (baked at 100°C; Examples i.e. Examples 14 and 15 of Fedynyshyn et al.).

Regarding claim 8, Guerrero et al. explicitly teach further heating (post-exposure bake; col. 4, lines 25-31) the substrate with the pattern coating material (examples) to a temperature of about 140°C for from about 30 seconds to about 120 seconds (½ minute to 2 minutes), which meets the limitation of about 150°C nm as defined by the claims when "about" is defined by one of ordinary skill in the art to be ±10 degrees C.

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 term "about" is ambiguous. However, one of ordinary skill in the art may define the term "about" to be ±10 degrees C, which may be understood by persons experienced in the field of the invention.

Regarding claim 10, Guerrero et al. explicitly teach the coating material prior to irradiation comprises metal ions with radiation sensitive ligands (col. 5, lines 59-61).and an interaction of the coating material with EUV (Examples and col. 3, lines 62-67).

Further regards to claim 10, the limitation "wherein interaction of the coating material with EUV alters the chemical properties of the coating material creating an exposed coating material with differential dissolution rates" is intended use language. *In re Leshin*, 125 USPQ 416, 417-418; 277 F2d 197 (CCPA 1960).

Regarding claim 11, Guerrero et al. explicitly teach the metal of the metal ions comprises Ti, Zr and Hf (col. 5, lines 56-61).

Response to Arguments

14. Applicant's arguments with respect to claims 1-19 have been considered but are moot because the arguments do not apply to any of the references being used in the current rejection.

Allowable Subject Matter

15. Claims 12 and 13 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

Conclusion

16. Any inquiry concerning this communication or earlier communications from the examiner should be directed to CHANCEITY N ROBINSON whose telephone number is (571)270-3786. The examiner can normally be reached on Monday-Friday (5:30 am-10:00 pm; IFP; PHP).

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 https://ppair-my.uspto.gov/pair/PrivatePair. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CHANCEITY N ROBINSON/
Primary Examiner, Art Unit 1722

Notice of References Cited	Application/Control No. 15/784,258	Applicant(s)/Patent Under Reexamination Stowers et al.	
	Examiner CHANCEITY N 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-8828493-B2	09-2014	Cheng; Joy	G03F7/0392	427/258
*	B	US-20100167217-A1	07-2010	Ando; Tomoyuki	G03F7/0035	430/326
*	C	US-8257910-B1	09-2012	Guerrero; Douglas J.	G03F7/091	430/322
*	D	US-20090214823-A1	08-2009	Cheng; Joy	B81C1/00031	428/137
*	E	US-8158338-B2	04-2012	Fedynyshyn; Theodore H.	G03F7/0045	430/270.1
	F					
	G					
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	I					
	J					
	K					
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	M					

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
	N					
	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.

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/784,258	Stowers et al.
	Examiner	Art Unit
	CHANCEITY N ROBINSON	1722

CPC - Searched*		
Symbol	Date	Examiner
G03F 7/00	01/05/2019	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 and IDS Search	01/05/2019	CR
East Search Updated	01/28/2020	CR

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner

/CHANCEITY N ROBINSON/ Primary Examiner, Art Unit 1722	

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	15/784,258	Stowers et al.
	Examiner	Art Unit
	CHANCEITY N ROBINSON	1722

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☑ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	01/28/2020								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
	8	✓								
	9	✓								
	10	✓								
	11	✓								
	12	O								
	13	O								
	14	O								
	15	O								
	16	O								
	17	O								
	18	O								
	19	O								

Lam Research Ex. 1009 - Page 308 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	99753	(forming adj pattern)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:07
L2	4415	(EUV or UV) with dosage	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:07
L3	1630	dosage with mJ	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:07
L4	14	1 and 2 and 3	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:08
L5	15186	(EUV or UV) with dose	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
L6	14182	dose with mJ	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
L7	5103	5 and 6	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
L8	477	1 and 7	US-PGPUB;	OR	ON	2020/01/28

			USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			08:15
L9	110	8 and pitch	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:15
L10	87	(pitch with nm) and 8	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:16
L11	67	10 and EUV	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 08:16
L12	36	11 and (double adj patterning)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:02
L13	504274	metal adj (ion or cation or suboxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:11
L14	59	peroxide adj ligand	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:11
L15	33	13 and 14	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:11
L16	0	1 and 15	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT;	OR	ON	2020/01/28 09:12

			IBM_TDB			
L17	16	pattern and 15	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:12
L18	18	"4877718"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:42
L19	9	18 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:42
L20	1	"20080020291".pn. and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:49
L21	0	"825710".pn. and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:57
L22	2	"8257910".pn. and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 09:58
L23	2	"8257910".pn. and pattern	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 10:00
L24	1	"8257910".pn. and pitch	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 10:52
L25	0	"8257910".pn. and suboxide	US-PGPUB; USPAT; USOCR; FPRS;	OR	ON	2020/01/28 11:21

			EPO; JPO; DERWENT; IBM_TDB			
L26	0	"8257910".pn. and peroxide	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:21
L27	0	"8257910".pn. and double	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:22
L28	22142	negative adj photoresist	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:22
L29	20232	negative adj resist	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:22
L30	39675	28 or 29	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:23
L31	108	2 and 30	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:23
L32	953433	(heat$3 or bak$3) with (substrate)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:23
L33	36	31 and 32	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:24
L34	36	33 and thickness	US-PGPUB; USPAT;	OR	ON	2020/01/28 11:24

			USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			
L35	2	34 and (double adj patterning)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:42
L36	91	(EUV with (dosage or dose)) and (double adj patterning)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:43
L37	77	32 and 36	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:43
L38	65	37 and (thickness with (nm or nanometer))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 11:43
L39	2	"20090214823".pn. and pattern	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:16
L40	4	(("8158338") or ("8828493") or ("8785113") or ("8124319")).PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/01/28 12:20
L41	4	L40	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:20
L42	16439977	41 adn (heat$3)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:20
L43	4	41 and (heat$3)	US-PGPUB; USPAT; USOCR; FPRS;	OR	ON	2020/01/28 12:20

			EPO; JPO; DERWENT; IBM_TDB			
L44	10	(peroxide adj ligand) and (metal adj suboxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:46
L45	600	(peroxide a) and (metal adj suboxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:46
L46	116	(peroxide) and (metal adj suboxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2020/01/28 12:46
S1	7	"12850867"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/01/05 16:41
S2	3847446	(method or process) with (substrate or support)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:44
S3	367748	(EUV or UV or ultraviolet) with radiation	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S4	155899	heat$3 with (coat$3) with (support or substrate)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S5	5772464	irraditat$4 or expos$4	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S6	24187	(EUV or UV or ultraviolet) with (dosage or dose)	US-PGPUB; USPAT;	OR	ON	2019/01/05 18:45

			USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			
S7	1271	S2 and S3 and S4 and S5 and S6	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:45
S8	1189	S7 and thickness	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:46
S9	691	S8 and (developer or developing)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:46
S10	54733	(TMAH or (tetramethylammonium adj hydroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S11	528	S9 and S10	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S12	527	S11 and pattern$3	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S13	20	S12 and ligands and (metal adj (ion or cation))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:47
S14	20	S13 AND ((G03F7/0042 OR G03F7/0043 OR G03F7/20 OR G03F7/325 OR G03F7/327 OR G03F7/022 OR G03F7/032 OR G03F7/033 OR G03F7/0382 OR G03F7/0385 OR G03F7/0392 OR G03F7/0397 OR G03F7/32 OR	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2019/01/05 18:48

		G03F7/322 OR G03F7/09 OR G03F7/2002 OR G03F7/2037 OR G03F7/30 OR G03F7/2004 OR G03F7/162 OR G03F7/168 OR G03F7/40 OR Y10T428/24355 OR H01M10/0525 OR H01M2004/021 OR H01M2004/025 OR H01M2004/027 OR H01M4/045 OR H01M4/049 OR H01M4/134 OR H01M4/1391 OR H01M4/1395 OR H01M4/48 OR H01M4/60 OR H01M4/66 OR H01M4/665 OR H01M4/667 OR H01M4/668 OR Y02E60/122 OR Y02P70/54 OR Y02T10/7011).CPC.)				
S15	1	("8415000").PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/06/09 21:42
S16	2	"15784258"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/06/09 21:50
S17	2	"8158338"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/01/27 19:05
S18	4	(("8158338") or ("8828493") or ("8785113") or ("8124319")).PN.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/01/27 19:05

EAST Search History (Interference)

< This search history is empty>

1/ 28/ 2020 12:52:47 PM
C:\ Users\ crobinson4\ Documents\ EAST\ Workspaces\ 15784258.wsp

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:	Attorney Docket No.: 5063.02US05
Stowers et al.	Confirmation No.: 9576
Application No.: 15/784,258	Examiner: Chanceity N. Robinson
Filed: October 16, 2017	Group Art Unit: 1722

For: RADIATION BASED PATTERNING METHODS

NOTICE OF APPEAL

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

Sir:

In accordance with 37 C.F.R. § 1.191, Applicant hereby appeals to the Patent Trial and Appeal Board from the Office Action mailed February 4, 2020, finally rejecting claims 1-11 in the above-identified patent application. A payment in the amount of **$800.00** to cover the fee was previously submitted on September 11, 2019, and it is believed that no further payment is necessary. The Office Action confirms that the previously paid Notice of Appeal fee can be applied to this new appeal. The Commissioner is authorized to charge to Deposit Account No. 60-1363 any underpayments, overpayments or additional required fees.

Respectfully submitted,

/Diane Bennett/

Diane E. Bennett, Ph.D.
Registration No. 63,240

Customer No. 62274
Christensen, Fonder, Dardi & Herbert PLLC
33 South Sixth Street
Suite 4540
Minneapolis, MN 55402
Telephone: (612) 315-4322

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No.60-1363.

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March 9, 2020	/Diane Bennett/
Date	Diane E. Bennett, Ph.D., Reg. #63,240

Electronic Acknowledgement Receipt

EFS ID:	38802487
Application Number:	15784258
International Application Number:	
Confirmation Number:	9576
Title of Invention:	RADIATION BASED PATTERNING METHODS
First Named Inventor/Applicant Name:	Jason K. Stowers
Customer Number:	62274
Filer:	Diane Elizabeth Bennett
Filer Authorized By:	
Attorney Docket Number:	5063.02US05
Receipt Date:	09-MAR-2020
Filing Date:	16-OCT-2017
Time Stamp:	11:18:15
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	Notice of Appeal Filed	NoticeOfAppeal.pdf	20816 5c12e0b0be6fbdd01f6acc05df1882e8f101d478	no	1

Warnings:

Information:	
Total Files Size (in bytes):	20816

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New Applications Under 35 U.S.C. 111

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

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

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

New International Application Filed with the USPTO as a Receiving Office

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

PTO/SB/06 (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 15/784,258	Filing Date 10/16/2017	☐ 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 $80 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $420 =	
☐ 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)			
AMENDMENT	05/11/2020	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 19	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 2	Minus	*** 3	= 0		x $460 =	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)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ 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.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/PAMELA V THERATT/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

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

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

Customer No. 62274
Christensen, Fonder, Dardi & Herbert PLLC
33 South Sixth Street
Suite 4540
Minneapolis, MN 55402
Telephone: (612) 315-4322
Facsimile: (612) 315-4321

Attorney Docket No.: 5063.02US05

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. 15/784,258, filed October 16, 2017 for: RADIATION BASED PATTERNING 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. [ ] Previously submitted

[ ] Please enter in the present application the unentered Amendment under 37 C.F.R. § 1.116, with any attachments, filed on _____ in said prior application.

[ ] Consider the arguments in the Appeal Brief or reply Brief previously filed on _____

[ ] Other _____

b. [X] Enclosed

[X] 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)

[X] 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	19	- 20	= 0	~~x 50~~	~~$~~		**x 100**	**$0**
Indep.	1	- 3	= 0	~~x 230~~	~~$~~		**x 460**	**$0**
RCE fee				~~+ 650~~	~~$~~		**+ 1300**	**$1300**
Mult. Dep.			= 0	~~[+ 410]~~	~~$~~		**[+ 820]**	**$0**
				~~TOTAL~~	~~$~~	OR	**TOTAL**	**$1300.00**

[ ] 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 **$1300.00** (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,

/Diane Bennett/

Diane E. Bennett, Ph.D.
Registration No. 63,240

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 60-1363.

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May 11, 2020	/Diane Bennett/
Date	Diane E. Bennett, Ph.D., Reg. #63,240

Lam Research Ex. 1009 - Page 322 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

PTO/SB/08a (03-15)
Approved for use through 07/31/2016. OMB 0651-0031
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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	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

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	4639208	A	1983-01-18	Okunaka et al.	
	2	4601917		1986-07-22	Russo et al.	Corresponds to JPS61-000586
	3	4851481		1989-01-25	Kuriyama et al.	Corresponds to JPS63-241061
	4	6566276		2003-05-20	Maloney et al.	Corresponds to CN1457504

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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	20110166268	A1	2011-07-07	Deelman et al.	
	2	20160116839	A1	2016-04-28	Meyers et al.	Corresponds to JP2018-502173.

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15784258
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Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

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	1457504	CN	A	2003-11-19	EKC Technology	English Abstract Only	
	2	1992665	EP	A1	2008-11-19	Kaneka Corporation		
	3	S63-241061	JP	A	1988-10-06	Sunstar Engineering Inc.	English Abstract Only	
	4	2003-218118	JP	A	2003-07-31	Samsung Electronics Co., Ltd.	English Abstract Only	
	5	2008-091215	JP	A	2008-04-17	Nitto Kasei Co., Ltd.	English Abstract Only	
	6	2009-533521	JP	A	2009-09-17	LG Chemical Ltd.	English Abstract Only	
	7	2010-094583	JP	A	2010-04-30	Nippon Soda Co.	English Abstract Only	
	8	2016-530565	JP	A	2016-09-29	Inpria Corporation	English Abstract Only	
	9	10-2003-0007904	KR		2003-01-23	EKC Technology, Inc.	English Abstract Only	
	10	10-2011-0132288	KR		2011-12-07	Inpria Corporation	English Abstract Only	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15784258
	Filing Date	2017-10-16
	First Named Inventor	Jason K. Stowers
	Art Unit	1722
	Examiner Name	Chanceity N. Robinson
	Attorney Docket Number	5063.02US05

	11	2009-138474	WO	A1	2009-11-19	Arkema France		
	12	2010-000504	WO	A1	2010-01-07	Centrum		
	13	2016-065120	WO	A1	2016-04-28	Inpria Corporation		
	14	2001-81560	JP	A	2001-03-27	Air Products & Chemicals, Inc.		
	15	2018-502173	JP	A	2018-01-25	Inpria Corporation	English Abstract Only	
	16	2014-150411	WO	A1	2014-09-25	The Sherwin Williams Company		

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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		

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EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	15784258
	Filing Date	2017-10-16
	First Named Inventor	Jason K. Stowers
	Art Unit	1722
	Examiner Name	Chanceity N. Robinson
	Attorney Docket Number	5063.02US05

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	15784258
Filing Date	2017-10-16
First Named Inventor	Jason K. Stowers
Art Unit	1722
Examiner Name	Chanceity N. Robinson
Attorney Docket Number	5063.02US05

CERTIFICATION STATEMENT

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

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

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	/Diane Bennett/	Date (YYYY-MM-DD)	2020-05-11
Name/Print	Diane E. Bennett, Ph.D.	Registration Number	63,240

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

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 record s.

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.

Espacenet

Bibliographic data: CN1457504 (A) — 2003-11-19

Method of making electronic materials

Inventor(s): MALONEY D J [US]; LEE W M [US]; ROMAN P J JR [US] ± (D.J. MALONEY, ; W.M. LEE, ; P.J. ROMAN JR, ; D.J. MALONEY,W.M. LEE,P.J. ROMAN JR)

Applicant(s): EKC TECHNOLOGY INC [US] ± (EKC TECHNOLOGY INC)

Classification:
- **international:** ***B05D3/00; B05D5/12; G03F7/004; G03F7/32; G03F7/40; H01L21/00; H01L21/027; H01L21/033; H01L21/06; H01L21/266; H01L21/3065; H01L21/308; H01L21/31; H01L21/311; H01L21/316; H01L21/3205; H01L21/469; H01L21/768; H01L23/52; H01L35/24;*** *H01L21/314;* (IPC1-7): H01L21/302; H01L21/461
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The present invention involves fabrication of a hard mask. An embodiment involves the conversion of a precursor into a top-surface imaging layer during a direct patterning step. Another embodiment of the present invention is a method of forming an etched pattern in a substrate. A further embodiment of the present invention is a method of forming an implanted region in a substrate. Preferred precursors are formed from a metal complex comprising at least one ligand selected from the group consisting of acac, carboxylato, alkoxy, azide, carbonyl, nitrato, amine, halide, nitro, and mixtures thereof and at least one metal selected from the group consisting of Li, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ba, La, Pr, Sm, Eu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Pb, Th, U, Sb, As, Ce, Mg, and mixtures thereof.

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权利要求书 8 页 说明书 44 页 附图 30 页

[54] 发明名称 电子材料的制造方法

[57] 摘要

本发明涉及构造硬掩膜。一个实施方案涉及到在直接形成图案的过程中把前驱体转化为顶表面图案层。本发明的另一个实施方案是在基底上形成刻蚀图案的方法。本发明的再一个实施方案是在基底上形成注入区的方法。优选的前驱体由一种金属络合物形成，该金属络合物含有至少一种配位体和至少一种金属，所述配位体选自乙酰丙酮化物、羧酸根、烷氧基、叠氮基、羰基、硝酸基、胺、卤素基、硝基和它们的混合物；所述金属选自 Li、Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、La、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce、Mg 和它们的混合物。

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1.在基底上形成硬掩膜的方法，该方法包括如下的步骤：

选择至少一种前驱体材料；

在基底的顶上形成一层含有该前驱体的层；

将至少一部分该前驱体层进行转化；

将该前驱体层显影，由此在该前驱体层上形成图案，以及

将该图案转移到基底上，由此在形成图案时不使用光刻胶。

2.如权利要求 1 的方法，该方法进一步包括用显影剂把该前驱体层的未转化部分显影去掉。

3.如权利要求 2 的方法，其中所述显影剂是液体显影剂，含有至少一种醇和至少一种酮，其中存在的所有醇的总体积大于在该液体显影剂中存在的所有醇的体积加上存在的所有酮的体积总和的 50%。

4.如权利要求 3 的方法，其中至少一种醇是异丙醇，至少一种酮是甲基异丁基酮，异丙醇和甲基异丁基酮的体积比大于大约 1:1，而小于大约 40:1。

5.如权利要求 1 的方法，该方法进一步包括用显影剂显影去掉该前驱体层的已转化部分。

6.如权利要求 5 的方法，其中所述显影剂是液体显影剂，含有至少一种醇和至少一种酮，其中存在的所有醇的总体积大于在该液体显影剂中存在的所有醇的体积加上存在的所有酮的体积总和的 50%。

7.如权利要求 6 的方法，其中至少一种醇是异丙醇，至少一种酮是甲基异丁基酮，异丙醇和甲基异丁基酮的体积比大于大约 1:1，而小于大约 40:1。

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8.如权利要求 1 的方法，该方法进一步包括从金属络合物中选择至少一种前驱体材料，该金属络合物包括至少一种配位体和至少一种金属，所述配位体选自乙酰丙酮化物、羧酸根、烷氧基、叠氮基、羰基、硝酸基、胺、卤素基、硝基和它们的混合物；所述金属选自 Li、Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、La、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce、Mg 和它们的混合物。

9.在基底上形成硬掩膜的方法，该方法包括如下的步骤：

选择至少一种前驱体材料；

在基底的顶上任选形成一保护层；

在该保护层的顶上形成一层含有该未转化前驱体的层；

将至少一部分该未转化前驱体层进行部分转化；

基本上除去至少一部分未转化前驱体层，形成图案，以及

通过把至少一部分部分转化的前驱体层进行转化，形成硬掩膜。

10.如权利要求 9 的方法，该方法进一步包括用选自光、电子束辐照、离子束辐照和它们的组合的能源，通过包括至少一部分对该能源基本上透明的带图案掩膜进行部分转化的步骤。

11.如权利要求 9 的方法，该方法进一步包括使用显影剂基本上除去至少一部分未转化前驱体层。

12.如权利要求 9 的方法，该方法进一步包括使用选自光、电子束辐照、离子束辐照、热退火和它们的组合的能源进行转化而形成硬掩膜的步骤。

13.如权利要求 9 的方法，该方法进一步包括从金属络合物中选择至少一种前驱体的步骤，该金属络合物包括至少一种配位体和至少一种金属，所述配位体选自乙酰丙酮化物、羧酸根、烷氧基、叠氮基、羰基、硝酸基、胺、卤素基、硝基和它们的混合物；所述金属选自 Li、

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Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、La、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce、Mg 和它们的混合物。

14.在基底上形成刻蚀图案的方法，该方法包括如下的步骤：

选择至少一种前驱体材料；

在基底的顶上形成一层含有未转化前驱体的层；

将至少一部分未转化前驱体层进行部分转化；

基本上除去至少一部分未转化前驱体层；

通过转化至少一部分部分转化前驱体层来形成硬掩膜，以及

通过刻蚀至少一部分基本上未被硬掩膜覆盖的基底在该基底上形成至少一个图案区。

15.如权利要求 14 的方法，该方法进一步包括从金属络合物选择至少一种前驱体材料的步骤，该金属络合物包括至少一种配位体和至少一种金属，所述配位体选自乙酰丙酮化物、羧酸根、烷氧基、叠氮基、羰基、硝酸基、胺、卤素基、硝基和它们的混合物；所述金属选自 Li、Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、La、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce、Mg 和它们的混合物。

16.形成带图案的薄顶表面的方法，该方法包括如下步骤：

选择至少一种含有金属络合物的前驱体材料；

在基底顶上形成图案转移层；

在图案转移层的顶上形成一层含有未转化前驱体的层；

通过包括至少一部分对光基本上透明的带图案掩膜将一部分未转化前驱体层曝光，由此将已曝光部分部分转化；

基本上除去至少一部分未转化前驱体层，因而至少一部分图案转移层被曝露出来；

通过转化至少一部分部分转化的前驱体层来形成硬掩膜；

刻蚀至少部分转化的前驱体层和图案转移层的曝露部分，由此从

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未覆盖的图案转移层形成至少一个被刻蚀的部分；以及

基本上除去保留的至少部分转化前驱体层和图案转移层，由此曝露出至少一部分基底。

17.如权利要求 16 的方法，该方法进一步包括从光刻胶、聚酰亚胺、聚甲基丙烯酸甲酯、线形酚醛树脂和环氧树脂中选择图案转移层。

18.如权利要求 16 的方法，该方法进一步包括选择金属络合物以使所述金属络合物含有至少一种配位体和至少一种金属，所述配位体选自乙酰丙酮化物、羧酸根、烷氧基、叠氮基、羰基、硝酸基、胺、卤素基、硝基和它们的混合物；所述金属选自 Li、Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、La、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce、Mg 和它们的混合物。

19.在一揭起层的上面形成带图案薄顶表面的方法，该方法包括如下步骤：

选择至少一种含有金属络合物的前驱体材料；

在基底的顶上形成一隔离层；

在该隔离层的顶上形成一揭起层；

在该揭起层的顶上形成一层含有未转化前驱体的层；

通过包含至少一部分对光基本上透明的带图案掩膜，将一部分未转化前驱体层曝光，由此将已曝光部分进行部分转化；

基本上除去至少一部分未转化前驱体层，由此曝露出至少一部分揭起层，该揭起层具有被部分转化前驱体层覆盖的揭起层的保留部分；

通过将至少一部分部分转化前驱体层进行转化，形成硬掩膜；

使至少部分转化前驱体和揭起层的曝露部分经受各向异性的去除方法，由此基本上除去揭起层的未覆盖部分和至少一部分在该揭起层未覆盖部分底下的隔离层，并曝露出至少一部分基底；

使至少部分转化的前驱体、揭起层的覆盖部分和至少一部分在揭起层覆盖部分底下的隔离层经受各向同性去除方法；

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在至少一部分曝露的基底顶上和在至少部分转化的前驱体顶上沉积上一层金属膜；

基本上除去至少部分转化前驱体顶上的金属；以及

基本上除去保留的至少部分转化前驱体、揭起层和隔离层，由此在基底顶上形成金属的图案。

20.如权利要求 19 的方法，该方法进一步包括选择金属络合物以使该金属络合物含有至少一种配位体和至少一种金属，所述配位体选自乙酰丙酮化物、羧酸根、烷氧基、叠氮基、羰基、硝酸基、胺、卤素基、硝基和它们的混合物；所述金属选自 Li、Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、La、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce、Mg 和它们的混合物。

21.在一揭起层上形成带图案薄顶表面的方法，该方法包括如下步骤：

选择至少一种含有金属络合物的前驱体材料；

在基底顶上形成一层含有未转化前驱体材料的层；

将至少一部分该未转化前驱体层进行部分转化；

基本上除去至少一部分未转化前驱体层，由此在部分转化前驱体部分形成向内呈锥形的侧壁断面并曝露出至少一部分基底；

通过转化至少一部分部分转化前驱体层来形成硬掩膜；

在至少一部分曝露的基底顶上和在至少部分转化前驱体的顶上沉积金属膜；

基本上除去在至少部分转化前驱体顶上的金属；以及

基本上除去保留的至少部分转化前驱体，由此在基底顶上形成金属图案。

22 如权利要求 21 的方法，该方法进一步包括选择金属络合物以使该金属络合物含有至少一种配位体和至少一种金属，所述配位体选自乙酰丙酮化物、羧酸根、烷氧基、叠氮基、羰基、硝酸基、胺、卤素基、

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硝基和它们的混合物；所述金属选自 Li、Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、La、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce、Mg 和它们的混合物。

23.在基底中形成注入区的方法，该方法包括如下步骤：

选择至少一种前驱体材料；

任选在该基底的顶上形成一保护层；

在该保护层的顶上形成一层含有至少一种未转化前驱体材料的层；

通过把至少一部分未转化前驱体层进行转化，形成前驱体层的部分转化部分；

使用显影剂基本上除去至少一部分未转化前驱体层；

通过转化至少一部分部分转化前驱体层来形成硬掩膜；以及

通过在至少一部分基本上未被硬掩膜覆盖的基底上注入离子来在该基底上形成至少一个注入区。

24.如权利要求 23 的方法，该方法进一步包括用选自光、电子束辐照、离子束辐照和它们的组合的能源通过包含至少一部分对所述能源基本上是透明的带图案掩膜进行部分转化。

25.如权利要求 23 的方法，该方法进一步包括使用选自光、电子束辐照、离子束辐照、热退火和它们的组合的能源进行转化而形成硬掩膜。

26.如权利要求 23 的方法，该方法进一步包括将未覆盖的基底曝露于离子束下而注入离子。

27.如权利要求 23 的方法，该方法进一步包括从金属络合物中选择至少一种前驱体材料的步骤，该金属络合物含有至少一种配位体和至少一种金属，所述配位体选自乙酰丙酮化物、羧酸根、烷氧基、叠氮

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基、羰基、硝酸基、胺、卤素基、硝基和它们的混合物；所述金属选自 Li、Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、La、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce、Mg 和它们的混合物。

28.在一个介电层中形成双波纹构筑的方法，该方法包括如下步骤：

选择至少一种前驱体材料；

在基底的顶上形成具有特征厚度的介电层；

在该介电层的顶上形成一层含有第一未转化前驱体的层；

通过在至少一部分未转化的第一前驱体层上使用第一部分转化方法，形成第一前驱体层的部分转化部分；

通过使用第一去除方法基本上除去至少一部分第一未转化前驱体层，曝露出至少一部分介电层，形成未被至少部分转化的第一前驱体层覆盖的第一图案；

在至少一部分部分转化的第一前驱体层上使用第一转化方法形成硬掩膜；

在介电层的曝露部分顶上和至少部分转化的第一前驱体层顶上形成一个旋转平面化层；

在该旋转平面化层的顶上形成一层含有第二未转化前驱体的层；

在至少一部分该未转化的第二前驱体层上使用第二部分转化方法形成第二前驱体层的部分转化部分；

使用第二去除方法基本上除去至少一部分第二未转化前驱体层，曝露出至少一部分旋转平面化层，形成未被至少部分转化的第二前驱体层覆盖的第二图案；

在至少一部分部分转化的第二前驱体层上使用第二转化方法形成硬掩膜；

在基本上未被第二硬掩膜覆盖的至少一部分介电层及其底下的旋转平面化层上使用第一刻蚀方法，在介电层上形成至少一个第二图案区，使得被第一刻蚀方法除去的深度小于介电层的厚度；

通过使用第三去除方法基本上除去剩下的至少部分转化的第二前

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驱体层和旋转平面化层，由此曝露出至少部分转化的第一前驱体层；

通过在至少一部分基本上未被第一硬掩膜覆盖的至少一部分介电层上使用第二刻蚀方法，在介电层上形成至少一个第一图案区，使得在第一图案区中用第二刻蚀方法除去介电层的深度小于其厚度，而且在第二图案区通过第二刻蚀方法基本上除去整个介电层的厚度，从而曝露出至少一部分基底；以及

任选地用第四去除方法基本上除去剩下的至少部分转化的第一前驱体层。

29.如权利要求 28 的方法，该方法进一步包括从低介电常数介电材料中选择介电层。

30.如权利要求 28 的方法，该方法进一步包括从金属络合物中选择至少一种前驱体材料的步骤，该金属络合物含有至少一种配位体和至少一种金属，所述配位体选自乙酰丙酮化物、羧酸根、烷氧基、叠氮基、羰基、硝酸基、胺、卤素基、硝基和它们的混合物；所述金属选自 Li、Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、La、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce、Mg 和它们的混合物。

31.如权利要求 28 的方法，该方法进一步包括选择第一和第二刻蚀方法中的至少一种作为各向异性含氧等离子体。

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电子材料的制造方法

发明领域

本发明涉及电子材料的织构方法，在此方法中涉及形成硬掩膜。在一个实施方案中，涉及在直接形成图案的步骤中，把一种前驱体转化为顶表面影像层。

发明背景

在半导体和封装工业中使用传统的方法在其产品中形成薄的金属和金属氧化物膜。这种方法的例子包括蒸发、溅射沉积或溅射、化学气相沉积（CVD）和热氧化方法等。蒸发是在希望沉积的基底附近加热待沉积金属的一种方法。一般在真空条件下进行，要沉积的材料挥发然后在基底上凝聚，在此基底上产生一个覆盖层，或者说无图案的所需材料的膜。此方法有几个缺点，包括须要把希望成膜的材料加热到高温并需要高真空的条件。除非在蒸发的过程中使用屏蔽或者掩蔽物，用此方法都会导致无图案的覆盖膜。

溅射是一种与蒸发相类似的技术，在此技术中通过用具有足够动能的入射原子轰击用于沉积的材料使之转化为气相，因而该材料的粒子被驱逐进入气相并随后在基底上凝聚。溅射具有和蒸发一样的缺点，另外还需要能够产生足够动能的入射粒子，以驱逐出这些沉积材料的粒子的设备和消耗品。

CVD 和蒸发以及溅射相似，但还要求在沉积的过程中使沉积在基底上的粒子经过化学反应，以在此基底上形成膜。虽然在需要化学反应这一点上 CVD 与蒸发和溅射不同，可是在膜沉积的过程中，CVD 方法仍然须要使用复杂的设备以及温度和压力的苛刻条件。

热氧化也需要温度和氧气气氛的苛刻条件。在这种技术中，通过对早先在基底上沉积的未氧化层进行氧化，在基底上产生一层氧化膜覆盖层。

有几种现有的膜沉积方法可以在环境温度和压力下进行，这包括

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溶胶-凝胶法和其它旋压法。在这些方法中，在基底上涂布含有一种前驱体粒子的溶液，这些颗粒随后可转变为所需的膜成分。可以用旋涂或旋注的方法进行此溶液的涂布，此时将基底围绕一根轴旋转，同时将溶液滴到基底的中间。在进行这样的涂布以后，使涂布好的基底经受高温处理，这样就把前驱体膜转变为所需材料的膜。因此，这些方法不允许直接成像以形成无定形膜的图案。相反，他们会产生由所需材料形成的无图案覆盖膜。这些方法与气相法相比，对设备的要求不那么苛刻，但对外界温度仍然有要求，以影响沉积膜向所需材料的转化。

在一种给覆盖膜形成图案的方法中，用光敏涂层涂布在覆盖膜上（一般是使用旋涂或其它溶液基的涂布方法，或者应用干光敏膜）。通过掩膜用特定波长的光使此光敏层进行选择性地曝光。曝光改变了光敏层曝光区的溶解性，使得能够用显影溶液选择性地除去曝光区或未曝光区。然后使用剩余的材料作为图案转移介质，或者叫刻蚀介质的掩膜，此刻蚀介质在所需材料上形成出图案。在此刻蚀步骤之后，除去剩下的材料（从前的光敏材料），如果需要，清洗掉在刻蚀方法的过程中产生的所有副产物。

在基底上形成有图案薄膜的另一种方法中，可以如上所述为光敏材料形成图案。在形成图案以后，在形成了图案的材料（从前的光敏材料）的表面上可沉积上所需材料的保形覆盖层，然后将带有所形成图案的材料和所需材料覆盖膜的基底进行曝光，对从前的光敏材料进行腐蚀处理。此处理除去残留的原光敏材料，与其一起还除去了在表面上的一部分所需材料的覆盖膜。以这样的方式得到了所需材料的带图案膜，在此“揭层(liftoff)”方法中，刻蚀步骤不是必需的。然而，仍然须要使用中间图案转移介质（光敏材料），这就是本方法的缺点。已知此“揭层”法对分辨率（最小尺寸）有严格的限制，这可由所需材料的图案来确定。此缺点严格地限制了此方法的用途。

因此很明显的是，沉积以后须要形成图案的覆盖膜都需要几个极其昂贵和困难的加工步骤。

在另外一个形成带图案膜的方法中，可以通过比如上述方法之一在一个比如用前面所述的刻蚀方法预先形成了图案的基底上沉积所需

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材料的覆盖膜。用这样的方法沉积的覆盖膜，使其厚度充满并完全覆盖在基底上现有的图案。然后按照各向同性的方式除去一部分覆盖膜，直到残留的所需材料和预先形成了图案的基底表面处于同一高度。因此，所需材料存在于镶嵌于预先形成了图案的基底中的图案中。可以通过刻蚀的方法来实现将所需材料进行的各向同性地去除；一般在制造半导体器件的情况下，通过已知的方法，比如化学机械平面化（CMP）来实现此去除。这就涉及到使用带有化学试剂的粒子浆液，通过化学作用和机械作用的结合，来除去有足够数量的所需材料，镶嵌在有图案的基底中的所需位置上留下了所需材料。这种形成带有图案膜的方法须要使用昂贵的和复杂的平面化设备和额外的消耗材料，包括平面化的垫子、浆液和化学试剂。另外，使用浆液的小颗粒要求这些颗粒以后要从平面化的表面上被除去，这也需要额外的加工步骤。

虽然这些方法中，某一些比另外一些对设备的要求更高，而且在使用溶液，还是使用气相的方法中是不同的，而对于形成金属膜和金属氧化物膜来说，这样的传统工艺都不是最佳的方法，因为比如它们各自都需要昂贵的设备、操作费时间、要求使用高温来达到希望的结果，而且得到的覆盖膜是没有形成图案的，如果须要形成图案，还需要另一个形成图案的步骤。许多这样的方法还具有另外的缺点，在许多情况下会形成多晶膜，对于许多应用，这种膜是不适用的。这些方法的另外一种有希望的方案，是使用一种前驱体材料，此材料可以涂布在基底上，并选择性地形成出影像和图案，无须中间步骤就能够形成无定形的膜。

在半导体加工中膜的一个用途就是形成薄的顶部表面影像层（在后面称为 TSI），一般是一种已经涂布在基底上的有机表层。在此情况下，此有机层无须是光活性的，因为要沉积的膜随后要用常规的方法形成图案。对于 TSI 来说，使用这样的膜赋予加工方法有几个优点，这包括不用光刻胶掩膜就能够提供耐等离子体刻蚀的性能，以及用很薄的膜提供增大的平版印刷的分辨率。对于 TSI 典型的膜包括金属和硅的氮化物和氧化物的膜，对已知是甲硅烷基化的方法已经进行了许多研究。此方法涉及在预先沉积的有机层的表面上有蒸汽沉积的方法沉积含硅化合物的膜。然后可在此含硅化合物膜上形成出影像，形成

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氧化硅膜，在下面的有机层进行氧-等离子体刻蚀图案时，它可作为 TSI 层。由于方法和成本的限制，半导体和封装工业对甲硅烷基化的接受是无关紧要的。

膜在半导体加工中的另一个应用是形成硬掩膜，比如用于离子注入方法中。离子注入(ion implantation)法是公知使用的技术，比如在半导体织构中用于在基底上形成掺杂区(doped regions)。离子注入经常要求带图案的阻隔层，此层已知作为硬掩膜，此膜使待要注入的离子只导向预先确定的区域。比如，在 Shimizu 等人的 US5,436,176 的实施方案 1 中公开了一种在被氧化硅膜覆盖的硅基底上进行无掩膜注入的技术，据公开是用硼原子进行的三次注入。另外同一个专利在实施方案 3 中公开了在三次重复法中使用多重硬掩膜进行注入的方法，此方法依次包括如下步骤：在氧化硅膜覆盖的硅基底上形成掩膜、用含磷化合物进行注入，形成二次掩膜、用硼注入，以及最后进行退火。

正如在前面所讨论的，用这些方法中的任何一种形成硬掩膜都要求比较多的加工步骤。取消在刻蚀或离子注入前的某些步骤将是有益的，因为这将比如简化使用的方法，提高其效率以及降低其成本。

解决此问题的一个办法涉及使用光刻胶作为掩膜。然而，众所周知的是，对某些等离子体的刻蚀化学品，特别是用于有机层形成图案时，光刻胶的耐受性很低，这种有机层可作为中间保护层，或者作为低介电常数（低 K 值）的介电材料和低离子终止能，发现了日益增多的用途。因此，需要难以接受的厚掩膜，使得在遮掩层被完全腐蚀掉以前完成待形成图案的层的刻蚀，或者避免在基底上涂布了掩膜的区域进行了注入。另一个缺点是，被注入了离子的光刻胶非常难以从晶片上除掉。也尝试过用另外的办法解决此问题，比如先涂布一层硬掩膜，然后在硬掩膜的上面再涂布一层光刻胶层，然后在进行刻蚀或离子注入前形成上图案。在等离子体刻蚀或离子注入前，合并现有技术方法中公开的多个步骤中的某一些，或者甚至取消一种或几种，将有助于使这些方法简化。因此，在等离子体形成图案或离子注入方法中取消某些步骤的方法将是我们十分希望的。

作为制造金属和金属氧化物硬掩膜的廉价的方法，开发出了用于金属络合物前驱体沉积的本方法。此方法的一个实施方案，即光化学

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金属有机化合物沉积法，涉及到使用金属络合物前驱体用的金属有机化合物，还涉及把金属有机化合物转化为金属或金属氧化物膜的方法，比如入射的辐射或热能。具体说，在此方法中，比如通过把金属有机化合物的前驱体溶解于适当的有机溶剂形成前驱体溶液，用任何已知的方法将其沉积在表面上，从而就把金属有机化合物前驱体涂布在表面上。然后通过部分转化方法和/或转化方法，比如在能源，如在光、离子束轰击、电子束轰击下曝光或在热处理或退火下曝光就把此前驱体至少部分转化为金属或金属氧化物层。因此，本方法在例如半导体和封装工业中具有用途。

Hill 等人的 US5,534,312 公开了一种在基底上制造带图案的含金属材料的不用光刻胶的方法，该方法包括在基底表面上沉积一层金属络合物的无定形膜、把膜放置在选择的气氛中以及用电磁辐射，优选用紫外线，任选经过掩膜对此膜被选择的区域进行曝光，以引起在此选择区的金属络合物发生光化学反应等步骤。然而，此参考材料没有设想使用带图案的含金属的材料作为硬掩膜来保护底层不受等离子体刻蚀环境的影响。

Thomson 等人的 US6,071,676 公开，其集成电路的制造方法引起所涂布化合物的降解，此时该化合物与辐射或离子束接触。换句话说，发生化合物降解的沉积层的尺度正比于辐射束的聚焦宽度。据公开，此方法可达到纳米级的尺度。在化合物降解之处就形成了金属或其它导体物质的沉积层，然后可使用该方法直接在基底上制造集成电路。据说此沉积层优选是金属或者金属合金，此金属可以是金、锡或者铬，或者此沉积层可以是非金属或半金属导体，比如锗。在另外一方面，提供一种集成电路的制造方法，此方法包括在基底上涂布一种在辐射或离子束作用下会发生降解，得到导体的，优选是金属的沉积层、在该化合物的选择表面区域上照射辐射或离子束，以及从基底上去掉降解的化合物和未受影响的化合物。

本发明的方法能够提供带图案的硬掩膜，以此代替在传统的 TSI 法和离子注入法中使用的氧化物层和光刻胶层，而且通过减少必须进行的加工步骤数简化这些方法。本发明的另一个优点是，得到的材料具有更好的耐受等离子体刻蚀化学品的性能。这还赋予本发明另外一

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个优点，就是允许使用极薄的膜作为掩膜，提高了平版印刷方法的最终分辨率，能够形成更小、更细的印刷外貌。本发明的再一个优点是，得到的材料具有更好的离子注入阻隔性能和终止能。另外，本发明的方法在如下方面是有利的，即使得能够将新材料用于形成图案层，比如用铂、铱、氧化铱、钌和氧化钌，已知在现有技术中这些材料是很难或者根本不能用传统方法刻蚀的。

发明概述

本发明的一个实施方案是在一个基底上形成硬掩膜的方法，该方法包括如下的步骤：

—选择至少一种前驱体材料；

—在基底的顶部形成含有该前驱体的一层；

—覆盖至少一部分该前驱体层；

—给该前驱体层显影，由此在该前驱体层上形成图案；以及

—将该图案转移到基底上，因此在形成图案时就不使用光刻胶。

可以用显影剂把前驱体层的未转化部分显影而去掉。另外，也可以用显影剂把前驱体层的转化部分显影而去掉。显影剂可以是含有至少一种醇和至少一种酮的液体显影剂，其中全部醇的总体积大于在此液体显影剂中所存在的所有醇的体积加上所有酮的体积总和的 50%。此显影剂的至少一种醇优选是异丙醇，至少一种酮优选是甲基异丁基酮，异丙醇和甲基异丁基酮的体积比大于大约 1:1，而小于大约 40:1。

本发明的另一个实施方案是在基底上形成硬掩膜的方法，该方法包括如下的步骤：

—选择至少一种前驱体材料；

—在基底顶部任选地形成一层保护层；

—在该保护层上形成含有未转化前驱体的一层；

—将至少部分未转化前驱体层进行部分转化；

—基本上去掉至少部分未转化前驱体层，形成图案；以及

—将至少一部分部分转化的前驱体层进行转化，形成硬掩膜。

可以用选自光、电子束辐照、离子束辐照和它们的组合的能源，经过包括至少一部分对此能源基本上是透明的带图案掩膜来实现部分

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转化。使用显影剂可以基本上去掉至少部分未覆盖的前驱体层。可以用选自光、电子束辐照、离子束辐照、热退火和它们组合的能源来实现转化。

本发明的再一个实施方案是一种在基底上形成刻蚀图案的方法，该方法包括如下步骤：

—选择至少一种前驱体材料；

—在基底的顶部形成含有未转化前驱体的一层；

—将至少一部分未转化的前驱体层进行部分转化；

—基本上去掉至少一部分未转化前驱体层；

—通过把至少一部分的部分转化的前驱体层进行转化，形成硬掩膜；以及

—通过刻蚀至少部分基本上被硬掩膜覆盖的基底，在基底上形成至少一个图案区。

本发明的又一个实施方案是形成带图案薄顶表面的方法，该方法包括如下步骤：

—选择至少一种含有金属络合物的前驱体材料；

—在基底的顶上形成图案转移层；

—在图案转移层的顶上形成含有未转化前驱体的一层；

—通过包括至少一部分对光基本上透明的部分的带图案掩膜使一部分未转化前驱体层曝光，由此将该曝光部分进行转化；

—基本上去掉至少一部分未转化前驱体层，由此去掉至少一部分图案转移层的覆盖；

—通过将至少一部分的部分转化前驱体层进行转化来形成硬掩膜；

—对至少部分转化的前驱体和图案转移层的未覆盖的部分进行刻蚀，由此从未覆盖的图案转移层形成至少一个刻蚀部分；以及

—基本上去掉剩下的至少部分转化的前驱体层和图案转移层，由此暴露至少一部分基底。

此图案转移层可选自光刻胶、聚酰亚胺、聚甲基丙烯酸甲酯、线型酚醛树脂和环氧树脂。

本发明的另外一个实施方案是在揭起层上形成带图案薄顶表面的

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方法，此方法包括如下步骤：

—选择至少一种含有金属络合物的前驱体材料；

—在基底顶上形成一个隔离层(release layer)；

—在隔离层的顶上形成一个揭起层；

—在此揭起层的顶上形成一层含有未转化前驱体的层；

—通过一个图案掩膜使一部分未转化前驱体层曝光，此掩膜包括至少一部分对光是基本上透明的，由此把曝光部分进行部分转化；

—基本上除去至少一部分未转化前驱体层，由此使至少一部分揭起层曝露出来，而其余部分揭起层被部分转化的前驱体层所覆盖；

—通过将至少一部分的部分转化的前驱体层进行转化来形成硬掩膜；

—使至少部分转化的前驱体和揭起层的暴露部分经受各向异性去除步骤(mean)，由此基本上除去揭起层的曝露部分和至少一部分在揭起层曝露部分下面的隔离层，曝露出至少一部分基底；

—将至少部分转化的前驱体、揭起层的覆盖部分和至少一部分在揭起层覆盖部分底下的隔离层经受各向同性去除方法(mean)；

—在至少一部分曝露的基底顶上和至少部分转化的前驱体顶上沉积上金属膜；

—基本上除去在至少部分转化的前驱体顶上的金属；以及

—基本上除去残留的至少部分转化的前驱体、揭起层和隔离层，由此在基底顶上形成金属图案。

本发明的另外一个实施方案是在揭起层的上面形成带图案薄顶表面的方法，该方法包括如下步骤：

—选择至少一种含有金属络合物的前驱体材料；

—在基底顶上形成含有未转化前驱体材料的一个层；

—将至少一部分未转化前驱体层进行部分转化；

—基本上除去至少一部分未转化前驱体层，由此在部分转化的前驱体部分形成向里具有锥度的侧壁轮廓并曝露至少一部分基底；

—通过转化至少一部分部分转化的前驱体层来形成硬掩膜；

—在至少一部分曝露的基底上和至少部分转化的前驱体顶上沉积上金属膜；

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—基本上除去在至少部分转化的前驱体顶上上的金属；以及

—基本上除去残留的至少部分转化的前驱体，由此在基底顶上形成金属的图案。

本发明的另一个实施方案是一种在基底上形成注入区的方法，该方法包括如下步骤：

—选择至少一种前驱体材料；

—任选地在基底顶上形成一保护层；

—在此保护层的顶上形成一含有至少一种未转化前驱体材料的层；

—通过把至少一部分未转化前驱体层进行部分转化，形成一部分部分转化的前驱体层；

—通过使用显影剂，基本上除去至少一部分未转化前驱体层；

—通过把至少一部分部分转化的前驱体层进行转化，形成硬掩膜；

—通过在至少一部分基本上没有被硬掩膜覆盖的基底上注入离子，在基底上形成至少一个注入区。

可以用选自光、电子束辐照、离子束辐照和它们的组合的能源，通过包括至少一个对这些能源透明部分的带图案掩膜来实现部分转化。可以用选自光、电子束辐照、离子束辐照、热退火和它们组合的能源来实现转化。可通过将未覆盖的基底曝露在离子束下来进行离子注入。

本发明还有一个实施方案是在一个介电层中形成双重波纹构筑(damascene architecture)的方法，此方法包括如下步骤：

—选择至少一种前驱体材料；

—在基底顶上形成具有特征厚度的介电层；

—在此介电层的顶上形成一个含有第一未转化前驱体的层；

—对至少一部分未转化的第一前驱体层使用第一部分转化方法(mean)，形成部分转化的第一前驱体层部分；

—使用第一除去方法基本上除去至少一部分第一未转化前驱体层，曝露出至少一部分介电层，形成没有被至少部分转化的第一前驱体层覆盖的第一图案；

—对至少一部分部分转化的第一前驱体层使用第一转化方法，形

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成硬掩膜；

—在介电层曝露部分的顶上和在至少部分转化的第一前驱体层的顶上形成旋转平面化层；

—在旋转平面化层的顶上形成含有第二未转化前驱体的一个层；

—通过对至少一部分第二未转化前驱体层使用第二部分转化方法，形成一部分部分转化的第二前驱体层；

—通过使用第二除去方法，基本上除去至少一部分第二未转化前驱体层，曝露出至少一部分旋转平面化层，形成没有被至少部分转化的第二前驱体层覆盖发第二图案；

—通过对至少一部分部分转化的第二前驱体层使用第二转化方法，形成硬掩膜；

—通过对至少一部分介电层和在其底下基本上没有被第二硬掩膜覆盖的旋转平面化层使用第一刻蚀方法，在介电层中形成至少一个图案区，使得第一刻蚀方法在深度方向上去掉比厚度小的一层介电层；

—通过使用第三去除方法，基本上除去残留的至少部分未转化第二前驱体层和旋转平面化层，由此曝露出至少部分转化的第一前驱体层；

—通过对至少一部分基本上没有被第一硬掩膜覆盖的介电层使用第二刻蚀方法，在介电层中形成至少一个第一图案区，使得在第一图案区中，通过第二刻蚀方法在介电层的深度方向上去掉比厚度小的一部分；还使得在第二图案区中，用第二刻蚀方法基本上在深度方向除去整个厚度的介电层，由此使至少一部分基底去掉覆盖，以及

—任选地，通过使用第四去除方法，基本上除去残留的至少部分转化第一前驱体层。

此介电层优选是低介电常数的介电材料。第一和第二刻蚀方法中至少一种优选是含氧的各向异性等离子体。

在这些实施方案中的每一种当中，优选的前驱体材料是含有至少一种配位体和至少一种金属的金属络合物，这些配位体选自乙酰丙酮化物、羧酸根、烷氧基、叠氮基、羰基、硝酸基、胺、卤素基、硝基和它们的混合物；而金属选自 Li、Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、

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La、Pr、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce、Mg 和它们的混合物。

附图概述

图 1 是一个方法流程图，该图把方法的步骤看作是方法的变量；

图 2 说明在本发明方法的一个实施方案中的步骤的基本顺序；

图 3 说明现有技术的制造方法以及在半导体接插件中使用的硬掩膜的用途；

图 4 说明按照本发明的制造方法和硬掩膜的用途；

图 5 说明用 TSI 形成图案的现有技术；

图 6 说明按照本发明的制造方法和 TSI 层的使用；

图 7 说明实施揭层方法的现有技术方法；

图 8 说明按照本发明实施揭层的方法；

图 9 说明按照本发明实施揭层的另一种方法；

图 10 说明用于双波纹方法集成的现有技术的方法；

图 11 说明按照本发明用于双波纹方法集成的方法，此方法的步骤比图 10 的方法更少；

图 12 说明制造离子注入硬掩膜和使用其注入离子的现有技术方法；

图 13 说明按照本发明的一个实施方案制造离子注入硬掩膜和使用其进行离子注入的现有技术方法；

图 14 显示由两种不同前驱体形成的 ZrO_2 膜显示出的不同折射率性能；

图 15 显示通过热转化和光化学转化形成的不同 ZrO_2 的折射率；

图 16 描述由在基底上涂布前驱体溶液后使用特殊溶剂引起的条纹；

图 17 显示对于 BST 的热对比曲线；

图 18 显示对于 BST 的光化学对比曲线；

图 19 显示对于 BST 的热/光化学组合对比曲线；

图 20 是对于线形酚醛树脂的厚度对刻蚀时间的图；

图 21 是对于完全转化的 PZT 和 TiO_2 的厚度对刻蚀时间的图。

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本发明的详细说明

本方法考虑到其它膜沉积和制造方法所不可能得到的优点。结果，使用户具有更强的控制和操纵所得到的膜，使之适应所需应用的能力。因此，本方法可用于广泛的应用中。

本发明提供一种制造所需材料的带图案膜的方法。重要的是要认识到无定形的膜与多晶膜和结晶膜的区别，同时要认识到无定形膜和更有序的膜的区别，此外还要认识到用不同成膜方法得到的无定形膜彼此是不同的。再有，由不同方法形成的不同无定形膜的不同性能可以得到控制，而且会造成可用于特定应用中的特殊化学、物理和机械性能，比如，作为半导体器件和/或其制造中的各种层。通过包括至少一个转化这样的无定形膜的步骤的本方法形成的硬掩膜优选是带有图案的，因此可用于把图案转移到基底上。硬掩膜包括但不限于注入掩膜、刻蚀掩膜和图案转移层或掩膜，比如揭起掩膜。

本方法实施方案的一个优点是，在形成图案时，它用不着使用传统的形成图案的材料，即光刻胶就能产生带图案的电子材料。本方法的另一个优点是，可以形成的前驱体材料的无定形膜可任选地直接在基底上形成图案，用不着使用中间的形成图案的材料。作为理解本发明实施方案的结果，可得到重要的和独特的性能，尽管此沉积方法没有使用其它的沉积和形成膜的方法。图 1 用流程图提供了本方法的总体情况，此流程图显示出作为例子的各个步骤，用这些相继的步骤得到对特定应用具有最佳性能的所需材料膜。这些步骤当中有许多都是可根据膜的最终应用而任意选择的。本发明也不限于这些步骤，根据膜的最终用途，可以包括另外一些步骤。本领域的专业人员都会知道，为了达到特定应用的希望的结果，哪些步骤应该包括，哪些不应该包括。

在每一步骤中都存在着不同的选择方案，操作这些选择方案都会对得到的膜有所影响。比如，在图 1 的步骤 1 中，选择方案可以包括前驱体材料的组成、在此前驱体材料中使用的溶剂，不管在此前驱体材料中是否使用溶剂，在前驱体材料中可以使用的添加剂和/或可以在此前驱体材料中包括的增强剂(rate enhancer)。

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在图 1 的步骤 2 中，选择方案可以包括基底的清洗、阻隔层的沉积、粘接促进剂的沉积和/或使用活性层。

在图 1 的步骤 3 中，选择方案可以包括涂布前驱体膜的方法、涂布前驱体时的气氛和/或沉积温度。

在图 1 的步骤 4 中，选择方案可包括热处理、用电子束进行的处理、用离子束进行处理、用微波进行处理和/或使用特殊的气氛。

在图 1 的步骤 5 中，选择方案可包括此膜是覆盖的、曝露的还是带有图案的，或者是彼此混合的，和/或使用特定的气氛。

在图 1 的步骤 6 中，选择方案可包括热退火、使用微波处理、用电子束处理、用离子束处理、电镀和/或使用特定的气氛。

在图 1 的步骤 7 中，选择方案可包括是使用湿技术还是干技术形成图案。

在图 1 的步骤 8 中，选择方案可包括退火和/或使用特定的气氛。在此步骤中，形成的任何无定形膜也可以通过例如应用高温或各种其它成核技术，如光诱发成核转化为多晶或结晶膜，而且对于某些应用，这可能是一个特别希望的步骤。

这些选择方案都是举例的性质，都不是可以操作以影响所得到膜性能的选择方案的穷举性清单。下面将详细叙述本发明的特定的特征和实施方案。

当需要带图案的膜时，在这里叙述的方法可以按光化学的方方式进行，用不着中间形成图案的材料，比如光刻胶，可以在环境条件下进行，也可以在另外的条件下进行，比如在空气或其它组成的气氛中和/或在不同的压力下，比如在环境压力、高于或低于环境压力下，可以结合使用其它的加工步骤，都产生唯一的材料、层和结构。

当按照光分解的方式实施此方法时，此方法基本在环境温度下实施，而其它的现有技术方法则要求使用高温来进行图案转移，此温度经常高于 100℃。从制造的观点出发，此限制赋予了严格的加工上的制约，限制了应用这些方法有关的器件组装时对使用材料的选择。

在基本上是环境压力下，本发明的方法一般可以满意地进行。反之，许多现有技术的沉积方法，除了具有上述限制以外，必须在高真空下进行，要使用难以运行和维护的昂贵而复杂的设备。

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本发明的方法使得能够很容易在基底上由前驱体材料形成薄层。此前驱体含有专门设计的分子，使其能够在基底上均匀地涂布，得到的膜具有很高的光学性能，在本方法的情况下，就是有很高的光敏感度。前驱体分子的特性是很不同的—各种各样的通式为 M_aL_b 的金属络合物，含有至少一种金属（M）和至少一种或几种适当的配位体（L），即 a 和 b 都是至少为 1 的整数，这样的金属络合物是本发明所设想的。

如果使用多种金属，所有的金属原子可以是一样的，也可以不都是一样原子的和/或具有不同价，比如 BaNa Fe（II）Fe（III），或者一些是一样的，而另外一些是不一样原子的和/或具有不同的价，比如 Ba_2Fe（II）Fe（III）。在任何情况下，金属 M 可以是碱金属或碱土金属，比如 Ba 或 Li、过渡金属，比如 Cr 或 Ni、主族金属，比如 Al 或 Sn 或镧系元素，比如 U 或 Th。优选每个金属独立地选自 Li、Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、La、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce 和 Mg。

如果使用多种配位体，所有的配位体可以是一样的，也可以是不同的，或者一些是一样的，而另一些是不同的。在任何情况下，选择配位体都要使得可以形成基本上未转化的前驱体络合物，并具有如下的性能：

1）可以以无定形的形式沉积在基底上；

2）无定形的膜是稳定的，或者至少是亚稳定的；

3）在吸收能量，例如所需能量的光子时，通过化学反应，此膜可转化为不同的含金属的材料，以及

4）任何由能量诱发的化学反应的副产物应该是可以除去的，即应该有足够的挥发性，使得能够从膜中除去。

为了得到这些结果中的前两个，此络合物应该具有低的极性和低的分子间力。由于有机基团一般具有低的分子间力，在其外周具有有机基团的配位体倾向于满足前两个要求。如果吸收的能量是光，已知步骤（3）的化学反应就是光诱导反应。

基本上未转化前驱体的沉积膜是无定形的，或者至少是基本上无定形的。因此，为了制造阻碍结晶的金属络合物，配位体 L 优选使得

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络合物成为不对称的。使用本身具有两个或多个立体异构形式的配位体就能够把络合物制成不对称的。例如，如果 L 是外消旋的 2-乙基己酸根，得到的金属络合物就是不对称的，因为此络合物具有几种不同的立体异构形式。可以选择配位体有机部分的尺寸和形状，使膜的稳定性达到最佳，并调节了通过选择的膜沉积方法所沉积的膜的厚度。

通过制造在每个金属原子上连接着几个不同配位体的络合物膜，也可以增强无定形膜对结晶的稳定性。这样的金属络合物具有几种异构体的形式。例如 $CH_3HNCH_2NHCH_3$ 与镍盐（II）和 KNCS 的混合物反应导致产生各种异构体的混合物。已知不同异构体的化学性能是明显不同的，在膜中有几种异构体存在就削弱了膜中络合物结晶的能力。

络合物必须是稳定的，或者至少是亚稳定的，意思是在此方法的条件下，络合物将不会迅速而自发地分解。对于给定金属络合物的稳定性可能取决于例如在络合物中的金属氧化态。例如已知在空气中 Ni（0）络合物是不稳定的，而 Ni（II）络合物在空气中是稳定的。因此，用于包含有在空气中加工步骤的沉积 Ni 基膜的方法，就应该包括优于 Ni（0）络合物的 Ni（II）络合物。

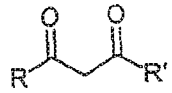
部分转化和转化是由在膜中的化学反应造成的，这将把部分转化区或转化区变成所需的转化材料。按照理想的方式，至少一个配位体与络合物反应并通过键连接，在络合物受到部分转化方法和/或转化方法的影响而产生激发状态时，该键裂解。在通过光，更优选通过紫外线作为部分转化方法和/或转化方法所引发的光化学反应中，优选从络合物上切下活性基团。为了使方法中这样的光化学步骤更加有效，特别优选中间产物在活性基团被切断而成为不稳定并自发转变为所需的新材料和挥发性副产物时产生。

有几种可以发生适当光化学反应的机理。按照本发明可以单独或组合操作的适当反应机理的例子如下：（a）吸收光子可把络合物置于配位体-金属电荷转移的激发态，在此状态下，金属络合物中的金属-配位体键是不稳定的，键断裂并且络合物的余下部分自发分解；（b）吸收光子可把络合物置于金属-配位体电荷转移激发态，在此状态下，络合物中的金属-配位体键是不稳定的，键回断裂，且络合物的剩下部分自发分解；（c）光子的吸收可把络合物置于 d-d 激发态，在此状态下，

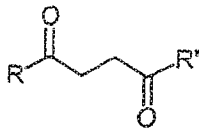
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络合物中的金属-配位体键是不稳定的，键断裂而络合物的余下部分自发分解；（d）吸收光子可把络合物置于分子内电荷转移激发态，在此状态下，络合物中的金属-配位体键是不稳定的，键断裂而络合物的余下部分自发分解；（e）吸收光子可把络合物的至少一个配位体置于局部配位体激发态，激发的配位体和络合物之间的键是不稳定的，键断裂而络合物的余下部分自发分解；（f）吸收光子可把络合物置于分子内电荷转移激发态，使得络合物的至少一个配位体是不稳定的，而且发生分解，然后络合物剩下的部分是不稳定的并自发分解；（g）吸收光子可把络合物的至少一个配位体置于局部化配位体激发态，其中受激发的配位体是不稳定的，并且发生了分解，然后络合物剩下的部分是不稳定的，并自发分解；以及（h）吸收光子可把络合物置于金属-配位体电荷转移激发态，在此状态下，络合物的至少一个配位体是不稳定的，并发生分解，然后络合物的剩下部分是不稳定的，并自发分解。然而，在本发明的广泛特征上，构成本发明并不限于这些反应机理。

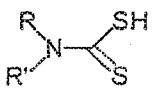
作为例子，在 US 5,534,312 中叙述了金属络合物及其金属和配位体组分，该专利整体在该引做参考。优选的金属络合物前驱体包括符合上面标准的各种配位体。更优选的配位体选自乙酰丙酮化物（已知还叫做 acac 或 2,4-戊二酮）及其阴离子、取代的乙酰丙酮化物，即：



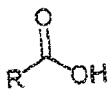
及其阴离子，丙酮基丙酮（已知也叫做 2,5-己二酮）及其阴离子、取代的丙酮基丙酮，即：



及其阴离子、二烷基二硫代氨基甲酸酯，即：

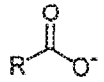


及其阴离子、羧酸，即：

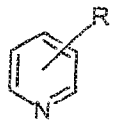


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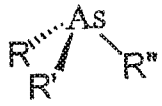
例如己酸，这里 R=$CH_3(CH_2)_4$，羧酸根，即：



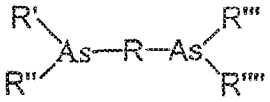
例如己酸根，这里 R=$CH_3(CH_2)_4$、吡啶和/或取代的吡啶，即：



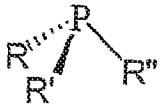
叠氮化合物，即 N_3^-、胺，即 RNH_2、二胺，例如 H_2NRNH_2、肼，即：



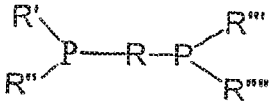
二肼，即：



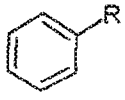
膦，即：



二膦，即：



芳烃，即：



羟基，即 OH^-、烷氧基配位体如 RO^-，配位体如$(C_2H_5)_2NCH_2CH_2O^-$、

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烷基配位体如 R–、芳基配位体和它们的混合物，这里每个 R、R'、R''、R'''和 R''''独立地选自有机基团，优选独立地选自烷基、烯基、芳烷基和芳烯基。

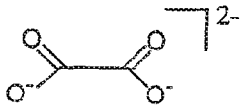
正如在本文中使用的，术语“烷基”指的是直链或分支的烃链。正如在本文中使用的，直链烃链或分支烃链意味着任何取代的或未取代的非环含碳化合物，包括烷烃、烯烃和炔烃。烷基的例子包括低级烷基，如甲基、乙基、正丙基、异丙基、正丁基、异丁基、叔丁基或异己基；高级烷基，例如正庚基、辛基、异辛基、壬基、癸基等。低级烯烃例如乙烯、丙烯、丙炔、丁烯、丁二烯、戊烯、正己烯或异己烯；以及高级烯烃，例如正庚烯、正辛烯、异辛烯、壬烯、癸烯等。一般专业人员都熟悉许多直链的，即线形的和分支的烷基，它们都在本发明的范围内。此外，这样的烷基还含有各种取代基，其中一个或几个氢原子被官能团或链内(in-chain)官能团取代。

正如在本文中使用的，术语“烯基”指的是其中至少一个碳-碳键是碳-碳双键的直链或分支的烃链。正如在本文中使用的，术语“芳烷基”指的是其端部被至少一个芳基取代的烷基，例如苄基。正如在本文中使用的，术语“芳烯基”指的是其端部被至少一个芳基取代的烯基。正如在本文中使用的，术语“芳基”指的是具有共轭双键系统，经常包括至少 6 个 π 电子的环烃。芳基的例子包括但不限于苯基、萘基、茴香基、甲苯基、二甲苯基等。

如相关领域的专业人员所理解的，在本发明的文字中，术语“官能团”普遍指的是具有链内的、侧键的和/或端部官能团的部分。作为链内官能团的例子可以举出酯、醚、酰胺、氨基甲酸酯及它们的硫代衍生物，即其中有至少一个氧原子被硫原子替代。作为侧键和/或端官能团的例子，可以举出卤素、例如氟和氯以及含氢的基团，如羟基、氨基、羧基、巯基和酰胺基、异氰酸酯基、氰基、环氧基和烯键式不饱和基团，例如烯丙基、丙烯酰基和甲基丙烯酰基以及马来酸根和马来酰亚胺基。

为了加强所需的光化学特性，包括光化学反应产物自发热分解的倾向，可以单独或与上面列出的配位体一起使用含有和/或选自下面的一个或几个基团的配位体：氧代，即 O_2^-、草酸根，即：

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卤化物、氢、氢化物，即 H^-、二氢化物，即 H_2、羟基、氰基，即 CN^-、羰基、硝基，即 NO_2、亚硝酸根，即 NO_2^-、硝酸根，即 NO_3^-、亚硝基，即 NO、乙烯、乙炔，即

R≡R'

硫氰酸根，即 SCN^-、异硫氰酸根，即 NCS^-、水合，即 H_2O、叠氮、碳酸根，即 CO_3^{-2}、胺和硫代羰基，这里每个 R 和 R'独立地选自有机基团，优选独立地选自烷基、烯基、芳烷基和芳烯基。每个配位体甚至更优选选自乙酰丙酮化物、羧酸根、烷氧基、草酸根、叠氮基、羰基、硝基、硝酸根、胺、氢及它们的阴离子。

优选地，金属络合物前驱体选自含有至少一个配位体和至少一个金属的络合物，其中该配位体选自乙酰丙酮化物、羧酸根、烷氧基、叠氮基、羰基、硝酸根、胺、卤素、硝基和它们的混合物；其中金属选自 Li、Al、Si、Ti、V、Cr、Mn、Fe、Ni、Co、Cu、Zn、Sr、Y、Zr、Nb、Mo、Ru、Rh、Pd、Ag、In、Sn、Ba、La、Pr、Sm、Eu、Hf、Ta、W、Re、Os、Ir、Pt、Au、Pb、Th、U、Sb、As、Ce、Mg 和它们的混合物。

前驱体可以直接涂布在基底上。另外也是优选地，可以把前驱体溶解于一种或几种溶剂形成前驱体溶液。这样使得可通过各种本领域专业人员公知的方法，很容易地涂布到基底上，例如把溶液旋涂或喷涂到基底上。可以根据几个单独或组合的标准来选择溶剂，这包括溶剂溶解前驱体的能力、溶剂对前驱体的惰性、溶剂的粘度、氧或其他环境或其他气体在溶剂中的溶解度、溶剂的紫外线、可见光和/或红外线的吸收光谱、溶剂相对于电子束和/或离子束的吸收截面、溶剂的挥发性、溶剂通过随后形成的膜的扩散能力、溶剂相对于存在的不同溶剂异构体的纯度、溶剂相对于存在的金属离子的纯度、溶剂的热稳定性、溶剂对随后形成的膜中缺陷点或成核点产生影响的能力、涉及溶剂的环境考虑。溶剂的例子包括烷烃，例如己烷、酮类，例如甲基异丁基酮（MIBK）和甲乙酮（MEK）以及丙二醇但甲醚醋酸酯（PGMEA）。

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溶液内前驱体的浓度可以在很宽的范围内变化，可由本领域的专业人员通过尽可能少的常规实验进行选择，使得包括其厚度和/或对光或粒子束辐照的敏感度在内的前驱体膜的性能符合所需的应用。

然而，对前驱体的选择对所需膜的性能可能有明显的影响，是本领域的专业人员不容易预测的。例如，两个前驱体 ML 和 ML'，每个都由金属 M 和两组不同的配体 L 或 L'中的一个组成，预期它们可形成相同的所需材料的膜，因为例如在该前驱体转化为硬掩膜的过程中，彼此不同的配位体部分将被去掉。实际上，这两个类似试剂假设相同的膜产物在其性能上可能有明显的不同。在该方法中可能被影响的性能的例子包括介电常数和在膜中有/无任何次级或三级结构存在。该差别可能的原因可以涉及无定形材料的形成速度和光逐出配位体从所需材料光致生成膜中除去能量的能力。在曝光过程中有配位体片段的存在可以影响成膜的方法，对例如膜的扩散性能、成核和晶体生长等现像造成影响。

再有，在成膜和光化学曝光时对前驱体的选择可能对所需材料膜对形成所需膜所处的气氛的气体组分的活性产生进一步的影响。这可能会影响到例如所沉积膜的氧化速度，而根据所需产物不同，高速度或低速度都可能是优点。另外，也认识到，通过选择前驱体可能对膜的复原能力，即尽可能减小裂纹的能力和收缩或致密化能力会有基本上的影响，而本领域的专业人员则会看到不同前驱体会产生同样的结果。

在前驱体或前驱体溶液中任选存在着化学添加剂。这可以是出于如下原因中的任何一个或几个：控制随后沉积的前驱体或膜的光敏感性、有助于在基底上沉积出均匀的、没有缺陷的膜、改变溶液的粘度、加大成膜速度、有助于避免在随后的曝光过程中膜开裂、改变溶液的其它整体性能以及以重要的方式改变所需材料膜的性能。除了在选择适当的溶剂时使用的标准以外，要按照这些标准来选择添加剂。优选该前驱体或前驱体溶液基本上不含有颗粒污染，以增强其成膜性能。

对该方法来说，将要涂布前驱体的基底的性质并不是关键的，虽然这会影响前驱体膜的沉积方法和沉积用的溶剂（如果使用的话）。基底可以包括但不限于简单盐，例如 CaF_2、半导体表面，包括硅、化合

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物半导体，包括硅-锗和 III-V 和 II-VI 半导体、印刷和/或层压电路板基底、金属、陶瓷和玻璃。硅晶片、陶瓷基底和印刷电路板已经得到普遍应用。在将它们使用于本方法之前，基底可以涂布上单层或多层涂层，例如介电层、光刻胶、聚酰亚胺、金属氧化物、热氧化物、导体材料、绝缘材料、铁电体材料或在电子器件的结构中使用的其它材料。在用氧等离子体进行形成图案，以及把前驱体材料用做 TSI 试剂的情况下，底层适合是有机材料，包括但不限于线形酚醛树脂、聚甲基丙烯酸甲酯（PMMA）、聚甲基戊二酰亚胺（PMGI）、聚酰亚胺和聚对羟基苯乙烯（PHOST）。

一旦形成了硬掩膜，其中的金属原子在一定程度上会在随后的步骤中“撞”到底下的基底上，这可通过仔细选择前驱体的配方条件和/或厚度加以克服。另外，可以在基底和前驱体层之间使用任选的保护层，在硬掩膜形成工艺完成以后，它仍然可以对基底构成保护。在涂布前驱体或前驱体溶液以前，基底上可任选涂布至少一层保护层。可以用本领域专业人员公知的各种方法在基底上涂布该保护层。当该方法包括离子注入步骤时，特别希望该保护层。

在沉积前驱体膜之前制备该基底对所需的硬掩膜的最终性能可能具有明显的影响。因此，例如某些表面性能可以是需要的，反之可能是须要避免的，这取决于所用的特定硬掩膜。基底制备可包括简单的清洗过程，以从基底表面上除去不希望的物质，在形成图案步骤之前，沉积阻隔材料、沉积粘接促进材料或沉积活性材料，用于诱发在所沉积材料膜中的化学变化，例如偶联剂。

前驱体或前驱体溶液的涂布方法可根据基底的情况和打算的应用情况进行选择。为本领域专业人员公知的可用的涂布方法的某些例子包括旋涂、喷涂、滴涂和辊涂、压印、弯月面式涂布和各种油墨印刷方法，例如喷墨(inkjet-type)的方法。可以选择涂布方法的各种变量以控制所沉积膜的厚度和均匀度，尽可能减小边缘效应并减少在膜中形成空隙或针孔，并确保在涂布过程中消耗的前驱体或前驱体溶液体积不比需要的更多。用最佳方法涂布前驱体膜会按照希望得到很光滑的膜。

沉积好的膜，任选经受烘烤或真空的步骤，在这些步骤中，在沉

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积膜中残留的任何溶剂都可被驱赶掉。当然，如果使用烘烤的步骤，重要的是要保持该步骤的温度低于前驱体分子的热分解温度。本发明的方法允许对前驱体浇注膜进行热覆盖或热处理或退火，以便通过热将其转化为所需材料的均匀覆盖涂层或者膜，其较不用热处理时转化为用于形成图案的部分转化和/或转化的剂量可能更少膜。在该加工步骤中，沉积的膜可任选地经受其它处理，包括但不限于覆盖式光化学曝光或电子束曝光和微波处理。

已经认识到在本方法步骤中的烘烤步骤可以有助于从前驱体膜中排出溶剂，也引起热分解过程。这两种机理都有助于本方法的总体效果，导致例如在随后的部分转化和/或转化步骤中降低所需的剂量。进一步还认识到，在这样的烘烤步骤中，可以形成与沉积的膜或所需材料的膜都不同的新材料。其效果可能明显地改变所需材料以后的性能，这包括介电常数、成核性能、形成材料品种的性能以及结晶性能，这都是本领域的专业人员不容易预见的。例如在某些应用中，优选使用一种双组分系统，其中一种材料在预烘烤步骤中被活化，而选择另一种化合物得以光化学或高能热方法活化。从前驱体混合物中进行沉积将使得能够有效地设计一个系统，该系统具有由烘烤和随后的部分转化和/或转化步骤形成的材料的不同化学性能的优点。

然后将沉积好的膜经受部分转化和/或转化，即能源的作用，使得该前驱体至少被部分转化。沉积好的膜的整体或者选择的部分可以对能源进行曝光。该能源可以是例如特殊波长的光源、特殊一段或几段波长的相干光源、宽带光源和电子束（e-束）源或离子束源。波长范围为大约 150~大约 600nm 的光是适合于使用的。优选的光波长是大约 157~大约 436nm。

在本发明的某些实施方案中，能源是通过用来在表面上界定影像的光学掩膜而定向的光源。该掩膜由基本上透明和基本上不透明的或光吸收区域构成。该掩膜还可以包括光学增强特征，例如相位移技术。然而，该能源无须一定要通过掩膜照射。例如如果给材料形成图案不是必须的，就可以使用漫射或覆盖式的能源进行曝光，由热能能源或宽的光束来提供曝光能源。

在其中使沉积膜进行至少部分转化的气氛和压力（既包括总压，

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也包括分压）可以是重要的方法参数。一般说来，作为是空气的气氛是适宜和经济的，但在至少部分转化的过程中，改变气氛的组成可能是优选的。这样做的一个原因是，如果使用短波的光，可以增大曝光光的透过率，因为空气可能削弱这样的光。因此，通过改变光的强度，例如增强光，就能够在膜中引发热反应，产生产物膜。也可能希望改变气氛的组成来改变产物膜的组成或性能。例如，在空气或氧气氛中对铜络合物曝光会导致产生氧化铜。通过从气氛中基本上除去氧，可以形成主要由还原的铜组成的膜。例如如果转化的前驱体必须是介电膜，优选在氧存在下进行部分转化或转化步骤，或者如果转化的前驱体必须是金属膜，就优选在还原性气体，例如氢存在下进行部分转化或转化步骤。另外，通过改变气氛中的湿度，可以改变膜中水的含量。

使用部分转化步骤或者已知也称为“基底预处理”的不同的依次进行的多个步骤，从工艺流的观点出发可以是有利的，例如使在昂贵的设备，例如步进器中，在基底顶上的前驱体进行曝光所需的时间尽可能短。

在沉积好的膜进行至少部分转化之后，前驱体膜可任选地被本领域已知的各种方法中任何一种进行处理，然后再除去至少一部分未转化的前驱体层。这些方法包括但不限于退火处理，例如热退火、激光退火或等离子体退火的步骤、曝露在特殊气氛中，例如氧化性或还原性气氛、离子注入、微波处理和电子束处理。如果部分转化的区域可以作为对前驱体未转化区无电电镀的成核点，在该步骤中可以使用任选的电镀步骤。

然后可以通过使用去除方法（或显影）除去沉积膜的未曝光区或部分未曝光区。例如，显影方法可以包括显影组合物，可将其作为液体或溶液以浆液显影法(puddle development)或浸渍湿法显影法进行涂布。另外，可以使用与半导体工业传统上使用的干法形成图案方法相类似的干法显影法作为显影方法。优选的去除方法包括喷雾显影法、浆液显影法和浸渍湿法显影法。

显影剂的配方和/或使用条件应该使得在膜的已曝光区和未曝光区之间存在着溶解度的差别。用该溶解度上的差别来除去膜的优选选择的区域，使得膜的某些选定区域被显影剂基本上去掉，而希望在基底

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上保留的区域基本上完整地保留下来。可以需要相当多的实验来优化显影剂的配方。例如，在一个希望把已对入射能曝光的区域在基底上保留下来的方法中，在对入射辐照曝光后使用浇注溶剂(casting solvent)对膜显影是太具有侵蚀性的。提供浇注溶剂在另一种液体中的稀溶液用于改进的显影方法，在该另外的液体中，（a）与浇注溶剂是可混溶的；（b）膜的未曝光区是微溶的（但无须完全溶解）；（c）膜的曝光区是基本上不溶的。

例如，在本发明的一个优选实施方案中，可以由酮类溶液浇注出无定形的膜。只使用酮作为显影剂，或者使用富含酮的醇-酮混合物，即含酮高于 50vol%的混合物，会导致比醇作为主要成分的显影剂效果更差的显影方法。例如 10:1（v/v）的 IPA:MIBK 溶液对于 $Ba_xSr_yTi_zO_3$（BST）是比单用 MIBK 或 1:1（v/v）的 IPA:MIBL 更为有效的显影剂，这里 IPA 表示异丙醇。10:1 的混合物本身不如 20:1 的 IPA:MIBK 有效。然而，无论 10:1，还是 20:1 的溶液都比 40:1（v/v）的 IPA:MIBK 更为有效。再有，这些溶液的相对效果与在形成带图案膜时使用的其它方法有很密切的关系，这包括例如入射辐照的类型和能量以及在涂布和形成图案的过程中的基底温度等。因此，为本发明确定适当的显影剂配方须要进行实验，对本领域的普通专业人员来讲并不是显而易见的。例如可以用与如上所述的光刻胶基方法中使用的显影方法相类似的方式，以物理方式涂布液体和/或溶液基的显影剂。

在显影以后，至少部分转化的前驱体可以任选地被本领域专业人员公知的各种方法中任何一种进行处理，然后再经受转化方法。这些方法包括但不限于退火处理，例如热退火、激光退火或等离子体退火。这样的退火的温度和时间都是重要的变量。该退火步骤也可以受到前面的表面处理的影响，例如氧等离子体、激光或快速热退火（RTA）方法等。能够选择适当的条件，使已经退火的至少部分转化的前驱体仍然保持其无定形的性质，而其物理性能或电性能中至少一种已经按照需要被改变了。另外，根据将要使用膜的应用不同，会引起膜转化为结晶状态的退火条件，例如高温可以是希望的。例如，在该阶段可以使用适当的热处理来诱发从无定形或至少基本上无定形的至少部分转化前驱体形成高度取向的结晶膜。以这样的方式，可以对无定形膜的

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性能进行细调，或者其物理性能可在很宽范围内变化—从一个极端的完全无定形相到半结晶的中间相，再到另一个极端的单取向的晶体相。这样的热处理一般起着进一步使前驱体转化的作用。

如果前驱体还要进行基本上充分的转化，随后前驱体膜就要任选，但是典型地经受转化方法的作用，使得该前驱体被基本上充分转化。可以把前驱体膜的整个膜或者选择的一部分对能源进行曝光。该转化方法可以是能源，该能源与前面使用的任何部分转化方法可以相同或者不同。例如，该转化方法可以是特殊波长的光源、特殊波长的相干光源、宽带光源、电子束源和/或离子束源。在本发明的某些实施方案中，如上面所讨论的能源，或者至少部分能源是通过用来在表面上界定影像的光学掩膜照射的光源。然而，该能源无须一定要通过掩膜照射。例如如果在转化步骤中给材料形成图案不是必须的，例如由于前驱体上已经形成有图案，就可以使用漫射或覆盖式的曝光作为转化方法。优选的转化方法包括光、电子束、离子束和热处理。如在上面对部分转化所讨论的，也是在本文中应用的，在其下进行转化的气氛条件，例如气氛的组成、压力（既包括总压也包括分压），还有湿度，都是重要的工艺变量。在转化的过程中，这些变量可以与在任何前面的部分转化步骤中使用的设定值相同，也可以不同。

当然应该理解，作为一个优选的膜，例如掩膜，可以通过将至少一部分部分转化的前驱体层基本上进行充分转化而得到，术语“基本上充分转化的前驱体”、“充分转化的前驱体”、“转化的前驱体”、“基本上充分转化的部分转化前驱体”、“充分转化的部分转化前驱体”和“已转化的部分转化前驱体”，如在本文中所使用的，都描述了这样的膜。

已经认识到，在把前驱体膜进行部分转化和/或基本上充分转化为所需材料的膜的过程中，膜会发生某些收缩，这就是说，所需材料膜的厚度经常比未转化的前驱体膜更薄。厚度上的这个变化是本发明的一个重要特征，给所需材料的膜赋予了有用的性能。例如，对于使电容最大化来说，形成极薄的膜是有利的，而同时，形成这样的膜从制造的观点出发又是一个挑战。本发明的方法提供了涂布比较薄浇注膜的能力，这样就赋予了制造上的便利，但也提供了比较更薄的所需至

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少部分转化前驱体材料的膜，这也就给所需材料的膜赋予了改善的性能。可以通过明智地操纵工艺变量来控制和调节沉积膜的收缩性能，这些变量包括选择前驱体、选择溶剂和溶剂的量、前驱体添加剂的种类、如沉积方法所决定的前驱体膜的厚度、在膜形成图案之前、过程中和以后的热处理以及已曝光膜的显影等。本发明的方法允许精确控制所需膜的厚度范围，使总厚度从埃（Å）的级别到微米（μm）级别。

在转化以后，随后任选的操作步骤可以包括转化后处理、包括但不限于如上所述的新显影方法的显影步骤以及显影后的处理步骤。要根据产物的最终应用选择具体的步骤。例如在 US5,534,312、5,821,017 和 6,071,676 中都叙述了使用的方法，这些专利的内容在该引做参考。

在本发明的某些实施方案中，在转化后是注入步骤，其中在基本上没有被硬掩膜覆盖的至少一部分基底上，通过使用注入方法，在该基底上形成至少一个注入区。使用离子束作为注入方法是本领域中已知的。然而，本方法不限于使用离子束，任何有效的注入方法都可以使用。适合于注入的离子包括但不限于砷、硼和磷。可以在高能结合低剂量的条件下进行离子注入，即高于大约 300KeV 的能量和小于约 10^{20} 个原子/cm^2的剂量，或者在低能，即小于大约 300KeV，结合高剂量，即大于大约 10^{20} 个原子/cm^2的条件下进行。在注入后可任选除去硬掩膜层。经过注入的基底可任选进行进一步的处理，例如退火，借该将注入的基底区转化为掺杂区(doped region)。如果这两个任选的步骤都进行，可以调节它们进行的次序，以适应本发明所涉及的特定应用。

本发明的其它实施方案设想，通过把本方法形成的至少部分转化前驱体作为耐刻蚀层。在一步或几步刻蚀步骤中，将例如等离子体、活性离子或湿刻蚀溶液等刻蚀方法通过硬掩膜提供的图案，与基底的选择区域相接触，只在这些需要的区域去掉基底。当前通常使用的硬掩膜材料，例如二氧化硅和氮化硅在使用刻蚀的电子制造方法中被用做保护掩膜。

本发明的一个优选实施方案设想，将通过本方法形成的至少部分转化的前驱体或硬掩膜作为耐刻蚀层。在一个或几个刻蚀步骤中，诸如等离子体、活性离子或湿刻蚀溶液的刻蚀方法通过由例如硬掩膜提供的图案与基底的选定区域接触，只在这些需要的区域除去基底。当

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前通常应用的硬掩膜材料，例如二氧化硅和氮化硅在使用刻蚀的电子制造方法中被用作保护掩膜。

图 2 说明对于本发明一个优选实施方案的各个步骤的基本顺序，即步骤 2A、2B、2C 和 2D，在加工前在步骤 2A 中所显示的基底 10 上进行这些步骤。例如，基底 10 可以是已经涂布有有机层的硅晶片。在步骤 2B 中，在基底 10 上涂布有未转化的前驱体 11。在步骤 2C 中，在至少一部分未转化前驱体 11 上施加转化方法，如在光化学金属有机沉积法中的光，或热处理，形成已转化的前驱体层 12。在步骤 2D 中，使用去除方法例如显影组合物除去至少一部分，优选基本上全部未转化前驱体层 11，剩下完整的已转化前驱体层 12，借该形成基底 10 的硬掩膜。这样的掩膜适当地允许某些形成图案方法通过到达基底的所需区域，同时对形成图案方法遮挡住或阻隔住某些另外的基底区域。

另外，在图 2 的步骤 2C 中，可以对至少一部分选择的未转化前驱体 11 施加部分转化方法，例如光或热处理，以形成部分转化前驱体层 12。在步骤 2D 中，使用去除方法例如显影组合物，除去至少部分，优选基本上全部未转化前驱体层 11，剩下完整的部分转化前驱体层 12。然后可在至少一部分部分转化前驱体使用在图上没有表示的转化方法，例如光或热处理，使得那部分发生基本上的转化，借该形成硬掩膜。该部分转化方法与转化方法可以相同，也可以不同。图 2 显示出在通过本发明的方法形成带图案的硬掩膜时很节省步骤。

相反，图 3 说明制造带图案硬掩膜时冗长的现有技术方法。在步骤 3A 中，如在图 2 中所说明的提供基底 200。在步骤 3B 中，在基底上形成硬掩膜层 210。该硬掩膜层可以是例如二氧化硅 210。在步骤 3C 中，在硬掩膜层 210 的顶上涂布光刻胶层 220。在步骤 3D 中，通过掩膜 235 将光刻胶层 220 对光 230 曝光。掩膜 235 包括透明的玻璃基底 240，它具有对光基本上不透明的区域 250，因此就阻隔了一部分光，在光刻胶层的已曝光部分 222 上形成了图案。在步骤 3E 中，已曝光的光刻胶区 222 被显影，借该曝露出硬掩膜层 210。在步骤 3F 中，通过用适当的刻蚀组合物刻蚀掉硬掩膜层 210 的未被保护部分，在硬掩膜层 210 中形成开口 255。在步骤 3G 中，除去剩下的部分光刻胶 220。在步骤 3H 中，选择使得能够刻蚀基底 200 而不刻蚀硬掩膜层 210 的等

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离子体刻蚀化学品在基底 200 上形成出图案。这就得到如在步骤 3I 中所定义的图案特征。因此，从图 3 可以明显看出，对于制造带图案的硬掩膜，传统的方法，例如通过带图案掩膜的离子注入技术与本发明的方法相比，需要更多的步骤。

图 4 说明本方法的一个优选实施方案，用来制造硬掩膜，使用的是金属络合物前驱体，形成带图案的硬掩膜，该方案去掉了与硬掩膜刻蚀有关的所有步骤，即上述步骤 3C 到步骤 3G。在步骤 4A 中，如在图 2 中所说明供应基底 300。在步骤 4B 中，在基底 300 的顶上形成了一个前驱体层 310，即含有金属络合物的层。在步骤 4C 中，通过胰脂酶 320 使前驱体 310 对部分转化方法，在该为光 315 曝光。掩膜 320 包括具有对部分转化方法基本上不透明区域 340 的透明玻璃基底 330。对部分转化方法 315 曝光的部分前驱体 310 被至少部分转化或反应，形成部分转化前驱体 350 的区域。在步骤 4D 中，整个组装体被曝露于去除方法（未显示），例如液体显影剂中。通过显影剂或去除方法除去基本上未转化前驱体 310，曝露出基底 310，同时把部分转化而又耐受去除方法的部分转化前驱体 350 被保留下来。在步骤 4E 中，对部分转化前驱体施加转化方法（未显示），形成基本上完全转化的前驱体 360，即带图案的硬掩膜。该转化可通过例如漫射光曝光步骤或热退火步骤来实现。在步骤 4C 和 4E 的每一步中，如果已转化前驱体 360 是介电膜，优选在氧存在下进行转化；而如果已转化前驱体 360 是金属膜，则优选在还原性气体存在下进行。在步骤 4F 中，刻蚀方法给基底形成上图案，在该该刻蚀方法选择是等离子体刻蚀化学品，它能够刻蚀基底 300，但不能刻蚀掩膜层 360。这样就形成了如在步骤 4G 中所定义的图案特征 390。

图 5 说明例如通过一般已知作为顶上甲硅烷基化形成影像的方法在光刻胶上形成 TSI 的现有技术的方法。在步骤 5A 中，提供一个基底 400。在步骤 5B 中，在基底 400 上涂布一层适合于进行顶上甲硅烷基化的光刻胶层 410。在步骤 5C 中，通过掩膜 435 使光刻胶层 410 对光 430 曝光。掩膜 435 包括一个具有对曝光方法基本上不透明的区域 450 的透明玻璃基底 440，从而阻挡一部分光，在光刻胶层的曝光部分 432 上形成图案。作为该曝光的结果，给予已曝光的光刻胶区不同的化学

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和/或物理性能。在步骤 5D 中，基底 400、光刻胶层 410 和已曝光的光刻胶区 432 都曝露在气体 TSI 试剂 460 中，它被选择性地吸收到已曝光的光刻胶区 432 中，形成改性的光刻胶表面 470。TSI 试剂 460 的例子是本领域已知的，包括含硅的气体。

在步骤 5E 中，把表面曝露在等离子体处理 480 中，使改性光刻胶表面更加惰性，由此形成耐蚀的硬掩膜 490。在步骤 5F 中，等离子体处理 495 除去直接在耐蚀硬掩膜表面 490 底下残留的光刻胶 410（。在步骤 5G 中，使用等离子体处理 497 给基底 400 形成图案，使用了由光刻胶层 410、改性光刻胶表面 470 和耐蚀硬掩膜表面 490 形成的复合堆积层来确定转移到基底 400 上的图案。通过在步骤 5H 中的刻蚀区 499 来说明得到的图案。在步骤 5I 中，使用了去除方法（未显示）来除去由光刻胶层 410、改性光刻胶表面 470 和耐蚀硬掩膜表面 490 形成的复合堆积层。同时在图 5 中说明的方法在形成用于形成图案的薄表面时可赋予其优点的，这有助于改善可得到的分辨率，而在松弛焦深时需要多个等离子体处理的步骤，这就产生需要 TSI 试剂的缺点，而且涉及到在其他的传统技术中不存在的图案转移时提高成本和复杂性。

反之，图 6 说明应用于 TSI 的本方法使用金属络合物形成带图案薄顶表面的一个优选实施方案。在步骤 6A 中，提供一个涂布有图案转移层 505 的基底 500。图案转移层 505 可任选地含有有机成膜树脂，这包括光刻胶、聚酰亚胺、PMMA、线形酚醛树脂、环氧树脂和本领域的专业人员已知的其他有机或相关涂层。在步骤 6B 中，在基底 500 的顶上形成前驱体层 510，直接覆盖在图案转移层 505 上面。在此情况下，前驱体 510 含有金属络合物。在步骤 6C 中，通过掩膜 520 将前驱体曝露于部分转化方法中，在此说明的是光 515。掩膜 520 包括透明的基底 530 例如说玻璃基底，该玻璃基底具有对部分转化方法基本上不透明的区域 540。对部分转化方法 515 曝光的部分前驱体 510 至少被部分转化或反应，形成部分转化前驱体的区域 550。在步骤 6D 中，整个组装体被曝露在去除方法（未显示）例如液体显影剂中。通过去除方法例如显影剂除去了基本上未转化的前驱体 510，曝露出图案转移层 505，同时留下了被部分转化并耐受去除方法的部分转化前驱体 550。在任选的步骤 6E 中，在部分转化前驱体 550 上施加转化方法（未显示），形成

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基本上充分转化的前驱体 560。该转化可通过例如漫射光曝光步骤或热退火步骤来实现。

在步骤 6F 中，表面曝露在刻蚀方法 570 中，举例说例如等离子体刻蚀化学品中。例如，等离子体刻蚀方法可主要由氧组成。该刻蚀方法除去图案转移层 505 的已曝光区域，而部分转化或基本上充分转化的前驱体层 560 被选择和加工，使得对刻蚀方法 570 基本上是惰性的，这样就形成了刻蚀区 580。在步骤 6G 中，通过刻蚀方法，使用在至少部分转化的前驱体 560 底下的图案转移层 505 中形成的图案为基底 500 形成图案（未显示），形成刻蚀区 590。在步骤 6H 中，去除方法（未显示）去掉了所有残留的图案转移层 505 和至少部分转化前驱体 560，曝露出所需的带有刻蚀区 590 的带图案基底 500。图 6 的方法优于在图 5 中显示的方法，因为它需要的步骤较少，等离子体步骤也少，而且不需要 TSI 试剂。同时，图 6 的方法保留下使用图 5 的方法所获得的全部优点。

图 7 说明在基底顶上沉积带图案金属层的现有技术方法。当所需的金属很难刻蚀时，例如是金或铂时习惯使用该方法。在步骤 7A 中，提供一个基底 600。在步骤 7B 中，在基底 600 的顶上涂布一层隔离层 605，而在隔离层 605 的顶上涂布一层揭起层 610。在步骤 7C 中，在揭起层 710 的顶上沉积上一层任选的硬掩膜层 620。在步骤 7D 中，在由任选的硬掩膜层 620、揭起层 610 和隔离层 605 组成的复合堆积层的顶上涂布上光刻胶层 630。在步骤 7E 中，通过掩膜 635 将光刻胶层 630 对光 645 曝光。掩膜 635 包括一个透明的玻璃基底 640，该基底具有对曝光方法基本上不透明的区域 650，这样就遮断了一部分光，并在光刻胶层的曝光部分 630 上形成了图案。在步骤 7F 中，使用去除方法，例如湿显影剂来除去在光刻胶层 630 上的已曝光部分 632。

在步骤 7G 中，使用等离子体刻蚀化学品 660 通过任选的硬掩膜层 620（如果存在）进行刻蚀。等离子体刻蚀化学品 660 也可以具有使光刻胶层 630 的大部分厚度受到侵蚀的作用。在步骤 7H 中，使用等离子体刻蚀化学品 670 通过揭起层 610 和隔离层 605 进行刻蚀。在该步骤中可以制造出侧壁，这可通过先以各向异性的模式使用等离子体刻蚀化学品 670，例如先将等离子体的带电粒子在垂直方向运动，然后转换

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为各向同性的模式，使等离子体中负责刻蚀的带电粒子在所有方向上均衡地运动来实现，该侧壁优选如在步骤 7H 中所说明的呈曲线状。在步骤 7I 中，使用一种沉积方法用所需的金属 680（例如金、铂或其他所需金属）来覆盖表面的特征。在步骤 7J 中，使用去除方法（未显示）例如通过溶剂处理来揭起所有残留的隔离层 605、揭起层 610、硬掩膜层 620（如果存在的话）和光刻胶层 630。这就在基底 600 上只剩下所需金属 680 的所需图案。这个给金属沉积物形成图案的方法是很困难的，涉及许多步骤，须要使用厚的光刻胶层。这样的厚光刻胶层消耗的量比需要的要更多，是很昂贵的。此外，除去光刻胶是很困难的，因为它比另外情况下使用得更厚。

相反，图 8 说明本方法的一个优选实施方案，使用金属络合物，应用于揭起方法，在揭起层上形成带图案的薄顶表面。在步骤 8A 中，提供一个基底 700。在步骤 8B 中，在基底 700 上涂布隔离层 705，而在隔离层 705 上涂布揭起层 710。在步骤 8C 中，把前驱体层 720 涂布在揭起层 710 上。在此情况下，前驱体 720 含有金属络合物。在步骤 8D 中，通过掩膜 735，将前驱体 720 对部分转化方法曝光，在该部分转化方法是例如光 745。掩膜 735 包括一个透明的玻璃基底 740，它具有对部分转化方法基本上不透明的区域 750。曝露于部分转化方法 745 的一部分前驱体 720 被至少部分转化或反应，形成部分转化前驱体 732 的区域。在步骤 8E 中，整个组装体曝露在去除方法（未显示）例如液体显影剂中。通过显影剂或去除方法去掉基本上未转化的前驱体 720，曝露出揭起层 710，同时留下被部分转化而且耐受去除方法的部分转化前驱体 732。在一个任选的步骤（未显示）中，对部分转化前驱体 732 施加转化方法（未显示），形成基本上充分转化的前驱体。

在步骤 8F 中，以各向异性的方式应用去除方法 760，例如等离子体刻蚀化学品，以除去不在前驱体 732 底下的揭起层 710 和底下的隔离层 705 的这些区域。在步骤 8G 中，通过让去除方法 760 以各向异性的方式刻蚀揭起层 710 和隔离层 705，从而形成如同所描述的曲线断面的揭起层。在步骤 8H 中，通过沉积方法在组合体上沉积上所需金属 770 的膜。在步骤 8I 中，通过显影方法，例如溶剂或干式显影法，与前驱体 732、揭起层 710 和隔离层 705 一起除去所需金属 770 的不需要

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部分，在基底 700 的顶上剩下所需金属 770 的所需图案。该方法优于在图 7 中概述的现有技术的方法，因为它需要的步骤较少，而且无须使用光刻胶。

图 9 说明本方法的另一个实施方案，使用金属络合物，应用于揭起方法，在揭起层的上面形成带图案的薄顶表面膜。在步骤 9A 中，提供一个基底 800。在步骤 9B 中，在基底 800 上涂布前驱体层 810。在该情况下，前驱体含有金属络合物。在步骤 9C 中，通过掩膜 835 使前驱体层 810 对部分转化方法曝光，在此部分转化方法是例如光 845。掩膜 835 包括透明的玻璃基底 840，它具有对部分转化方法基本上不透明的区域 850。曝露于此部分转化方法的部分前驱体 850 被至少部分转化或反应，形成已曝光区 832。在步骤 9D 中，整个组装体曝露于去除方法（未显示）如液体显影剂中。通过该去除方法除去基本上未转化的前驱体 810，曝露出基底 800，同时留下被部分转化而且耐受去除方法的已曝光区域 832。如在本发明的其他实施方案中所叙述的，已曝光区域 832，在去除方法步骤 9D 以后，可任选地再进行转化。如在步骤 9D 中所描述，通过对曝光和在步骤 9C 和 9D 中介绍的去除方法的控制，可以在已曝光区域 832 中得到向内具有锥度的侧壁断面，这些方法分别如在上面步骤 8D、8F 和 8G 中叙述过。在步骤 9E 中，通过沉积方法，在组装体上沉积上所需金属 870 的膜。在步骤 9F 中，通过显影方法例如溶剂或干式显影法，与前驱体 832 一起除去所需金属 870 的不需要的部分，在基底 800 的顶上剩下金属 870 的所需图案。

在本发明的另一个优选实施方案中，可使用 TSI 层集成的方法，制造把铜集成到半导体接插结构时使用的双波纹结构。图 10，从步骤 A 到步骤 H 说明了制造波纹结构的现有技术的方法，该方法被称为“via-first”方法。在步骤 10A 中，提供一个基底 900，如在图上所示，该基底上相继涂布有第一介电层 905、隔离层 915、第二介电层 910 和硬掩膜 920。介电层 905 和 910 一般是，但不必须是相同的材料，而隔离层和掩膜层 915 和 920 可以是相同的材料，也可以是不同的材料，但经常是氮化硅和/或氧化硅。在步骤 10B 中，在硬掩膜 920 的顶上，用底部抗反射涂层（BARC）925 和光刻胶层 930 涂布组装体。如图所示，光刻胶上形成上图案并通过传统方法显影。在步骤 10C 中，使用

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等离子体刻蚀化学品除去 BARC 层 925、硬掩膜 920、介电层 910、隔离层 915 和介电层 905 上所指出的部分。在步骤 10D 中，在步骤 10C 的等离子体方法以后，从组装体上除去剩余的光刻胶 930 和 BARC 层 925。在步骤 10E 中，如图所示，在组装体硬掩膜 920 的顶上涂布第二 BARC 层 935 和第二光刻胶层 940，该光刻胶层 940 上形成了图案并被传统方法显影。在步骤 10F 中，使用了第二等离子体刻蚀化学品步骤除去 BARC 层 935 和介电层 910 的指定部分。在步骤 10G 中，在步骤 10F 的等离子体方法以后，除去剩余的光刻胶 940 和 BATC935。

与此相反，图 11 说明本发明的方法如何可用更少的步骤制造双波纹结构。在步骤 11A 中，提供一个涂布有介电层 1005 的基底 1000。在步骤 11B 中，在该介电层的顶上涂布上例如含有金属络合物的前驱体层，通过至少部分转化而形成上图案，然后用如前面在本发明的另一个实施方案中所讨论的技术进行显影，得到如图所示的带图案层 1010。例如，可以通过例如溶剂或如上所述的干式显影法进行图案显影步骤。然后在带图案层 1010 的顶上涂布上旋转平面化层 1015。该旋转平面化层 1015 可以是任何有机基的涂层，可以旋涂在组装体这。在步骤 11C 中，如图所示，例如使用与形成带图案层 1010 时使用的相同技术沉积上带图案层 1020，并形成图案和显影。在步骤 11D 中，应用刻蚀方法(未显示)，例如等离子体刻蚀化学品，除去旋转平面化层 1015 的所显示区域和介电层 1005 的一部分厚度。对刻蚀方法进行控制是很重要的，如图所示使其只除去一部分介电层 1005 的厚度。例如，可以使用的等离子体刻蚀，限制其时间短于刻蚀介电层整个厚度所需的时间。

在步骤 11E 中，通过去除方法，例如用溶剂处理组装体来除去带图案层 1020 和旋转平面化层 1015，旋转平面化层在该溶剂中是可溶的，而且该溶剂对组装体的其他部分没有基本上的不良影响。在步骤 11F 中，应用受到控制的刻蚀方法（未显示），例如如上所述的等离子体刻蚀化学品除去介电层 1005 上所描绘的区域。该受控制的刻蚀在由带图案层 1020 所形成的图案中同时除去了介电层 1005 的剩余厚度，而在带图案层 1010 所形成的图案中只除去介电层 1005 的一部分厚度。可以以这样的方式组合出双波纹的模式。

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在步骤 11F（未显示）以后可以任选地除去带图案层 1010，另外把带图案层 1010 剩下，在沉积了铜和平面化以后用做 CMP 终止点。

很明显，在图 11 中所描述的方法优于在图 10 中叙述的方法，因为前者使用的步骤较少，无需多层光刻胶和 BARC 的步骤，避免了在传统方法中使用的隔离层和硬掩膜。

图 12 说明一个由现有技术使之简化的复杂的离子注入的方法，用来制造带图案离子注入掩膜。在步骤 12A 中，如在图 2 中所述提供一个基底 1200。在步骤 12B 中，在基底 1200 上形成一个任选的保护层 1205，然后是注入掩膜层 1210。在一个实施例中，注入掩膜层是氧化硅。在步骤 12C 中，在注入掩膜层 1210 的顶上，在基底 1200 上涂布光刻胶层 1220。在步骤 12D 中，通过掩膜 1235 使光刻胶层 1220 对光 1230 曝光。掩膜 1235 包括一个透明的玻璃基底 1240，它具有对曝光方法 1250 基本上不透明的区域，因该遮挡住一部分光，在光刻胶层的已曝光部分 1222 上形成了图案。在步骤 12E 中，已曝光的光刻胶区 1222 被显影，曝露出注入掩膜层 1210。在步骤 12F 中，用适当的刻蚀组合物，通过刻蚀掉注入掩膜层的未保护部分，在注入掩膜层 1210 上形成了开口。在步骤 12G 中，除去剩余部分的光刻胶层 1220。在步骤 12H 中，将基底在离子束下曝光，以在注入掩膜中的开口下直接形成注入区 1270。在任选的步骤 12I 中，除去注入掩膜层 1210，将基底退火，由此把注入区 1270 转化为搀杂区 1280。因此，由图 12 可以明显地看出，传统的方法需要比本方法更多的步骤来形成带图案的注入掩膜并通过该掩膜进行离子注入。

反之，图 13 说明本方法的另一个优选实施方案，使用金属络合物，用来制造离子注入掩膜，形成带图案的注入掩膜，该方法去掉了与注入掩膜刻蚀有关的所有步骤，即如上所述的步骤 12C 到 12G。在步骤 13A 中，提供一个基底 1300。在步骤 13B 中，在基底 1300 上形成一个任选的保护层 1312，在保护层 1312 的顶上形成一个前驱体层 1310。在此情况下，前驱体 1310 是金属络合物。在步骤 13C 中，通过掩膜 1320 使前驱体 1310 对部分转化方法曝光，在该部分转化方法是光 1315。掩膜 1320 包括一个透明的玻璃基底 1330，它具有对部分转化方法基本上不透明的区域 1340。对部分转化方法 1315 曝光的一部分前驱

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体 1310 被至少部分转化或反应，形成部分转化前驱体区 1350。在步骤 13D 中，该组合体曝露在去除方法（未显示），例如液体显影剂中。通过显影剂或去除方法除去未转化前驱体 1310，曝露出保护层 1312，同时留下被部分转化而且耐受去除方法的部分转化前驱体 1350。在步骤 13E 中，对部分转化前驱体 1350 施加转化方法（未显示），形成基本上充分转化的前驱体 1360。该转化可通过例如漫射光曝光步骤或热退火步骤来实现。在步骤 13C 和 13E 的每一步，如果已转化前驱体 1360 将是介点膜，该转化优选在氧存在下进行；而如果已转化前驱体将是金属膜，则优选在还原性气体，例如氢存在下进行。在步骤 13F 中，基底 1300 经受离子注入方法例如离子束 1370 的处理，以在基底上形成注入区 1380。在任选的步骤 13G 中，除去注入掩膜并进行热退火，以把基底上的注入区 1370 转化为掺杂区 1390。

本发明方法很宽的范围使得能够广泛地得到应用。本发明的一个优选实施方案包括无定形的金属氧化物膜，用于在印刷线路板（PWB）中形成集成的电容结构，其中使用适当的前驱体溶液按照本发明涂布和直接在 PWB 基底上形成图案。本发明的优点包括能够直接形成图案，并与此有关省略掉其他的工艺步骤、使用 PWB 加工所要求的环境温度和环境压力，以及形成的膜是高电容所能够接受的。

在另一个优选的实施方案中，通过本发明，在透明的基底形成带图案的金属氧化物或混合金属氧化物膜，成为不透明的图案。这样实施本发明，在半导体制造方法中进行平版印刷的图案转移时，可用做图案掩膜。

在本发明另外的一个优选实施方案中，使用无定形的金属氧化物或混合金属氧化物膜在高级的连接半导体器件的连接界面中，形成去偶电容结构，其中按照本发明的方法，在改性硅基底上用适当的前驱体溶液进行涂布并形成图案。在该实施方案中固有的优点包括直接形成图案的能力，由此可以省去许多其他的工艺步骤，再一个优点是使用环境温度和环境压力，这与这样的高级连接件组装时的条件没有什么不同。

本发明的再一个实施方案设想，使用的前驱体膜可用于给记忆储存元件制造图案，无论是以电容性储存节点的方式，即动态随机存取

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存储器（DRAM），还是作为铁电体记忆存储节点（FeRAM），再有，在该实施方案中固有的优点包括能够直接形成图案，这样就省略了许多其他的工艺步骤，再一个优点是使用环境温度和环境压力，这与这样的记忆器件组装时是没有什么不同的。

本发明还有一个实施方案设想在半导体制品的前端形成门介电材料，因为高级硅基器件在优选的门介电材料中可以使氧化硅转变为具有更高介电常数的新材料。这种具有高介电常数的新材料，对于同样的电气性能，允许把门介电材料的物理厚度制造得比二氧化硅更厚。该更厚的物理厚度使得更容易制造，也使通过该门的量子通道效应更小。很明显，当把本发明的方法用于线前端（FEOL）半导体工艺时，比其他已知的要求较低温度和严格低真空的方法具有更大的优点。有各式各样的高介电常数的材料适合于本发明的方法，这包括但不限于$Ba_xSr_yTi_2O_3$（BST）、$BaTiO_3$、$SrTiO_3$、$PbTiO_3$、$Pb_xZr_yTi_zO_3$（PZT）、(Pb,La)(Zr,Ti)O_3（PLZT）、(Pb,La)TiO_3（PLT）、$LiNbO_3$、Ta_2O_5、$SrBi_2Ti_2O_9$、Al_2O_3、TiO_2、ZrO_2和HfO_2。

与此类似，本发明可用于制造 FEOL 半导体制品的门电极材料。这些材料在与门介电材料形成电接触的门介电材料的顶上。过去，门电极一直是由硅制造的。按照与门介电材料从二氧化硅向外迁移相类似的方式，具有推动力，使门电极转变为基本上比硅具有更好特性的材料。可供门电极的用途候选材料包括铂、铱、钌、氧化钌、氧化铱和其他新材料。所有这些材料提出都对沉积和形成图案进行挑战，然而它们都适合于本发明的应用。另外，在传统方法中的许多步骤都要求高温、严格的真空要求以及使用苛刻的等离子体加工条件，这些都预示着会损害敏感的硅基底。使用本发明的方法就可以避免这些苛刻的条件。对传统方法更大的挑战是如在 US-P-6048769 中所述，须要把不同的电极材料放置在不同偏压的门晶体管上。对于传统集成路径的这个要求就使本来已经很多的步骤再次加倍，因此从制造的观点出发，本发明的这个优选实施方案为减少步骤数提供了戏剧性的优势。

贵金属和导电金属氧化物的应用并不限于制造门电极。对于这些材料有几个隔离层的应用，无论是导电层还是绝缘层，都用在 FEOL 半导体的加工中。很明显，这些应用中有几个依赖于形成所需材料的

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膜，这些材料具有作为电容性材料使用的高介电常数（高 k 值）。按照类似的方式，可以对膜进行优化，使膜对于作为感应材料的磁导率（μ）达到最佳。类似地可能是电阻元件，就像是磁性元件、压电元件、热电元件和铁电元件一样。

本发明方法的其他可能的应用是非常宽广的。某些例子包括：用于半导体制造（晶体管门电路组、电容性结构等）的高介电常数材料的直接图案沉积、用于微电子包（电容性结构）的高介电常数材料的直接图案沉积、用于半导体制造（晶体管门电路组、电容性结构等）的高介电常数材料的低温沉积、用于微电子包（电容性结构等）高介电常数材料的低温沉积、用于半导体制造（晶体管门电路组、电容性结构等）的高介电常数材料的非真空基沉积、用于微电子包（电容性结构等）的高介电常数材料的非真空基沉积、用于半导体制造（绝缘子结构等）的金属氧化物的直接图案沉积、用于微电子包的金属氧化物的直接图案沉积、用于半导体制造的金属氧化物低温沉积、用于微电子包（电容性结构）的金属氧化物的低温沉积、用于半导体制造的金属氧化物非真空基沉积、用于微电子包的金属氧化物非真空基沉积、用于半导体制造（晶体管门电路组）的金属的直接图案沉积、用于微电子包（连接件等）的金属直接图案沉积、用于半导体制造的金属低温沉积、用于微电子包的金属低温沉积、用于半导体制造的金属非真空基沉积、用于微电子包的金属非真空基沉积、用于半导体制造（片上电阻元件）的电阻材料的直接图案沉积、用于微电子包（包封电阻器）的高电阻材料的直接图案沉积、用于半导体制造的电阻材料的低温沉积、用于微电子包（包封电阻器）的电阻材料的低温沉积、用于半导体制造的电阻材料的非真空基沉积、用于微电子包的电阻材料的非真空基沉积、通过混合金属/氧化物沉积受控制的电阻材料、用于半导体制造（片上感应器）的制造感应器材料的直接图案沉积、用于微电子包（包封感应器）制造感应器材料的直接图案沉积、用于半导体制造的制造感应器材料的低温沉积、用于微电子包（包封感应器）的感应器制造材料的低温沉积、用于半导体制造的感应器制造材料的非真空基沉积、用于微电子包的感应器制造材料的非真空基沉积、用于制造使用有机半导体和/或有机基底的器件的金属和氧化物材料的直接

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图案沉积、用于制造使用有机半导体和/或有机基底的器件的金属和氧化物材料的低温沉积、用于制造使用有机半导体和/或有机基底的器件的金属和氧化物材料的低温沉积、用于制造使用有机半导体和/或有机基底的器件的金属和氧化物材料的非真空基沉积、在双层或 TSI 光刻胶方法中用做光敏、电子束敏层、磁性材料的直接图案沉积、低温沉积、非真空基沉积、混合金属和混合氧化物材料的沉积、金属和金属氧化物结构的喷墨状（液滴）打印、在基底上的喷雾涂布、使用用于厚膜的液相涂布（旋涂或弯月面涂布）的材料，以简化和改善涂布方法和性能，然后利用转化时的体积收缩以得到薄涂层（这样的应用是制造包封的电容器，这里涂布上厚层以得到最终薄的膜，用以改善该结构的电容）的用途、在聚合物/天然纤维上液态涂布金属有机前驱体，然后通过光化学转化或低温热转化，沉积出金属或金属氧化物涂层（例如涂布银/氧化银制造抗微生物纤维和织物，用于医院的应用、抗臭味的服装例如袜子或衬垫等）、将前驱体进行液相渗透，然后进行热转化，形成具有催化活性的多孔材料、用做聚合物溶液的添加剂，通过形成纳米级组合物以改善得到的材料的物理、化学、光学和电性能的应用、合成和配合水溶性前驱体以减少上述方法中的挥发份的排放、门电极材料、平面显示器、FeRAM、直写材料、微细流体、掩膜和波导。

对于制造电子材料用的方法的补充叙述包括在同时提交的 US 专利申请 09/_____中叙述的内容，题目是《基底预处理的方法和设备》，其公开的内容在该引做参考。

实施例

下面的实施例进一步说明本发明的某些实施方案。提供这些实施例仅用于说明的目的，不以任何方式对本发明构成限制。

实施例 1

通过将其溶解于适当的溶剂并将该溶液旋涂在硅芯片表面上，浇注出两种不同的含锆前驱体膜，即 Zr(乙酰丙酮)$_4$（也已知作为 Zr(acac)$_4$ 和四(2,4-戊二酮基)锆(IV)）和 Zr(羧酸根)$_4$。每一种都经受长时间的覆盖式热处理，即直到前驱体膜的厚度不再有变化为止。在该处理之后，使用可变角光谱椭圆仪（VASE）测量每个试样的折光指数与波长的关

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系。在图 14 中描述了得到的结果。在图 14 中，曲线 101 来自由 $Zr(acac)_4$ 前驱体形成的试样，曲线 102 来自由 Zr(羧酸根)$_4$ 前驱体形成的试样。这些结果显示出，在每个试样的折光指数性能上存在着明显的差别，这直接与前驱体的化学组成有关。$Za(acac)_4$ 前驱体形成的膜具有的折光指数为对于 3%，高于由 Zr(羧酸根)$_4$ 形成的膜的折光指数。

实施例 2

先制造两种不同的铜前驱体，即 $Cu(OH_2)_2(O_2C(CH_2)_4CH_3)_4$ 和(μ-$(C_2H_5)_2NCH_2CH_2O)_2Cu_2(N_3)_2$。据认为每种前驱体都经受光化学反应，这导致失去配位体并产生铜原子。然后认为铜原子互相结合，形成金属铜，或者与氧结合形成氧化铜，然而，作为先形成的金属铜氧化的结果，也可能生成氧化铜。基于现有技术的化学，没有理由假设在类似的条件下这些不同的前驱体将提供不同的产物，虽然都承认作为对前驱体进行选择的结果，反应的成膜性能和效率会有很大的差别。

因此，把这两种前驱体的每一种都进行溶解，通过旋涂的方法在硅片上使每种溶液沉积，然后在真空中通过光分解，使在涂布的每块晶片上的前驱体层进行基本上的充分转化。光分解一直持续到在对膜进行 DTIR 光谱分析时不再观察到与配位体有关的吸收。然后把试样转移到烧结炉中，在 400℃的氮气下加热。

然后用已知的宽角度 X 射线衍射法对每个试样进行检测。发现 $Cu(OH_2)_2(O_2C(CH_2)_4CH_3)_4$ 前驱体在转化后得到更多的氧化铜，而对于(μ-$(C_2H_5)_2NCH_2CH_2O)_2Cu_2(N_3)_2$ 前驱体则产生更多的晶体金属铜。这样的结果显示出这些方法结果的依存性，即在转化以后，对前驱体的组成具有现有技术无法预见的依存性。

给定前驱体材料的膜转化为无定形膜的方法，例如热方法或光分解方法，对这些膜的性能可以具有明显的影响。如在实施例 3 和 4 中所显示的，在汇总光学的折射率数据中就显示出这一点，通过比较介电常数的数据也清楚地显示出这一点。

实施例 3

将前驱体 $Zr(acac)_4$（乙酰丙酮锆(IV)，来自 Chemat Technology 公司，Northridge，CA）溶解于甲苯，以 1250rpm 的转速在 30sec 将该溶液旋涂在硅晶片上。得到的未转化前驱体膜的厚度为 436Å。在 180℃

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的加热板上加热 1hr，将 ZrO_2 进行热转化。在 180℃的加热板上再进行延长的热转化。使用具有 220 nm 冷镜的 Karl SussMJB-3 型掩膜直线对准器对 ZrO_2 进行光化学转化。由于掩膜直线对准器在深紫外线区的输出强度比较小（大约 0.38mW/cm²），要使用 5hr 的曝光时间，因为已经发现再多的曝光剂量也不会使厚度进一步缩减。使用 VASE 测定得到的膜的厚度和折光指数与波长的关系。这些膜测量的厚度如下：

未转化的 $Zr(acac)_4$ 前驱体	436Å
热转化	360Å
延长热转化	316Å
光转化	330Å

将前驱体 $Zr(O(O)CC_7H_{15})_4$（2-乙基己酸锆(IV)，来自 Chemat Technology 公司，Northridge，CA）溶解于己烷，以 1500rpm 的转速在 30sec 将该溶液旋涂在硅晶片上。得到的未转化前驱体膜的厚度为 2335Å。在 180℃的加热板上加热 3hr，将 ZrO_2 进行热转化。在 180℃的加热板上再进行延长的热转化。包括热转化时间总共达到 6hr。如上面对 $ZrO(acac)_4$ 所述，ZrO_2 进行光化学转化，只是由于前驱体 $Zr(O(O)CC_7H_{15})_4$ 的光敏感度比较低，曝光强度也低，所以使用的曝光时间大约是 30hr。也是使用 VASE 测定得到的膜的厚度和折光指数与波长的关系。这些膜测量的厚度如下：

未转化的 $Zr(O(O)CC_7H_{15})_4$ 前驱体	2335Å
热转化	1141Å
延长热转化	977Å
光转化	1487Å

在图 15 上显示的是折光指数的结果，这里光化学转化的 $Zr(acac)_4$ 是曲线 1，热转化的 $Zr(acac)_4$ 是曲线 2，热转化的 $Zr(O(O)CC_7H_{15})_4$ 是曲线 3，而光化学转化的 $Zr(O(O)CC_7H_{15})_4$ 是曲线 4，延长热转化的 $Zr(O(O)CC_7H_{15})_4$ 是曲线 5，延长热转化的 $Zr(acac)_4$ 是曲线 6。

这些结果显示出，对于每种试样的折光率性能有明显的差别，这直接关系到前驱体的化学组成及其制备方法。

实施例 4

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在涂铝的硅晶片上旋涂上大约 7000Å 的前驱体在己烷中的溶液，该前驱体设计其在在至少部分转化后会得到 BST 膜。通过将 3.7gTi(二(乙酰丙酮)二(异丙氧基))、2.8g2-乙基己酸钡和 5.6g2-乙基己酸根（在 2-乙基己酸中，浓度 40wt%）溶解于 182g 己烷中制备 BST 前驱体膜，相当于 Ba:Sr:Ti(IV)的摩尔比为 1:0.8:1。通过热处理或者通过光分解材料把前驱体膜转化为 BST 膜。把得到的薄的 BST 膜制成膜电容器并测量膜的电性能。如同在下面的结果可以看出的，每种膜的介电常数和平均电导率都有着戏剧性的不同：

由热转化得到的 BST 膜	
介电常数	4.66
平均电导率	0.009992S
由光化学转化得到的 BST 膜	
介电常数	27.26
平均电导率	0.04311S

这些结果显示出对于每个试样，在电性能上有着明显的差别，这直接涉及到转化前驱体的制备方法。

实施例 5

在例如旋涂膜前驱体时，对溶剂的选择是重要的，因为它可以影响到膜的光学质量。例如，该实施例显示出，由含有用于转化为 BST 膜的前驱体在 MIBK 和正庚烷中的溶液浇注得到的膜，可得到很高的光学质量，而从 PGMEA 的溶液就得到带斑纹的膜。

在这些溶剂的每一种当中，通过将前驱体溶解于溶剂，或者用所需的溶剂替代前驱体溶液中的一部分或全部溶剂。每种溶液都用旋涂法沉积在覆盖有铝的硅晶片上。硅晶片以 1500rpm 的转速旋转 30sec。在旋涂以后，在 110 的加热板上烘烤 2min，以除去任何残留的溶剂。使用带有 220nm 冷镜的 Karl Suss MJB-3 型掩膜直线对准器以大约 1.2mW/cm²的强度把前驱体膜转化为氧化物。每块晶片曝光 1.5hr，以确保完全转化。在转化以后，进行显影和去除步骤，这时用与旋涂试样同样的溶剂漂洗，洗掉每块前驱体膜的未转化、未曝光的部分。使用 VASE 测量在转化前（即未转化的）、刚刚在转化以后的和显影后的膜厚度。

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由 MIBK 和正庚烷得到的高光学质量的前驱体膜表面，基本上没有上面表面特征，所以就没有图可以显示这个。反之，由 PGMEA 溶液旋涂得到的BST前驱体膜显示出明显的条纹，这可以在图16中看出。在上述溶剂中，MIBK 得到最均匀的和可以重现的膜。

实施例 6

在如何使用热处理把前驱体膜转化为所需材料的膜的实施例中，用设计在转化时用来形成 BST 膜的前驱体溶液旋涂一系列的裸硅晶片。通过在 160℃的加热板上以 10min 的间隔加热每块晶片，使总加热时间为 120min，从而使晶片进行至少部分转化。在每次转化间隔以后，用异丙醇漂洗给前驱体图案显影，除去未转化的前驱体。这样就能够测定出热印该膜所需的时间，即在用异丙醇显影后具有明显量的残留膜所需的时间。如在图 17 上所看到的，对于热转化，测定的这个时间大约是 20min。

用光化学转化代替热转化进行类似的实验，该结果显示在图 18 中。该图显示出，光化学印膜所需的时间为大约 30~60min。在第三个实验中，设计的是将热部分转化或预处理与光化学转化结合起来，晶片先在 160℃下进行 10min 的预热处理，然后如上所述进行光化学转化的操作。热/光化学打印的结果如在图 19 中所示，该图显示出热/光化学转化组合方法所需的时间，即形成图案所需的最大时间，从只用光化学转化的 30~60min 缩短为大约 20min。

实施例 7

缩短成像光的波长和增加透镜系统的数字光圈都可以改善光投射系统的分辨率。然而，在整个光刻胶膜上保持图像聚焦的能力，随着厚度增加而降低。减小光刻胶膜的厚度可保持焦深，但对于图案转移步骤所需的刻蚀的要求限制了光刻胶的最大厚度。为了减弱焦深的限制，使用的薄的膜成像，只在光刻胶顶层上形成图案。在给光刻胶顶层成像以后，把图案显影，然后使用刻蚀的方法转移到基底上。

对于使用金属络合物前驱体的双层方法，可以使用含有底层和金属络合物前驱体的两组膜，每一层都是例如旋涂的。金属络合物前驱体的作用是刻蚀掩膜的要求，而底层被用于使用刻蚀把图案转移到基底上。测试了三种不同的底层：PMMA、PHOST 和线形酚醛树脂。

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PHOST 和线形酚醛树脂是在 160℃的加热板上进行 2hr 的硬烘烤以后进行金属络合物前驱体的旋涂的。在实验中使用的金属络合物前驱体，设计得能够形成 BST、PZT 或二氧化钛（TiO_2）。按照在实施例 4 中叙述的操作程序制备 BST 前驱体。通过把 18.48g2-乙基己酸铅溶解于 57.4g 己烷中，加入 24.2g2-乙基己酸锆(IV)和 9.5gTi(二(乙酰丙酮)二(异丙氧基))，然后再添加 327g 己烷来制备 PZT 前驱体，这相当于 Pb(II):Zr(IV):Ti(IV)的摩尔比是 2.5:1:1.3。下面的表列出了使用的不同组合以及底层和金属络合物前驱体是否被认为是相容的。

底层	前驱体	使用己烷浇注溶剂的相对相容性
PMMA	BST	差
PMMA	PZT	差
PHOST	BST	差
PHOST	PZT	差
线形酚醛树脂	BST	好
线形酚醛树脂	PZT	好
线形酚醛树脂	TiO_2	好

发现硬烘烤的线形酚醛树脂与 BST、PZT 和 TiO_2 前驱体都是相容的，而测试的 PMMA 和 PHOST 底层材料在旋涂金属络合物层的时候会溶解。在有 BST 和 PZT 前驱体使用的浇注溶剂己烷存在下，PMMA 和 PHOST 会溶解掉。硬烘烤的线形酚醛树脂与 BST 和 PZT 的相容性使得能够进行图案的形成和转移。

实施例 8

通过监测刻蚀时厚度的变化来确定在硬烘烤线形酚醛树脂和两种金属络合物之间的刻蚀选择性。按照实施例 7 制备硬烘烤线形酚醛树脂和充分转化的 PZT 或 TiO_2 试样，把试样装入刻蚀室，用氧等离子体进行 30sec 间隔的刻蚀，总刻蚀时间至少是 120sec。在每个刻蚀间隔之后测量试样的厚度。从厚度对刻蚀时间的图上确定每个试样的刻蚀速度。图 20 显示的是硬烘烤线形酚醛树脂的厚度对刻蚀时间图，而图 21 是对于充分转化的 PZT 和 TiO_2 的同样的图。下面的表格列出了各自的斜率和线形最小二乘方线的相关系数。

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被氧刻蚀的层	厚度~刻蚀时间图的斜率	相关系数
硬烘烤线形酚醛	–76.3	0.999
充分转化 PZT	–0.195	0.985
充分转化 TiO_2	–0.0866	0.992

由各个刻蚀速度图的斜率比确定出刻蚀选择性。硬烘烤线形酚醛树脂和充分转化 PZT 之间的刻蚀选择性是大约 390:1。硬烘烤线形酚醛树脂和充分转化的 TiO_2 之间的刻蚀选择性是大约 880:1。在同样条件下，TIO_2 的刻蚀选择性与 SiO_2 的刻蚀选择性大致相当。

实施例 9

进行了 BST 和 PZT 的电子束对比度测试，通过给每种材料的一系列充分转化的膜曝光，增加电子束的剂量，并注意在显影以后保留膜的百分比是 0 的最高剂量和保留膜的比例达到 1 的最低剂量，以确定这些材料的光速。PZT 和 BST 的对比度在大约相同的范围，从大约 60 至大约 100 μ C/cm^2。

本领域的专业人员将能够理解，本发明的范围并不限于在此所公开的内容，而且还要包括其扩展的内容。

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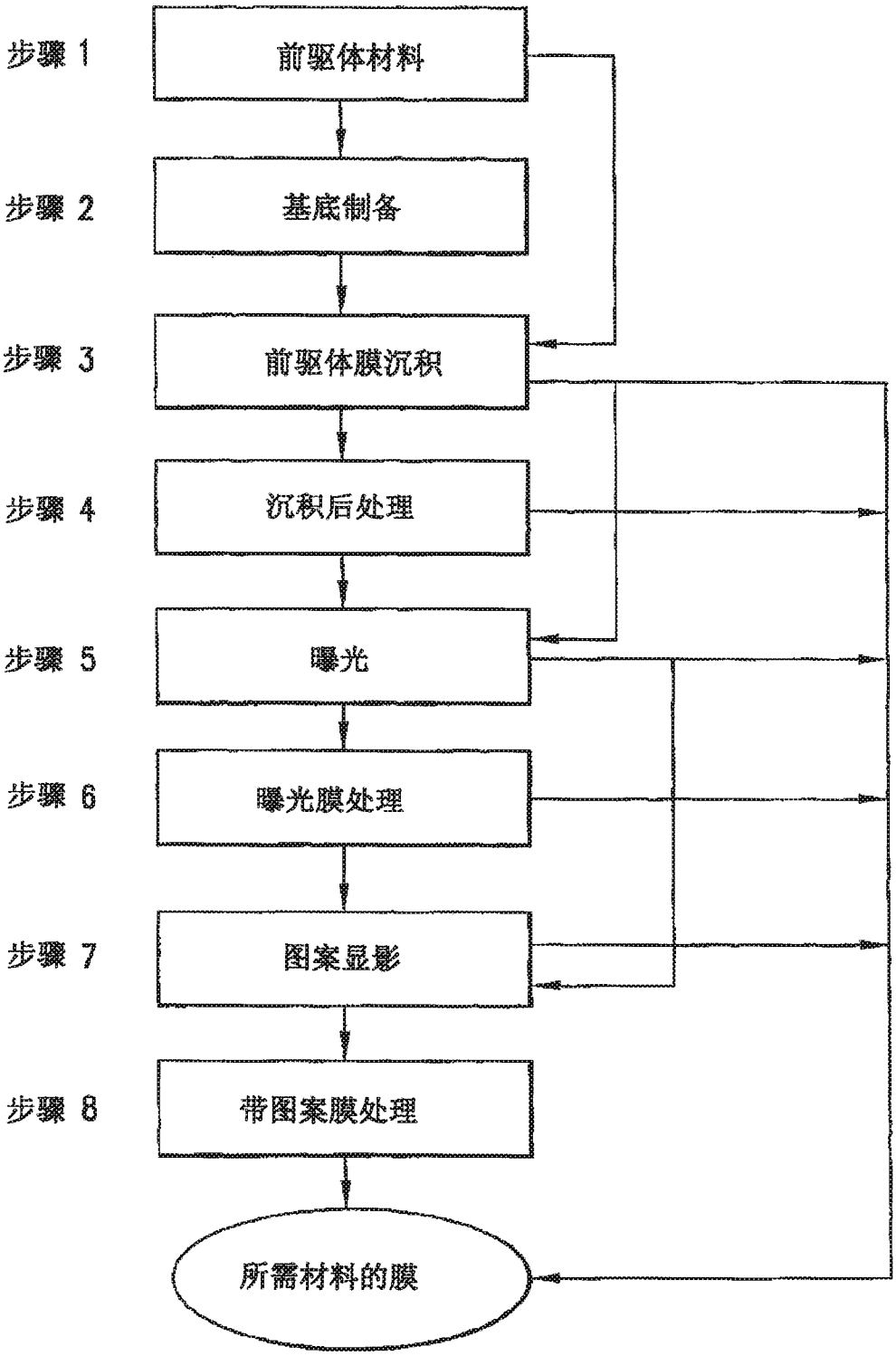


图1

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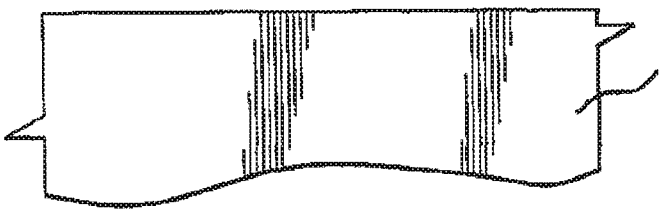


图2A

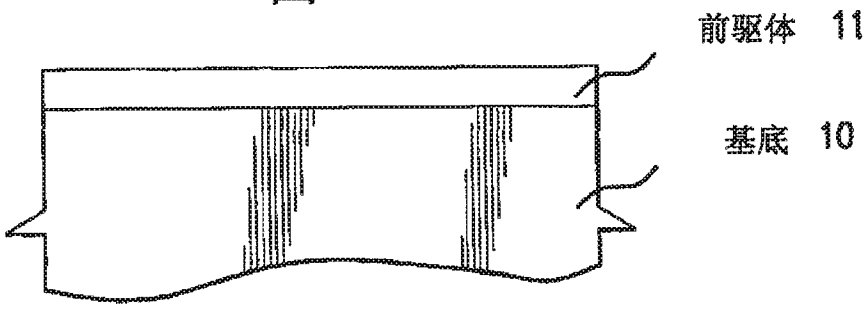


图2B

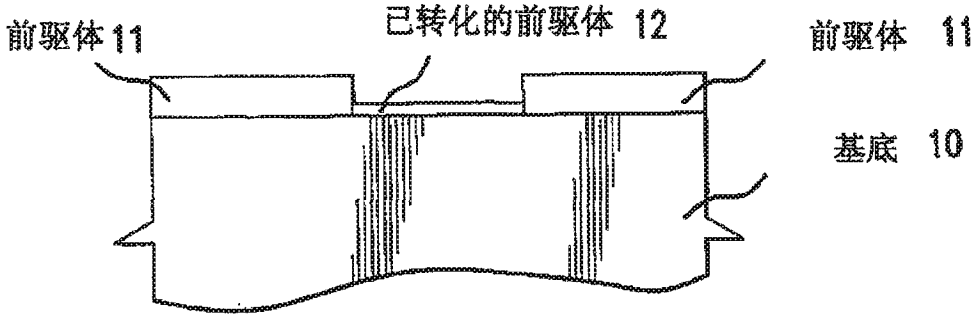


图2C

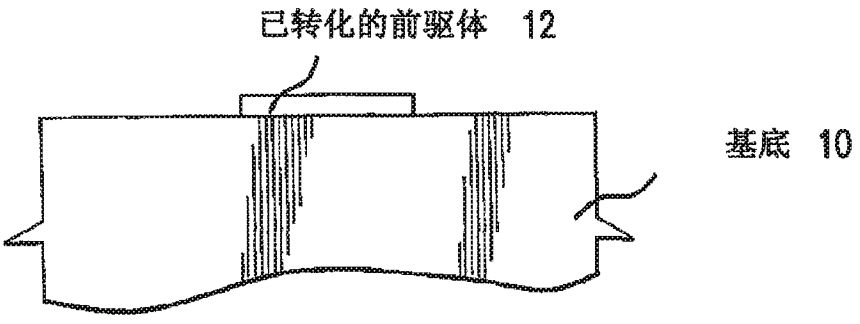
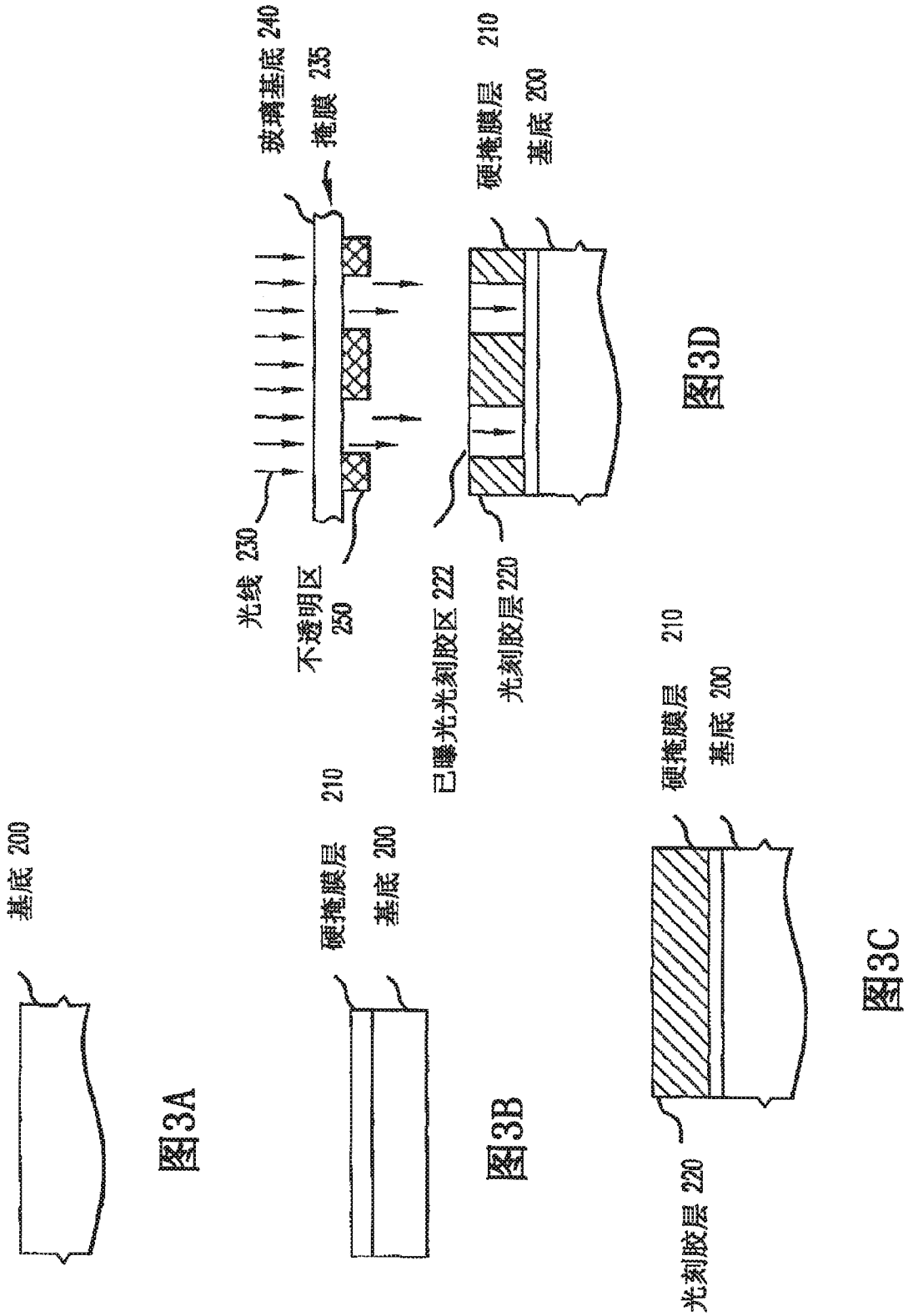
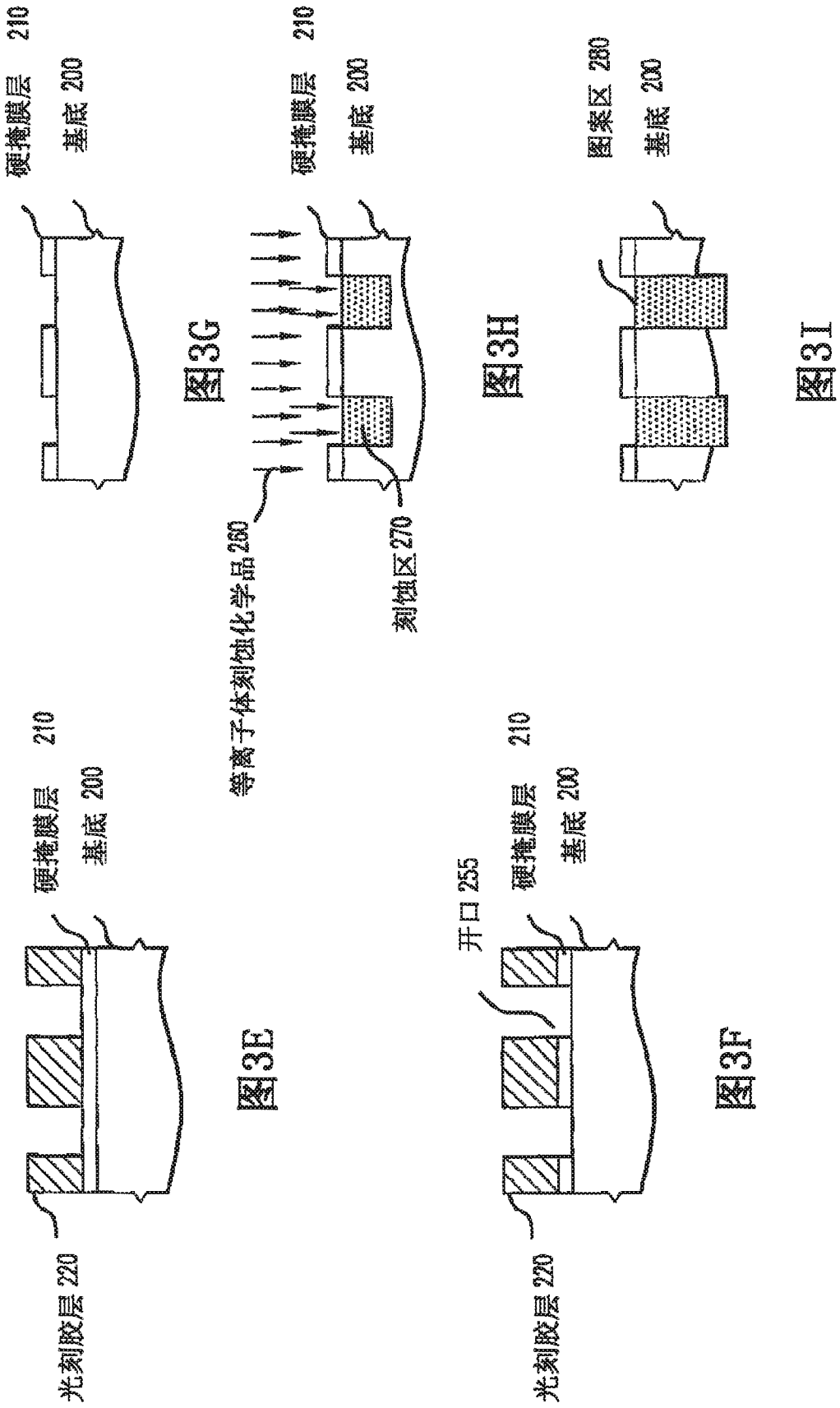


图2D

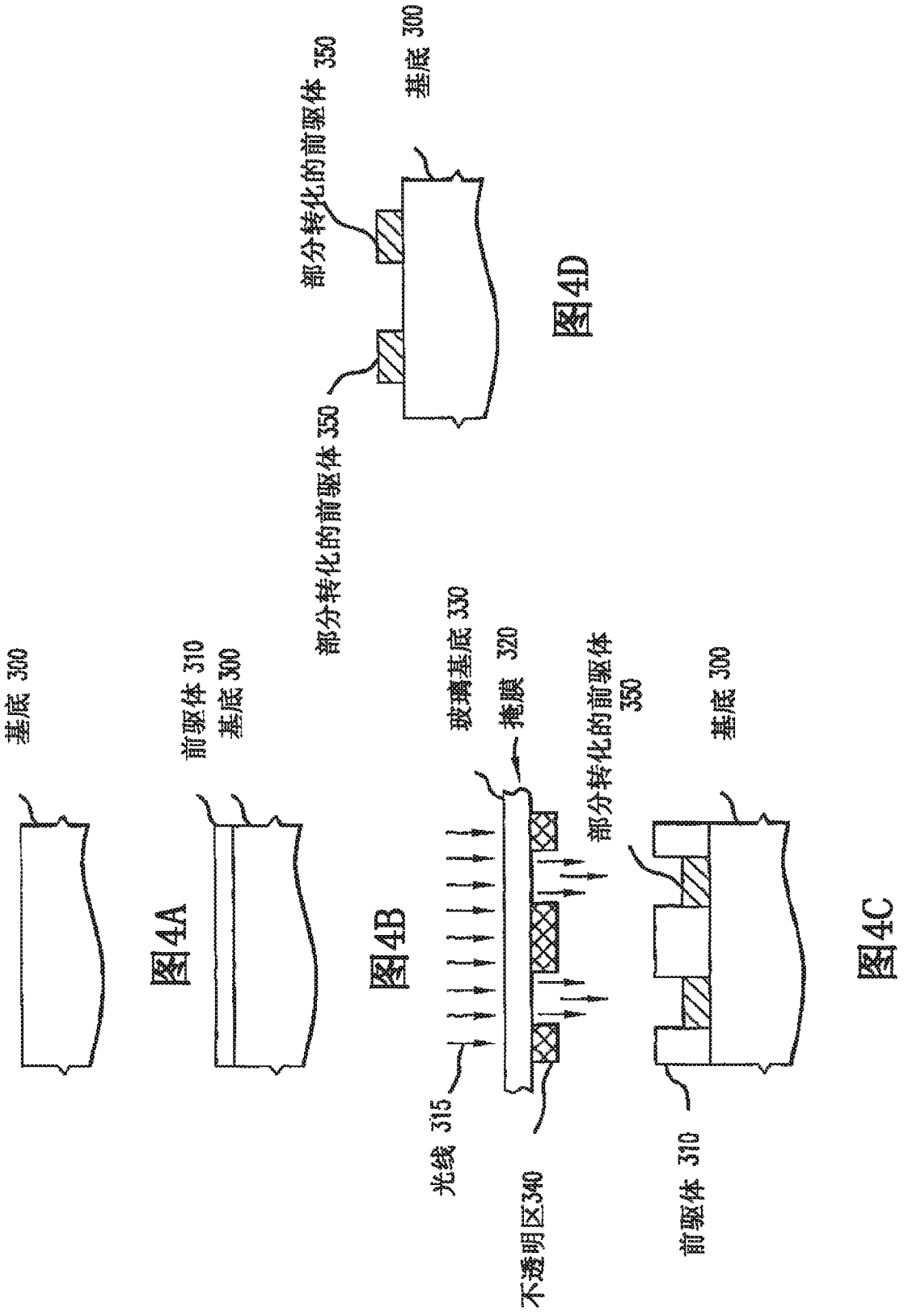
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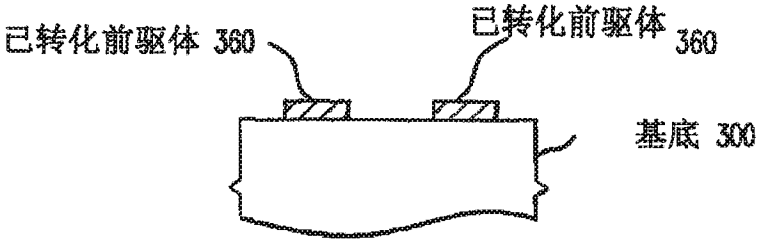


图4E

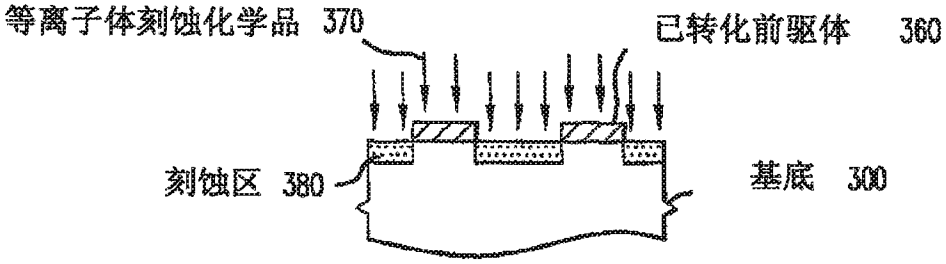


图4F

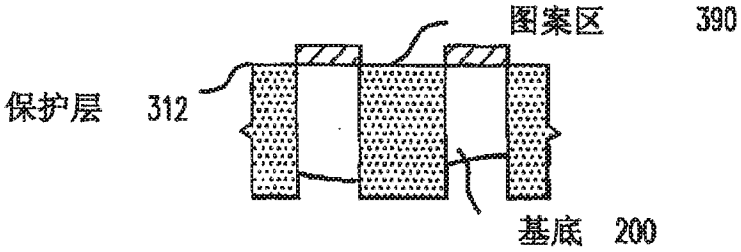
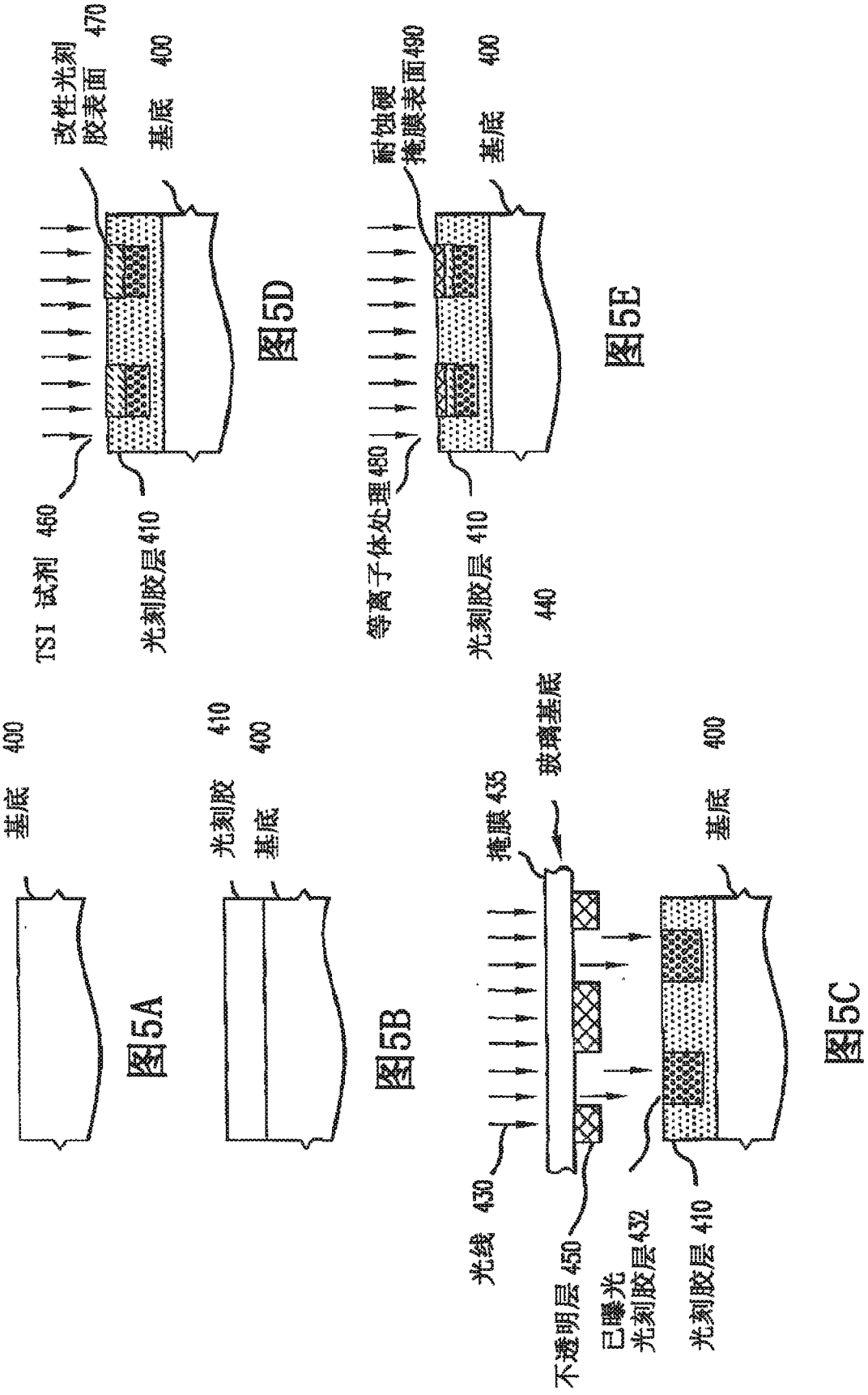


图4G

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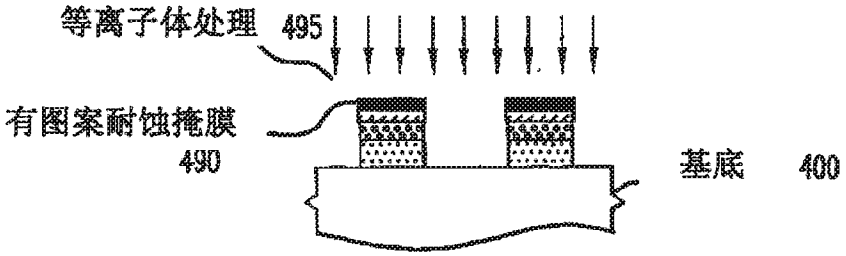


图5F

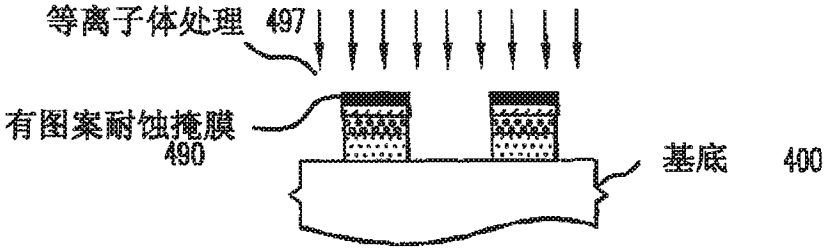


图5G

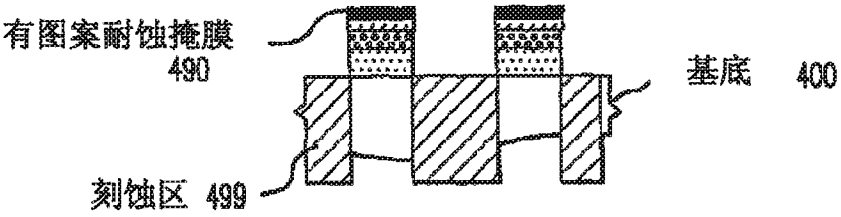


图5H

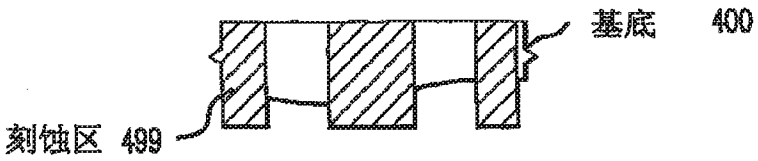


图5I

Lam Research Ex. 1009 - Page 391 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

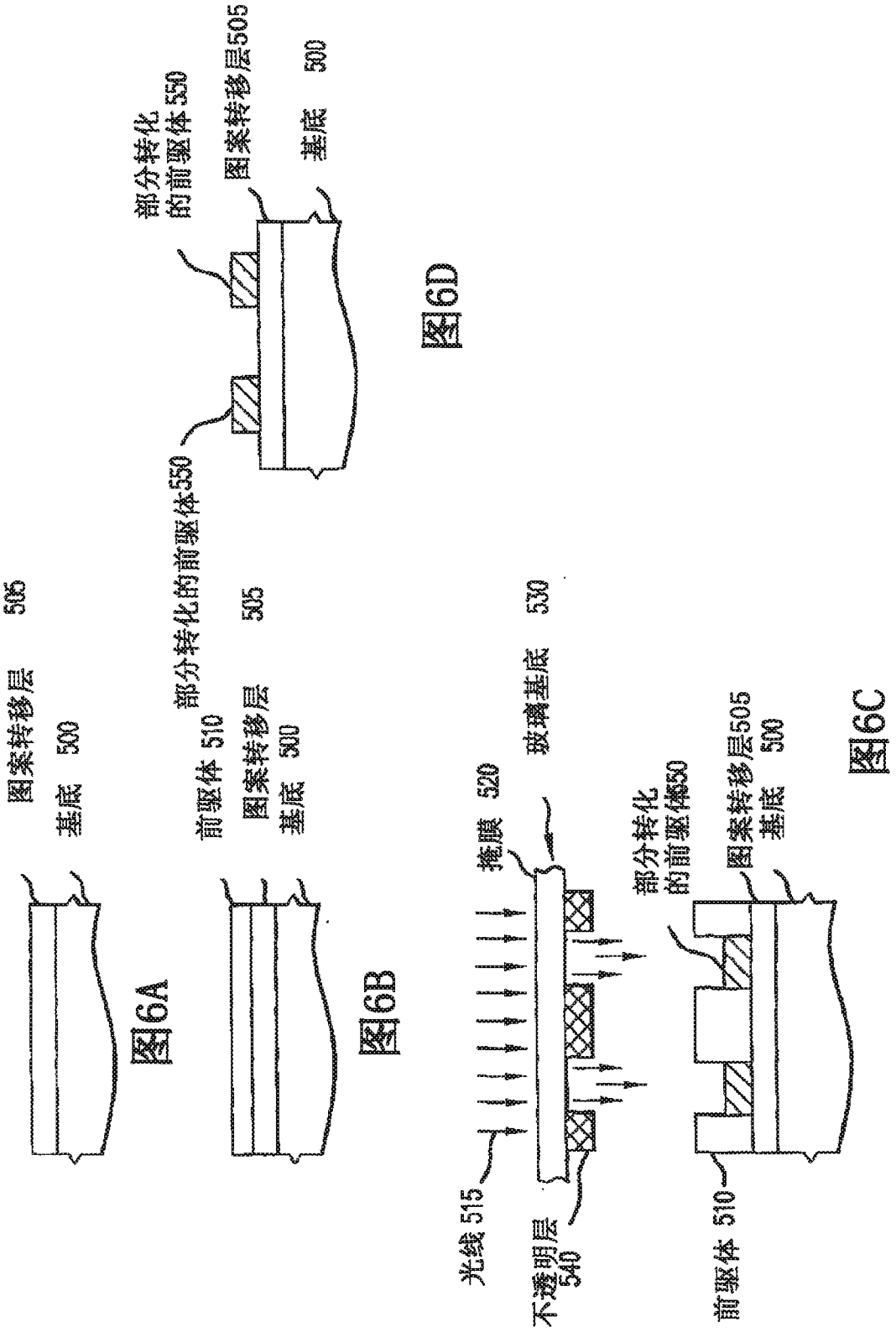


图6A 图6B 图6D 图6C

Lam Research Ex. 1009 - Page 392 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

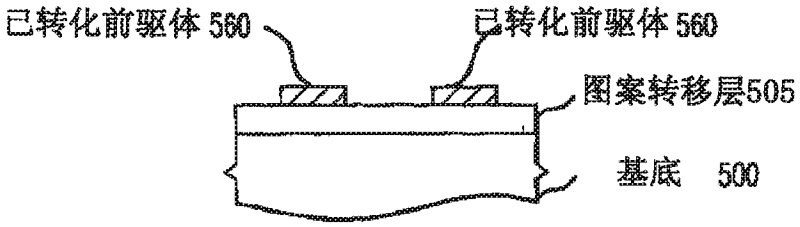


图6E

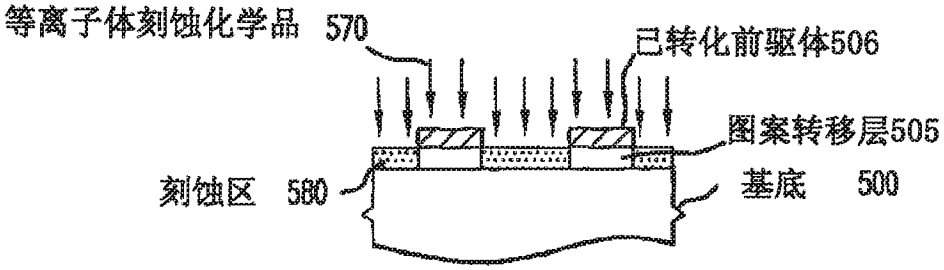


图6F

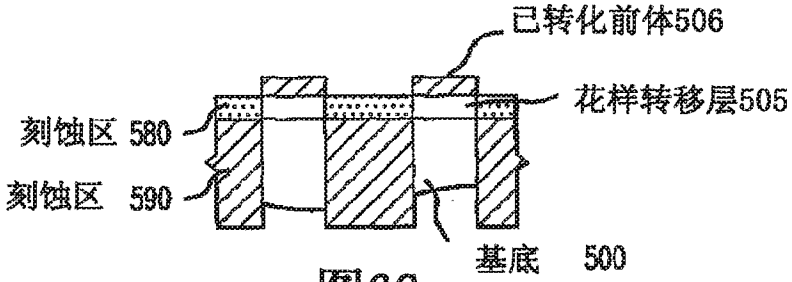


图6G

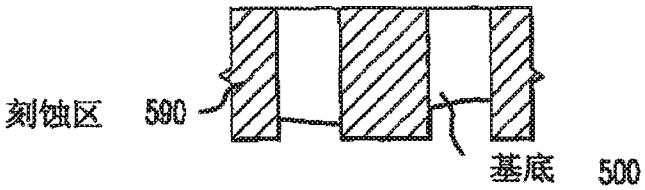


图6H

Lam Research Ex. 1009 - Page 393 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

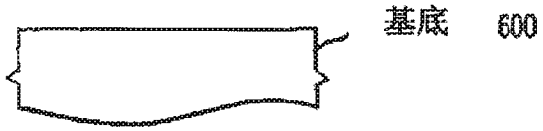


图7A

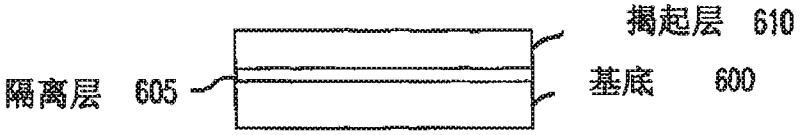


图7B

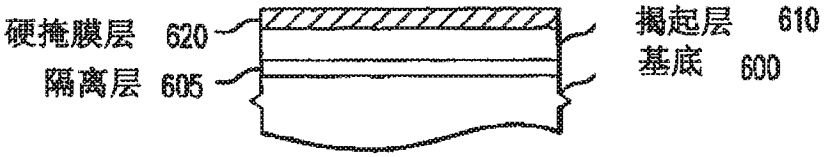


图7C

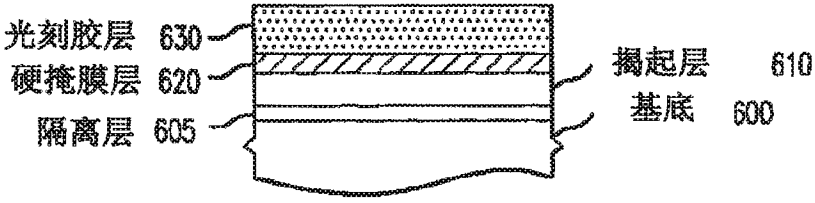


图7D

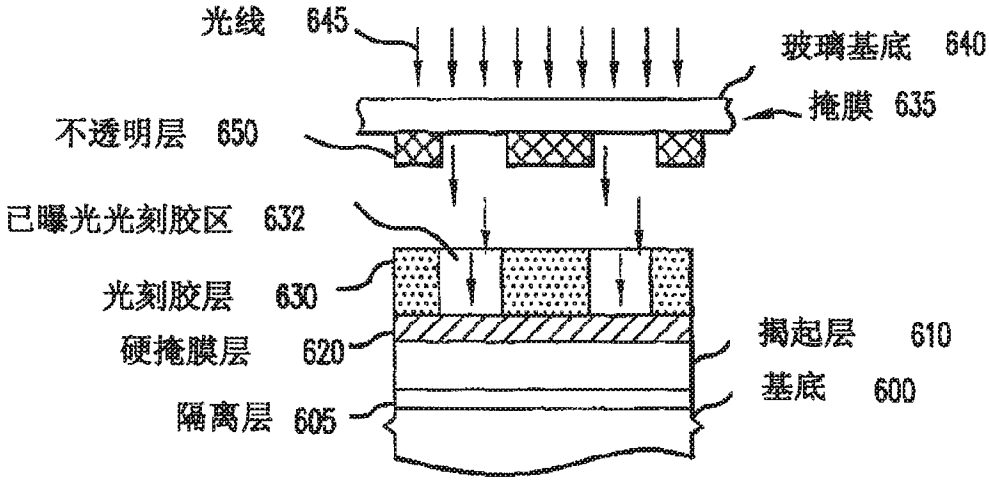


图7E

Lam Research Ex. 1009 - Page 394 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

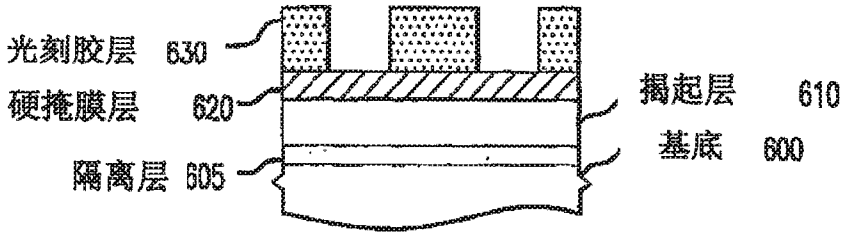


图7F

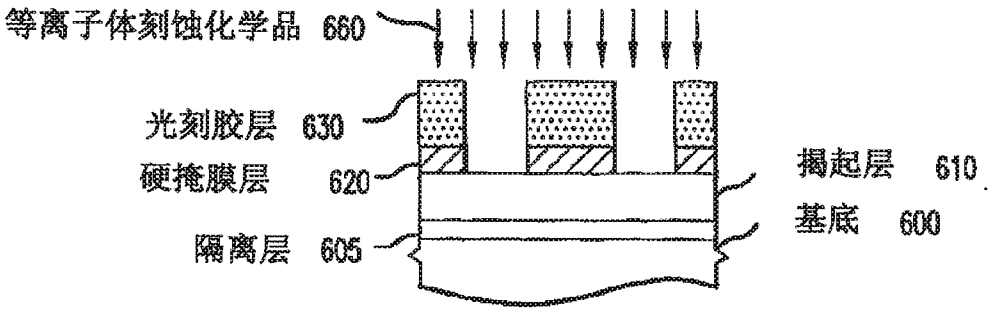


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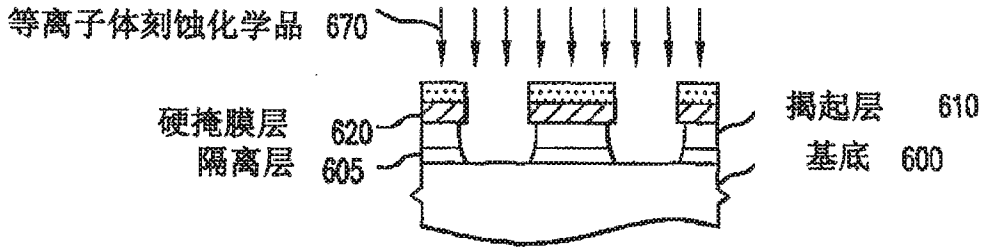


图7H

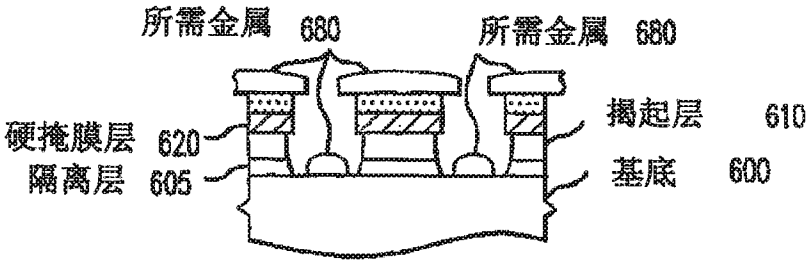


图7I

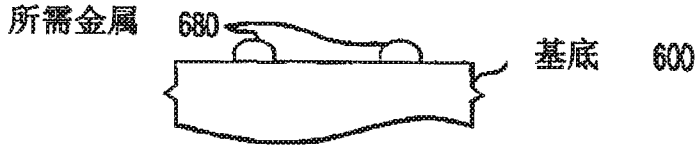
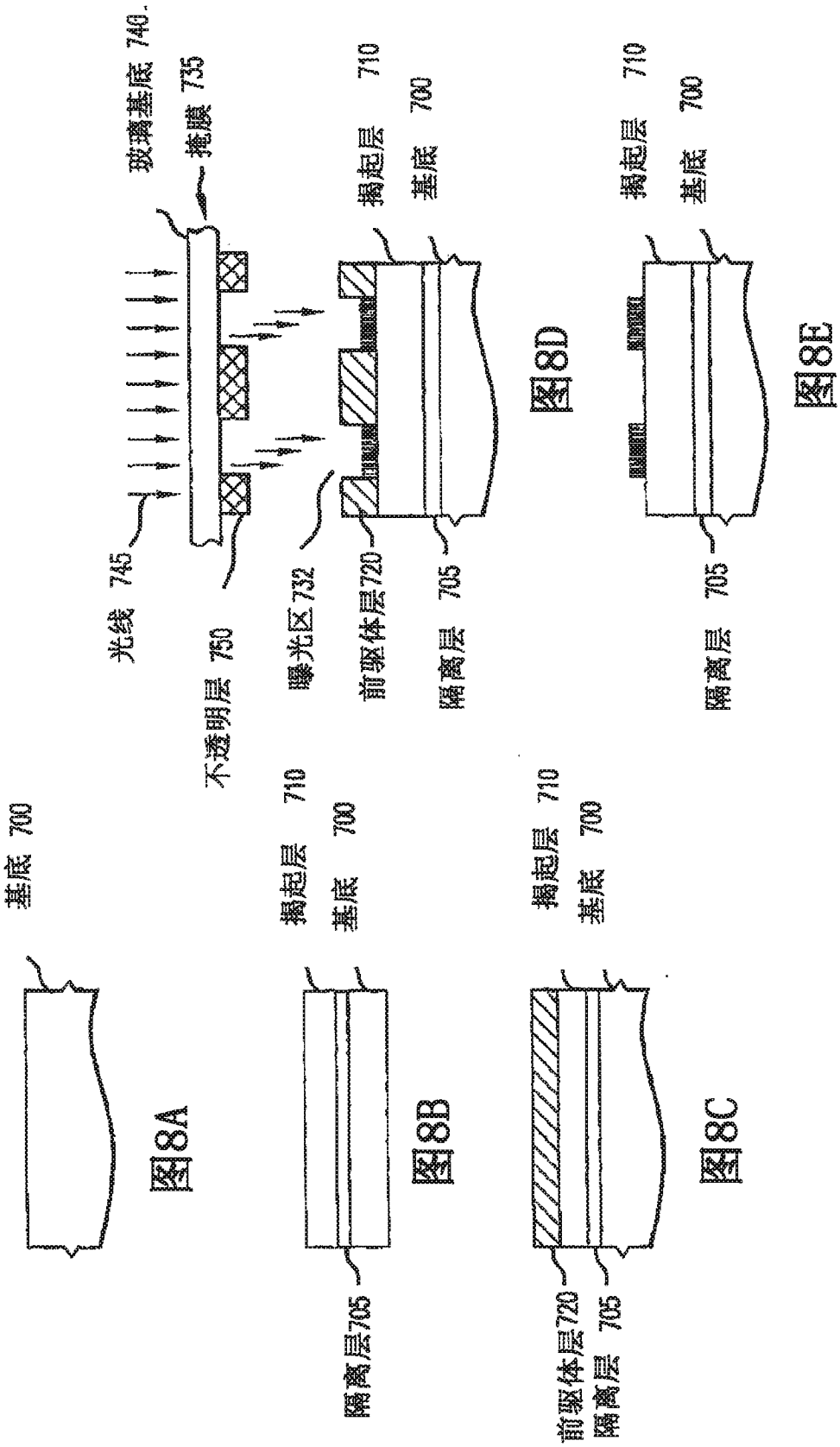


图7J

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Lam Research Ex. 1009 - Page 396 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

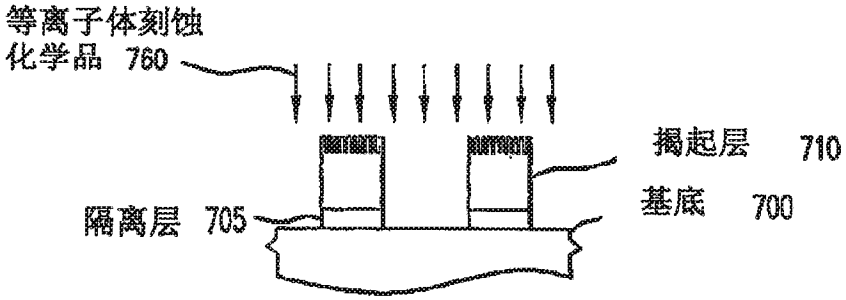


图8F

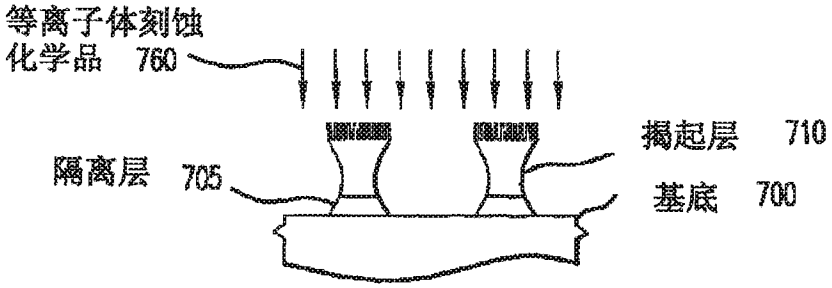


图8G

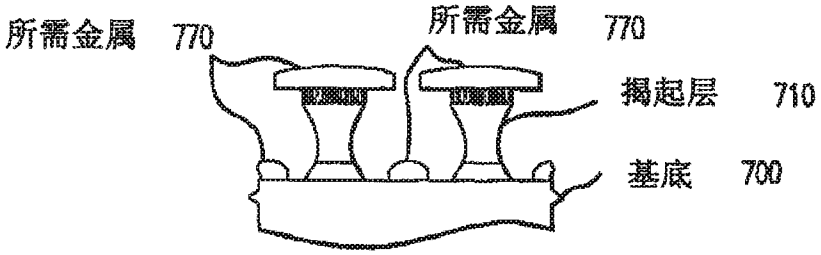


图8H



图8I

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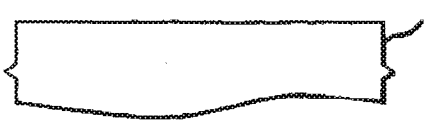


图9A

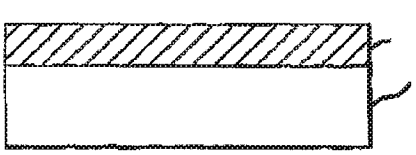


图9B

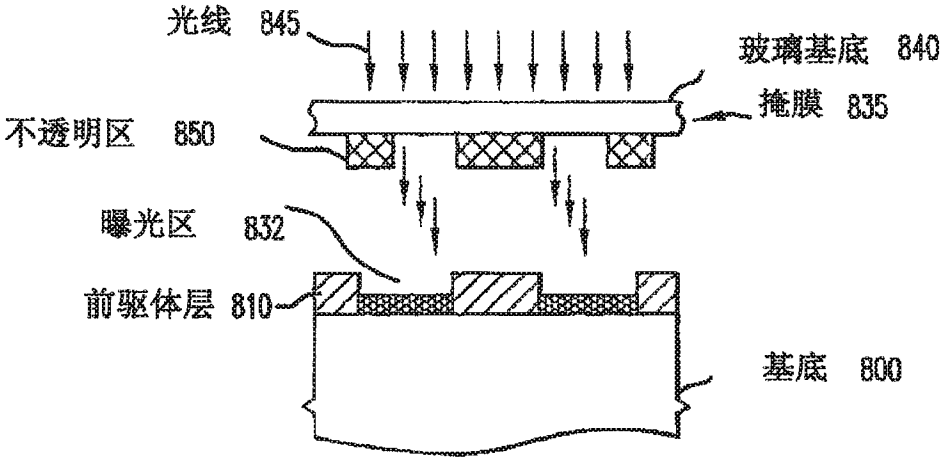


图9C

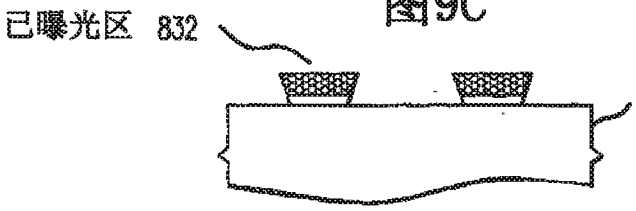


图9D

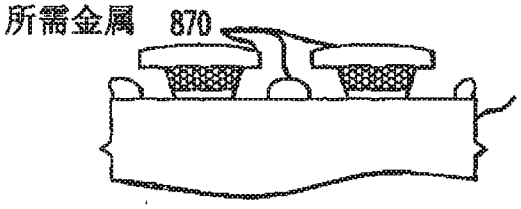


图9E

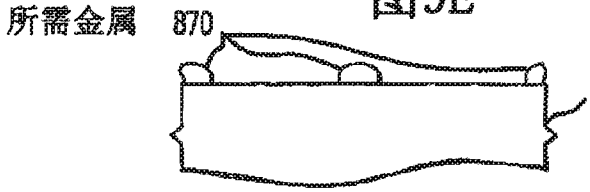


图9F

Lam Research Ex. 1009 - Page 398 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

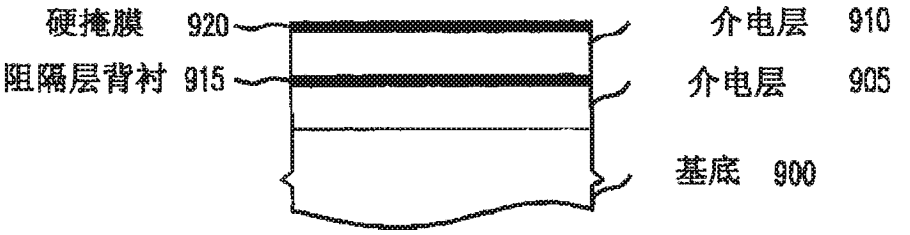


图10A

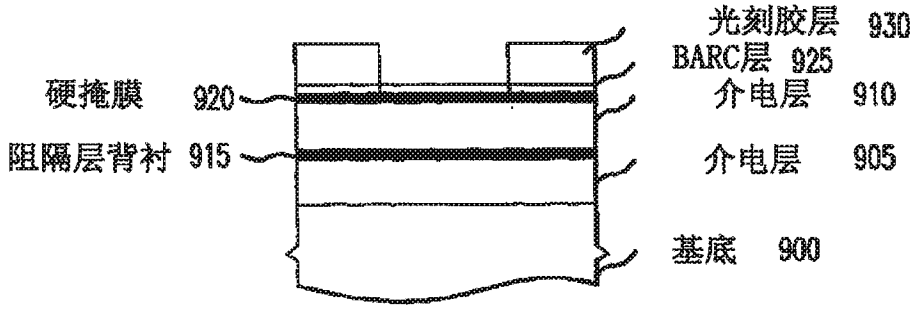


图10B

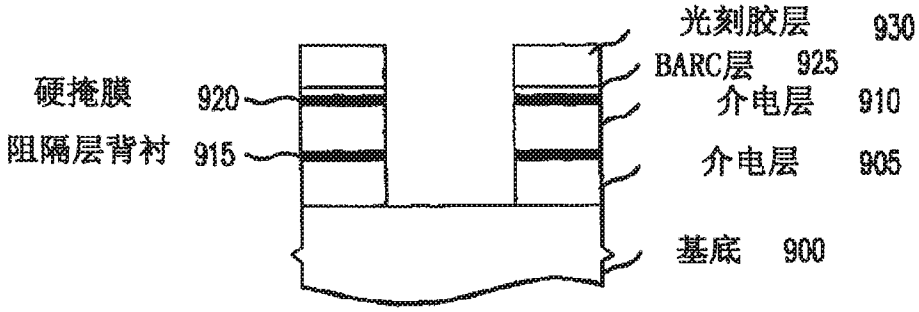


图10C

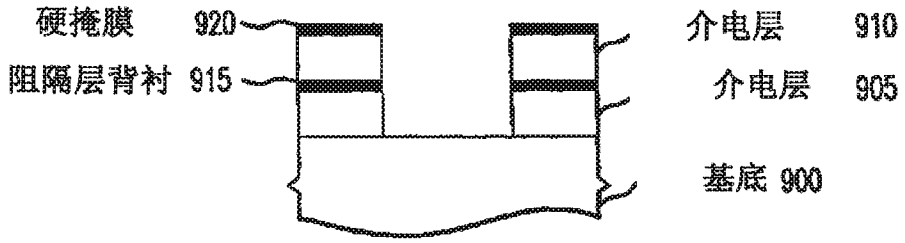


图10D

Lam Research Ex. 1009 - Page 399 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

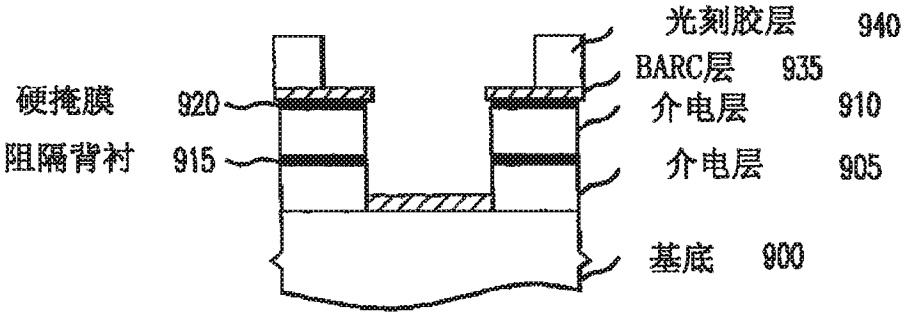


图10E

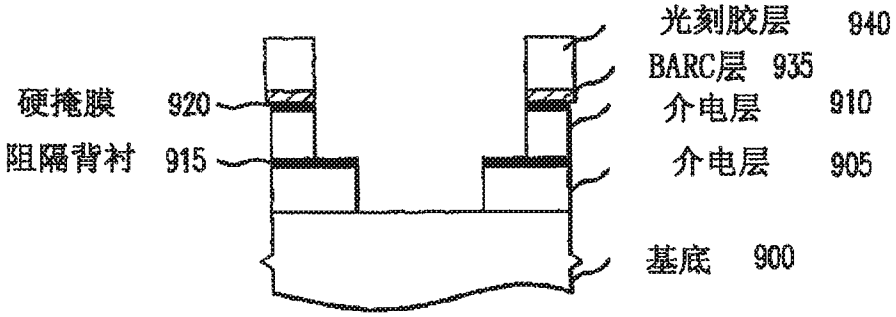


图10F

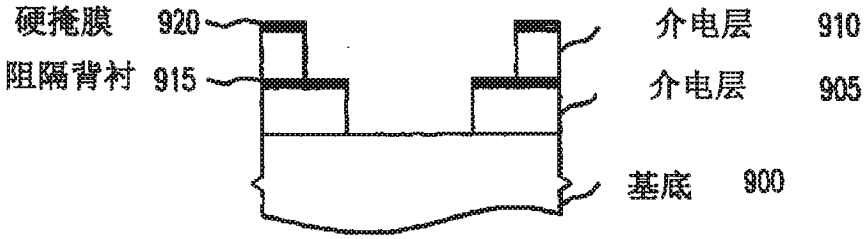
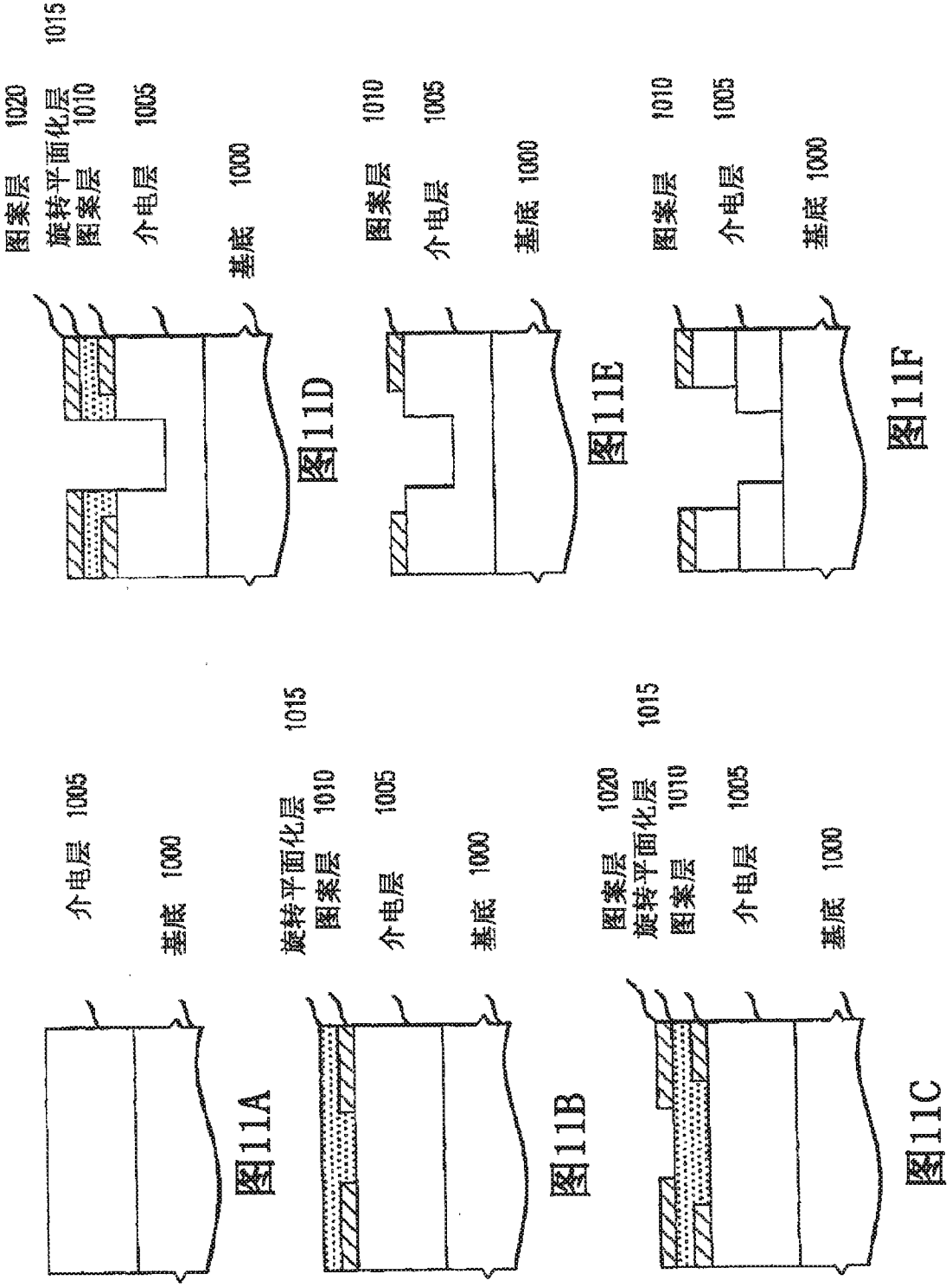


图10G

Lam Research Ex. 1009 - Page 400 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564



Lam Research Ex. 1009 - Page 401 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

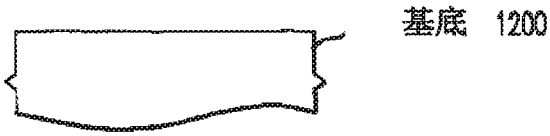


图12A

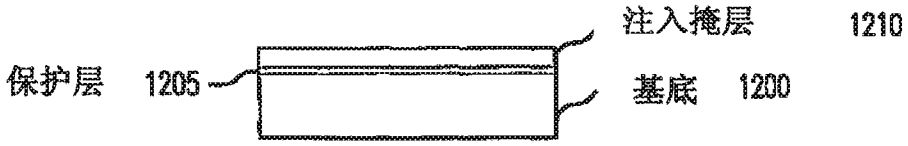


图12B

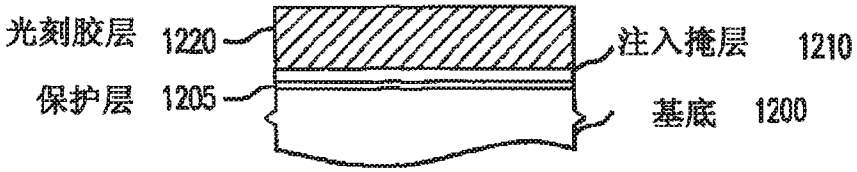


图12C

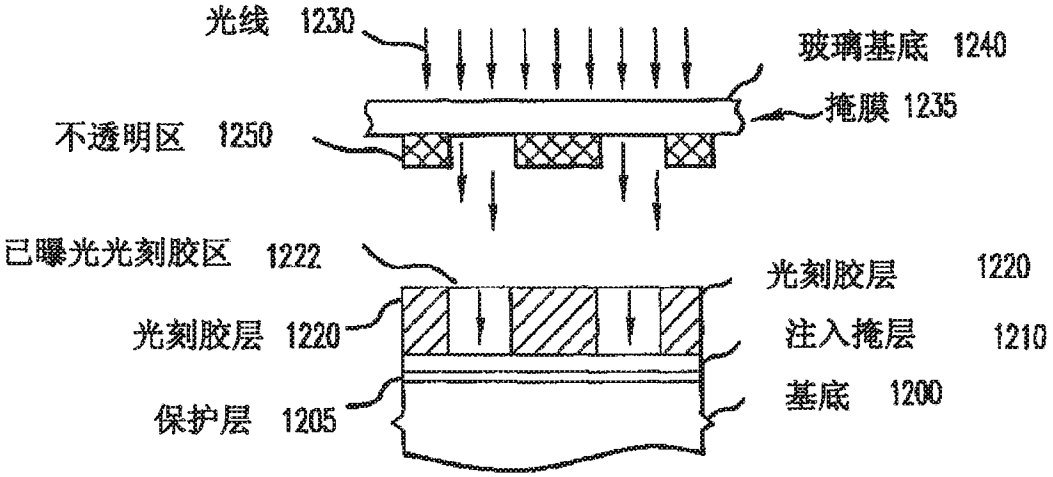


图12D

Lam Research Ex. 1009 - Page 402 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

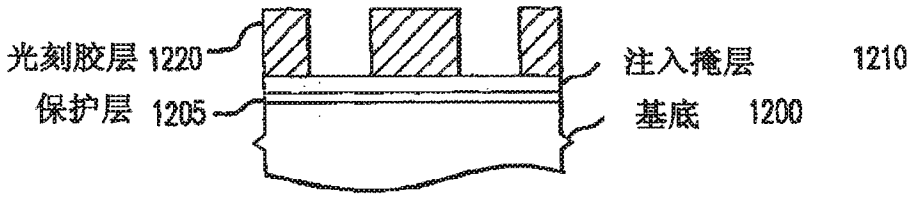


图12E

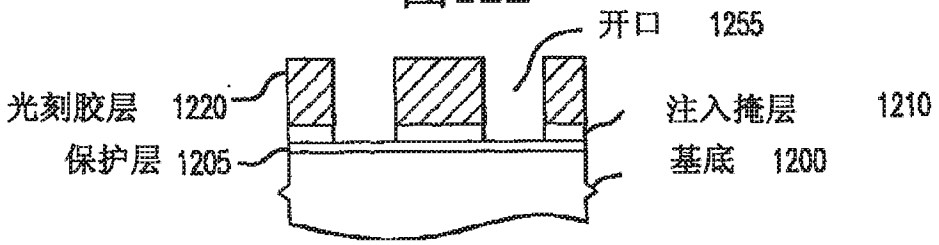


图12F

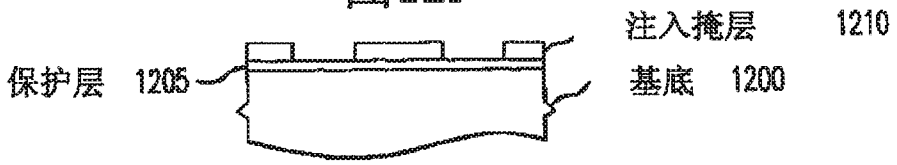


图12G

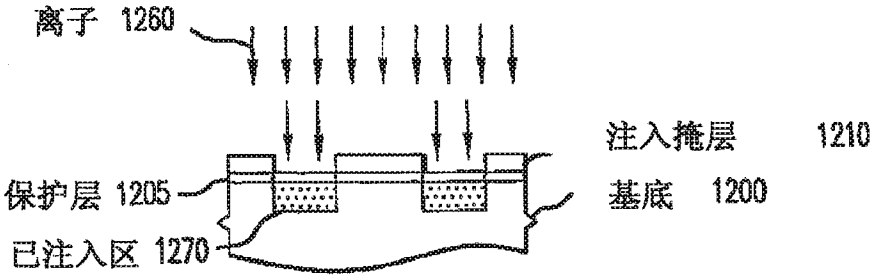


图12H

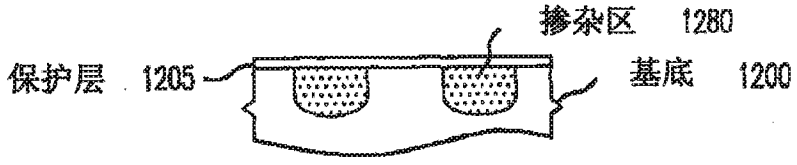


图12I

Lam Research Ex. 1009 - Page 403 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

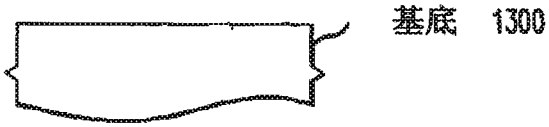


图13A

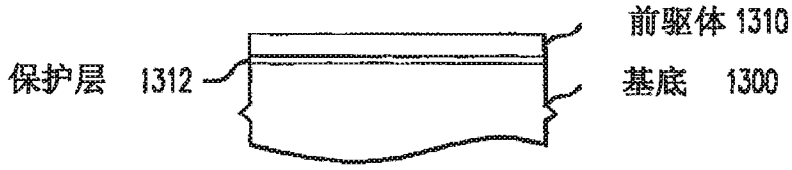


图13B

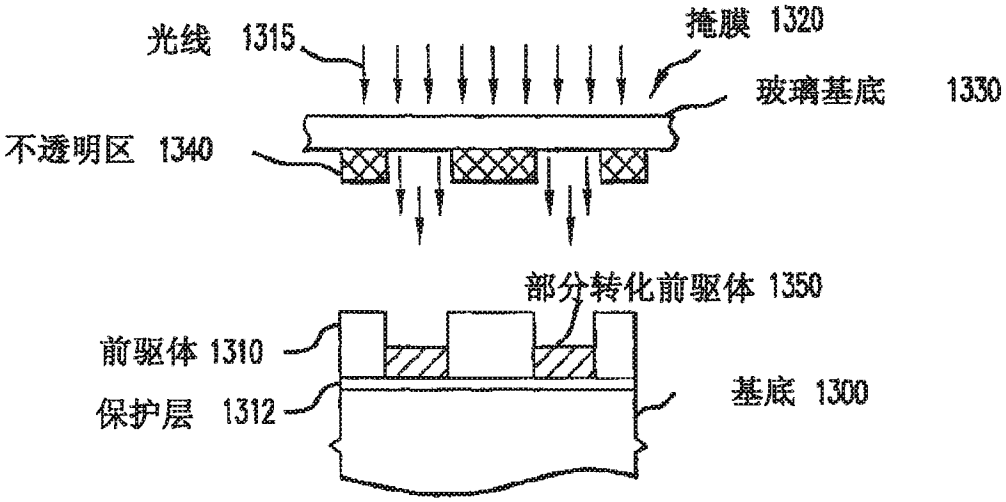


图13C

Lam Research Ex. 1009 - Page 404 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

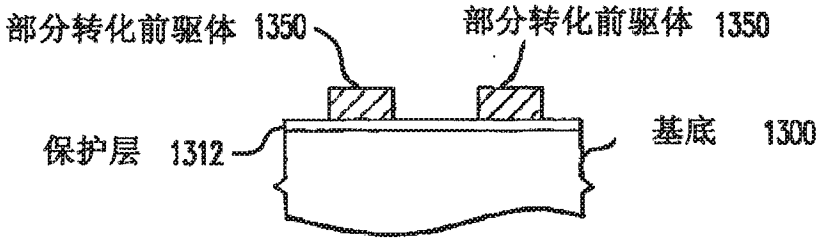


图13D

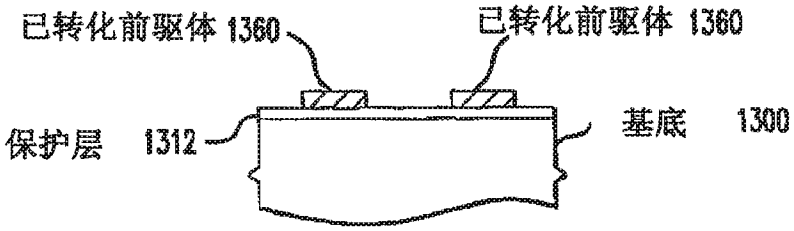


图13E

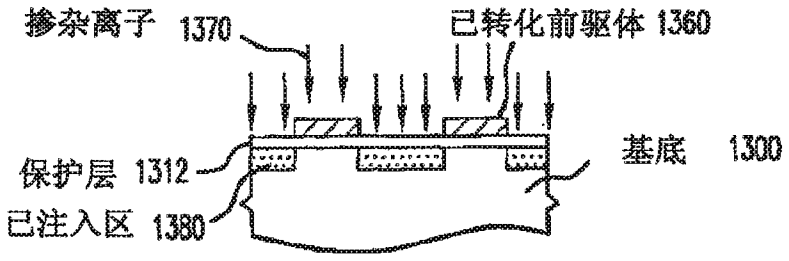


图13F

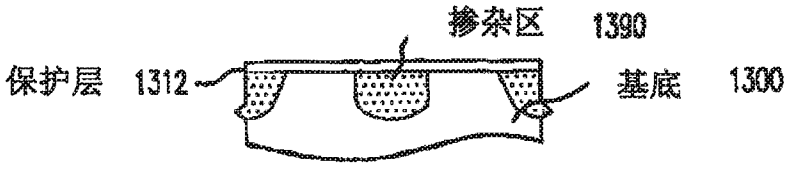


图13G

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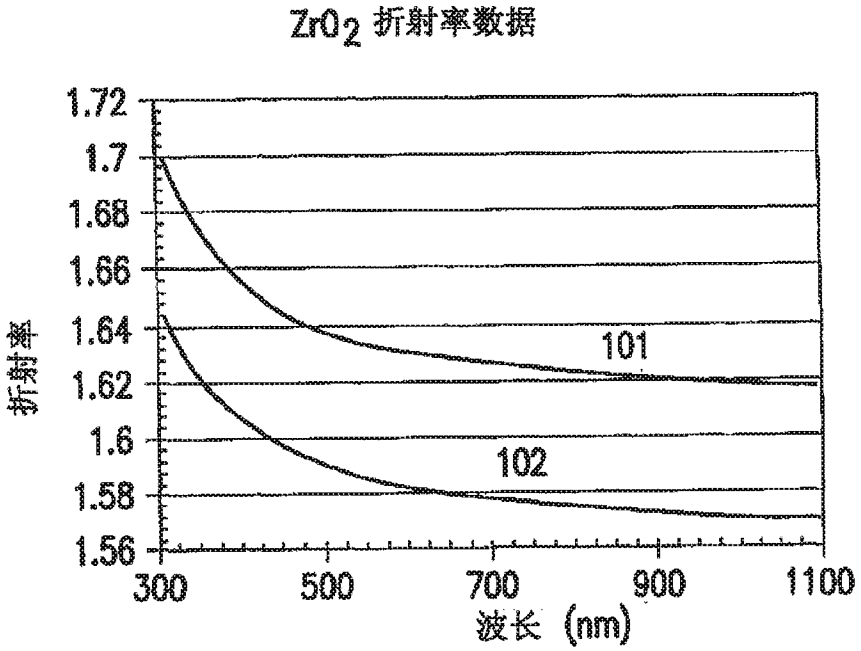


图14

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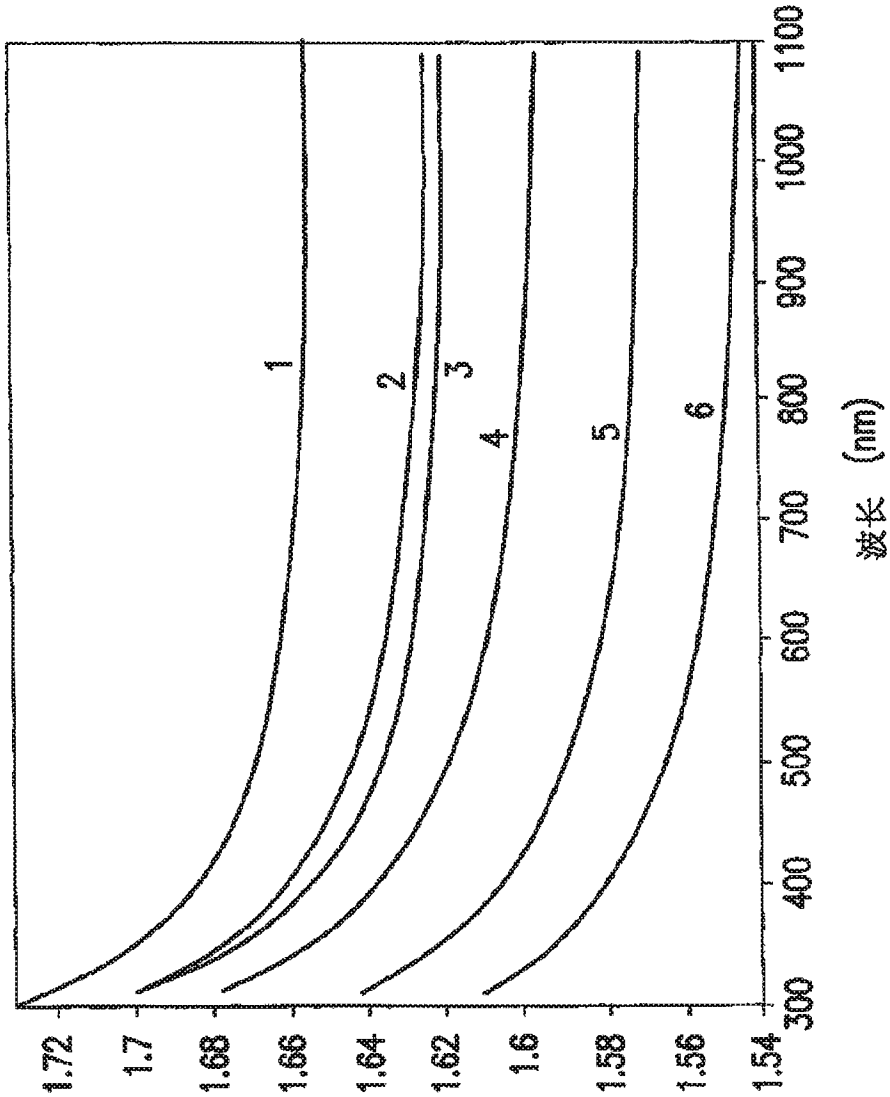


图15

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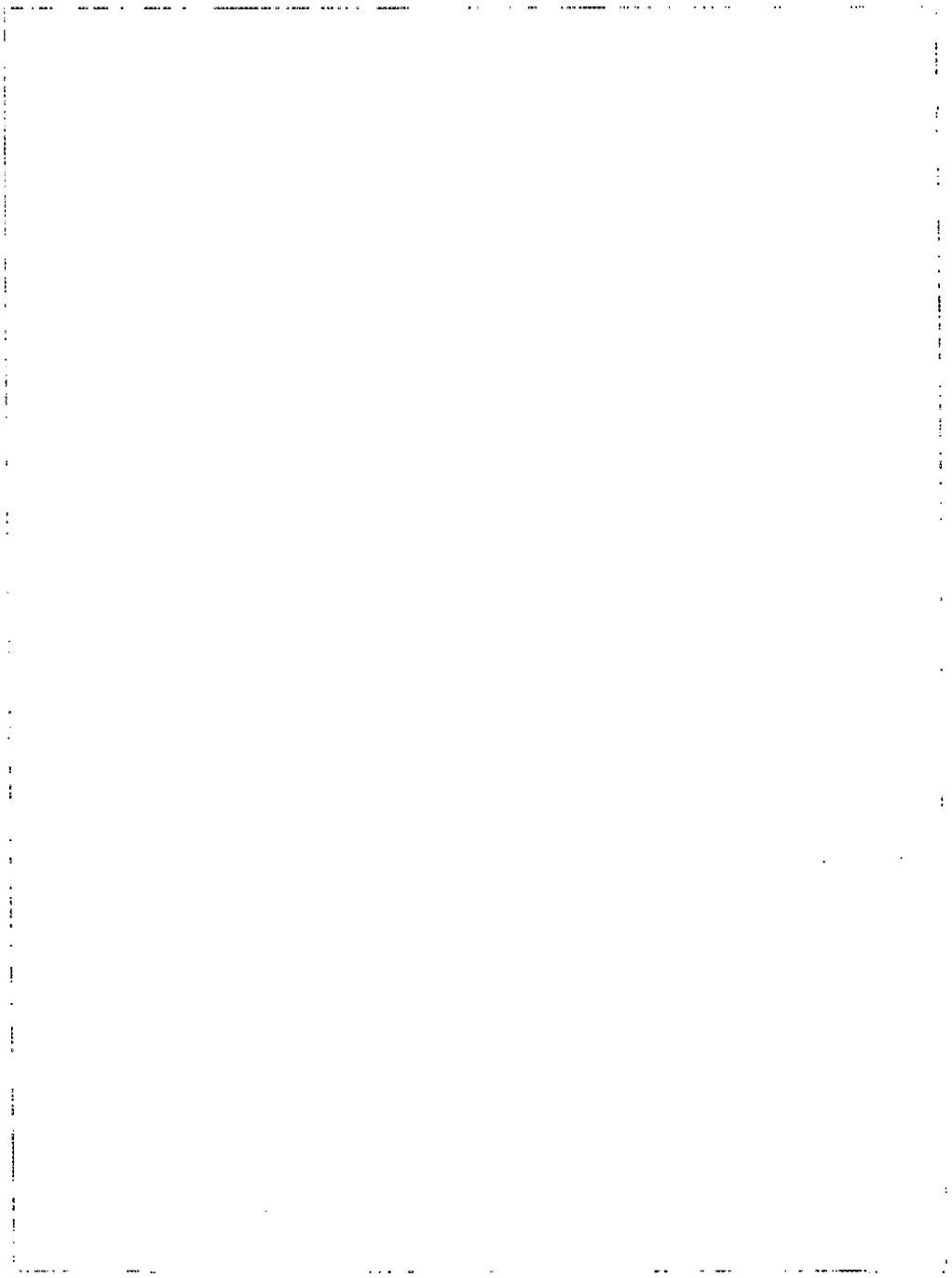


图16

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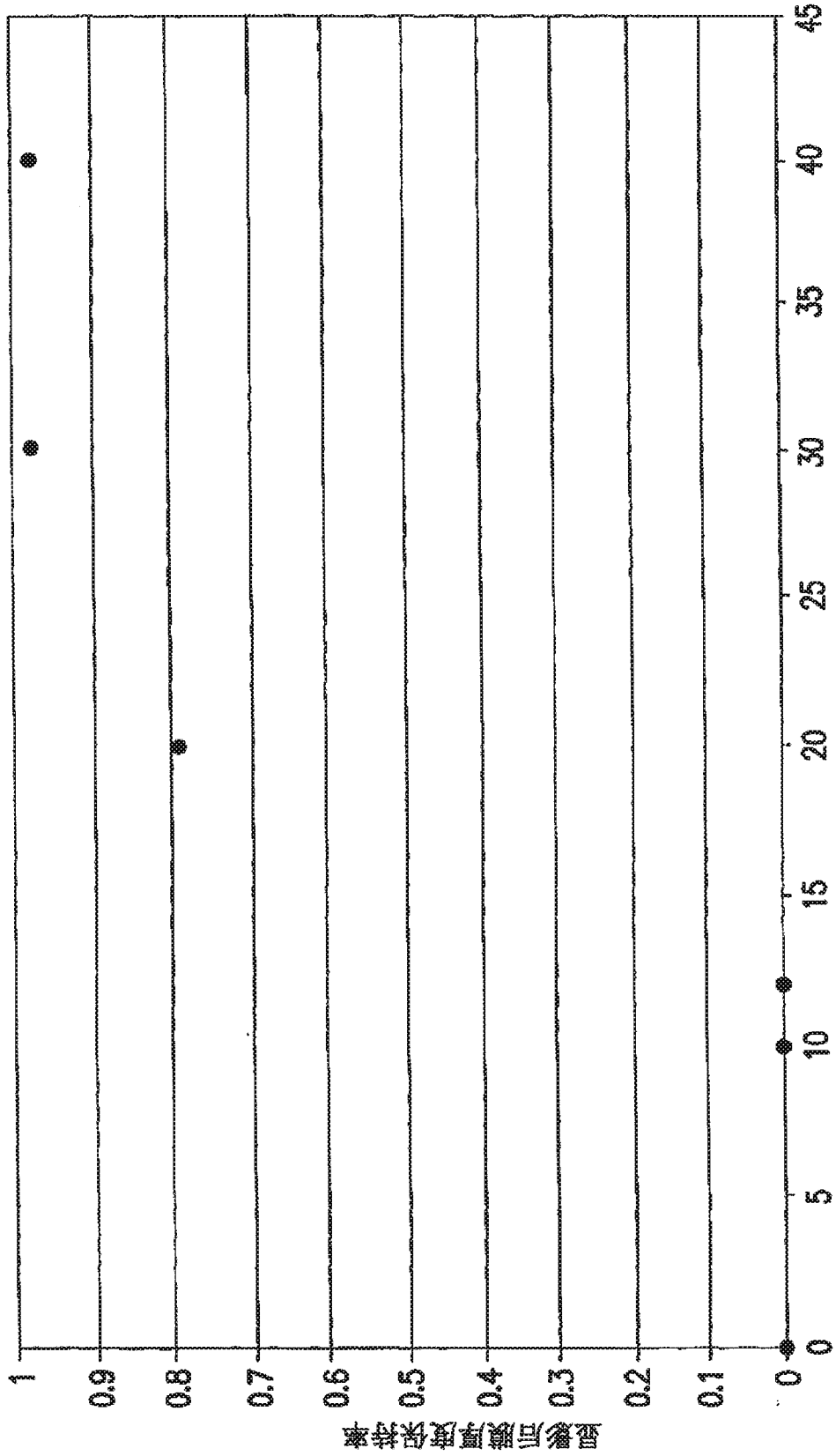


图17

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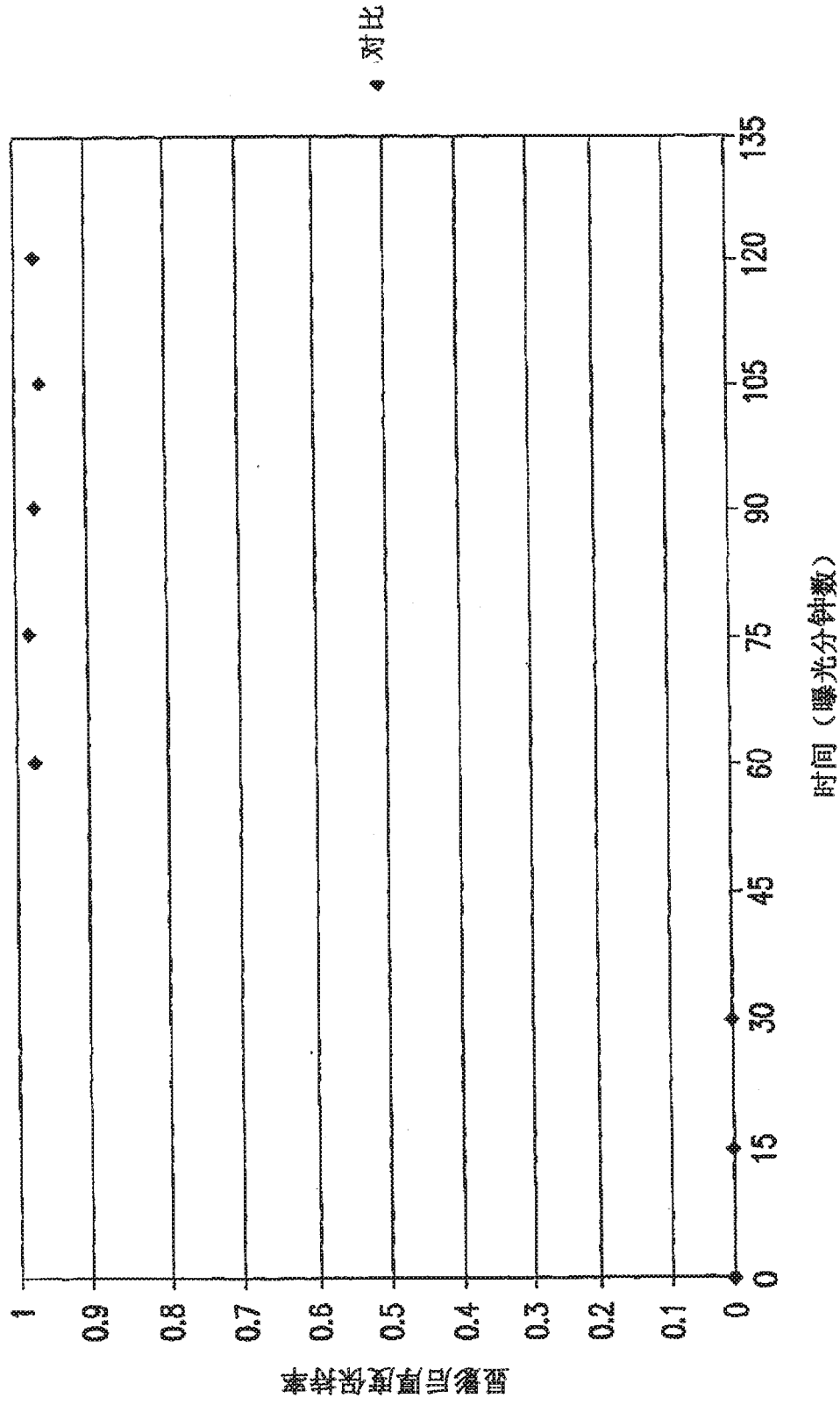


图18

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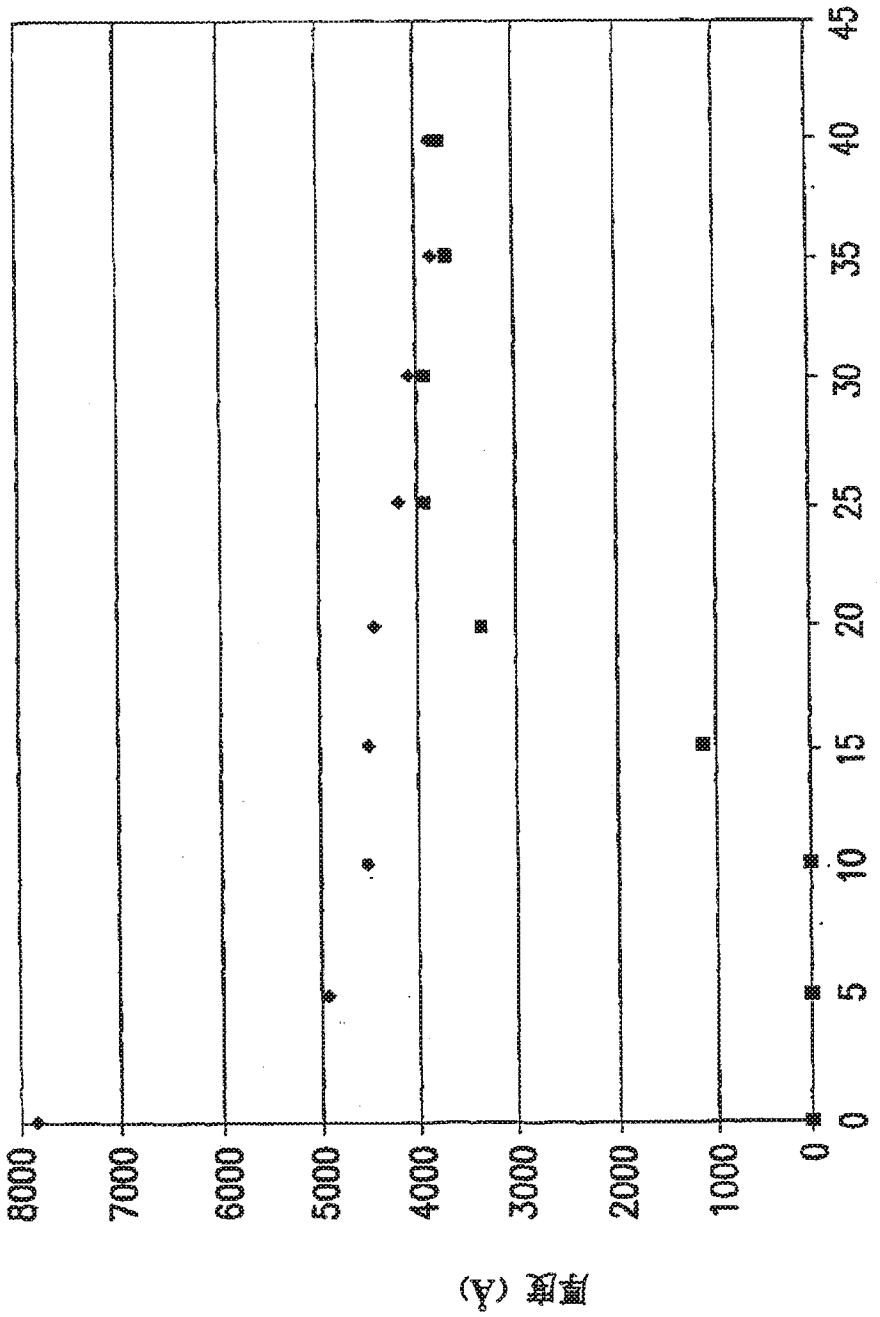


图19

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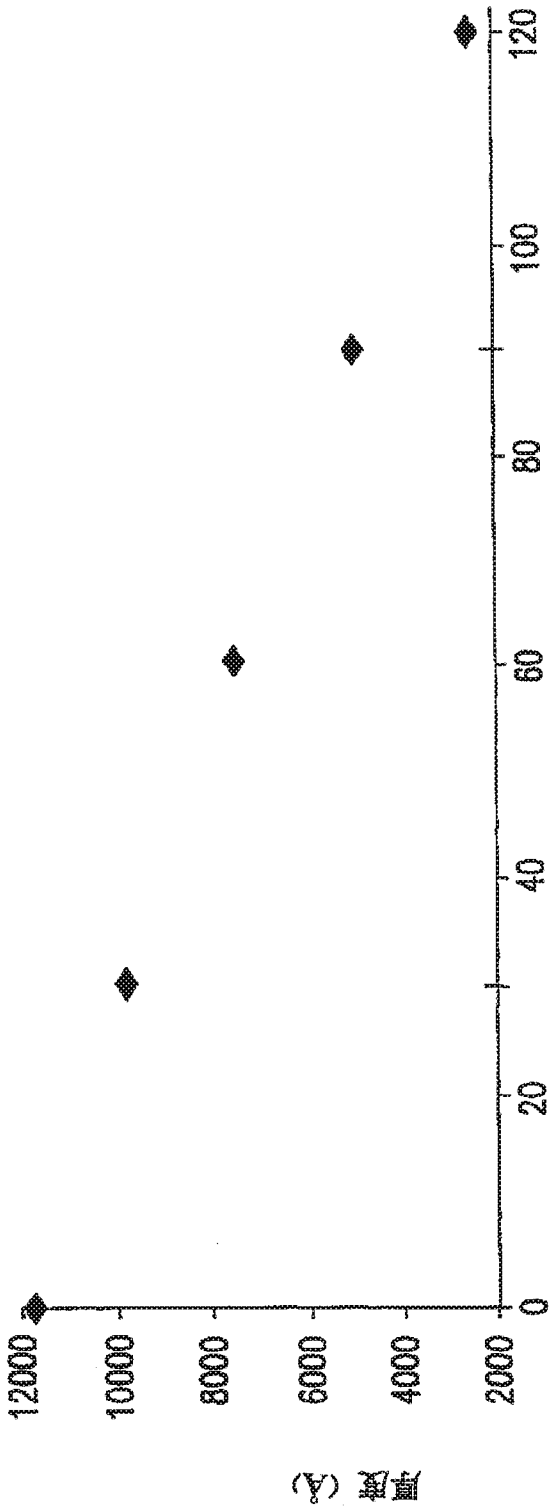


图20

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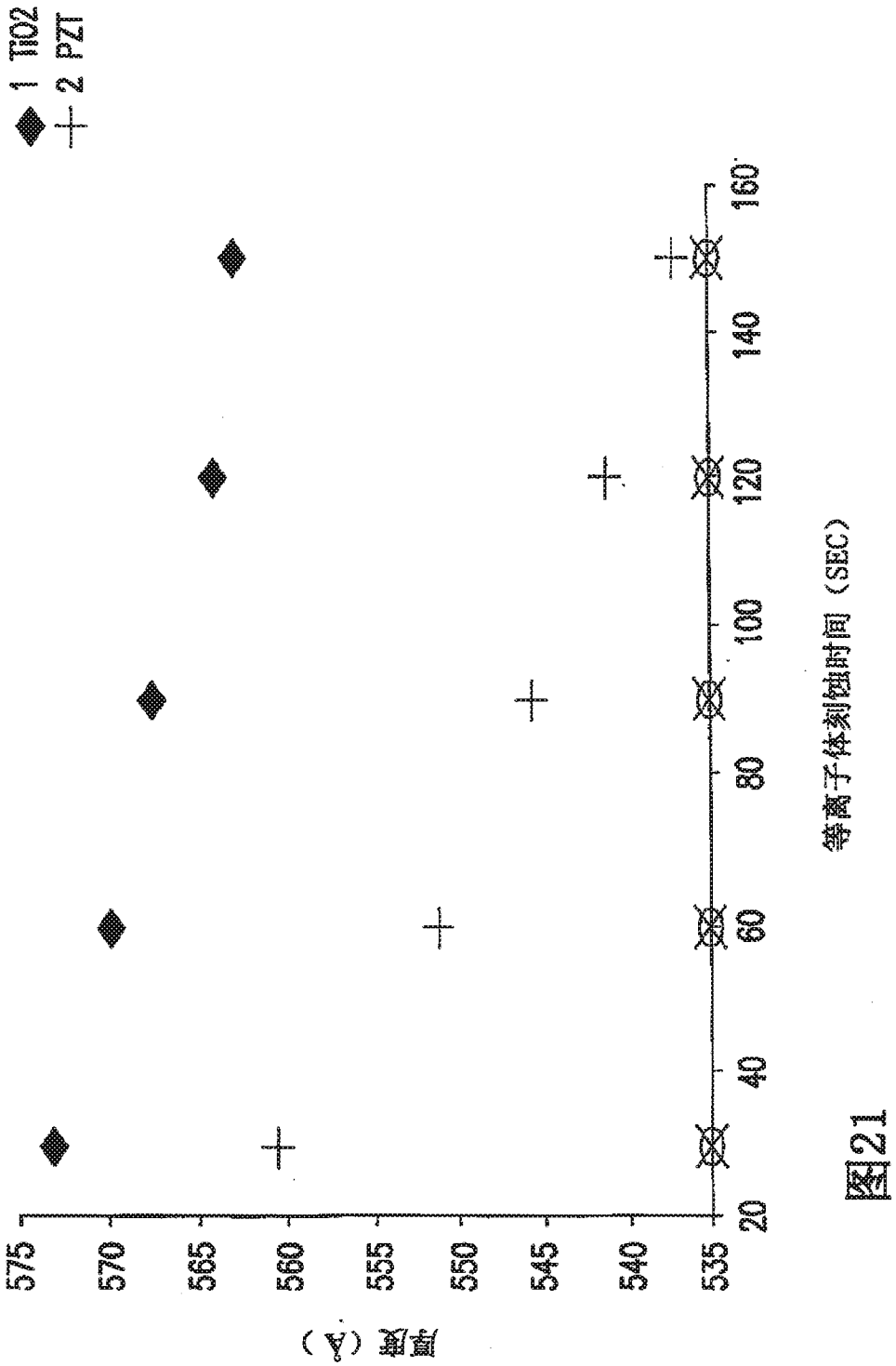


图21

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(54) CURABLE COMPOSITION

(57) The present invention ha's its object to provide a curable composition which shows practical level of curability, without using any toxic organotin type curing catalyst. Further, The present invention has its object to provide a curable composition which has good tensile characteristics and good weather resistance while retaining practical levels of surface curability and depth curability; the above objects can be achieved by a curable composition which comprises: (A) 1 to 80 parts by weight of an organic polymer containing a reactive silyl group such as an alkyldialkoxysilyl group in a molecule; (B) 99 to 20 parts by weight of an organic polymer containing a reactive silyl group such as an alkyldialkoxysilyl group in a molecule, and having a main chain skeleton comprising a repeating unit different from that of the component (A); and (C) 0.1 to 30 parts by weight of a guanidine compound per 100 parts by weight of the sum of the component (A) and the component (B).

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Description

TECHNICAL FIELD

[0001] The present invention relates to a curable composition which comprises an organic polymer containing a silicon atom-bound hydroxyl or hydrolyzable group and containing a silyl group capable of crosslinking under siloxane bond formation (hereinafter referred to as a "reactive silyl group").

BACKGROUND ART

[0002] It is known that organic polymers containing at least one reactive silyl group in the molecule have properties such that they are crosslinked under siloxane bond formation resulting from hydrolysis and other reactions of the reactive silyl group due to moisture and the like, even at room temperature to give rubber-like cured products.

[0003] Among these reactive silyl group-containing polymers, those polymers which have a polyoxyalkylene type or polyisobutylene type main chain skeleton are disclosed in Patent Document 1, Patent Document 2 and the like and have already been produced industrially and are in wide use in such fields as sealants, adhesives and coatings.

[0004] For achieving curability of a curable composition comprising such reactive silyl group-containing organic polymers, a silanol condensation catalyst is used. Generally used as the silanol condensation catalyst are organotin type catalysts having a carbon-tin bond such as dibutyltin bis(acetylacetonate). In recent years, however, the toxicity of organotin type compounds have been pointed out and development of non-organotin catalysts has been looked for. Patent Document 3, Patent Document 4, Patent Document 5, Patent Document 6 and Patent Document 7 disclose carboxylic acid tin salts and other carboxylic acid metal salts as silanol condensation catalysts and further disclose that the addition of an amine compound as a promoter results in improved curability. Further, from the environmental stress viewpoint, substantially metal-free curing catalysts are desired and, Patent Document 8 discloses that the combined use of an amine compound and a carboxylic acid gives a metal-free silanol condensation catalyst.

[0005] While it is known in the art that the use of an amine compound in combination with another silanol condensation catalyst results in improved curability, as mentioned above, there is almost no disclosure about catalyst systems in which amine compounds are used singly as silanol condensation catalysts. Further, when the non-organotin type catalysts described in the patents mentioned above are used, there arises a problem, namely the adhesiveness tends to be inferior as compared with the use of organotin type catalysts.

[0006] Patent Document 9 discloses a technology which comprises utilizing certain amine compounds known in the art as silanol condensation catalysts and specifically mentions 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and the like. However, when the amine compounds described in Patent Document 9 were used as silanol condensation catalysts for reactive silyl group-containing organic polymers, no practical curability was obtained in some cases. Furthermore, in certain cases, when practical levels of curability could be secured, the curable compositions failed to secure adhesiveness.

[0007] Patent Document 10 discloses biguanide compounds, which is one of amine compounds; they are, however, disadvantageous in that they provide poor depth curability in the early stage of curing.

[0008] Patent Document 11 and Patent Document 12 disclose a technology of increasing the rate of surface curing by using a reactive silyl group-containing organic polymer, which comprises using a trialkoxysilyl group-containing organic polymer and an alkyldialkoxysilyl group-containing organic polymer in combination. By using a trialkoxysilyl group-containing organic polymer, it becomes possible to reduce the addition level of an organotin type catalyst, which is toxic; however, the documents do not teach any organotin-free one-pack formulations.

[0009] Patent Document 13, Patent Document 14 and Patent Document 15 disclose a technology which comprises using a polyoxyalkylene type resin containing a silicon atom with two alkoxy groups bound thereto, a polyoxyalkylene type resin containing a silicon atom with three alkoxy groups bound thereto and a polymerization product obtained by polymerizing a polymerizable vinyl group-containing monomer; however, biguanide compounds are not exemplified.

[0010] Patent Document 16 discloses a technology which comprises using a polyoxyalkylene type resin containing a silyl group with three groups selected from a hydroxyl group and hydrolyzable group bound thereto and a polymer obtained by polymerizing a polymerizable unsaturated group-containing monomer having a hydrolyzable silyl group; however, biguanide compounds are not exemplified.

Patent Document 1: Japanese Kokai Publication S52-73998
Patent Document 2: Japanese Kokai Publication S63-6041
Patent Document 3: Japanese Kokai Publication H05-39428
Patent Document 4: Japanese Kokai Publication H09-12860
Patent Document 5: Japanese Kokai Publication 2000-313814
Patent Document 6: Japanese Kokai Publication 2000-345054
Patent Document 7: Japanese Kokai Publication 2003-206410
Patent Document 8: Japanese Kokai Publication H05-117519

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Patent Document 9: WO2004/022618
Patent Document 10: Japanese Kokai Publication 2005-248175
Patent Document 11: Japanese Kokai Publication H10-245484
Patent Document 12: Japanese Kokai Publication 2001-55503
Patent Document 13: Japanese Kokai Publication 2001-200230
Patent Document 14: Japanese Kokai Publication 2001-220568
Patent Document 15: Japanese Kokai Publication 2002-69289
Patent Document 16: WO98/47939

SUMMARY OF THE INVENTION

[0011] It is an object of the present invention to provide a curable composition which comprises a reactive silyl group-containing organic polymer, shows practical levels of surface curability and depth curability, without using any toxic organotin type curing catalyst as a silanol condensation catalyst, and gives cured products showing high strength and high elongation upon stretching and having good surface weather resistance.

[0012] The present inventors made investigations to solve such problems as mentioned above and, as a result, found that guanidine compounds having a specific structure, instead of organotin type curing catalysts, can act as curing catalysts for silyl group-containing organic polymers.

[0013] When, however, when they were combined with alkyldialkoxysilyl group-containing organic polymers, the cured products exhibited high strength and elongation values but the time required for surface curing and the time required for curing to the depth were both long and, therefore, they were unpractical.

[0014] When, on the other hand, they are combined with trialkoxysilyl group-containing organic polymers, the cured products show low values both in strength and in elongation although the time required for surface curing or depth curing is shortened, and the use thereof may be restricted in certain fields of application.

[0015] Then, the inventors used an alkyldialkoxysilyl group-containing organic polymer and a trialkoxysilyl group-containing organic polymer whose main chain skeleton comprises a different repeating unit from that in the alkyldialkoxysilyl group-containing organic polymer in a specific quantity ratio and further used a guanidine compound having a specific structure as a silanol condensation catalyst, and found that the thus-obtained composition can secure practical levels of surface curability and depth curability and the cured products, when stretched, exhibit sufficient levels of strength and elongation and have good surface weather resistance, in spite of the fact that the guanidine compound is a non-organotin type catalyst. The present invention has been completed based on such findings.

[0016] That is, the present invention relates to a non-organotin curable composition, which comprises:

(A) an organic polymer containing, in a molecule, a reactive silyl group represented by the formula $-SiR^1X^1_2$ (wherein R^1 represents a group selected from among alkyl groups containing 1 to 20 carbon atoms, aryl groups containing 6 to 20 carbon atoms and aralkyl groups containing 7 to 20 carbon atoms, and the two X^1S each independently is a hydroxyl group or a hydrolyzable group);
(B) an organic polymer containing, in a molecule, a reactive silyl group represented by the formula $-SiX^2_3$ (wherein the three x^2s each independently is a hydroxyl group or a hydrolyzable group) and having a main chain skeleton comprising a repeating unit different from a repeating unit of a main chain skeleton of the component (A); and
(C) a guanidine compound represented by the general formula (1):

$$R^2N=CNR^3_2\text{-}NR^4_2 \qquad (1)$$

(wherein R^2, the two R^3s and the two R^4s each independently is a hydrogen atom or an organic group),

wherein the weight ratio of component (A) /component (B) is 1/99 to 80/20 and the component (C) amounts to 0.1 to 30 parts by weight per 100 parts by weight of the sum of the component (A) and the component (B).

[0017] One preferred embodiment of the present invention relates to the curable composition, wherein one of the main chain skeleton of the (A) component organic polymer and the main chain skeleton of the (B) component organic polymer is a polyoxyalkylene and the other is a (meth)acrylate ester polymer.

[0018] One particularly preferred embodiment of the present invention relates to the curable composition, wherein the component (C) is a guanidine compound represented by the general formula (1), in the formula (1), R^2 being a hydrocarbon group wherein the carbon atom at position 1 is saturated, or a hydrogen atom.

[0019] One further preferred embodiment of the present invention relates to the curable composition, wherein the component (C) is a biguanide compound represented by the general formula (1), in the formula (1), the $-NR^3_2$ group being an $-NR^5\text{-}C(=NR^6)\text{-}NR^7_2$ group (wherein R^5, R^6 and the two R^7s each independently is a hydrogen atom or an organic group) and/or an $-N=C(NR^8_2)\text{-}NR^9_2$ group (wherein the two R^8s and the two R^9s each independently is a hydrogen

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atom or an organic group).

[0020] One particularly preferred embodiment of the present invention relates to the curable composition, wherein a polyether plasticizer is used in combination.

[0021] Preferred as applications of the curable composition according to the present invention is a sealant or an adhesive which comprises any of the curable composition described above.

[0022] The curable composition of the invention has practical levels of surface curability and depth curability without containing any of those tetravalent organotin compounds the toxicity of which is currently a matter of concern; further, after curing, the cured products exhibit sufficient levels of strength and elongation upon stretching and retain good surface curability for a long period of time.

DETAILED DESCRIPTION OF THE INVENTION

[0023] In the following, the present invention is described in detail.

[0024] The present invention includes a non-organotin type curable composition which comprises a specific reactive silyl group-containing organic polymer and a specific silanol condensation catalyst. The "non-organotin type curable composition", so referred to herein, is a composition in which the addition level of an organotin compound is not higher than 50% by weight of the addition level of the compounds each acting as a silanol condensation catalyst.

[0025] The curable composition of the invention comprises, as an essential constituent (A), a reactive silyl group-containing organic polymer (hereinafter referred to also as "component (A)", "reactive silyl group-containing organic polymer (A) " or "organic polymer (A)") and, as an essential constituent (B), a reactive silyl group-containing organic polymer (hereinafter referred to also as "component (B)", "reactive silyl group-containing organic polymer (B)" or "organic polymer (B)").

[0026] The main chain skeleton of the organic polymer (A) and that of the organic polymer (B) are different from each other since the difference imparts particularly good weather resistance to the cured products.

[0027] The organic polymer (A) and the organic polymer (B) have, on an average, at least one reactive silyl group per molecule. The reactive silyl group, so referred to herein, is an organic group containing hydroxyl groups or hydrolyzable groups each bound to a silicon atom. The reactive silyl group-containing organic polymer (A) and the reactive silyl group-containing organic polymer (B) are crosslinked under siloxane bond formation as a result of a reaction promoted by a silanol condensation catalyst.

As the reactive silyl group in the organic polymer (A), there may be mentioned groups represented by the general formula (2):

$$-SiR^1X^1_2 \qquad (2)$$

(R^1 is at least one selected from among alkyl groups containing 1 to 20 carbon atoms, aryl groups containing 6 to 20 carbon atoms, aralkyl groups containing 7 to 20 carbon atoms, and $-OSi(R')_3$ (each R' is independently a hydrocarbon group containing 1 to 20 carbon atoms). Two X^1s are independently a hydroxyl group or a hydrolyzable group).

[0028] As the reactive silyl group in the organic polymer (B), there may be mentioned groups represented by the general formula (3):

$$-SiX^2_3 \qquad (3)$$

(three X^2s are independently a hydroxyl group or a hydrolyzable group).

The organic polymer (B) may contain a reactive silyl group having a structure other than that represented by the general formula (3) in the same molecule; namely, the organic polymer (B) may further contain a reactive silyl group represented by the general formula (2) which is contained in the organic polymer (A) in addition to a reactive silyl group represented by the general formula (3).

[0029] The curable composition of the present invention, which comprises a reactive silyl group-containing organic polymer (A) and a reactive silyl group-containing organic polymer (B) as the main component, is better in compatibility with the silanol condensation catalyst (component C), namely the guanidine compound, as compared with a composition which comprises, as the main component, such an inorganic polymer as polydimethylsiloxane, hence is preferred. The curable composition comprising an organic polymer (A) and an organic polymer (B) is excellent in curability and the cured products obtained therefrom are characterized by excellent adhesiveness.

[0030] Further, for the same reasons, the organic polymer (A) and the organic polymer (B) each preferably has a main chain skeleton containing at least one atom selected from among a hydrogen atom, a carbon atom, a nitrogen atom, an oxygen atom and a sulfur atom.

[0031] The main chain skeleton of the organic polymer (A) and of the organic polymer (B) is not particularly restricted but include, polyoxyalkylene type polymers such as polyoxyethylene, polyoxypropylene, polyoxybutylene, polyoxyte-

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tramethylene, polyoxyethylene-polyoxypropylene copolymers and polyoxypropylene-polyoxybutylene copolymers; ethylene-propylene type copolymers, polyisobutylene, copolymers of isobutylene and isoprene or the like, polychloroprene, polyisoprene, copolymers of isoprene or butadiene and acrylonitrile and/or styrene or the like, polybutadiene and copolymers of isoprene or butadiene and acrylonitrile and styrene or the like, hydrocarbon type polymers such as hydrogenated polyolefin polymers derived from these polyolefin type polymers by hydrogenation; polyester type polymers obtained by condensation of a dibasic acid such as adipic acid and a glycol, or ring-opening polymerization of a lactone (s); (meth) acrylate ester polymers obtained by radical polymerization of such a compound as ethyl (meth) acrylate and butyl (meth) acrylate; vinyl polymers obtained by radical polymerization of such a compound as a (meth)acrylate ester compound, vinyl acetate, acrylonitrile and styrene; graft polymers obtained by polymerizing a vinyl compound in such polymers as mentioned above; polysulfide type polymers; polyamide type polymers such as polyamide 6 produced by ring-opening polymerization of ε-caprolactam, polyamide 6.6 produced by polycondensation of hexamethylenediamine and adipic acid, polyamide 6.10 produced by polycondensation of hexamethylenediamine and sebacic acid, polyamide 11 produced by polycondensation of ε-aminoundecanoic acid, polyamide 12 produced by ring-opening polymerization of ε-aminolaurolactam, and copolymer polyamides composed of a plurality of the polyamides mentioned above; polycarbonate type polymers such as polycarbonates produced by polycondensation of bisphenol A and carbonyl chloride; diallyl phthalate type polymers; and like organic polymers. Further, polysiloxane type polymers such as polydiorganosiloxane can be also included.

[0032] Preferred among those mentioned above are organic polymers (A) and organic polymers (B) each having, as the main chain skeleton, saturated hydrocarbon type polymers such as polyisobutylene, hydrogenated polyisoprene and hydrogenated polybutadiene, polyoxyalkylene type polymers, (meth)acrylate ester polymers and polysiloxane type polymers, in view of their relatively low glass transition temperature and of good low'-temperature resistance of cured products obtained therefrom.

[0033] The glass transition temperature of the reactive sily group-containing organic polymer (A) and of the reactive silyl group-containing organic polymer (B) is not particularly restricted but preferably is not higher than 20°C, more preferably not higher than 0°C, most preferably not higher than -20°C. When the glass transition temperature is higher than 20°C, the viscosity of the curable composition increases in the winter season or in cold districts, developing a tendency toward lowered workability and, further, the flexibility of cured products obtained decreases and the elongation thereof tends to decrease.

[0034] The glass transition temperature mentioned above can be determined by DSC measurement according to the method prescribed in JIS K 7121.

[0035] A curable composition comprising, as the main component, a saturated hydrocarbon type polymer and an organic polymer whose main chain skeleton is a polyoxyalkylene type polymer and a (meth)acrylate ester polymer is more preferred since, when it is used as an adhesive or sealant, low-molecular-weight components scarcely migrate to (i.e. stain) adherends.

[0036] Further, an organic polymer whose main chain skeleton is a polyoxyalkylene type polymer and a (meth)acrylate ester polymer is particularly preferred since it is high in moisture permeability and, when used as a main component of a one-pack type adhesive or sealant, it is excellent in depth curability and gives cured products excellent in adhesiveness. Most preferred is an organic polymer whose main chain skeleton is a polyoxyalkylene type polymer.

[0037] The polyoxyalkylene type polymer to be used as the main chain skeleton of the organic polymer (A) or of the organic polymer (B) is a polymer having a repeating unit represented by the general formula (4):

$$-R^{10}-O- \qquad (4)$$

(R^{10} is a straight or branched alkylene group containing 1 to 14 carbon atoms).

[0038] The group R^{10} in the general formula (4) is not particularly restricted but may be any of the straight or branched alkylene groups containing 1 to 14 carbon atoms and, among those, straight or branched alkylene groups containing 2 to 4 carbon atoms are preferred.

[0039] The repeating unit defined by the general formula (4) is not particularly restricted but includes, for example, $-CH_2O-$, $-CH_2CH_2O-$, $-CH_2CH(CH_3)O-$, $-CH_2CH(C_2H_5)O-$, $-CH_2C(CH_3)_2O-$ and $-CH_2CH_2CH_2CH_2O-$.

[0040] The polyoxyalkylene type polymer may have one repeating unit species or a plurality of repeating unit species. In the case of use in the field of sealants and the like, in particular, an organic polymer (A) and an organic polymer (B) in which the main component of the main chain skeleton is a propylene oxide polymer are preferred since such polymers are noncrystalline and relatively low in viscosity.

[0041] A method of producing such a polyoxyalkylene type polymer is not particularly restricted but may be any of the methods known in the art. For example, mention may be made of the method using an alkali catalyst such as KOH, the method disclosed in Japanese Kokai Publication S61-215623 which uses, as a catalyst, a transition metal-porphyrin complex, such as a complex obtained by reacting an organoaluminum compound with porphyrin, the methods disclosed in Japanese Kokoku Publications S46-27250 and S59-15336 and United States Patents 3,278,457, 3,278,458,

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3,278,459, 3,427,256, 3,427,334 and 3,427,335, among others, which use, as a catalyst, a composite metal cyanide complex, the method disclosed in Japanese Kokai Publication H10-273512 which uses, as a catalyst, a polyphosphazene salt, and the method disclosed in Japanese Kokai Publication H11-060722 which uses, as a catalyst, a phosphazene compound.

[0042] The method of producing a reactive silyl group-containing polyoxyalkylene type polymer is not particularly restricted but may be any of the methods known in the art. For example, mention may be made of the methods disclosed in Japanese Kokoku Publications S45-36319 and S46-12154, Japanese Kokai Publications S50-156599, S54-6096, S55-13767, S55-13468 and S57-164123, Japanese Kokoku Publication H03-2450 and United States Patents 3,632,557, 4,345,053, 4,366,307 and 4,960,844, among others, and the methods disclosed in Japanese Kokai Publications S61-197631, S61-215622, S61-215623, S61-218632, H03-72527, H03-47825 and H08-231707, among others, according to which polymers high in molecular weight (number average molecular weight of 6,000 or higher) and narrow in molecular weight distribution (Mw/Mn of 1.6 or below) can be obtained.

[0043] In formulating the curable composition using the reactive silyl group-containing polyoxyalkylene type polymer mentioned above, the polymer may comprise a single species or a combination of a plurality of species thereof.

[0044] The saturated hydrocarbon type polymer to be used as the main chain skeleton of the organic polymer (A) or of the organic polymer (B) is a polymer whose molecules are substantially free of any carbon-carbon unsaturated bond, except for an aromatic ring, and is excellent in heat resistance, weather resistance, durability and a moisture barrier property.

[0045] The saturated hydrocarbon type polymer is not particularly restricted but there may be mentioned (i) polymers derived from an olefin compound containing 2 to 6 carbon atoms, such as ethylene, propylene, 1-butene and isobutylene as the repeating unit species, (ii) polymers derived from a diene type compound, such as butadiene and isoprene as the repeating unit species, and (iii) polymers obtained by copolymerizing the above-mentioned diene type compound and the above-mentioned olefin type compound, followed by hydrogenation. Among these, isobutylene type polymers and hydrogenated polybutadiene type polymers are preferred in view of ease of functional-group introduction into an end thereof, ease of molecular weight control and adjustability of the number of terminal functional groups, among others; isobutylene type polymers are more preferred.

[0046] The isobutylene type polymer may be such one that all of the repeating units are derived from isobutylene or a copolymer with another compound. When the isobutylene type copolymer is used as the main chain skeleton, the polymer preferably has an isobutylene-derived repeating unit content, in each molecule, of not lower than 50% by weight, more preferably not lower than 80% by weight, particularly preferably 90 to 99% by weight, so that the cured products obtained may have excellent rubber characteristics.

[0047] A method of producing the saturated hydrocarbon type polymer is not particularly restricted but may be any of various conventional polymerization methods. Among them, the living polymerization method the development of which has been remarkable in recent years is preferred and, for example, the Inifer polymerization found by Kennedy et al. (J. P. Kennedy et al., J. Polymer Sci., Polymer Chem. Ed., 1997, 15, p. 2843) may be mentioned as a method of producing isobutylene-based polymers using the living polymerization method. This polymerization method enables introduction of various functional groups into molecular ends and the isobutylene type polymers obtained are known to have a molecular weight of about 500 to 100,000 with a molecular weight distribution of not broader than 1.5.

[0048] A method of producing the reactive silyl group-containing saturated hydrocarbon polymer is not particularly restricted but may be any of the methods known in the art, for example the methods disclosed in Japanese Kokoku Publications H04-69659 and H07-108928, Japanese Kokai Publications S63-254149, S64-22904 and H01-197509 and Japanese Patents Nos. 2539445 and 2873395 and Japanese Kokai Publication H07-53882.

[0049] In formulating the curable composition using the above-mentioned reactive silyl group-containing saturated hydrocarbon type polymer, the polymer may comprise a single species or a combination of a plurality of species thereof.

[0050] A (meth) acrylate ester polymer to be used as the main chain skeleton of the organic polymer (A) or of the organic polymer (B) is a polymer in which the repeating unit is derived from a (meth)acrylate ester compound. The expression "(meth)acrylate ester" refers to an acrylate ester and/or a methacrylate ester and has the same meaning also in the description which follows.

[0051] The (meth)acrylate ester compound to be used as the repeating unit is not particularly restricted but includes such (meth)acrylate compounds as (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth) acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-heptyl (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, phenyl (meth)acrylate, toluyl (meth)acrylate, benzyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, stearyl (meth)acrylate, glycidyl (meth)acrylate, γ-(methacryloyloxypropyl)trimethoxysilane, γ-(methacryloyloxypropyl)dimethoxymethylsilane, (meth)acrylic acid-ethylene oxide adducts, trifluoromethylmethyl (meth)acrylate, 2-trifluoromethylethyl (meth)acrylate, 2-perfluoroethylethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, perfluoroethyl (meth)acrylate, trifluoromethyl (meth)acrylate, bis

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(trifluoromethylmethyl) (meth)acrylate, 2-trifluoromethyl-2-perfluoroethylethyl (meth)acrylate, 2-perfluorohexylethyl (meth)acrylate, 2-perfluorodecylethyl (meth) acrylate and 2-perfluorohexadecylethyl (meth)acrylate.

The (meth)acrylate ester polymer includes copolymers of a (meth)acrylate ester compound and a vinyl compound copolymerizable therewith. The vinyl compound is not particularly restricted but includes: styrene compounds such as styrene, vinyltoluene, α-methylstyrene, chlorostyrene, and styrenesulfonic acid and salts thereof; silyl group-containing vinyl compounds such as vinyltrimethoxysilane and vinyltriethoxysilane; maleic acid, maleic anhydride, and maleic acid monoalkyl esters and dialkyl esters; fumaric acid and fumaric acid monoalkyl esters and dialkyl esters; maleimide type compounds such as maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and cyclohexylmaleimide; nitrile group-containing vinyl compounds such as acrylonitrile and methacrylonitrile; amide group-containing vinyl compounds such as acrylamide and methacrylamide; vinyl esters such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate; alkenes such as ethylene and propylene; conjugated dienes such as butadiene and isoprene; vinyl chloride, vinylidene chloride, allyl chloride and allyl alcohol. It is also possible to use a plurality of these as copolymerization components.

[0052] Among the (meth) acrylate ester polymers obtained from the compounds mentioned above, those organic polymers which comprise, as the main chain skeleton, a copolymer of a styrene compound and a (meth) acrylate compound are preferred since they give cured products excellent in physical properties; those organic polymers which comprise, as the main chain skeleton, a copolymer of an acrylate ester compound and a methacrylate ester compound are more preferred, and those organic polymers which comprise, as the main chain skeleton, a polymer of an acrylate ester compound are particularly preferred.

[0053] For use in general architectural fields, the curable composition is required to be low in viscosity, while the cured products obtained therefrom are required to be excellent in weather resistance and thermal stability, low in modulus and high in elongation.

[0054] More preferred as ones meeting these requirements are organic polymers (A) or organic polymers (B) whose main chain skeleton is derived from a butyl acrylate compound.

[0055] On the other hand, for use in automotive or like fields, the cured products obtained are required to be excellent in oil resistance.

[0056] More preferred as one giving cured products excellent in oil resistance is an organic polymer (A) or an organic polymer (B) whose main chain skeleton is a copolymer mainly derived from ethyl acrylate.

[0057] Curable compositions comprising the organic polymer (A) and the organic polymer (B) whose main chain skeleton is an ethyl acrylate-based copolymer tend to give cured products somewhat inferior in low-temperature characteristics (low-temperature resistance) in spite of their being excellent in oil resistance. For improving the low-temperature characteristics, replacement is made of a part of ethyl acrylate with butyl acrylate. Since, however, an increased proportion of butyl acrylate tends to impair the good oil resistance, the proportion thereof is preferably not higher than 40%, more preferably not higher than 30%, in cases of a field where oil resistance is required.

[0058] The use, as a comonomer component, of 2-methoxyethyl acrylate or 2-ethoxyethyl acrylate which has an oxygen atom introduced into the side chain alkyl group is also preferred for improving low-temperature characteristics and the like without causing decrease in oil resistance.

[0059] Since, however, the introduction of an alkoxy group having an ether bond in the side chain tends to render the cured products obtained inferior in thermal stability, the proportion thereof is preferably not higher than 40% in cases of use where thermal stability is required.

[0060] As mentioned above, it is possible to obtain an organic polymer (A) or an organic polymer (B) whose main chain skeleton is an ethyl acrylate-based copolymer and which is suited for various uses or can meet requirements by selecting the comonomer component species and varying the proportion thereof taking into consideration such physical properties as oil resistance, thermal stability and low temperature characteristics as required of the cured products obtained. For example, there may be mentioned, without any limitative meaning, copolymers of ethyl acrylate, butyl acrylate and 2-methoxyethyl acrylate copolymer (weight ratio: 40-50/20-30/30-20) as examples excellent in balance among such physical properties as oil resistance, thermal stability and low-temperature characteristics.

[0061] In the practice of the present invention, these preferred compounds may be copolymerized and, further, block-copolymerized with another compound and, on such occasion, the content of these preferred compounds is preferably not lower than 40% by weight.

A method of producing the (meth)acrylate ester polymer is not particularly restricted but may be any of the methods known in the art. Among them, the living radical polymerization method is preferably used in particular in view of the ease of high-rate introduction of a crosslinking functional group into a molecular chain end and the possibility of obtaining polymers narrow in molecular weight distribution and low in viscosity.

[0062] The polymers obtained by ordinary free radical polymerization using, for example, an azo compound or peroxide as a polymerization initiator tend to show an increased molecular weight distribution value generally not lower than 2 and an increased level of viscosity.

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[0063] Among the methods of producing (meth)acrylate ester polymers using the above-mentioned "living radical polymerization method", the "atom transfer radical polymerization method" which uses an organic halide or sulfonyl halide compound as an initiator and a transition metal complex as a catalyst is preferred as the method of producing (meth) acrylate ester polymers containing a specific functional group since it has not only such characteristics of the "living radical polymerization" as the narrowness in molecular weight distribution and the capability to give polymers low in viscosity but also a high degree of freedom in selecting the initiator and catalyst and the capability to provide the polymers with a halogen or the like at ends thereof relatively advantageous to functional-group exchange reactions. As for the atom transfer radical polymerization method, there may be mentioned, for example, the method described in Matyjaszewski et al. , Journal of the American Chemical Society (J. Am. Chem. Soc.), 1995, 117, p. 5614.

[0064] A method of producing the reactive silyl group-containing (meth) acrylate ester polymer is not particularly restricted but includes, for example, the free radical polymerization method using a chain transfer agent, as disclosed in Japanese Kokoku Publications H03-14068 and H04-55444 and Japanese Kokai Publication H06-211922, the atom transfer radical polymerization method disclosed in Japanese Kokai Publication H09-272714, and the like.

[0065] It is also possible to use a (meth) acrylate ester copolymer derived from a plurality of the (meth) acrylate ester compounds mentioned above as the main chain skeleton of the organic polymer (A) or of the organic polymer (B).

[0066] As typical examples of the (meth)acrylate ester copolymer derived from a plurality of (meth)acrylate ester compounds, there may be mentioned copolymers whose main chain skeleton substantially comprises: a repeating unit having an alkyl group containing 1 to 8 carbon atoms as represented by the general formula (5):

$$-CH_2-C(R^{11})(COOR^{12})- \quad (5)$$

(R^{11} is a hydrogen atom or a methyl group and R^{12} is an alkyl group containing 1 to 8 carbon atoms); and a repeating unit having an alkyl group containing 9 or more carbon atoms as represented by the general formula (6):

$$-CH_2-C(R^{11})(COOR^{13})- \quad (6)$$

(R^{11} is as defined above and R^{13} is an alkyl group containing 9 or more carbon atoms).

[0067] The group R^{12} in the general formula (5) is not particularly restricted but may be any of the alkyl groups containing 1 to 8 carbon atoms, for example a methyl group, an ethyl group, a propyl group, an n-butyl group, a t-butyl group and a 2-ethylhexyl group; among these, alkyl groups containing 1 to 4 carbon atoms are preferred. The group R^{12} contained in the copolymers is not always restricted to a single alkyl group species.

[0068] The group R^{13} in the general formula (6) is not particularly restricted but may be any of the alkyl groups containing 9 or more carbon atoms, for example a lauryl group, an tridecyl group, a cetyl group, a stearyl group and a behenyl group; among these, alkyl groups containing 10 to 30 carbon atoms are preferred, and alkyl groups containing 10 to 20 carbon atoms are more preferred. The group R^{13} contained in the copolymers is not always restricted to a single alkyl group species.

The (meth)acrylate ester copolymer substantially comprises, the repeating units defined by the general formula (5) and general formula (6). The term "substantially" as used herein means that the content of the polymer containing the repeating units defined by the general formulas (5) and (6) in the copolymer is not lower than 50% by weight, and the content of the polymer containing the repeating units defined by the general formulas (5) and (6) in the copolymer is preferably not lower than 70%.

[0069] The content ratio between the repeating units of general formulas (5) and (6) occurring in the copolymer as expressed in terms of the weight ratio (general formula (5): general formula (6)) is preferably 95:5 to 40:60, more preferably 90:10 to 60:40.

The (meth)acrylate ester copolymer comprises a copolymer of (meth)acrylate ester compounds used as the repeating units defined by the general formulas (5) and (6) and a vinyl compound copolymerizable therewith.

[0070] As the vinyl compound, there may be mentioned, for example, acrylic acids such as acrylic acid and methacrylic acid; amide group-containing compounds such as acrylamide, methacrylamide, N-methylolacrylamide and N-methylolmethacrylamide, epoxy group-containing compounds such as glycidyl acrylate and glycidyl methacrylate, amino group-containing compounds such as diethylaminoethyl acrylate, diethylaminoethyl methacrylate and aminoethyl vinyl ether; and, further, such compounds as acrylonitrile, styrene, α-methylstyrene, alkyl vinyl ethers, vinyl chloride, vinyl acetate, vinyl propionate and ethylene.

In the main chain skeleton of the organic polymer (A), there may further be present, if necessary, another repeating unit containing, for example, a urethane bond, so long as the effects of the present invention are not significantly lessened thereby.

[0071] The urethane bond-containing repeating unit is not particularly restricted but there may be mentioned, for example, a repeating unit comprising a group formed by the reaction between an isocyanato group and an active hydrogen group (the group thus formed is hereinafter referred to also as an "amide segment").

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[0072] The amide segment is an organic group represented by the general formula (7):

$$-NR^{14}-C(=O)- \qquad (7)$$

(R^{14} is a hydrogen atom or an organic group).

[0073] The amide segment is not particularly restricted but includes, for example, a urethane group formed by the reaction between an isocyanato group and a hydroxyl group; a urea group formed by the reaction between an isocyanato group and an amino group; and a thiourethane group formed by the reaction between an isocyanato group and a mercapto group.

[0074] Those organic groups formed by the reaction of an active hydrogen in the urethane group, the urea group and the thiourethane group with an isocyanato group also fall within the definition of "amide segment" as given herein.

[0075] A method of producing the reactive silyl group-containing organic polymer containing an amide segment in the main chain skeleton thereof is not particularly restricted but there may be mentioned, for example, the method comprising reacting an active hydrogen-terminated organic group-containing organic polymer with an excess of a polyisocyanate compound to give a polymer having an isocyanato group at a polyurethane type main chain end and, thereafter or simultaneously therewith, reacting all or part of the isocyanato groups in the polymer with a group W in a silicon compound represented by the general formula (8):

$$R^{15}\text{-}SiR^{16}_{3-a}X^{3}_{a} \qquad (8)$$

(R^{15} is a divalent organic group, more preferably a divalent hydrocarbon group containing 1 to 20 carbon atoms; the (3-a) R^{16}s are a hydrogen atom or an organic group, the a X^3s are a hydroxyl group or a hydrolyzable group, and a is 2 or 3; and W is a group containing at least one active hydrogen selected from the group consisting of a hydroxyl group, a carboxyl group, a mercapto group and an amino (primary or secondary) group), as disclosed in Japanese Kokoku Publication S46-12154 (United States Patent 3,632,557), Japanese Kokai Publications S58-109529 (United States Patent 4,374,237), S62-13430 (United States Patent 4,645,816), H08-53528 (EP 0676403), and H10-204144 (EP 0831108), Japanese Kohyo Publication 2003-508561 (United States Patent 6,197,912), Japanese Kokai Publications H06-211879 (United States Patent 5,364,955), H10-53637 (United States Patent 5,756,751), H11-100427, 2000-169544, 2000-169545 and 2002-212415, Japanese Patent 3,313,360, United States Patents 4,067,844 and 3,711,445, Japanese Kokai Publication 2001-323040, and the like.

[0076] Mention may also be made of a method comprising reacting an active hydrogen-containing group occurring at an end of an organic polymer with the isocyanato group of a reactive silyl group-containing isocyanate compound represented by the general formula (9):

$$O=C=N\text{-}R^{15}\text{-}SiR^{16}_{3-a}X^{3}_{a} \qquad (9)$$

(R^{15}, R^{16} X^3 and a are as defined above referring to the general formula (8)), as disclosed in Japanese Kokai Publications H11-279249 (United States Patent 5,990,257), 2000-119365 (Unites States Patent 6,046,270), S58-29818 (United States Patent 4,345,053), H03-47825 (United States Patent 5,068,304), H11-60724, 2002-155145 and 2002-249538, WO 03/018658, WO 03/059981, and the like.

[0077] The active hydrogen-terminated group-containing organic polymer is not particularly restricted but includes, for example, hydroxyl group-terminated oxyalkylene polymers (polyether polyols), polyacrylic polyols, polyester polyols, hydroxyl group-terminated saturated hydrocarbon type polymers (polyolefin polyols), polythiol compounds and polyamine compounds.

[0078] Preferred among these are those organic polymers whose main chain skeleton comprises a polyether polyol, polyacrylic polyol and polyolefin polyol components, since they have a relatively low glass transition temperature and give cured products excellent in low-temperature resistance.

[0079] Those organic polymers comprising a polyether polyol component are low in viscosity, have good workability and give cured products showing good depth curability and adhesiveness, hence are particularly preferred. Curable compositions in which an organic polymer containing a polyacrylic polyol and saturated hydrocarbon type polymer component are more preferred since they give cured products having good weather resistance and thermal stability.

[0080] The polyether polyol preferably has, on an average, at least 0.7 terminal hydroxyl group per molecule.

[0081] The production method thereof is not particularly restricted but may be any of the methods known in the art, including, for example, a polymerization method using an alkali metal catalyst, and a polymerization method of an alkylene oxide using a polyhydroxy compound containing at least two hydroxyl groups per molecule as an initiator in the presence of a double metal cyanide complex or cesium.

[0082] Among the polymerization methods mentioned above, the polymerization method using a double metal cyanide complex is preferred since it gives polymers low in degree of unsaturation, narrow in molecular weight distribution

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(Mw/Mn) and low in viscosity, which give cured products excellent in acid resistance and weather resistance, among others.

[0083] The term "polyacrylic polyol" refers to a polyol whose skeleton is a (meth)acrylic acid alkyl ester (co)polymer and whose molecule contains a hydroxyl group.

[0084] As for the production method thereof, the living radical polymerization method is preferred and the atom transfer radical polymerization method is more preferred because of capability of their giving polymers narrow in molecular weight distribution and possibly low in viscosity. Also preferred is the polymerization method involving the so-called SGO process in which an acrylic acid alkyl ester type compound is continuously bulk-polymerized under high-temperature and high-pressure conditions, as disclosed in Japanese Kokai Publication 2001-207157. As such a polyacrylic polyol, there may be mentioned ARUFON UH-2000 (product of Toagosei Co., Ltd.), and the like.

[0085] The polyisocyanate compound is not particularly restricted but includes, for example, an aromatic type polyisocyanate such as toluene (tolylene) diisocyanate, diphenylmethane diisocyanate and xylylene diisocyanate; and an aliphatic type polyisocyanate such as isophorone diisocyanate and hexamethylene diisocyanate.

[0086] The silicon compound defined by the general formula (8) is not particularly restricted but there may be mentioned, for example, amino group-containing silane compounds such as γ-aminopropyltrimethoxysilane, N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane, γ-(N-phenyl)aminopropyltrimethoxysilane, N-ethylaminoisobutyltrimethoxysilane, N-cyclohexylaminomethyltriethoxysilane, N-cyclohexylaminomethyldiethoxymethylsilane and N-phenylaminomethyltrimethoxysilane; hydroxyl group-containing silane compounds such as γ-hydroxypropyltrimethoxysilane; and mercapto group-containing silane compounds such as γ-mercaptopropyltrimethoxysilane.

[0087] As the silicon compound represented by the general formula (8); there may further be mentioned Michael addition products derived from various α,β-unsaturated carbonyl compounds and a primary amino group-containing silane compound or Michael addition products derived from various (meth)acryloyl group-containing silane compounds and a primary amino group-containing compound, as disclosed in Japanese Kokai Publications H06-211879 (United States Patent 5,364,955), H10-53637 (United States Patent 5,756,751), H10-204144 (EP 0831108) 2000-169544 and 2000-169545.

[0088] The reactive silyl group-containing isocyanate compound defined by the general formula (9) is not particularly restricted but includes, for example, γ-trimethoxysilylpropyl isocyanate, γ-triethoxysilylpropyl isocyanate, γ-methyldimethoxysilylpropyl isocyanate, γ-methyldiethoxysilylpropyl isocyanate, trimethoxysilylmethyl isocyanate, triethoxymethylsilylmethyl isocyanate, dimethoxymethylsilylmethyl isocyanate, and diethoxymethylsilylmethyl isocyanate.

[0089] As the reactive silyl group-containing isocyanate compound defined by the general formula (9), there may further be mentioned the reaction products derived from a silicon compound of the general formula (8) and an excess of a polyisocyanate compound, as disclosed in Japanese Kokai Publication 2000-119365 (United States Patent 6,046,270).

[0090] The hydrolyzable group represented by X^1 in the general formula (2) and X^2 in the general formula (3) is not particularly restricted but includes those hydrolyzable groups which are known in the art, for example, a hydrogen atom, halogen atoms, and an alkoxy group, an acyloxy group, a ketoxymate group, an amino group, an amide group, an acid amide group, an aminooxy group, a mercapto group and an alkenyloxy group. Among these, a hydrogen atom, an alkoxy group, an acyloxy group, a ketoxymate group, an amino group, an amide group, an aminooxy group, a mercapto group and an alkenyloxy group are preferred, and an alkoxy group is more preferred from the viewpoints of mild hydrolyzability and easy handleability.

[0091] Two groups selected from among a hydroxyl group and hydrolyzable groups are bound to one silicon atom, and three groups selected from among a hydroxyl group and hydrolyzable groups are bound to one silicon atom; each of the two groups may be the same or different, and each of the three groups may be the same or different.

[0092] The group R^1 in the general formula (2) is not particularly restricted but includes, for example, an alkyl group such as a methyl group and an ethyl group, a cycloalkyl group such as a cyclohexyl group, an aryl group such as a phenyl group, an aralkyl group such as a benzyl group, and a triorganosiloxy group represented by $-OSi(R')_3$ wherein R' is a methyl group, a phenyl group or the like. Among these, a methyl group is preferred.

[0093] The reactive silyl group defined by the general formula (2) is not particularly restricted but includes, for example, a dimethoxymethylsilyl group, a dimethoxyethylsilyl group, a diethoxymethylsilyl group, a diethoxyethylsilyl group and a diisopropoxymethylsilyl group.

Among these, a dimethoxymethylsilyl group is most preferred since it affords good curability and good storage stability in the curable composition.

Further, a diethoxymethylsilyl group and a diethoxyethylsilyl group are preferred since the alcohol formed upon hydrolysis reaction of the reactive silyl group is highly safe ethanol.

[0094] The reactive silyl group defined by the general formula (3) is not particularly restricted but includes, for example, a trimethoxysilyl group, a triethoxysilyl group, a triisopropoxysilyl group, a methoxydiethoxysilyl group and a ethoxydimethoxysilyl group. Among these, a trimethoxysilyl group and a triethoxysilyl group are preferred since it affords good curability in the curable composition, and when rapid curability is particularly required, a trimethoxysilyl group is preferred.

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Further, a triethoxysilyl group is preferred since the alcohol formed upon hydrolysis reaction of the reactive silyl group is highly safe ethanol.

[0095] A method of introducing the reactive silyl group is not particularly restricted but includes such methods known in the art as the methods (a) to (c) shown below.

(a) A method comprising: reacting a polymer containing such a functional group as a hydroxyl group in the molecule with an organic compound containing an active group reactive with this functional group as well as an unsaturated group to give an unsaturated group-containing polymer; or copolymerizing a polymer containing such a functional group as a hydroxyl group in the molecule with an unsaturated group-containing epoxy compound to give an unsaturated group-containing polymer, and then reacting the reaction product obtained with a reactive silyl group-containing hydrosilane for hydrosilylation.

(b) A method comprising reacting the unsaturated group-containing organic polymer obtained in the same manner as described above in (a) with a compound containing a mercapto group and a reactive silyl group.

(c) A method comprising reacting an organic polymer containing such a functional group as a hydroxyl group, an epoxy group or an isocyanato group in the molecule with a compound containing a functional group reactive with this function group and a reactive silyl group.

[0096] Among these methods, the method (a) or the method (c) in such a mode that a hydroxyl group-terminated polymer is reacted with a compound containing an isocyanato group and reactive silyl group is preferred in view of the fact that a high conversion rate can be attained in a relatively short period of time. The method (a) is more preferred since curable compositions based on the reactive silyl group-containing organic polymer obtained by the method (a) tends to be lower in viscosity than curable compositions based on the organic polymer obtained by the method (c) and, as a result, curable compositions having good workability can be obtained and, further, the organic polymer obtained by the method (b) has a stronger mercaptosilane-due odor as compared with the organic polymer obtained by the method (a).

The hydrosilane compound to be used in carrying out the method (a) is not particularly restricted but includes, for example, halogenated hydrosilanes such as trichlorosilane, methyldichlorosilane, dimethylchlorosilane and phenyldichlorosilane; alkoxysilanes such as trimethoxysilane, triethoxysilane, methyldiethoxysilane, methyldimethoxysilane, phenyldimethoxysilane and 1-[2-(trimethoxysilyl)ethyl]-1,1,3,3-tetramethyldisiloxane; acyloxyhydrosilanes such as methyldiacetoxysilane and phenyldiacetoxysilane; and ketoxymatehydrosilanes such as bis(dimethylketoxymate)methylsilane and bis(cyclohexylketoxymate)methylsilane. Among these, halogenated hydrosilanes and alkoxyhydrosilanes are preferred, and alkoxyhydrosilanes are more preferred because of the mild hydrolyzability and easy handleability of curable compositions based on the organic polymer (A) and organic polymer (B) obtained. Among the alkoxyhydrosilanes, methyldimethoxysilane is preferred because of its ready availability and excellent various characteristics (curability, storage stability, elongation characteristic, tensile strength, etc.) of curable compositions based on the organic polymer (A) and organic polymer (B) obtained and cured products.

The synthetic method (b) is not particularly restricted but may be, for example, the method of introducing a mercapto group- and reactive silyl group-containing compound into an unsaturated-bond site in the organic polymer by a radical addition reaction in the presence of a radical initiator and/or a radical generation source. The mercapto group- and reactive silyl group-containing compound is not particularly restricted but includes, for example, γ-mercaptopropyltrimethoxysilane, γ-mercaptopropylmethyldimethoxysilane, γ-mercaptopropyltriethoxysilane, γ-mercaptopropylmethyldiethoxysilane, mercaptomethyltrimethoxysilane and mercaptomethyltriethoxysilane.

The method of reacting a hydroxyl group-terminated polymer with an isocyanato group- and reactive silyl group-containing compound according to the synthetic method (c) is not particularly restricted but may be, for example, a method disclosed in Japanese Kokai Publication H03-47825. The isocyanato group- and reactive silyl group-containing compound is not particularly restricted but includes, for example, γ-isocyanatopropyltrimethoxysilane, γ-isocyanatopropylmethyldimethoxysilane, γ-isocyanatopropyltriethoxysilane, γ-isocyanatopropylmethyldiethoxysilane, isocyanatomethyltrimethoxysilane, isocyanatomethyltriethoxysilane, isocyanatomethyldimethoxymethylsilane and isocyanatomethyldiethoxymethylsilane.

[0097] In the case of silane compounds containing a silicon atom with three hydrolyzable groups bound thereto, for example trimethoxysilane, the disproportionation reaction may proceed rapidly in certain cases. The progress of the disproportionation reaction may sometimes result in the formation of such a dangerous compound as dimethoxysilane.

[0098] In the case of γ-mercaptopropyltrimethoxysilane and γ-isocyanatopropyltrimethoxysilane, however, such disproportionation reaction will not proceed. Therefore, in the case of using, as the silyl group, a group containing a silicon atom with three hydrolyzable groups bound thereto, for example a trimethoxysilyl group, the synthetic method (b) or (c) is preferably employed.

[0099] On the other hand, in the case of silane compounds represented by the general formula (10):

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$$H\text{-}(SiR^{17}_2O)_mSiR^{17}_2\text{-}R^{18}\text{-}SiX^4_3 \qquad (10)$$

(wherein the three X^4s each independently is a hydroxyl group or a hydrolyzable group; the (2m+2) R^{17}s each independently is a hydrocarbon group, preferably, from the availability and cost viewpoint, a hydrocarbon group containing 1 to 20 carbon atoms, more preferably a hydrocarbon group containing 1 to 8 carbon atoms, particularly preferably a hydrocarbon group containing 1 to 4 carbon atoms; R^{18} is a divalent organic group, preferably, from the availability and cost viewpoint, a divalent hydrocarbon group containing 1 to 12 carbon atoms, more preferably a divalent hydrocarbon group containing 2 to 8 carbon atoms, particularly preferably a divalent hydrocarbon group containing 2 carbon atoms; and m is an integer of 0 to 19, preferably, from the availability and cost viewpoint, 1), the disproportionation reaction will not proceed. Therefore, for introducing a group containing a silicon atom with three hydrolyzable groups bound thereto by the synthetic method (a), a silane compound represented by the general formula (10) is preferably used.

[0100] As the silane compound represented by the general formula (10), there may be mentioned 1-[2-(trimethoxysilyl) ethyl]-1,1,3,3-tetramethyldisiloxane, 1-[2-(trimethoxysilyl)propyl]-1,1,3,3-tetramethyldisiloxane and 1-[2-(trimethoxysilyl) hexyl]-1,1,3,3-tetramethyldisiloxane.

[0101] The organic polymer (A) and the organic polymer (B) to be used may have either a straight chain structure or a branched chain structure in the molecule thereof, and the number average molecular weight thereof, as expressed in terms of the value on a polystyrene equivalent basis as derived from the value measured by GPC, is preferably 500 to 100, 000, more preferably 1, 000 to 50, 000, particularly preferably 3, 000 to 30,000. When the number average molecular weight is lower than 500, the cured products obtained tend to be inferior in elongation characteristics and, when it is in excess of 100,000, the resulting curable composition becomes high in viscosity and tends to be inferior in workability.

[0102] The number of reactive silyl groups contained in each molecule of the organic polymer (A) and the organic polymer (B) is preferably not smaller than 1 on an average; it is preferably 1.1 to 5. When the number of reactive silyl groups contained in each molecule is smaller than 1 on an average, the curable composition tends to be inferior in curability and the cured products obtained show a tendency toward failure to exhibit a good rubber elastic behavior.

[0103] For the curable composition to have practically rapid levels of surface curability and depth curability and for the cured products obtained therefrom to have good mechanical characteristics (high strength, high elongation, etc.) and surface weather resistance for a long period of time, it is preferable that either one of the main chain skeleton of the organic polymer (A) containing a reactive silyl group represented by $-SiR^1X^1_2$ and the main chain skeleton of the organic polymer (B) containing a reactive silyl group represented by $-SiX^2_3$ be a polyoxyalkylene type polymer and the other be a (meth)acrylate ester polymer (R^1, X^1 and X^2 being as defined above referring to the general formulas (2) and (3)). Specifically, there may be mentioned a case where the main chain of the component (A) is a polyoxyalkylene type polymer and the main chain of the component (B) is a (meth)acrylate ester polymer, and a case where the main chain of the component (A) is a (meth)acrylate ester polymer and the main chain of the component (B) is a polyoxyalkylene type polymer.

[0104] As for the addition level of the component (A) and component (B), the weight ratio between the component (A) and component (B) is important for securing practically rapid rates of surface curability and depth curability for the curable composition, and the weight ratio (component (A) /component (B)) is preferably 1/99 to 80/20, more preferably 1/45 to 99/55.

[0105] For achieving good workability and rapid depth curability of the curable composition and satisfactory strength and elongation of the cured products, the content of a polyoxyalkylene type polymer is desirably increased to preferably 30% by weight or more, more preferably 50% by weight or more, and still more preferably 70% by weight or more when the sum of both is set to 100% by weight; the content of a (meth)acrylate ester polymer is desirably increased to preferably 30% by weight or more, more preferably 50% by weight or more, and still more preferably 70% by weight or more.

[0106] The curable composition of the invention essentially comprises a guanidine compound represented by the general formula (1):

$$R^2N{=}CNR^3_2\text{-}NR^4_2 \qquad (1)$$

(R^2, the two R^3s and the two R^4s each independently is a hydrogen atom or an organic group) as a curing catalyst (component (C)) (such guanidine compound is hereinafter sometimes referred to as "guanidine compound (C)").

[0107] Owing to the use of a guanidine compound (C) as a curing catalyst therein, the curable composition of the invention shows a practical level of curability and the cured products obtained show good adhesiveness to various adherends, in spite of the fact that the curing catalyst is a non-organotin type catalyst.

[0108] R^2 appearing in the general formula (1) is preferably a hydrocarbon group in which the carbon at position 1 is saturated, or a hydrogen atom since excellent curability can be imparted to the above-mentioned component (A) and component (B). In cases where R^2 is an organic group or a hydrocarbon group, the number of carbon atoms contained therein is preferably 1 to 20, more preferably 1 to 10, from the availability viewpoint.

[0109] R^3 appearing in the general formula (1) is preferably a hydrogen atom or an organic group since excellent

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curability can be imparted to the above-mentioned component (A) and component (B).

[0110] Since the cured products obtained show excellent adhesiveness, an $-NR^3_2$ group appearing in the general formula (1) is preferably an $-NR^5-C(=NR^6)-NR^7_2$ group (in which R^5, R^6 and the two R^7s each independently is a hydrogen atom or an organic group) and/or an $-N=C(NR^8_2)-NR^9_2$ group (in which the two R^8s and the two R^9s each independently is a hydrogen atom or an organic group). In cases where an $-NR^3_2$ group is an $-NR^5-C(=NR^6)-NR^7_2$ group (R^5, R^6 and the two R^7s being as defined above), R^5, R^6 and the two R^7s each independently is preferably a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, more preferably a hydrogen atom or a hydrocarbon group containing 1 to 10 carbon atoms, since the cured products obtained show excellent adhesiveness and the corresponding compound is readily available.

[0111] Further, it is preferred that at least any one of R^2, the two R^4s, R^5, R^6 and the two R^7s be an aryl group, since the cured products obtained show excellent adhesiveness.

In cases where an $-NR^3_2$ group is an $-N=C(NR^8_2)-NR^9_2$ group (in which the two R^8s and the two R^9s being as defined above), R^5, R^6 and the two R^7s each independently is preferably a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, more preferably a hydrogen atom or a hydrocarbon group containing 1 to 10 carbon atoms, from the adhesiveness and availability viewpoint.

[0112] Those guanidine compounds of the general formula (1) in which $-NR^3_2$ is such an organic group as the above-mentioned $-NR^5-C(=NR^6)-NR^7_2$ and $-N=C(NR^8_2)-NR^9_2$ are called biguanide compounds.

[0113] Each of the two R^4s in the general formula (1) is preferably a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, more preferably a hydrogen atom or a hydrocarbon group containing 1 to 10 carbon atoms, since, in such a case, the amidine compound is readily available and can provide the component (A) and the component (B) with good curability.

[0114] In view of their ready availability and their ability to provide the component (A) and the component (B) with good curability, those guanidine compounds represented by the general formula (1) in which any two or more of R^2, R^3 and the two R^4s are bound together to form a ring structure are preferred. The number of carbon atoms contained in the guanidine compound (C) represented by the general formula (1) is preferably 2 or more, more preferably 6 or more, and particularly preferably 7 or more.

[0115] When the number of carbon atoms is smaller than 2 (namely when the molecular weight is low), the volatility of the compound becomes increased, causing a tendency toward pollution of the work environment. It is not necessary to particularly specify the upper limit to the number of carbon atoms contained in the guanidine compound (C); it is generally preferred, however, that the number be not larger than 10,000.

[0116] For the same reasons as mentioned above, the guanidine compound (C) preferably has a molecular weight of not lower than 60, more preferably not lower than 12 0, particularly preferably not lower than 130. It is not necessary to particularly specify the upper limit to the molecular weight; it is generally preferred, however, that the molecular weight be not higher than 100,000.

The guanidine compound (C) (inclusive of the biguanide compound) is not particularly restricted but includes pyrimidine compounds such as 2-aminopyrimidine and 2-amino-4,6-dimethylpyrimidine; imidazoline compounds such as 1,3-dimethyl-2-iminoimidazolidine and 1-methyl-2-iminoimidazolidine-4-one; guanidine compounds such as guanidine, dicyandiamide, 1-methylguanidine, 1-ethylguanidine, 1-cyclohexylguanidine, 1-phenylguanidine, 1,1-dimethylguanidine, 1,3-dimethylguanidine, 1,2-diphenylguanidine, 1,1-di-o-tolylguanidine, 1,2-bis(o-tolyl)guanidine, 1,1,3-trimethylguanidine, 1,2,3-trimethylguanidine, 1,1,3,3-tetramethylguanidine, 1,1,2,3,3-pentamethylguanidine, 2-ethyl-1,1,3,3-tetramethylguanidine, 1,1,3,3-tetramethyl-2-n-propylguanidine, 1,1,3,3-tetramethyl-2-isopropylguanidine, 2-n-butyl-1,1,3,3-tetramethylguanidine, 2-tert-butyl-1,1,3,3-tetramethylguanidine, 1,2,3-tricyclohexylguanidine, 1-benzyl-2,3-dimethylguanidine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-ethyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-n-propyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-isopropyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-n-butyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-cyclohexyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, and 7-n-octyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene; and biguanide compounds such as biguanide, 1-methylbiguanide, 1-ethylbiguanide, 1-n-butylbiguanide, 1-(2-ethylhexyl)biguanide, 1-n-octadecylbiguanide, 1,1-dimethylbiguanide, 1,1-diethylbiguanide, 1-cyclohexylbiguanide, 1-allylbiguanide, 1-phenylbiguanide, 1-(o-tolyl)biguanide,1-morpholinobiguanide, 1-n-butyl-N^2-ethylbiguanide, 1,1'-ethylenebisbiguanide, 1,5-ethylenebiguanide, 1-[3-(diethylamino)propyl]biguanide, 1-[3-(dibutylamino)propyl]biguanide, and N',N"-dihexyl-3,12-diimino-2,4,11,13-tetraazatetradecanedia midine.

[0117] Either a single species among these guanidine compounds may be incorporated in the curable composition or a combination of a plurality thereof may be incorporated in the curable composition.

[0118] Preferred among those guanidine compounds mentioned above are 1,1,2,3,3-pentamethylguanidine, 1-phenylguanidine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene and like guanidine compounds, since they are highly active and can impart good curability to the component (A) and component (B), and the cured products obtained show excellent adhesiveness; more preferred are 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene and like cyclic guanidine compounds.

Further, 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine, 1-phenylguanidine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-methyl-

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1,5,7-triazabicyclo[4.4.0]dec-5-ene and 1-(o-tolyl)biguanide are preferred since they are readily available and can impart good curability to the component (A) and component (B) and the cured products obtained show excellent adhesiveness; 1-(o-tolyl)biguanide is more preferred.

The addition level of the guanidine compound (C) is preferably 0.1 to 30 parts by weight, more preferably 0.1 to 12 parts by weight, per 100 parts by weight of the sum of the (A) component organic polymer and (B) component organic polymer.

[0119] When the addition level of the guanidine compound (C) is below 0.1 part by weight, the curable composition may fail to obtain a practical rate of curing and it becomes sometimes difficult for the curing reaction to proceed to a sufficient extent. On the other hand, when the level of addition of the guanidine compound (C) is above 30 parts by weight, the pot life becomes too short, hence the workability tends to become worsened.

[0120] While such an guanidine compound is used as a curing catalyst according to the invention, another curing catalyst may also be used in combination so long as the effects of the invention will not be lessened. As typical examples, there may be mentioned: carboxylic acid metal salts such as tin carboxylates, lead carboxylates, bismuth carboxylates, potassium carboxylates, calcium carboxylates, barium carboxylates, titanium carboxylates, zirconium carboxylates, hafnium carboxylates, vanadium carboxylates, manganese carboxylates, iron carboxylates, cobalt carboxylates, nickel carboxylates and cerium carboxylates; titanium compounds such as tetrabutyl titanate, tetrapropyl titanate, titanium tetrakis(acetylacetonate), bis(acetylacetonato)diisopropoxytitanium and diisopropoxytitanium bis(ethyl acetoacetate); organotin compounds such as dibutyltin dilaurate, dibutyltin maleate, dibutyltin phthalate, dibutyltin dioctanoate, dibutyltin bis(2-ethylhexanoate), dibutyltin bis(methyl maleate), dibutyltin bis (ethyl maleate), dibutyltin bis (butyl maleate), dibutyltin bis(octyl maleate), dibutyltin bis(tridecyl maleate), dibutyltin bis(benzyl maleate), dibutyltin diacetate, dioctyltin bis(ethyl maleate), dioctyltin bis(octyl maleate), dibutyltin dimethoxide, dibutyltin bis(nonylphenoxide), dibutenyltin oxide, dibutyltin oxide, dibutyltin bis(acetylacetonate), dibutyltin bis(ethyl acetoacetonate), dibutyltin oxide-silicate compound reaction products and dibutyltin oxide-phthalic acid ester reaction products; aluminum compounds such as aluminum tris(acetylacetonate), aluminum tris(ethyl acetoacetate) and diisopropoxyaluminum ethyl acetoacetate; zirconium compounds such as zirconium tetrakis(acetylacetonate); various metal alkoxides such as tetrabutoxyhafnium; organic acidic phosphoric acid esters; organic sulfonic acids such as trifluoromethanesulfonic acid; and inorganic acids such as hydrochloric acid, phosphoric acid and boric acid.

The combined use of these curing catalysts is expected to increase the catalytic activity and improve such characteristics as depth curability, thin layer curability and adhesiveness. Since, however, the toxicity of the curable composition obtained may increase depending on the addition level of the organotin compound, the addition level of the organotin compound in the curable composition of the invention is preferably low. Thus, the addition level of the organotin is preferably not higher than 5 parts by weight, more preferably not higher than 0.5 part by weight, still more preferably not higher than 0.05 part, per 100 parts by weight of the sum of the component (A) and component (B) ; substantial absence of any organotin is particularly preferred. Furthermore, from the environmental stress viewpoint, it is preferred that the addition level of metal compounds other than organotins be also low.

The addition level of metal compounds other than organotins is preferably not higher than 10 parts by weight, more preferably not higher than 5 parts by weight; substantial absence thereof is particularly preferred.

[0121] Further, carboxylic acids can be used in combination as a promoter so long as the effects of the invention will not be lessened. The specific examples thereof include: straight-chain saturated fatty acids such as acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, 2-ethylhexanoic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, heptadecylic acid, stearic acid, nonadecanoic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, melissic acid and lacceric acid; monoenoic unsaturated fatty acids such as undecylenic acid, linderic acid, tsuzuic acid, physeteric acid, myristoleic acid, 2-hexadecenoic acid, 6-hexadecenoic acid, 7-hexadecenoic acid, palmitoleic acid, petroselinic acid, oleic acid, elaidic acid, asclepic acid, vaccenic acid, gadoleic acid, gondoic acid, cetoleic acid, erucic acid, brassidic acid, selacholeic acid, ximenic acid, lumequeic acid, acrylic acid, methacrylic acid, angelic acid, crotonic acid, isocrotonic acid and 10-undecenoic acid; polyenoic unsaturated fatty acids such as linoelaidic acid, linolic acid, 10,12-octadecadienoic acid, hiragonic acid, α-eleostearic acid, β-eleostearic acid, punicic acid, linolenic acid, 8,11,14-eicosatrienoic acid, 7,10,13-docosatrienoic acid, 4,8,11,14-hexadecatetraenoic acid, moroctic acid, stearidonic acid, arachidonic acid, 8,12,16,19-docosatetraenoic acid, 4,8,12,15,18-eicosapentaenoic acid, clupanodonic acid, nisinic acid and docosahexaenoic acid; branched fatty acids such as 1-methylbutyric acid, isobutyric acid, 2-ethylbutyric acid, isovaleric acid, tuberculostearic acid, pivalic acid, 2,2-dimethylbutyric acid, 2-ethyl-2-methylbutyric acid, 2,2-diethylbutyric acid, 2,2-dimethylvaleric acid, 2-ethyl-2-methylvaleric acid, 2,2-diethylvaleric acid, 2,2-dimethylhexanoic acid, 2,2-diethylhexanoic acid, 2,2-dimethyloctanoic acid, 2-ethyl-2,5-dimethylhexanoic acid, neodecanoic acid and versatic acid; triple bond-containing fatty acids such as propiolic acid, tariric acid, stearolic acid, crepenynic acid, xymenynic acid and 7-hexadecynoic acid; alicyclic carboxylic acids such as naphthenic acid, malvalic acid, sterculic acid, hydnocarpic acid, chaulmoogric acid, gorlic acid, 1-methylcyclopentanecarboxylic acid, 1-methylcyclohexanecarboxylic acid, 2-methylbicyclo[2.2.1]-5-heptene-2-carboxylic acid, 1-adamantanecarboxylic acid, bicycle[2.2.1]heptanes-1-carboxylic acid and bicycle[2.2.2]octane-1-carboxylic acid; oxygen-containing fatty acids such as acetoacetic acid, ethoxyacetic acid, glyoxylic acid, glycolic acid, gluconic

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acid, sabinic acid, 2-hydroxytetradecanoic acid, ipurolic acid, 2,2-dimethyl-3-hydroxypropionic acid, 2-hydroxyhexadecanoic acid, jalapinolic acid, juniperic acid, ambrettolic acid, aleuritic acid, 2-hydroxyoctadecanoic acid, 12-hydroxyoctadecanoic acid, 18-hydroxyoctadecanoic acid, 9,10-dihydroxyoctadecanoic acid, ricinolic acid, camlolenic acid, licanic acid, pheronic acid, cerebronic acid and 2-methyl-7-oxabicyclo[2.2.1]-5-heptene-2-carboxylic acid; and halogen-substituted monocarboxylic acids such as chloroacetic acid, 2-chloroacrylic acid and chlorobenzoic acid. As far as aliphatic dicarboxylic acids are concerned, there may be mentioned saturated dicarboxylic acids such as adipic acid, azelaic acid, pimelic acid, suberic acid, sebacic acid, ethylmalonic acid, glutaric acid, oxalic acid, malonic acid, succinic acid, oxydiacetic acid, dimethylmalonic acid, ethylmethylmalonic acid, diethylmalonic acid, 2,2-dimethylsuccinic acid, 2,2-diethylsuccinic acid, 2,2-dimethylglutaric acid and 1,2,2-trimethyl-1,3-cyclopentanedicarboxylic acid; and unsaturated dicarboxylic acids such as maleic acid, fumaric acid, acetylenedicarboxylic acid and itaconic acid. As far as aliphatic polycarboxylic acids are concerned, there may be mentioned tricarboxylic acids such as aconitic acid, 4,4-dimethylaconitic acid, citric acid, isocitric acid and 3-methylisocitric acid. As aromatic carboxylic acids, there may be mentioned aromatic monocarboxylic acids such as benzoic acid, 9-anthracenecarboxylic acid, atrolactic acid, anisic acid, isopropylbenzoic acid, salicylic acid and toluic acid; and aromatic polycarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, carboxyphenylacetic acid and pyromellitic acid. The combined use of these curing catalysts is expected to increase the catalytic activity and improve such characteristics as curability and depth curability. The addition level of the carboxylic acid is preferably not 0.01 to 20 parts by weight, more preferably 0.1 to 10 parts by weight, per 100 parts by weight of the sum of the component (A) and component (B)

[0122] The curable composition of the invention preferably contains a polyether type plasticizer as a component (D).

[0123] The polyether type plasticizer functions as an agent for adjusting the viscosity and slump characteristics of the curable composition and adjusting the tensile strength, elongation and like mechanical characteristics of the cured products obtained. Further, the incorporation thereof in one-pack type curable compositions is preferred since the change in curing rate is thereby rendered less even after long-term storage and the rate of curing in the depth upon exposure to the air is increased thereby.

[0124] The polyether type plasticizer is not particularly restricted but includes, for example, polyether polyols such as polyethylene glycol, polypropylene glycol and polytetramethylene glycol, derivatives of such polyether polyols as obtained by converting the hydroxyl groups thereof to ester groups or ether groups and like polyethers. Among these, polypropylene glycol is preferred from the compatibility viewpoint.

[0125] The polypropylene glycol preferably has a number average molecular weight of 500 to 15000, more preferably 1000 to 5000.

[0126] When the molecular weight of polypropylene glycol is too low, the cured products obtained cannot retain their initial physical characteristics over a long period of time as a result of the plasticizer being eluted therefrom by heat or rainfall with the lapse of time; such elution may possibly cause contamination due to adhesion of dust, for instance. On the other hand, when the molecular weight is excessively high, the viscosity of the curable composition increases and the workability tends to become poor.

[0127] The molecular weight distribution of the polyether type plasticizer is not particularly restricted but is preferably narrow; the value obtained by dividing the weight average molecular weight by the number average molecular weight is preferably lower than 1.80, more preferably 1.50 or lower.

[0128] In the case of polyether type polymers, the number average molecular weight is determined by terminal group analysis and, in the case of other polymers, it is determined by GPC. The molecular weight distribution (Mw/Mn) is determined by GPC (on a polystyrene equivalent basis).

[0129] The polyether type plasticizer may be one containing at least one reactive silyl group within the molecule or may be one containing no such group. The addition of a reactive silyl group-containing polymeric plasticizer is preferred since the polymeric plasticizer added is involved in the curing reaction and thus is prevented from migrating from the cured products obtained.

[0130] As the reactive silyl group, there may be mentioned the same ones as the above-mentioned reactive silyl groups to be contained in the component (A) or component (B). The average number of reactive silyl groups per molecule, when contained in the plasticizer, is preferably not greater than 1, more preferably not greater than 0.8. When a reactive silyl group-containing plasticizer, in particular a reactive silyl group-containing oxyalkylene polymer, is used, it is necessary that the number average molecular weight thereof be lower than those of the component (A) and component (B).

[0131] The polyether type plasticizer to be incorporated may comprise one single species or a combination of a plurality of species. A low-molecular-weight plasticizer and a polymeric plasticizer may be used in combination. These plasticizers may be incorporated on the occasion of polymer production.

[0132] The addition level of the polyether type plasticizer is preferably 1-150 parts by weight, more preferably 10-120 parts by weight, particularly preferably 20-100 parts by weight, per 100 parts by weight of the sum of the component (A) and component (B). At levels lower than 1 part by weight, the effects as the plasticizer tend to become insignificant and, at levels exceeding 150 parts by weight, the mechanical strength of the cured products tends to become insufficient.

[0133] Other plasticizers may be added to the curable composition of the present invention in combination with the

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(D) component polyether type plasticizer. The plasticizer other than the polyether type plasticizers is not particularly restricted but includes: phthalic acid esters such as dibutyl phthalate, diheptyl phthalate, di(2-ethylhexyl) phthalate and butyl benzyl phthalate; nonaromatic dibasic acid esters such as dioctyl adipate, dioctyl sebacate, dibutyl sebacate and diisodecyl succinate; aliphatic esters such as butyl oleate and methyl acetylricinoleate; phosphoric acid esters such as tricresyl phosphate and tributyl phosphate; trimellitic acid esters; chlorinated paraffins; hydrocarbon type oils such as alkyldiphenyls and partially hydrogenated terphenyl; process oils; and epoxy plasticizers such as epoxidized soybean oil and benzyl epoxystearate.

[0134] A polymeric plasticizer other than the polyether type plasticizers may also be added as the plasticizer. As compared with the case of addition of a low-molecular-weight plasticizer containing no polymer constituent within the molecule, the addition of a polymeric plasticizer produces such effects as the following: the curable composition can retain the initial characteristics for a long period of time and, when the cured products obtained are coated with an alkyd paint, the drying characteristics (also referred to as coatability) can be improved.

[0135] The polymeric plasticizer is not particularly restricted but includes: vinyl polymers obtained by polymerization of vinyl monomers by various methods; polyalkylene glycol esters such as diethylene glycol dibenzoate, triethylene glycol dibenzoate and pentaerythritol esters; polyester type plasticizers derived from a dibasic acid such as sebacic acid, adipic acid, azelaic acid and phthalic acid and a dihydric alcohol such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol and dipropylene glycol; polystyrenes such as polystyrene and poly-α-methylstyrene; polybutadiene, polybutene, polyisobutylene, butadiene-acrylonitrile copolymers, polychloroprene and the like.

[0136] Among these polymeric plasticizers, vinyl polymers are preferred since they have high compatibility with the component (A) and the component (B) and provide the resulting cured products with good weather resistance and thermal stability; among them, acrylic polymers and/or methacrylic polymers are more preferred, and such acrylic polymers as polyacrylic acid alkyl esters are particularly preferred.

[0137] While the method of producing the polyacrylic acid alkyl esters is not particularly restricted, the living radical polymerization method is preferred because of capability of their giving polymers narrow in molecular weight distribution and possibly low in viscosity, and the atom transfer radical polymerization method is more preferred. Also particularly preferred is the method called "SGO process" and disclosed in Japanese Kokai Publication 2001-207157, which comprises continuously bulk-polymerizing an acrylic acid alkyl ester type compound under high temperature and high pressure conditions.

[0138] The number average molecular weight of the polymeric plasticizer is generally 500 to 15000, preferably 800 to 10000, more preferably 1000 to 8000, particularly preferably 1000 to 5000, most preferably 1000 to 3000. When the molecular weight of the polymeric plasticizer is too low, the plasticizer may escape from the cured products obtained with the lapse of time due to heat or rainfall and, as a result, it becomes no longer possible to maintain the initial physical characteristics, staining by adhesion of dust may possibly be caused and the alkyd applicability tends to become poor. On the other hand, when the molecular weight is excessively high, the viscosity of the curable composition will increase and the workability tends to become poor.

[0139] The molecular weight distribution of the polymeric plasticizer is not particularly restricted but preferably is narrow, for example narrower than 1.80, preferably not wider than 1.70, more preferably not wider than 1.60, still more preferably not wider than 1.50, particularly preferably not wider than 1.40, most preferably not wider than 1.30.

[0140] In the case of polyether type polymers, the number average molecular weight is determined by the end-group analysis and, in the case of other polymers, it is determined by the GPC method. The molecular weight distribution (Mw/Mn) is measured by the GPC method (on the polystyrene equivalent basis).

[0141] The polymeric plasticizer may be a reactive silyl group-containing one or a silyl group-free one and, in cases where a reactive silyl group-containing polymeric plasticizer is added, the polymeric plasticizer is preferably involved in the curing reaction and thus, the plasticizer can be prevented from migrating from the cured products obtained.

[0142] The reactive silyl group-containing polymeric plasticizer is preferably a compound whose silyl group content is, on an average, not more than one, preferably not more than 0.8, per molecule. When a reactive silyl group-containing plasticizer, in particular a reactive silyl group-containing oxyalkylene polymer, is added, it is preferred that the number average molecular weight thereof be lower than that of the component (A) and of the component (B) so that a satisfactory plasticizing effect may be obtained.

[0143] The plasticizer to be added may comprise a single species or a combination of a plurality of species. It is also possible to add a low-molecular-weight plasticizer and a polymeric plasticizer in combination. The plasticizer addition may also be made on the occasion of the production of the component (A) and the component (B).

[0144] The addition level thereof is preferably 5 to 150 parts by weight, more preferably 10 to 120 parts by weight, particularly preferably 20 to 100 parts by weight, per 100 parts by weight of the sum of the component (A) and the component (B) . At addition levels lower than 5 parts by weight, there is a tendency for the plasticizing effect to be little produced and, at levels exceeding 150 parts by weight, there arises a tendency for the mechanical strength of the cured products to become insufficient.

[0145] In the curable composition of the present invention, there may be incorporated an adhesiveness-imparting

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agent, if necessary.

The adhesiveness-imparting agent is a compound containing a hydrolyzable silyl group and other functional group (s) in the molecule and, when incorporated into the curable composition, effectively improves the adhesiveness of the resulting cured products to various adherends and/or effectively removes (dehydrates) the moisture contained in the curable composition. Further, the adhesiveness-imparting agent is a compound capable of not only producing the effects mentioned above but also functioning as a physical property modifier and/or a dispersibility-improving agent for inorganic fillers.

[0146] The hydrolyzable silyl group occurring in the adhesiveness-imparting agent may be any of those enumerated hereinabove as examples of the hydrolyzable group. Among those, a methoxy group, an ethoxy group, and the like are preferred because of their proper rate of hydrolysis. The number of hydrolyzable groups contained in each molecule of the adhesiveness-imparting agent is preferably not smaller than 2, particularly preferably not smaller than 3.

[0147] As examples of the functional group other than the hydrolyzable silyl group as occurring in the adhesiveness-imparting agent, there may be mentioned a substituted or unsubstituted amino group, mercapto group, epoxy group, carboxyl group, vinyl group, isocyanato group and isocyanurate group, and halogen atoms. In particular, substituted or unsubstituted amino group-containing adhesiveness-imparting agents are preferred since they show good compatibility with the guanidine compound (C) and the like. Substituted or unsubstituted amino group-containing adhesiveness-imparting agents are preferred also in view of their ability to enhance the adhesiveness between the cured products obtained and adherends.

[0148] The adhesiveness-imparting agent is not particularly restricted but includes aminosilanes such as γ-aminopropyltrimethoxysilane, γ-aminopropyltriethoxysilane, γ-aminopropyltriisopropoxysilane, γ-aminopropylmethyldimethoxysilane, γ-aminopropylmethyldiethoxysilane, γ-(2-aminoethyl)aminopropyltrimethoxysilane, γ-(2-aminoethyl)aminopropylmethyldimethoxysilane, γ-(2-aminoethyl)aminopropyltriethoxysilane, γ-(2-aminoethyl)aminopropylmethyldiethoxysilane, γ-(2-aminoethyl)aminopropyltriisopropoxysilane, γ-(2-(2-aminoethyl)aminoethyl)aminopropyltrimethoxysilane, γ-(6-aminohexyl)aminopropyltrimethoxysilane, 3-(N-ethylamino)-2-methylpropyltrimethoxysilane, 2-aminoethylaminomethyltrimethoxysilane, N-cyclohexylaminomethyltriethoxysilane, N-cyclohexylaminomethyldiethoxymethylsilane, γ-ureidopropyltrimethoxysilane, γ-ureidopropyltriethoxysilane, N-phenyl-γ-aminopropyltrimethoxysilane, N-phenylaminomethyltrimethoxysilane, N-benzyl-γ-aminopropyltrimethoxysilane, N-vinylbenzyl-γ-aminopropyltriethoxysilane, N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole, N-cyclohexylaminomethyltriethoxysilane, N-cyclohexylaminomethyldiethoxymethylsilane, N-phenylaminomethyltrimethoxysilane, (2-aminoethyl)aminomethyltrimethoxysilane and N,N'-bis[3-(trimethoxysilyl)propyl]ethylenediamine; ketimine type silanes such as N-(1,3-dimethylbutylidene)-3-(triethoxysilyl)-1-propanamine, and condensation products resulting from partial condensation of the silanes mentioned above.

[0149] Among the adhesiveness-imparting agents mentioned above, γ-aminopropyltrimethoxysilane is particularly preferred from the viewpoints of compatibility, transparency and availability.

[0150] The adhesiveness-imparting agent to be incorporated in the curable composition may comprise a single species or a combination of a plurality of species. In selecting the adhesiveness-imparting agent, it is preferred that one containing a hydrolyzable group of the same structure as the hydrolyzable group occurring in the component (A) and the component (B) so that the surface curability of the curable composition may be prevented from changing during storage. Thus, when the hydrolyzable silyl group in the component (A) and the component (B) is a methoxysilyl group, an adhesiveness-imparting agent with a methoxysilyl group structure should be selected and, when the hydrolyzable silyl group in the component (A) and the component (B) is an ethoxysilyl group, an adhesiveness-imparting agent with an ethoxysilyl group structure should be selected.

[0151] To the curable composition of the present invention, there may be added a filler, if necessary. The filler is not particularly restricted but includes: reinforcing fillers such as fumed silica, precipitated silica, crystalline silica, fused silica, dolomite, silicic anhydride, hydrous silicic acid and carbon black; heavy calcium carbonate, colloidal calcium carbonate, magnesium carbonate, diatomaceous earth, calcined clay, clay, talc, titanium oxide, bentonite, organic bentonite, ferric oxide, fine aluminum powder, flint powder, zinc oxide, activated zinc white, shirasu balloons, glass microballoons, organic microballoons based on a phenol resin or a vinylidene chloride resin, organic powders such as PVC powder and PMMA powder; and fibrous fillers such as asbestos, glass fibers and filaments.

[0152] When a filler is added, the addition level thereof is preferably 1 to 250 parts by weight, more preferably 10 to 200 parts by weight, per 100 parts by weight of the sum of the component (A) and the component (B).

[0153] On the occasion of using the curable composition as a one-pack type adhesive or sealant, it is preferred, for obtaining good storage stability, that such a filler as mentioned above be uniformly mixed with a dehydrating agent such as calcium oxide and the mixture be allowed to stand in a sealed bag made of an airtight material for a proper period of time for dehydrating and drying, and then used, as disclosed in Japanese Kokai Publication 2001-181532 and the like.

[0154] When the cured products obtained are to be used in the fields of application where transparency is required, a polymer powder containing a polymer of methyl methacrylate and the like, and noncrystalline silica, are preferred as the filler to be added, as disclosed in Japanese Kokai Publication H11-302527 and the like; hydrophobic silica and the like, as disclosed in Japanese Kokai Publication 2000-38560 and the like, is more preferred.

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[0155] The hydrophobic silica, so referred to herein, is a product derived by treating the surface of the silicon dioxide fine powder generally occupied by silanol (-SiOH) groups with an organosilicon halide or an alcohol for conversion of those groups to (-SiO-hydrophobic) groups. The hydrophobic silica is not particularly restricted but includes, for example, products obtained by treating silanol groups occurring on a silicon dioxide fine powder with dimethylsiloxane, hexamethyldisilazane, dimethyldichlorosilane, trimethoxyoctylsilane, trimethylsilane, and the like. The untreated silicon dioxide fine powder whose surface is occupied by silanol (-SiOH) groups is called hydrophilic silica fine powder.

[0156] When the cured products obtained are to be used in the fields of application where high strength is required, silicon compounds such as fumed silica, precipitated silica, crystalline silica, fused silica, dolomite, silicic anhydride and hydrous silicic acid; carbon black, surface-treated finely divided calcium carbonate, calcined clay, clay, activated zinc white and the like are preferred as the filler to be added, and the addition level thereof is preferably 1 to 200 parts by weight per 100 parts by weight of the sum of the component (A) and the component (B).

[0157] Further, when the cured products obtained are to be used in the fields of application where low strength and high elongation modulus are required, titanium oxide, calcium carbonate such as heavy calcium carbonate, magnesium carbonate, talc, ferric oxide, zinc oxide and shirasu balloons are preferred as the filler to be added, and the addition level thereof is preferably 5 to 200 parts by weight per 100 parts by weight of the sum of the component (A) and the component (B).

When calcium carbonate is added, the tendency toward improvements in the breaking strength, breaking elongation and adhesiveness of the cured products obtained increases as the specific surface area increases. Only one of these filler species may be added or a plurality of species thereof may be added in combination.

[0158] The example of addition of a plurality of additives is not particularly restricted but the combined use of a surface-treated fine calcium carbonate and a calcium carbonate larger in particle diameter such as heavy calcium carbonate is preferred since cured products excellent in physical characteristics can be obtained.

[0159] Preferred as the surface-treated fine calcium carbonate are those whose particle diameter is not larger than 0.5 μm and whose particle surface has been treated with a fatty acid and a fatty acid salt.

[0160] Preferred as the calcium carbonate having a large particle diameter are those whose particle diameter is not smaller than 1 μm and whose particle surface has not been treated.

[0161] In cases where the curable composition is required to have good workability (releasability, etc.) or where the surface of the cured products obtained is required to be matted, organic balloons or inorganic balloons are preferred as the filler to be added. These fillers may be surface-treated or non-surface-treated, and only one species thereof may be added or a plurality of species thereof may be added in admixture. For improving the workability (releasability, etc.), the particle diameter of the balloons is preferably not larger than 0. 1 mm and, for rendering the cured product surface matted, it is preferably 5 to 300 μm.

[0162] The curable composition of the present invention, which gives cured products excellent in chemical resistance, is suited for use, in particular, as a sealant, adhesive or like composition for siding boards in ceramic and like systems and for housing outside-wall joints and outside-wall tiles.

[0163] On the occasion of use in such fields of application, the cured products obtained appear or exist on the joints or like observable surfaces and, therefore, it is desirable that the cured product design be in harmony with the outside wall design. In recent years, in particular, the sputtering coating and the addition of colored aggregates, among others, have been employed for providing luxurious outside walls, so that the designs of cured products are becoming more and more important.

[0164] For obtaining luxurious designs, a scaly or granular substance is incorporated in the curable composition of the present invention. The addition of a granular substance gives sandy or sandstone-like rough surfaces, and the addition of a scaly substance gives surfaces rendered uneven due to scales.

[0165] The cured products obtained are in harmony with luxurious outside walls and are excellent in chemical resistance, so that the luxurious appearance thereof can be maintained for a long period of time.

[0166] The scaly or granular substance is not particularly restricted but includes, for example, one disclosed in Japanese Kokai Publication H09-53063, and the diameter thereof is properly selected according to the outside wall material and design and is preferably not smaller than 0.1 mm, more preferably 0.1 to 5.0 mm. In the case of a scaly substance, the thickness of scales is preferably 1/10 to 1/5 (0.01 to 1.00 mm) of the diameter.

[0167] The addition level of the scaly or granular substance is properly selected according to the size of the scaly or granular substance, the outside-wall material and design and other factors; preferably, the addition level is 1 to 200 parts by weight per 100 parts by weight of the curable composition.

[0168] The material of the scaly or granular substance is not particularly restricted but includes natural products such as silica sand and mica, synthetic rubbers, synthetic resins, and inorganic materials such as alumina. These may be appropriately colored according to the outside wall material, design, and so forth so that the design quality of the composition applied to joints and so forth may be enhanced.

[0169] Preferred methods of finishing are those disclosed in Japanese Kokai Publication H09-53063 and the like.

[0170] The scaly or granular substance may be incorporated in advance in the curable composition or may be admixed

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with the curable composition of the occasion of use thereof.

[0171] It is also possible, for the same purposes, to add balloons (preferably having an average particle diameter of not smaller than 0.1 mm) to the curable composition, thereby providing the resulting cured product surface with a coarse feel such as a sandy or sandstone feel and, further, contributing to weight reduction. The "balloons" are spherical hollow fillers.

[0172] The balloons are not particularly restricted but include, for example, those disclosed in Japanese Kokai Publications H10-251618, H02-129262, H04-8788, H04-173867, H05-1225, H07-113073, H09-53063, 2000-154368 and 2001-164237 and WO 97/05201.

[0173] As the material of balloons, there may be mentioned inorganic materials such as glass, shirasu and silica; and organic materials such as phenol resins, urea resins, polystyrene and Saran. Mention may further be made of composite materials of an inorganic material and an organic material; and laminates comprising a plurality of layers. These may be used singly or a plurality species thereof may be used in combination.

[0174] It is also possible to use balloons subjected to surface coating treatment, treatment with various surface treatment agents or some other treatment; as typical examples, there may be mentioned organic balloons coated with calcium carbonate, talc, titanium oxide or the like, and inorganic balloons surface-treated with an adhesiveness-imparting agent.

[0175] Further, the balloons preferably have a particle diameter of not smaller than 0.1 mm, more preferably 0.2 mm to 5.0 mm, particularly preferably 0.5 mm to 5.0 mm. When the diameter is smaller than 0.1 mm, the addition even in large amounts only increases the viscosity of the composition, sometimes failing to provide the resulting cured products with a coarse feel.

[0176] When balloons are added, the addition level thereof can be properly selected according to the intended decorative effect; it is preferred that balloons having a particle diameter of not smaller than 0.1 mm be added in an amount such that the volume concentration thereof in the curable composition amounts to 5 to 25% by volume, more preferably 8 to 22% by volume. When the volume concentration of balloons is below 5% by volume, the desired coarse feel tends to become lost. At level exceeding 25% by volume, the viscosity of the curable composition increases and the workability thereof tends to become poor; further, the modulus of the cured products increases and the fundamental performance characteristics of the sealant or adhesive tend to become impaired.

[0177] On the occasion of adding balloons, it is also possible to add, in combination, such an anti-slip agent as the one disclosed in Japanese Kokai Publication 2000-154368 or such an amine compound capable of rendering the resulting cured product surface uneven and matted as the one disclosed in Japanese Kokai Publication 2001-164237. Preferred as the amine compound mentioned above are primary and/or secondary amines having a melting point of 35°C or higher.

[0178] Also usable as the balloons are thermally expandable minute hollow particles disclosed in Japanese Kokai Publication 2004-51701 or 2004-66749, for instance. The "thermally expandable minute hollow particles" are spherical plastic bodies made of a polymer shell material (vinylidene chloride type copolymer, acrylonitrile type copolymer or vinylidene chloride-acrylonitrile copolymer) with a low-boiling compound such as a hydrocarbon containing 1 to 5 carbon atoms as spherically enclosed therein.

[0179] By adding thermally expandable minute hollow particles to the curable composition of the present invention, it becomes possible to obtain, without using any organic solvent at all, a thermally removable adhesive composition which, when no more required, can be peeled off with ease only by heating without destruction of the adherend materials. This is based on the mechanism such that when the adhesive portion is heated, the gas pressure inside the shells of the thermally expandable minute hollow particles increases and the polymer shell material is softened and dramatically expanded to cause peeling at the adhesive interface.

[0180] When the curable composition of the present invention contains sealant curing particles as well, the cured products obtained can have an uneven rough surface and, thus, the decorative feature thereof can be improved. The preferred diameter, addition level, material and the like of the sealant curing particles are disclosed in Japanese Kokai Publication 2001-115142, and the diameter is preferably 0.1 mm to 1 mm, more preferably 0.2 to 0.5 mm. The addition level is preferably 5 to 100 parts by weight, more preferably 20 to 50 parts by weight, per 100 parts by weight of the curable composition. The material is not particularly restricted but may be any of the materials used in sealing compositions; thus, mention may be made of urethane resins, silicones, modified silicones and polysulfide rubbers, for example. Among those mentioned above, modified silicone type sealant curing particles are preferred.

[0181] To the curable composition of the present invention, there may be added a silicate, if necessary. The silicate acts as a crosslinking agent on the component (A) and the component (B) and functions to bring about improvements in the restorability, durability and creep resistance of the cured products obtained.

[0182] Further, the addition of a silicate brings about improvements in the adhesiveness and water-resistant adhesiveness and in the bond durability under high-temperature and high-pressure conditions. The silicate is not particularly restricted but includes, for example, tetraalkoxysilanes or partial hydrolysis condensation products derived therefrom; more specifically, there may be mentioned tetraalkoxysilanes (tetraalkyl silicates) such as tetramethoxysilane, tetraethoxysilane, ethoxytrimethoxysilane, dimethoxydiethoxysilane, methoxytriethoxysilane, tetra-n-propoxysilane, tetra-i-propoxysilane, tetra-n-butoxysilane, tetra-i-butoxysilane and tetra-t-butoxysilane as well as partial hydrolysis conden-

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sation products derived therefrom.

[0183] When a silicate is added, the addition level thereof is preferably 0.1 to 20 parts by weight, more preferably 0.5 to 10 parts by weight, per 100 parts by weight of the sum of the component (A) and the component (B).

[0184] The tetraalkoxysilane-derived partial hydrolysis condensation product mentioned above is not particularly restricted but includes, for example, products derived from tetraalkoxysilanes by addition of water thereto to cause partial hydrolysis and condensation.

[0185] The addition of a tetraalkoxysilane-derived partial hydrolysis condensation product is preferred since such condensation product produces significant improvements in restorability, durability and creep resistance of the cured products obtained as compared with the corresponding composition containing the tetraalkoxysilane added thereto.

[0186] Commercially available as the tetraalkoxysilane-derived partial hydrolysis condensation product are, for example, Methyl Silicate 51 and Ethyl Silicate 40 (both being products of Colcoat Co., Ltd.); these can be used as additives.

[0187] For the purpose of inhibiting the surface curability of the curable composition from changing during storage, it is preferred that the silicate be selected from among those in which the silicon atom-bound hydrolyzable groups are the same as the hydrolyzable groups in the reactive silyl group occurring in the component (A) and the component (B). Thus, when the component (A) and the component (B) each contains methoxysilyl groups, a methoxysilyl group-containing silicate is preferably selected and, when the component (A) and the component (B) each contains ethoxysilyl groups, an ethoxysilyl group-containing silicate is preferably selected.

[0188] In the curable composition of the invention, there may be incorporated a tackifier, if necessary.

The tackifier is not particularly restricted provided that it is one in common use, irrespective of whether it occurs as a solid or liquid at ordinary temperature. For example, there may be mentioned styrene block copolymers, hydrogenation products derived therefrom, phenol resins, modified phenol resins (e.g. cashew oil-modified phenol resins, tall oil-modified phenol resins), terpene-phenol type resins, xylene-phenol type resins, cyclopentadiene-phenol type resins, coumarone-indene type resins, rosin type resins, rosin ester type resins, hydrogenated rosin ester type resins, xylene type resins, low-molecular-weight polystyrene type resins, styrene copolymer resins, petroleum resins (e.g. C5 hydrocarbon type resins, C9 hydrocarbon type resins, C5C9 hydrocarbon copolymer resins), hydrogenated petroleum resins, terpene type resins, DCPD resins, and petroleum resins. These may be added singly or a plurality thereof may be added in combination.

[0189] The styrene block copolymers and hydrogenation products derived therefrom mentioned above are not particularly restricted but include, for example, styrene-butadiene-styrene block copolymers (SBSs), styrene-isoprene-styrene block copolymers (SISs), styrene-ethylenebutylene-styrene block copolymers (SEBSs), styrene-ethylenepropylene-styrene block copolymers (SEPSs) and styrene-isobutylene-styrene block copolymers (SIBSs).

[0190] When a tackifier is added, the addition level thereof is preferably 5 to 1,000 parts by weight, more preferably 10 to 100 parts by weight', per 100 parts by weight of the sum of the component (A) and the component (B).

[0191] In the curable composition of the present invention, there may be incorporated a solvent or diluent, if necessary.

The solvent or diluent is not particularly restricted but includes, for example, aliphatic hydrocarbons, aromatic hydrocarbons, alicyclic hydrocarbons, halogenated hydrocarbons, alcohols, esters, ketones and ethers. These may be added singly or a plurality thereof may be added in combination.

[0192] When a solvent or diluent is added, the solvent or diluent preferably has a boiling point of 150°C or higher, more preferably 200°C or higher, so that the volatile components in the solvent or diluent may be inhibited from dissipating into the air on the occasion of indoor use of the curable composition.

[0193] In the curable composition of the present invention, there may be incorporated a physical property modifier, if necessary. The physical property modifier functions so as to adjust the tensile characteristics and hardness of the resulting cured products.

The physical property modifier is not particularly restricted but includes, for example, alkylalkoxysilanes such as methyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane and n-propyltrimethoxysilane; alkylisopropenoxysilanes such as dimethyldiisopropenoxysilane, methyltriisopropenoxysilane and γ-glycidoxypropylmethyldiisopropenoxysilane; functional group-containing alkoxysilanes such as γ-glycidoxypropylmethyldimethoxysilane, γ-glycidoxypropyltrimethoxysilane, vinyltrimethoxysilane, vinyldimethylmethoxysilane, γ-aminopropyltrimethoxysilane, N-(β-aminoethyl)aminopropylmethyldimethoxysilane, γ-mercaptopropyltrimethoxysilane and γ-mercaptopropylmethyldimethoxysilane; silicone varnishes; and polysiloxanes. These may be added singly or a plurality thereof may be added in admixture.

[0194] Among such physical property modifiers, those which form, upon hydrolysis, a compound containing a monovalent silanol group in the molecule are preferred since they are effective in reducing the modulus of the resulting cured products without worsening the surface stickiness thereof; among them, those which form, upon hydrolysis, trimethylsilanol are more preferred.

[0195] The compounds which form, upon hydrolysis, a compound containing monovalent silanol group in the molecular are not particularly restricted but include: those compounds disclosed in Japanese Kokai Publication H05-117521; compounds derived from an alkyl alcohol, such as hexanol, octanol and decanol, and capable of forming, upon hydrolysis, such an organosilicon compound represented by R_3SiOH as trimethylsilanol; and those compounds disclosed in Japa-

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nese Kokai Publication H11-241029 which are compounds derived from a polyhydric alcohol containing 3 or more hydroxyl groups in each molecule, for example trimethylolpropane, glycerol, pentaerythritol or sorbitol, and capable of forming, upon hydrolysis, such an organosilicon compound represented by R_3SiOH as trimethylsilanol.

[0196] Further, mention may be made of those compounds disclosed in Japanese Kokai Publication H07-258534 which are derived from an oxypropylene polymer and capable of forming, upon hydrolysis, such an organosilicon compound represented by R_3SiOH as trimethylsilanol and, further, those compounds disclosed in Japanese Kokai Publication H06-279693 which contain a crosslinkable hydrolyzable silyl group and a silyl group capable of forming, upon hydrolysis, a monovalent silanol group-containing compound.

[0197] When a physical property modifier is added, the addition level thereof is preferably 0.1 to 20 parts by weight, more preferably 0.5 to 10 parts by weight, per 100 parts by weight of the sum of the component (A) and the component (B).

[0198] In the curable composition of the present invention, there may be incorporated a thixotropic agent (anti-sagging agent), if necessary. The term "thixotropic agent" refers to an agent functioning to prevent the curable composition from sagging and improve the workability thereof.

[0199] The thixotropic agent is not particularly restricted but includes, for example, polyamide waxes; hydrogenated castor oil derivatives; and metal soaps such as calcium stearate, aluminum stearate and barium stearate. Further, mention may be made of those rubber powders having a particle diameter of 10 to 500 μm which are disclosed in Japanese Kokai Publication H11-349916, and those organic fibers disclosed in Japanese Kokai Publication 2003-155389. These thixotropic agents (antisagging agents) may be added singly or a plurality of species may be added in combination.

[0200] When a thixotropic agent is added, the addition level thereof is preferably 0.1 to 20 parts by weight per 100 parts by weight of the sum of the component (A) and the component (B).

[0201] In the curable composition of the present invention, there may be incorporated, for example, a compound containing an epoxy group in each molecular, if necessary. By adding an epoxy group-containing compound, it becomes possible to enhance the restorability of the cured products obtained.

[0202] The epoxy group-containing compound is not particularly restricted but includes, for example, epoxidized unsaturated fats and oils; epoxidized unsaturated fatty acid esters; alicyclic epoxy compounds; epichlorohydrin derivatives and like compounds; and mixtures thereof. More specifically, there may be mentioned epoxidized soybean oil, epoxidized linseed oil, bis(2-ethylhexyl)-4,5-epoxycyclohexane-1,2-dicarboxylate (E-PS), epoxyoctyl stearate, epoxybutyl stearate and the like. Among these, E-PS is preferred.

[0203] When an epoxy compound is added, the addition level thereof is preferably 0.5 to 50 parts by weight per 100 parts by weight of the sum of the component (A) and the component (B).

[0204] In the curable composition of the present invention, there may be added a photocurable substance, if necessary. The photocurable substance is a substance capable of undergoing, under the action of light, chemical changes in molecular structure in a short period of time which lead to changes in physical properties such as curing. The addition of a photocurable substance to the curable composition results in the formation of a photocurable substance-based layer on the surface of the cured products obtained and thus in improvements in the stickiness and weather resistance of the cured products.

[0205] The photocurable substance is not particularly restricted but includes those known in the art, such as organic monomers, oligomers, resins, and compositions containing any of them; for example, there may be mentioned unsaturated acrylic compounds, vinyl cinnamate polymers and azidized resins.

[0206] As the unsaturated acrylic compounds, there may be mentioned monomers, oligomers, or mixtures thereof, containing one or a plurality of acrylic or methacrylic unsaturated groups in each molecule, and, specifically, propylene (or butylene or ethylene) glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate and like monomers or oligoesters having a molecular weight not exceeding 10,000. More specifically, there may be mentioned, for example, such special acrylates as (bifunctional) Aronix M-210, Aronix M-215, Aronix M-220, Aronix M-233, Aronix M-240 and Aronix M-245; (trifunctional) Aronix M-305, Aronix M-309, Aronix M-310, Aronix M-315, Aronix M-320 and Aronix M-325, and (polyfunctional) Aronix M-400 (all Aronix products being available from Toagosei Co., Ltd.). Among these, acrylic functional group-containing compounds are preferred, and compounds containing, on an average, 3 or more acrylic functional groups in each molecule are more preferred.

[0207] The vinyl cinnamate polymers are photosensitive resins having cinnamoyl groups as photosensitive groups, which are compounds resulting from esterification of polyvinyl alcohol with cinnamic acid, and many other derivatives of vinyl cinnamate polymers.

[0208] The azidized resins are known as photosensitive resins in which azide groups are photosensitive groups and include rubber photosensitive solutions generally containing a diazide compound added as a photosensitizer and, further, those detailed examples are described in "Kankosei Jushi (Photosensitive Resins)" (published March 1, 1972 by Insatsu Gakkai Shuppanbu Ltd., p. 93 ff., p. 106 ff., and p. 117 ff.). These may be used either singly or in admixture, if necessary together with a sensitizer.

[0209] In some cases, the addition of a sensitizer such as a ketone and nitro compound or a promoter such as an amine enhances the effect.

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[0210] When a photocurable substance is added, the addition level thereof is preferably 0.1 to 20 parts by weight, more preferably 0.5 to 10 parts by weight, per 100 parts by weight of the sum of the component (A) and the component (B). At levels of 0.1 part by weight or below, the effect of enhancing the weather resistance of the cured products obtained is very little and, at levels of 20 parts by weight or above, the cured products obtained are too hard, tending to undergo cracking or the like.

[0211] In the curable composition of the present invention, there may be incorporated an oxygen-curable substance, if necessary. The oxygen-curable substance can be cured upon reaction with oxygen in the air, and the addition of an oxygen-curable substance makes it possible to reduce the stickiness of the cured product surface and to prevent dirt and dust from adhering to the surface through the formation of a cured layer in the vicinity of the cured product surface obtained.

[0212] The oxygen-curable substance is not particularly restricted but may be any of the compounds containing an unsaturated compound capable of reacting with oxygen in the air; thus, for example, there may be mentioned drying oils such as tung oil and linseed oil, and various alkyd resins obtained by modifying such compounds; drying oil-modified acrylic polymers, epoxy type resins and silicone type resins; liquid polymers obtained by polymerizing or copolymerizing such a diene compound(s) as butadiene, chloroprene, isoprene and 1,3-pentadiene, for example 1,2-polybutadiene, 1,4-polybutadiene and C5-C8 diene polymers; liquid copolymers obtained by copolymerizing such a diene compound with a vinyl compound, such as acrylonitrile and styrene, copolymerizable with the diene compound, in a manner such that the diene compound serve as the main component, for example NBR and SBR; and, further, various modifications thereof (maleinated modifications, boiled oil modifications, etc.). Among those mentioned above, tung oil and liquid diene type polymers are preferred. The oxygen-curable substance to be added may comprise a single species or a combination of a plurality of species.

[0213] When a catalyst and/or metal dryer which are capable of promoting the curing reaction are added in admixture with the oxygen-curable substance, the effect may be enhanced. The catalyst and metal dryer for promoting the curing reaction are not particularly restricted but include, for example, metal salts such as cobalt naphthenate, lead naphthenate, zirconium naphthenate, cobalt octylate and zirconium octylate, and amine compounds.

[0214] When an oxygen-curable substance is added, the addition level thereof is preferably 0.1 to 20 parts by weight, more preferably 0.5 to 10 parts by weight, per 100 parts by weight of the sum of the component (A) and the component (B). At addition levels below 0.1 part by weight, the effect of improving the stain resistance of the cured products obtained tends to become insufficient and, at levels exceeding 20 parts by weight, the tensile characteristics and the like of the cured products obtained tend to become impaired.

[0215] Further, the oxygen-curable substance is preferably added in admixture with a photocurable substance, as disclosed in Japanese Kokai Publication H03-160053.

[0216] In the curable composition of the present invention, there may be incorporated an antioxidant, if necessary. By adding an antioxidant, it becomes possible to enhance the thermal stability of the cured products obtained.

[0217] The antioxidant is not particularly restricted but includes hindered phenol type, monophenol type, bisphenol type and polyphenol type antioxidants. Among these, hindered phenol type antioxidants are preferred. Also preferred are hindered amine type light stabilizers such as Tinuvin 622LD and Tinuvin 144; Chimassorb 944 LD and Chimassorb 119FL (all four being products of Chiba Specialty Chemicals) ; ADK STAB LA-57, ADK STAB LA-62, ADK STAB LA-67, ADK STAB LA-63 and ADK STAB LA-68 (all five being products of Adeka Corporation) ; and Sanol LS-770, Sanol LS-765, Sanol LS-292, Sanol LS-2626, Sanol LS-1114 and Sanol LS-744 (all six being product of Sankyo Lifetech Co., Ltd.). Specific examples of the antioxidants are disclosed also in Japanese Kokai Publications H04-283259 and H09-194731.

[0218] When an antioxidant is added, the addition level thereof is preferably 0.1 to 10 parts by weight, more preferably 0.2 to 5 parts by weight, per 100 parts by weight of the sum of the component (A) and the component (B).

[0219] In the curable composition of the present invention, there may be incorporated a light stabilizer, if necessary. By adding a light stabilizer, the cured products obtained can be prevented from undergoing photooxidative degradation.

[0220] The light stabilizer is not particularly restricted but includes benzotriazole type, hindered amine type and benzoate type compounds. Among these, hindered amine type light stabilizers are preferred.

[0221] When a light stabilizer is added, the addition level thereof is preferably 0.1 to 10 parts by weight, more preferably 0.2 to 5 parts by weight, per 100 parts by weight of the sum of the component (A) and the component (B). A specific example of the light stabilizer is disclosed in Japanese Kokai Publication H09-194731 as well.

[0222] When such a photocurable substance as an unsaturated acrylic compound is added to the curable composition of the present invention, a tertiary amine group-containing hindered amine type light stabilizer is preferably added as disclosed in Japanese Kokai Publication H05-70531 since, then, the storage stability of the curable composition is improved.

[0223] The tertiary amine group-containing hindered amine type light stabilizer is not particularly restricted but includes Tinuvin 622LD, Tinuvin 144 and Chimassorb 119FL (all three being products of Ciba Specialty Chemicals Inc.); ADK STAB LA-57, LA-62, LA-67 and LA-63 (all four being products of Adeka Corporation); and Sanol LS-765, LS-292, LS-

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2626, LS-1114 and LS-744 (all five being products of Sankyo Lifetech Co., Ltd.).

[0224] To the curable composition of the present invention may be added an ultraviolet absorber, if necessary. When an ultraviolet absorber is added to the curable composition, the surface weather resistance of the cured products obtained is improved.

[0225] The ultraviolet absorber is not particularly restricted but includes benzophenone type, benzotriazole type, salicylate type, substituted tolyl type and metal chelate type compounds.

[0226] Among these, benzotriazole type ultraviolet absorbers are preferred.

[0227] When an ultraviolet absorber is added to the curable composition, the addition level thereof is preferably 0.1 to 10 parts by weight, more preferably 0.2 to 5 parts by weight, per 100 parts by weight of the sum of the component (A) and the component (B).

[0228] The antioxidant, light stabilizer and ultraviolet absorber mentioned above are preferably added in combination to the curable composition and, for example, a phenol or hindered phenol antioxidant, a hindered amine type light stabilizer and a benzotriazole type ultraviolet absorber are preferably added in admixture with the curable composition.

[0229] To the curable composition of the present invention may be added a flame retardant, if necessary. The flame retardant is not particularly restricted; thus, for example, phosphorus type flame retardants such as ammonium polyphosphate and tricresyl phosphate; aluminum hydroxide, magnesium hydroxide, and flame retardants such as thermally expandable graphite may be added to the curable composition. The flame retardant to be added thereto may comprise a single species or a combination of a plurality of species.

[0230] When a flame retardant is added to the curable composition, the addition level thereof is preferably 5 to 200 parts by weight, more preferably 10 to 100 parts by weight, per 100 parts by weight of the organic polymer.

[0231] To the curable composition of the present invention may be added, if necessary, various additives other than those mentioned above for the purpose of adjusting various physical properties of the curable composition or of the cured products to be obtained. As such additives, there may be mentioned, for example, curability modifiers, radical inhibitors, metal deactivators, antiozonants, phosphorus type peroxide decomposers, lubricants, pigments, blowing agents, antitermites and antifungal agents. Specific examples of these are disclosed in publications such as Japanese Kokoku Publications H04-69659 and H07-108928, and Japanese Kokai Publications S63-254149, S64-22904 and 2001-72854. These additives may be added singly to the curable composition or a plurality thereof may be added in combination to the curable composition.

[0232] In cases where the curable composition is of the one-pack type, the composition contains all components as mixed up in advance and, thus, curing may proceed during storage if moisture is present in formulation components. Therefore, those formulation components which contain moisture are preferably dehydrated and dried prior to addition or dehydrated during compounding and kneading by reducing the pressure, for instance.

[0233] When the curable composition is of the two-pack type, it is not necessary to incorporate the curing catalyst in the main component having a reactive silyl group-containing organic polymer and, therefore, even if some moisture is contained in the formulation components, the risk of the progress of curing (gelation) is low; in cases where long-term storage stability is required, however, it is preferred that the formulation components be dehydrated or dried.

[0234] As for the method of dehydrating or drying, the method comprising drying by heating or the method comprising dehydrating under reduced pressure are preferred in cases where the formulation components are solids such as powders and, in cases where they are liquids, the vacuum dehydration method and the dehydration method using a synthetic zeolite, activated alumina, silica gel, quick lime, magnesium oxide or the like are preferred and, further, the dehydration method comprising adding an alkoxysilane compound such as n-propyltrimethoxysilane, vinyltrimethoxysilane, vinylmethyldimethoxysilane, methyl silicate, ethyl silicate, γ-mercpatopropylmethyldimethoxysilane, γ-mercaptopropylmethyldiethoxysilane and γ-glycidoxypropyltrimethoxysilane; an oxazolidine compound such as 3-ethyl-2-methyl-2-(3-methylbutyl)-1,3-oxazolidine; and an isocyanate compound to the curable composition and allowing the same to react with water contained in the formulation components is also preferred. In this way, the storage stability of the curable composition is improved by the addition of such an alkoxysilane compound, oxazolidine compound and isocyanate compound.

[0235] In using vinyltrimethoxysilane or a like alkoxysilane compound capable of reacting with water for the purpose of drying, the addition level thereof is preferably 0.1 to 20 parts by weight, more preferably 0.5 to 10 parts by weight, per 100 parts by weight of the sum of the component (A) and the component (B).

[0236] The method of preparing the curable composition of the present invention is not particularly restricted but there may be employed, for example, such a method known in the art as a method comprising combining the formulation components mentioned above and kneading the resulting mixture at ordinary temperature or with heating using a mixer, roller, kneader, or the like, or a method comprising dissolving the formulation components using small portions of an appropriate solvent and then mixing up the solutions.

[0237] When exposed to the air, the curable composition of the present invention forms a three-dimensional network structure under the action of atmospheric moisture and thus is cured to give a solid having rubber elasticity.

[0238] The curable composition of the present invention can be suitably used in such fields of application as pressure-

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sensitive adhesives; sealants for buildings, ships, automobiles, roads, etc.; adhesives; impression materials; vibration-proof materials; damping materials; soundproof materials; expanded/foamed materials; coating compositions; spray coatings, etc. Among such fields of application, the use as sealants or adhesives is more preferred since the cured products obtained are excellent in flexibility and adhesiveness.

[0239] The curable composition of the present invention can also be used in such fields of application as back cover sealants for a solar cell and like electric and electronic part materials; insulating cover materials for electric wires and cables and other electric insulating materials; elastic adhesives; contact adhesives; spray sealants; crack repair materials; tiling adhesives; powder coating compositions; casting materials; rubber materials for medical use; pressure-sensitive adhesives for medical use; sealants for medical devices; food packaging materials; joint sealants for siding boards and other exterior materials; coating materials; primers; electromagnetic wave shielding conductive materials, thermally conductive materials; hot melt materials; potting agents for electrics and electronics; films; gaskets; various molding materials; rustproof and waterproof sealants for wired glass and laminated-glass edges (cut end faces); liquid sealants for use in automotive parts, electrical machinery parts, various machinery parts, etc.

[0240] Further, the curable composition can also be used as various types of hermetically sealants and adhesives since it, either alone or with the aid of a primer, can adhere to a wide range of substrates such as glass, ceramics, wood, metals and resin moldings.

[0241] The curable composition of the present invention can also be used in the form of interior panel adhesives, exterior panel adhesives, tiling adhesives, stone pitching adhesives, ceiling finishing adhesives, floor finishing adhesives, wall finishing adhesives, vehicle panel adhesives, electric, electronic and precision apparatus assembling adhesives, direct glazing sealants, double glazing sealants, sealants for SSG systems, or building working joint sealants.

BEST MODE FOR CARRYING OUT THE INVENTION

[0242] The following examples and comparative examples illustrate the present invention more specifically. These are, however, by no means limitative of the scope of the present invention.

(Synthesis Example 1)

[0243] A 1-L flask was charged with 2.84 g of Copper (I) bromide and 39 mL of acetonitrile, and heated with stirring under nitrogen stream at 70°C for 20 minutes. Thereto were added 5.93 g of diethyl 2,5-dibromoadipate, 254 mL of n-butyl acrylate, 61 mL of ethyl acrylate and 71 mL of stearyl acrylate, and the mixture was further heated with stirring at 80°C for 20 minutes. Pentamethyldiethylenetriamine (hereinafter referred to as triamine) (0.41 mL) was then added thereto and the reaction was allowed to start. Triamine was further added in an amount of 0.14 mL. While heating with stirring was allowed to continue to proceed at 80°C, 0.14 mL of triamine was added thereto. After 180 minutes from the start of the reaction, the pressure inside the reaction container was reduced and volatile components were removed. After 240 minutes from the start of the reaction, 118 mL of acetonitrile, 49 mL of 1,7-octadiene and 1.38 mL of triamine were added. The mixture was continuously heated with stirring at 80°C, followed by stopping heating after 620 minutes from the start of the reaction. The reaction solution was heated under reduced pressure to remove volatile components, and then diluted by toluene to be filtrated and the filtrate was condensed, thereby obtaining a polymer.

The polymer obtained, aluminum silicate (product of Kyowa Chemical Industry, trade name: Kyoward 500SH, 2 parts by weight per 100 parts by weight of the polymer) and aluminum silicate (product of Kyowa Chemical Industry, trade name: Kyoward 700SL, 2 parts by weight per 100 parts by weight of the polymer) were admixed with xylene (100 parts by weight per 100 parts by weight of the polymer), and the mixture was stirred at 130°C. After 3 hours, aluminum silicate was filtrated and the volatile components of the filtrate were heated under reduced pressure to be distilled off. The polymer was heated at 180°C for 12 hours for devolatilization (pressure reduction degree: 10 torr or less), thereby eliminating the Br groups from the copolymer. The polymer, aluminum silicate (product of Kyowa Chemical Industry, trade name: Kyoward 500SH, 3 parts by weight per 100 parts by weight of the polymer) and aluminum silicate (product of Kyowa Chemical Industry, trade name: Kyoward 700SL, 3 parts by weight per 100 parts by weight of the polymer) were admixed with xylene (100 parts by weight per 100 parts by weight of the polymer), and the mixture was stirred at 130°C. After 5 hours, aluminum silicate was filtrated and the volatile components of the filtrate was heated under reduced pressure and distilled off to give an alkenyl-terminated polymer. Next, 23.3 g of the polymer, 2.55 mL of methyldimethoxysilane, 0.38 mL of dimethyl orthoformate and a platinum catalyst were put into a 200-mL pressure-resist glass reaction container. The content of the platinum catalyst was set to 2×10^{-4} equivalents in the mole ratio to the content of an alkenyl group of the polymer. The reaction mixture was heated at 100°C for 3 hours. The volatile components of the mixture were distilled off under reduced pressure to give a methyldimethoxysilyl group-terminated acrylate ester polymer (A-1). The number average molecular weight of the polymer (A-1) was 27,000 determined by GPC (polystyrene-equivalent value measured by using a TOSOH model HLC-8120 GPC solvent delivery system, a TOSOH model TSK-GEL H type column, with THF as a solvent), and the molecular weight distribution thereof was 1.3. As a result of ^{1}H-NMR measurement

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(made in $CDCl_3$ solvent using a Nippon Denshi (JEOL Ltd.) model JNM-LA400), the average number of terminal methyldimethoxysilyl groups per molecule was found to be 1.7.

(Synthesis Example 2)

[0244] Using polyoxypropylene diol with a number average molecular weight of about 2, 000 as an initiator, propylene oxide was polymerized in the presence of a zinc hexacyanocobaltate-glyme complex catalyst to give polypropylene oxide with a number average molecular weight of 25,500 (polystyrene equivalent value measured in the same manner as in Synthesis Example 1). To this hydroxyl group-terminated polypropylene oxide was then added a methanol solution of NaOMe in an amount of 1.2 equivalents relative to the hydroxyl groups in the polymer, the methanol was distilled off and, further, allyl chloride was added to convert the terminal hydroxyl groups to allyl groups. The unreacted allyl chloride was removed by volatilization under reduced pressure. To 100 parts by weight of the crude allyl-terminated polypropylene oxide obtained were added 300 parts by weight of n-hexane and 300 parts by weight of water and, after mixing with stirring, the water was removed by centrifugation. The hexane solution obtained was further mixed with 300 parts by weight of water with stirring, and after the water was removed again by centrifugation, the hexane was removed by volatilization under reduced pressure. In the above manner, allyl-terminated bifunctional polypropylene oxide with a number average molecular weight of about 25,500 was obtained. The allyl group-terminated polypropylene oxide (P-1) (100 parts by weight) was reacted with 0.8 part by weight of methyldimethoxysilane at 90°C for 5 hours by adding 150 ppm of an isopropanol solution of a platinum-vinylsiloxane complex (platinum content: 3% by weight) thereto as a catalyst to give a methyldimethoxysilyl group-terminated polyoxypropylene type polymer (A-2). As a result of ^{1}H-NMR measurement in the same manner as described above, the average number of terminal methyldimethoxysilyl groups per molecule was found to be about 1.3.

(Synthesis Example 3)

[0245] Using polyoxypropylene triol with a number average molecular weight of about 3, 000 as an initiator, propylene oxide was polymerized in the presence of a zinc hexacyanocobaltate-glyme complex catalyst to give polypropylene oxide (P-1) with a number average molecular weight of about 26,000 (polystyrene equivalent value measured in the same manner as in Synthesis Example 1). To this hydroxyl group-terminated polypropylene oxide was then added a methanol solution of NaOMe in an amount of 1.2 equivalents relative to the hydroxyl groups in the polymer, the methanol was distilled off and, further, allyl chloride was added to convert the terminal hydroxyl groups to allyl groups. The unreacted allyl chloride was removed by volatilization under reduced pressure. To 100 parts by weight of the crude allyl-terminated polypropylene triol obtained were added 300 parts by weight of n-hexane and 300 parts by weight of water and, after mixing with stirring, the water was removed by centrifugation. The hexane solution obtained was further mixed with 300 parts by weight of water with stirring, and after the water was removed again by centrifugation, the hexane was removed by volatilization under reduced pressure. In the above manner, allyl-terminated trifunctional polypropylene oxide (P-2) with a number average molecular weight of about 26,000 was obtained.

[0246] The allyl group-terminated trifunctional polypropylene oxide with a number average molecular weight of about 26,000 obtained in the above manner (100 parts by weight) was reacted with 1.3 parts by weight of trimethoxysilane at 90°C for 5 hours by adding 150 ppm of an isopropanol solution of a platinum-divinyldisiloxane complex (platinum content: 3% by weight) thereto as a catalyst to give a trimethoxysilyl-terminated polyoxypropylene type polymer (B-1). As a result of ^{1}H-NMR measurement in the same manner as mentioned above, the average number of terminal trimethoxysilyl groups per molecule was found to be about 2.0.

(Synthesis Example 4)

[0247] The allyl-terminated polypropylene oxide (P-2) obtained in Synthesis Example 3 (100 parts by weight) was reacted with 3.3 parts by weight of 1-[2-(trimethoxysilyl)ethyl]-1,1,3,3-tetramethyldisiloxane at 90°C for 5 hours by adding 150 ppm of an isopropanol solution of a platinum-vinylsiloxane complex (platinum content: 3% by weight) thereto as a catalyst to give a trimethoxysilyl-terminated polyoxypropylene type polymer (B-2). As a result of ^{1}H-NMR measurement in the same manner as mentioned above, the average number of terminal trimethoxysilyl groups per molecule was found to be about 2.1.

(Synthesis Example 5)

[0248] To 100 parts by weight of the hydroxyl group-terminated polypropylene oxide (P-1) obtained in Synthesis Example 3 was added 1.8 parts by weight of γ-isocyanatopropyltrimethoxysilane, and the reaction was allowed to proceed at 90°C for 5 hours to give a trimethoxysilyl group-terminated polyoxypropylene type polymer (B-3).

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As a result of ^{1}H-NMR measurement in the same manner as mentioned above, the average number of terminal trimethoxysilyl groups per molecule was found to be about 2.1.

(Synthesis Example 6)

[0249] Into a flask were put 66 g of n-butyl acrylate, 14.5 g of methyl methacrylate, 15 g of stearyl methacrylate, 4.5 g of 3-methacryloxypropyltrimethoxysilane and 23.0 g of isobutanol, and 1.3 g of azobisisobutyronitrile was dissolved therein to prepare a mixture solution. Isobutanol (44 g) was put into a separable flask provided with a stirrer, thermometer, and nitrogen introducing port and heated to 105°C. Then, nitrogen was subjected to bubbling, and after the air inside the flask system was substituted by nitrogen, the above monomer solution was dropped for 4 hours; 2 hours later, post-polymerization was carried out. Trimethoxysilyl group-containing methacryl type polymer (B-4) obtained was an isobutanol solution having 60% of solid concentration and the number average molecular weight (Mn) was 11,000 in polystyrene-equivalent value determined by GPC (same method as in Synthesis Example 1). As calculated from the put amount and the average molecular weight, the average number of trimethoxysilyl groups of the methacryl type polymer (B-4) per molecule was found to be about 2.0.

(Example 1)

[0250] Surface-treated colloidal calcium carbonate (120 parts by weight; product of Shiraishi Kogyo Kaisha Ltd., trade name: Hakuenka CCR), 55 parts by weight of a polypropylene glycol type plasticizer (product of Mitsui Takeda Chemicals, trade name: Actocol P-23), 20 parts by weight of titanium oxide (white pigment) (product of Ishihara Sangyo Kaisha Ltd., trade name: Tipaque R-820), 2 parts by weight of an antisagging agent (product of Kusumoto Chemicals Ltd., trade name: Disparlon 6500), 1 part by weight of styrenated phenol (hindered phenol type antioxidant) (product of YSK, Inc., trade name: Unox KC), 1 part by weight of a benzoate type ultraviolet absorber (product of Sumitomo Chemical, trade name: Sumisorb 400) and 1 part by weight of a hindered amine type light stabilizer (product of Sankyo Lifetech, trade name: Sanol LS-770) were weighed and admixed with 70 parts by weight of the methyldimethoxysilyl group-terminated acrylate ester polymer (A-1) obtained in Synthesis Example 1 and 30 parts by weight of the trimethoxysilyl group-terminated polyoxypropylene type polymer (B-1) obtained in Synthesis Example 3 and, after thorough kneading, the mixture was passed through a three-roll paint mill three times for dispersion. Thereafter, the mixture was dehydrated at 120°C for 2 hours under reduced pressure and, after cooling to a temperature not higher than 50°C, 3 parts by weight of N-β-(aminoethyl)-γ-aminopropyltrimethoxysilane (product of Dow Corning Toray Co., Ltd., trade name: A-1120) and 2 parts by weight of vinyltrimethoxysilane (product of Dow Corning Toray Co., Ltd., trade name: A-177), each as an adhesiveness-imparting agent, and 4 parts by weight of 1-(o-tolyl)biguanide (product of Ouchi Shinko Chemical Industrial, trade name: Nocceler BG) as a curing catalyst were added and kneaded. After kneading under substantially water-free conditions, the resulting mixture was hermetically packed in a moisture-proof container. A one-pack type curable composition was thus obtained.

(Example 2)

[0251] A curable composition was obtained in the same manner as in Example 1 except that the trimethoxysilyl group-terminated polyoxypropylene type polymer (B-2) obtained in Synthesis Example 4 was used in lieu of the polymer (B-1) used in Example 1.

(Example 3)

[0252] A curable composition was obtained in the same manner as in Example 1 except that the trimethoxysilyl group-terminated polyoxypropylene type polymer (B-3) obtained in Synthesis Example 5 was used in lieu of the polymer (B-1) used in Example 1.

(Example 4)

[0253] The methyldimethoxysilyl group-terminated polyoxypropylene type polymer (A-2) obtained in Synthesis Example 2 and the isobutanol solution of the trimethoxysilyl group-containing methacryl type polymer (B-4) obtained in Synthesis Example 6 was mixed in a solid content ratio (weight ratio) of 70/30, and then isobutanol was volatilized with heating at 110°C under reduced pressure by a rotary evaporator to give a polymer having 99% or more of solid content concentration. A curable composition was obtained in the same manner as in Example 1 except that 100 parts by weight of the above-obtained polymer mixture was used in lieu of the polymer (A-1) and polymer (B-1) used in Example 1.

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(Comparative Example 1)

[0254] A curable composition was obtained in the same manner as in Example 1 except that 100 parts by weight of the methyldimethoxysilyl group-terminated polyoxypropylene type polymer (A-2) obtained in Synthesis Example 2 was used in lieu of the polymer (A-1) and polymer (B-1) used in Example 1.

(Comparative Example 2)

[0255] A curable composition was obtained in the same manner as in Example 1 except that the polymer (A-1) was used in an amount of 90 parts by weight and the polymer (B-1) was used in an amount of 10 parts by weight.

(Comparative Example 3)

[0256] A curable composition was obtained in the same manner as in Example 1 except that 100 parts by weight of the trimethoxysilyl group-terminated polyoxypropylene type polymer (B-3) obtained in Synthesis Example 5 was used in lieu of the polymer (A-1) and polymer (B-1) used in Example 1.

(Comparative Example 4)

[0257] A curable composition was obtained in the same manner as in Example 1 except that the methyldimethoxysilyl group-terminated polyoxypropylene type polymer (A-2) obtained in Synthesis Example 2 was used in an amount of 50 parts by weight in lieu of the polymer (A-1) used in Example 1 and the trimethoxysilyl group-terminated polyoxypropylene type polymer (B-2) was used in an amount of 50 parts by weight in lieu of the polymer (B-1).

[0258] The one-pack type moisture-curable compositions obtained in Examples 1 to 4 and Comparative Examples 1 to 4 were evaluated for surface curability, depth curability, cured product tensile characteristics and cured product weather resistance by the methods described below; the results obtained are shown in Table 1. The environmental compatibility as judged depending on the use or nonuse of an organotin compound is also shown for each composition.

(Surface curability)

[0259] Under conditions of 23°C and 50% RH, each of the above curable compositions was spread to a thickness of about 3 mm, and the surface of the curable composition was touched gently with a microspatula from time to time and the time required for the composition to become no more sticking to the microspatula was determined. The results thus obtained are shown in Table 1.

(Depth curability)

[0260] Under conditions of 23ºC and 50% RH, each of the above curable compositions was packed into a polyethylene tube with a diameter of 12 mm without allowing entrance of bubbles, and the excess was scraped away with a spatula to make the surface level to give a test sample. The test sample was allowed to stand under the same conditions for 7 days, the cured surface layer portion was then stripped off and, after removing the uncured portion thoroughly, the cured portion thickness was measured using vernier calipers.

(Cured product tensile characteristics)

[0261] A 3-mm-thick sheet-shaped test sample was prepared from each of the above curable compositions, and then, set and cured by allowing the specimen to stand under conditions of 23°C and 50% RH for 3 days and further at 50°C for 4 days. No. 3 dumbbell specimens defined in JIS K 6251 were punched out from the sheet and subjected to tensile testing using a Shimadzu model autograph at a pulling rate of 200 mm/minute, and the 100% tensile modulus, strength at break and elongation at break were measured. The curable composition of the invention is mainly suitable for using as sealants for building materials and when aluminum panels on an outer wall expand or contract by heat, the sealants are required to follow the expansion and contraction. The cured products may be required to have about 300% in elongation at break in order to follow the expansion and contraction of the outer wall.

(Cured product weather resistance)

[0262] A 3-mm-thick sheet-shaped test sample was prepared from each of the above curable compositions, and then, set and cured by allowing the specimen to stand under conditions of 23°C and 50% RH for 3 days and further at 50°C

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for 4 days. The product was put in an accelerated weather resistance tester (Product of Suga Test Instruments, trade name; Sunshine Weather Meter WEL-SUN-DC), and the surface of the product was visually observed per 500-hours irradiation to evaluate the degree of deterioration. The product was designated as "+" when the surface was not changed from the initial state and thus the weather resistance was evaluated as good; as "-" when a crack or chalking occurred on the surface. Table 1 shows the results on the surface states after 2,000-hours irradiation.

(Environmental compatibility)

[0263] The composition was designated as "+" when no organotin compound was used or as "-" when an organotin compound was used therein.

[0264]

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[Table 1]

			Examples				Comparative Examples			
			1	2	3	4	1	2	3	4
(A)	Alkyldialkoxysilyl group-containing organic polymer	A-1	70	70	70			90		
		A-2				70	100			50
(B)	Trialkoxysilyl group-containing organic polymer	B-1	30					10		
		B-2		30						50
		B-3			30				100	
		B-4				30				
(C)	Biguanide compound	1-(o-tolyl) biguanide	4	4	4	4	4	4	4	4
	Calcium carbonate	Hakuenka CCR	120	120	120	120	120	120	120	120
	Plasticizer	Actcol P-23	55	55	55	55	55	55	55	55
	Pigment	Tipaque R-820	20	20	20	20	20	20	20	20
	Antisagging agent	Disparlon 6500	2	2	2	2	2	2	2	2
	Antioxidant	Styrenated phenol	1	1	1	1	1	1	1	1
	Ultraviolet absorber	Sumisorb 400	1	1	1	1	1	1	1	1
	Light stabilizer	Sanol LS-770	1	1	1	1	1	1	1	1
	Aminosilane	A-1120	3	3	3	3	3	3	3	3
	Vinylsilane	A-171	2	2	2	2	2	2	2	2
Surface curability		Time required for film production on surface	80 minutes	110 minutes	60 minutes	60 minutes	40 hours	10 hours	30 minutes	115 minutes

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(continued)

			Examples				Compartive Examples			
			1	2	3	4	1	2	3	4
	Comprehensive evaluation of Surface curability (+: within 2 hours, -: more than 2 hours)		+	+	+	+	-	-	+	+
Depth curability		Depth of cured portion in 7 days (mm)	7.1	7.0	7.3	8.0	5.4	5.9	9.8	9.5
Cured product tensile characteristics		100% modulus (MPa)	0.75	0.61	0.78	0.80	0.68	0.60	0.63	0.66
		Strength at break (MPa)	1.70	1.50	1.74	1.55	1.64	1.72	1.80	1.68
		Elongation at break (%)	320	330	370	330	440	340	280	420
	Comprehensive evaluation of tensile characteristics (+: 1.2 MPa or more in strength and 300% or more in elongation, -: others)		+	+	+	+	+	+	-	+
Cured product weather resistance (+: surface not changed after 2,000 irradiation by SWM, -: surface deteriorated)			+	+	+	+	-	+	-	-
Environmental compatibility (+: organotin-free, -: organotin-used)			+	+	+	+	+	+	+	+

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[0265] As is evident from Table 1, in Examples 1 to 4 in which 70 parts by weight of the alkyldialkoxysilyl group-containing organic polymer (A) and 30 parts by weight of the trialkoxysilyl group-containing organic polymer (B) whose main chain skeleton comprises a different repeating unit from that of the component (A), the curable compositions showed practical rate in surface curability and depth curability, and cured products showed high tensile strength at break and tensile elongation at break. No deterioration was observed even after such a long period of time as 2, 000 hours in the accelerated weather resistance evaluation. On the other hand, in Comparative Example 1 in which only the component (A) was used and in Comparative Example 2 in which 90 parts by weight of the component (A) and 10 parts by weight of the component (B) were used in combination, 10 hours or more were required for film production on the surface, and the depth of the cured portion after 7 days were less than 6 mm. These are disadvantageous in practical use for sealants and adhesives. In Comparative Example 3 in which 100 parts by weight of the component (B) was used, although surface curability was as rapid and good as 30 minutes, cured product tensile elongation at break was as low as 280% and cured product weather resistance on the surface was poor. Further, in Comparative Example 4 in which 50 parts by weight of the component (A) and of the component (B) both having polyoxyalkylene type main chain skeleton, cured product weather resistance on the surface was poor while surface curability and depth curability in the curable composition and cured product tensile characteristics were good.

[0266] From the above results, it becomes clear that an appropriate ratio of addition levels of the component (A) and the component (B) having different main chain skeleton from that of the component (A) is important for obtaining a curable composition excellent in surface curability, depth curability, tensile characteristics of cured products obtained and surface weather resistance when guanidine compounds having environmental compatibility are used as an curing catalyst.

Claims

1. A non-organotin curable composition
which comprises:

(A) an organic polymer containing, in a molecule, a reactive silyl group represented by the formula $-SiR^1X^1_2$ (wherein R^1 represents a group selected from among alkyl groups containing 1 to 20 carbon atoms, aryl groups containing 6 to 20 carbon atoms and aralkyl groups containing 7 to 20 carbon atoms, and the two X^1s each independently is a hydroxyl group or a hydrolyzable group);
(B) an organic polymer containing, in a molecule, a reactive silyl group represented by the formula $-SiX^2_3$ (wherein the three X^2s each independently is a hydroxyl group or a hydrolyzable group) and having a main chain skeleton comprising a repeating unit different from a repeating unit of a main chain skeleton of the component (A); and
(C) a guanidine compound represented by the general formula (1):

$$R^2N=CNR^3_2-NR^4_2 \qquad (1)$$

(wherein R^2, the two R^3s and the two R^4s each independently is a hydrogen atom or an organic group),

wherein the weight ratio of component (A)/component (B) is 1/99 to 80/20 and the component (C) amounts to 0.1 to 30 parts by weight per 100 parts by weight of the sum of the component (A) and the component (B).

2. The curable composition according to Claim 1,
wherein one of the main chain skeleton of the (A) component organic polymer and the main chain skeleton of the (B) component organic polymer is a polyoxyalkylene and the other is a (meth)acrylate ester polymer.

3. The curable composition according to Claim 1 or 2,
wherein the component (C) is a guanidine compound represented by the general formula (1),
in the formula (1), R^2 being a hydrocarbon group wherein the carbon atom at position 1 is saturated, or a hydrogen atom.

4. The curable composition according to any of Claims 1 to 3,
wherein the component (C) is a biguanide compound represented by the general formula (1),
in the formula (1), the $-NR^3_2$ group being an $-NR^5-C(=NR^6)-NR^7_2$ group (wherein R^5, R^6 and the two R^7s each independently is a hydrogen atom or an organic group) and/or an $-N=C(NR^8_2)-NR^9_2$ group (wherein the two R^8s and the two R^9s each independently is a hydrogen atom or an organic group).

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5. The curable composition according to any of Claims 1 to 4, which further comprises a polyether plasticizer as a component (D).

6. A sealant which comprises the curable composition according to any of Claims 1 to 5.

7. An adhesive which comprises the curable composition according to any of Claims 1 to 5.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/052421

A. CLASSIFICATION OF SUBJECT MATTER
C08L101/10(2006.01)i, *C08K5/00*(2006.01)i, *C08K5/31*(2006.01)i, *C08L23/26*(2006.01)i, *C08L33/14*(2006.01)i, *C08L71/02*(2006.01)i, *C09J123/26*(2006.01)i, *C09J133/04*(2006.01)i, *C09J143/04*(2006.01)i,
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)
C08L101/10, C08K5/00, C08K5/31, C08L23/26, C08L33/14, C08L71/02, C09J123/26, C09J133/04, C09J143/04, C09J171/02, C09J201/10, C09K3/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2007
Kokai Jitsuyo Shinan Koho 1971-2007 Toroku Jitsuyo Shinan Koho 1994-2007

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 2005-248175 A (The Yokohama Rubber Co., Ltd.), 15 September, 2005 (15.09.05), Claims; Par. Nos. [0015] to [0019], [0057] to [0068] (Family: none)	4

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* 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
29 March, 2007 (29.03.07)	10 April, 2007 (10.04.07)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

Lam Research Ex. 1009 - Page 446 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/052421

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2003-313418 A (Kaneka Corp.), 06 November, 2003 (06.11.03), Claims; Par. Nos. [0057] to [0059] (Family: none)	1-7

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

Lam Research Ex. 1009 - Page 447 Lam Research Corp. v. Inpria Corp. IPR2024-00033 - U.S. Patent No. 9,823,564

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/052421

Continuation of A. CLASSIFICATION OF SUBJECT MATTER
(International Patent Classification (IPC))

C09J171/02(2006.01)i, *C09J201/10*(2006.01)i, *C09K3/10*(2006.01)i

(According to International Patent Classification (IPC) or to both national classification and IPC)

Form PCT/ISA/210 (extra sheet) (April 2005)

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Espacenet

Bibliographic data: JPS63241061 (A) — 1988-10-06

EPOXY RESIN COMPOSITION

Inventor(s): OKUNO TATSUYA; KURIYAMA AKIRA ± (OKUNO TATSUYA, ; KURIYAMA AKIRA)

Applicant(s): SUNSTAR ENGINEERING INC ± (SUNSTAR GIKEN KK)

Classification: **- international:** ***C08G59/00; C08G59/40; C08K5/54; C08K5/544; C08L63/00; C08L83/04; C08L83/06;***
(IPC1-7): C08K5/54; C08L63/00; C08L83/06
- cooperative:

Application number: JP19870179653 19870717

Priority number (s): JP19860270682 19861113

Also published as: JPH07733 (B2)

Abstract of JPS63241061 (A)

PURPOSE:To impart crack resistance and toughness to epoxy resins, by dispersing specific silicone resin particles formed from an organopolysiloxane having silanol groups at both terminals and an organosilane compd. in an epoxy resin. CONSTITUTION:This epoxy resin compsn. is obtd. by dispersing silicone resin particles formed from 5-200pts.wt. component (a) and a compd. selected from the group consisting of components (b)-(e) in a specific ratio in 100pts.wt. epoxy resin. Component (a) is an organopolysiloxane having silanol groups at both terminals, represented by formula I, etc. (wherein R1 is methyl or the like; p is 9-500); (b) is an aminosilane compd. of formula II, etc. (wherein R3 is H or the like; R4 is -C2H4- or the like; R5 and R6 are each methyl or the like; m is 0 or 1); (C) is a mercaptosilane compd. of formula III (wherein R9 is -C3H6- or the like); (d) is an epoxysilane compd. of formula IV, etc. (wherein R10 is a group of formula V or the like); and (e) is an isocyanatosilane compd. of formula VI [wherein R11 is -A- (wherein A is an alkylene) or the like].

⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　昭63－241061

⑤1Int.Cl.⁴	識別記号	庁内整理番号	㊸公開　昭和63年(1988)10月6日
C 08 L 63/00	NKB	6609－4J	
C 08 K 5/54	LRU	B－6845－4J	
	NLC	A－6845－4J	
C 08 L 83/06	LRY	6609－4J	審査請求　未請求　発明の数 1　（全9頁）

㊹発明の名称　エポキシ樹脂組成物

㉑特　願　昭62－179653

㉒出　願　昭62(1987)7月17日

優先権主張　㉜昭61(1986)11月13日㉝日本(JP)㉞特願　昭61－270682

㉗発明者　奥野　辰弥　大阪府高槻市明田町7番1号　サンスター技研株式会社内

㉗発明者　栗山　晃　大阪府高槻市明田町7番1号　サンスター技研株式会社内

㉛出願人　サンスター技研株式会社　大阪府高槻市明田町7番1号

㉔代理人　弁理士　青山　葆　外1名

明　細　書

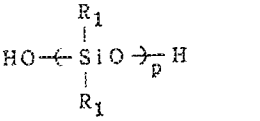
1.発明の名称

エポキシ樹脂組成物

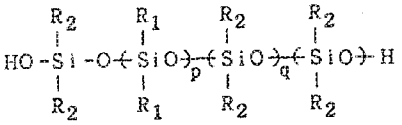
2.特許請求の範囲

1.エポキシ樹脂100重量部に対し、

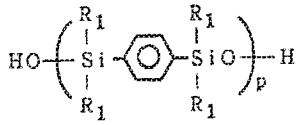
(a)式：



〔I〕



〔I'〕



〔I''〕

〔式中、R_1はメチルまたはフエニル、R_2はフエニル、pは9～500、およびqは0またはpの6％以下である〕

で示される両末端シラノールオルガノポリシロキサンの1種または2種以上の混合物5～200重量部と、下記化合物群：

(b)式：



〔II〕

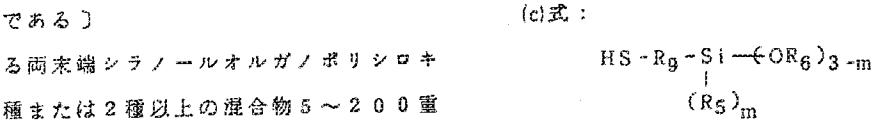
または

〔III〕

〔式中、R_3は水素、フエニル、ベンジル、シクロヘキシル、ビニルベンジルまたはアリル、R_4は$-C_2H_4-$、$-C_3H_6-$または$-C_2H_4SC_2H_4-$、R_5およびR_6は同一もしくは異なつてメチルまたはエチル、R_7は$-C_2H_4-$、$-C_2H_4SC_2H_4-$、$-C_2H_4NHC_2H_4-$または$-\overset{\overset{O}{\|}}{C}-$、$R_8$は$-C_2H_4-$または$-C_3H_6-$、およびmは0または1である〕

で示されるアミノシラン化合物、

(c)式：



〔IV〕

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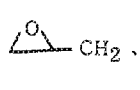
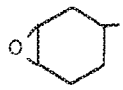
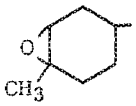
〔式中、R_5、R_6およびmは前記と同意義、およびR_9は$-C_3H_6-$または$-CH_2-$である〕

で示されるメルカプトシラン化合物、

(d)式：

$$R_{10}-\left(CH_2\right)_3-\underset{\underset{(R_5)_m}{|}}{Si}-\left(OR_6\right)_{3-m} \quad [V]$$

$$CH_3-\underset{\underset{R_{10}}{|}}{CH}-CH_2-\underset{\underset{(R_5)_m}{|}}{Si}-\left(OR_6\right)_{3-m} \quad [V']$$

〔式中、R_5、R_6およびmは前記と同意義、およびR_{10}は  または   である〕

で示されるエポキシシラン化合物および

(e)式：

$$OCN-R_{11}-\underset{\underset{(R_5)_m}{|}}{Si}-\left(OR_6\right)_{3-m} \quad [VI]$$

〔式中、R_5、R_6およびmは前記と同意義、およびR_{11}は$-A-$または$-Q-NHCOX-A-$（ここで、Aはアルキレン基、Qはジイソシアネート残基、およびXは$-NH-$、$-O-$または$-S-$）である〕

で示されるイソシアネートシラン化合物

から選ばれる1種または2種以上の混合物とを、それらの水酸基とアルコキシ基のモル比率：〔OR_6〕／〔OH〕が0.1～15となるように併用して成るシリコーン樹脂粒子を分散させたことを特徴とするエポキシ樹脂組成物。

2.(b)～(e)の化合物群の1種または2種以上に、(f)式：

$$\left(R_{12}O\right)_{4-r}-\underset{\underset{(R_5)_m}{|}}{Si}-\left(R_{13}-Y\right)_{r-m} \quad [VII]$$

〔式中、R_5は前記と同意義、R_{12}はメチルまたはエチル、R_{13}は$-CH_2-$、$-C_2H_4-$または$-C_3H_6-$、Yは$CH_2=CH-$、C_6H_5、C_nF_{2n+1}（n＝1～10）、$CF_3\overset{\overset{O}{\|}}{C}-O-$、NC－またはNC$(CH_2)_3S-$、および

rは0、1または2、mはrが2のとき0または1である〕

または(g)式：

$$\left(R_{12}O\right)_{4-r}-\underset{\underset{(R_5)_m}{|}}{Si}-\left(R_{14}\right)_{r-m} \quad [VIII]$$

〔式中、R_5、R_{12}は前記と同意義、R_{14}は$C_{n'}H_{2n'+1}$（n'＝1～20）、$CH_2=CH-$またはC_6H_5、およびrは0、1または2、mはrが2のとき0または1である〕

で示される他の有機シラン化合物を加えた前記第1項記載のエポキシ樹脂組成物。

3.発明の詳細な説明

産業上の利用分野

本発明はエポキシ樹脂組成物、更に詳しくは、エポキシ樹脂マトリックス中に特定のシリコーン樹脂粒子を安定分散させたことから成り、特にエポキシ樹脂に対し耐クラック性や靱性を付与した新規なエポキシ樹脂組成物に関する。

従来技術と解決すべき問題点

周知の如く、エポキシ樹脂組成物は引張り強度，曲げ強度等の機械的性質、誘電特性，体積抵抗率等の電気的性質に優れ、このため接着剤材料、コーテイング材料，各種電機・電子機器用絶縁材料へと幅広く応用されている。

しかし、主成分であるエポキシ樹脂は通常、耐クラック性や靱性に欠け、さらには硬化時の収縮によるストレスの緩和が困難であるため、これら欠点を改良すべく、これまでにさまざまな工夫がなされてきた。主な工夫として、たとえば

(1)可撓性を付与する特殊なエポキシ樹脂、たとえばポリエチレングリコールジグリシジルエーテル、ヘキサンジオールジグリシジルエーテル、ウレタン変性エポキシ樹脂、チオコール変性エポキシ樹脂、ドデセニルサクシニックアンハイドライド、ポリアゼライン酸ポリ無水物等を配合したり、あるいは

(2)変性アクリロニトリル－ブタジエンゴムやアクリルゴム等のTgの低いゴム粒子を分散させるといつた手法が知られている。しかしながら、(1)の手法では硬化速度が遅くなつたり、耐熱強度の低下を招いたり、硬化物が経時的に可撓性を失つ

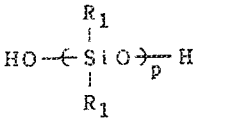
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たりするため十分な改良ができない。また(2)の手法では、樹脂の吸水率が大となる。

本発明者らは、かかるエポキシ樹脂の改質について鋭意研究を進めた結果、通常のエポキシ樹脂に対して特定の両末端シラノールオルガノポリシロキサンと、1分子内に少なくとも2個のアルコキシシリル基を有する有機シラン化合物とを加え、要すれば加温下で撹拌混合すれば、両末端シラノールオルガノポリシロキサンと有機シラン化合物の架橋反応生成物であるシリコーン樹脂粒子がエポキシ樹脂マトリックス中に均一安定に分散して存在し、エポキシ樹脂の改質効果を発揮しうることを見出し、本発明を完成させるに至つた。

発明の構成と効果

すなわち、本発明は、エポキシ樹脂100部(重量部、以下同様)に対し、(a)式：

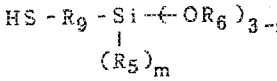


〔I〕

〔式中、R_3は水素、フエニル、ベンジル、シクロヘキシル、ビニルベンジルまたはアリル、R_4は$-C_2H_4-$、$-C_3H_6-$または$-C_2H_4SC_2H_4-$、R_5およびR_6は同一もしくは異なつてメチルまたはエチル、R_7は$-C_2H_4-$、$-C_2H_4SC_2H_4-$、$-C_2H_4NHC_2H_4-$または、R_8は$-C_2H_4-$または$-C_3H_6-$、およびmは0または1である〕

で示されるアミノシラン化合物、

(c)式：

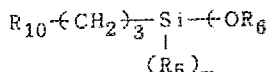


〔IV〕

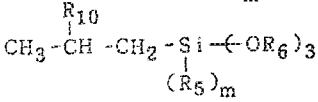
〔式中、R_5，R_6およびmは前記と同意義、およびR_9は$-C_3H_6-$または$-CH_2-$である〕

で示されるメルカプトシラン化合物、

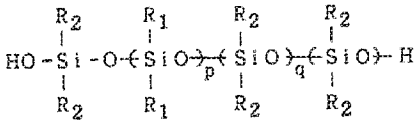
(d)式：



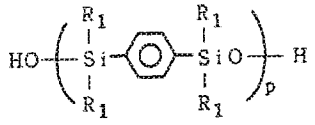
〔V〕



〔V'〕



〔I'〕

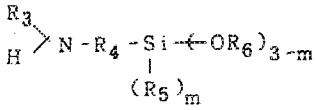


〔I'〕

〔式中、R_1はメチルまたはフエニル、R_2はフエニル、pは9～500、およびqは0またはpの6%以下である〕

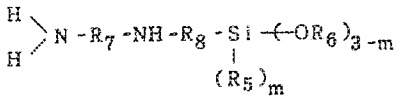
で示される両末端シラノールオルガノポリシロキサン(以下、シリコーン樹脂という)の1種または2種以上の混合物5～200部と、

(b)式：

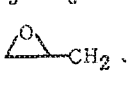
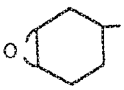
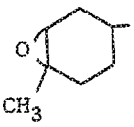


〔II〕

または

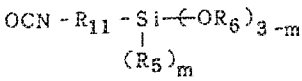


〔III〕

〔式中、R_5，R_6およびmは前記と同意義、およびR_{10}は、またはである〕

で示されるエポキシシラン化合物および

(e)式：



〔VI〕

〔式中、R_5，R_6およびmは前記と同意義、およびR_{11}は-A-または-Q-NHCOX-A-(ここで、Aはアルキレン基、好ましくは炭素数2以上、特に3以上の低級アルキレンでたとえば$-(CH_2)_2-$、$-(CH_2)_3-$等、Qはジイソシアネート残基、たとえば2,4-もしくは2,6-トリレンジイソシアネート、4,4'-ジフエニルメタンジイソシアネートなどの芳香族ジイソシアネート残基またはヘキサメチレンジイソシアネート、リジンジイソシアネート、イソホロンジイソシアネート、水添MDI、

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水添ＴＤＩなどの脂肪族系ジイソシアネート残基、およびＸは-NH-、-O-または-S-）である〕で示されるイソシアネートシラン化合物の群から選ばれる１種または２種以上の混合物とを、それらの水酸基とアルコキシ基のモル比率：〔OR_6〕/〔OH〕が0.1～15となるように併用して成るシリコーン樹脂粒子を分散させたことを特徴とするエポキシ樹脂組成物を提供するものである。

本発明におけるエポキシ樹脂は通常のものが使用されてよく、特に制限はない。具体例としては以下のものが挙げられ、１種または２種以上の混合物を使用に供する。

(1)グリシジルアミン型エポキシ樹脂

N,N-ジグリシジルアミノ基を少なくも１個有するエポキシ樹脂で、N,N,N',N'-テトラグリシジルアミノジフエニルメタン、N,N-ジグリシジルメタ（またはパラ）アミノフエノールグリシジルエーテルおよびそれらの縮合物。これらはアラルダイトＭＹ７２０（チバガイギー社製）、エポトートＹＨ４３４，ＹＨ１２０（東都化成社製）として市販。

(2)ノボラック型エポキシ樹脂

フエノールノボラック型エポキシ樹脂としてエピコート１５２，１５４（シエル化学社製）、ダウエポキシ樹脂ＤＥＮ４３１，４３８，４３９，４８５（ダウケミカル社製）、チバガイギーＥＰＮ１１３８，１１３９（チバガイギー社製）等。

クレゾールノボラック型エポキシ樹脂としてチバガイギーＥＣＮ１２３５，１２７３，１２８０，１２９９（チバガイギー社製）、ＥＯＣＮ１０２，１０３，１０４（日本化業社製）等。

(3)ビスフエノールＡ型エポキシ樹脂としてエピコート８２８，８３４，８２７，１００１，１００２，１００４，１００７，１００９（油化シエル社製）、ダウエポキシＤＥＲ３３１，３３２，６６２，６６３Ｕ，６６２Ｕ（ダウケミカル社製）、アラルダイト６０７１，７０７１，７０７２（チバガイギー社製）、エピクロン８４０，８５０，８５５，８６０，１０５０，３０５０，４０５０，７０５０（大日本インキ化学工業社製）等。

ウレタン変性ビスフエノールＡ型エポキシ樹脂としてアデカレジンＥＰＶ－６，ＥＰＶ－９，ＥＰＶ－１５（旭電化社製）等。

臭素化ビスフエノールＡ型エポキシ樹脂としてアラルダイト８０１１（チバガイギー社製）、ダウエポキシ樹脂ＤＥＲ５１１（ダウケミカル社製）等。

(4)脂環式エポキシ樹脂としてアラルダイトＣＹ－１７９，ＣＹ－１７８，ＣＹ－１８２，ＣＹ－１８３（チバガイギー社製）等。

(5)その他：ビスフエノールＦ型、レゾルシン型、テトラヒドロキシフエニルエタン型、ポリアルコール、ポリグリコール型、グリセリントリエーテル型、ポリオレフイン型、エポキシ化大豆油、エステル型エポキシ樹脂等も使用することができる。

なお、これらのエポキシ樹脂にあつて、常温液状のものはそのまま使用できるが、常温固形のものについては、その融点以上に加熱溶融するか、あるいは液状エポキシ樹脂を併用して液状化すればよい。

本発明における式〔Ⅰ〕，〔Ⅰ'〕，〔Ⅰ''〕のシリコーン樹脂(a)は、たとえばチツソ(株)製の末端シラノールポリジメチルシロキサン、末端シラノールジフエニルシロキサン、末端シラノールポリジメチル-ジフエニルシロキサン、ポリテトラメチル-p-シルフエニレンシロキサンが市販されている。使用量は、エポキシ樹脂１００部に対して５～２００部、好ましくは５～５０部の範囲で選定する。５部未満であると、改質効果が得られず、また２００部を越えると、樹脂全体がゲル化状態となる。

本発明における式〔Ⅱ〕，〔Ⅲ〕のアミノシラン化合物(b)の具体例について、その構造式および化合物名を以下に列挙する。

式〔Ⅱ〕のアミノシラン化合物

$H_2NC_3H_6Si(OC_2H_5)_3$

γ-アミノプロピルトリエトキシシラン

$H_2NC_2H_4Si(OCH_3)_3$

β-アミノエチルトリメトキシシラン

$H_2NC_3H_6Si(OC_2H_5)_2$
　　|
　　CH_3

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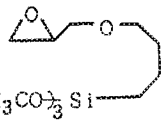
γ－アミノプロピルジエトキシメチルシラン

$CH_2=CHCH_2NHC_3H_6Si(OCH_3)_3$

γ－アリルアミノプロピルトリメトキシシラン

$H_2NC_2H_4SC_2H_4Si(OC_2H_5)_2$
$\quad\quad\quad

（３－グリシドキシプロピル）メチルジエトキシシラン



$(H_3CO\rightarrow_3 Si$

３－グリシドキシプロピルトリメトキシシラン

本発明における式〔VI〕のイソシアネートシラン化合物(e)の具体例について、その構造式および化合物名を以下に列挙する。

$OCN-CH_2CH_2CH_2-Si(OC_2H_5)_3$

γ－イソシアネートプロピルトリエトキシシラン

$OCN-CH_2CH_2CH_2-Si(OCH_3)_3$

γ－イソシアネートプロピルトリメトキシシラン

これらの有機シラン化合物(b)～(e)はいずれも、分散安定剤および硬化剤として機能し、かかる群の中から１種または２種以上の混合物を選定して使用に供すればよい。使用量（２種以上の混合物の場合はその合計量）は一般的に、シリコーン樹脂(a)に対してそれらの水酸基とアルコキシ基のモル比率：〔OR_6〕/〔OH〕 が0.1～15となるように選定する。この比率が0.1未満であると、分散安定効果が発揮されず、また15を越えると、シリコーン樹脂粒子を分散して得られるエポキシ樹脂組成物の粘度安定性が劣る。本発明では、エポキシ樹脂とシリコーン樹脂粒子界面の接着性も考慮しており、アルコキシ基が水酸基（シラノール基）に対してかなり過剰のモル比で使用することもある。

なお、これらの有機シラン化合物(b)～(e)群に加えて、(f)式：

$$(R_{12}O\rightarrow_{4-r} \underset{(R_5)_m}{Si}(R_{13}-Y)_{r-m} \qquad \text{〔VII〕}$$

〔式中、R_5は前記と同意義、R_{12}はメチルまたはエチル、R_{13}は$-CH_2-$、$-C_2H_4-$または$-C_3H_6-$、Yは$CH_2=CH-$、C_6H_5、C_nF_{2n+1}（n＝1～10）、$CF_3\overset{\overset{O}{\|}}{C}-O-$、NC－またはNC$(CH_2)_3S-$、および

rは0、1または2、mはrが2のとき0または1である〕

または(g)式：

$$(R_{12}O\rightarrow_{4-r} \underset{(R_5)_m}{Si}(R_{14})_{r-m} \qquad \text{〔VIII〕}$$

〔式中、R_5，R_{12}は前記と同意義、R_{14}は$C_{n'}H_{2n'+1}$（n'＝1～20）、$CH_2=CH-$ またはC_6H_5、およびrは0、1または2、mはrが2のとき0または1である〕

で示される有機シラン化合物を使用してもよい。この有機シラン化合物(f)または(g)の使用によつて、エポキシ樹脂を架橋させることなくシリコーン樹脂のみを架橋し粒子化できる。かかる有機シラン化合物(f)または(g)の具体例（構造式と化合物名）を以下に列挙する。

$(C_2H_5O\rightarrow_4 Si$

テトラエトキシシラン

$CH_2=CHCH_2Si(OC_2H_5)_3$

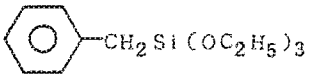
アリルトリエトキシシラン

$CH_2=CHCH_2Si(OCH_3)_3$

アリルトリメトキシシラン

$C_5H_{11}Si(OC_2H_5)_3$

アミルトリエトキシシラン



ベンジルトリエトキシシラン

$C_4H_9Si(OCH_3)_3$

n－ブチルトリメトキシシラン

$C_2H_5Si(OC_2H_5)_3$

エチルトリエトキシシラン

$C_2H_5Si(OCH_3)_3$

エチルトリメトキシシラン

$CH_3(CH_2)_5Si(OCH_3)_3$

n－ヘキシルトリメトキシシラン

$CH_3Si(OC_2H_5)_3$

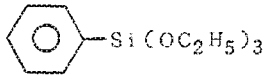
メチルトリエトキシシラン

$CH_3Si(OCH_3)_3$

メチルトリメトキシシラン

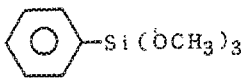
$CH_3(CH_2)_{17}Si(OC_2H_5)_3$

n－オクタデシルトリエトキシシラン



フエニルトリエトキシシラン

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フエニルトリメトキシシラン

$CH_3(CH_2)_2Si(OCH_3)_3$

n-プロピルトリメトキシシラン

$(CH_3O)_4Si$

テトラメトキシシラン

$CH_2=CHSi(OC_2H_5)_3$

ビニルトリエトキシシラン

$CH_2=CHSi(OCH_3)_3$

ビニルトリメトキシシラン

$NC(CH_2)_2Si(OC_2H_5)_3$

シアノエトキシトリエトキシシラン

$NC(CH_2)_3S(CH_2)_3Si(OCH_3)_2$
$\quad\quad\quad

錫オキサイド0.5部を加え、80℃で撹拌しながら、これに末端シラノールポリジメチルシロキサン〔I〕（p＝350～380、R_1＝CH_3）50部およびγ-アミノプロピルトリエトキシシラン1部を加え、さらに6時間加熱撹拌を続ける。反応混合物は乳白色の液体となり、反応終了後室温で放置・冷却してエポキシ樹脂中にシリコーン樹脂粒子が均一に分散したエポキシ樹脂組成物を得る。25℃でのB型粘度計による粘度26000 cps。光学顕微鏡観察の結果、シリコーン樹脂粒子径0.5～3μであつた。

次に、このエポキシ樹脂組成物に変性脂肪族ポリアミンを配合し、硬化させたところ、硬化物の弾性率（20℃）は8.5×10^9（dyne/cm²）であつた。これに対し、「エピコート828」単独の場合の弾性率は1.1×10^{10}（dyne/cm²）であつた。

実施例2

実施例1と同様に、ビスフエノールF型エポキシ樹脂（シエル化学社製、エピコート807）100部とt-ブチル錫オキサイド0.5部を80℃で撹拌、これに実施例1と同じ液状シリコーン樹脂130部およびγ-アミノプロピルトリエトキシシラン8部を加え、6時間加熱撹拌、次いで放置・冷却して乳白色液体のエポキシ樹脂組成物を得る。粘度180000 cps、粒子径1～10μ。変性脂肪族ポリアミンによる硬化物の弾性率3.6×10^9（dyne/cm²）。

実施例3

実施例1と同様に、ビスフエノールA型エポキシ樹脂（油化シエル社製、エピコート1001）90部、エステル型エポキシ樹脂（シエル化学社製、エピコート871）10部およびt-ブチル錫オキサイド0.5部を90℃で撹拌、これに実施例1と同じ液状シリコーン樹脂15部およびN-β-（アミノエチル）-γ-アミノプロピルトリメトキシシラン0.8部を加え、3時間加熱撹拌、次いで放置・冷却して半固体のエポキシ樹脂組成物を得る。粒子径1～3μ。

実施例4

ビスフエノールF型エポキシ樹脂である「エピコート807」100部に対しt-ブチル錫オキサイド0.5部、平均分子量1700（n≒20）の液状シリコーン樹脂〔I〕（R_1＝CH_3）5部、N-β-（アミノエチル）-γ-アミノプロピルトリメトキシシラン0.5部およびテトラエトキシシラン0.5部を加え、室温で6時間撹拌混合して、乳白色液体のエポキシ樹脂組成物を得る。粘度4000 cps、粒子径0.5～2μ。

実施例5

ノボラック型エポキシ樹脂である「エピコート154」100部に対し、t-ブチル錫オキサイド0.5部を加え、80℃で撹拌しながら、これに実施例1と同じ液状シリコーン樹脂50部およびγ-アミノプロピルトリエトキシシラン1部を加え、80℃で3時間撹拌混合して乳白色高粘稠液体のエポキシ樹脂組成物を得る。80℃でのB型粘度計における粘度50000 cps、粒子径2～12μ。

実施例6

ビスフエノールA型エポキシ樹脂（油化シエル社製、エピコート1001）100部に、分子量150000のシラノール末端ポリテトラメチル-p-シルフエニレンシロキサン10部を加え、150℃で撹拌しながら、t-ブチル錫オキサイド0.5部およびγ-アミノプロピルトリエトキシシラン0.5部を加え、3時間加熱撹拌を続ける。得られるエポキシ樹脂組成物は、室温で淡黄色の固形であつた。粒子径2～5μ程度。

実施例7

ビスフエノールA型エポキシ樹脂（油化シエル社製、エピコート828）100部にt-ブチル錫オキサイド0.5部を加え、80℃で撹拌しながら末端シラノールポリジメチル-ジフエニルシロキサン〔I〕（p＝28、q＝1）50部およびγ-アミノプロピルトリエトキシシラン1部、フエニルトリメトキシシラン7部を加え、さらに6時間加熱撹拌を続ける。得られるエポキシ樹脂組成物は、乳白色の液体であつた。25℃でのB型粘度計における粘度は42000 cps。光学顕微鏡

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観察の結果、シリコーン樹脂粒子径0.5～2μであつた。

実施例8

ビスフエノールA型エポキシ樹脂（油化シエル社製、1001）100部にt-ブチル錫オキサイド0.5部を加え、N_2雰囲気下100℃で撹拌しながらγ-イソシアネートプロピルトリメトキシシラン4部を加え、5時間加熱撹拌を行つた後、IRでイソシアネート基の吸収がないことを確認した。その後、実施例1と同様の液状シリコーン樹脂30部を加え、エアー中でさらに6時間加熱撹拌を行う。得られるエポキシ樹脂組成物は、固形であつた。粒子径2～5μ。

実施例9

ビスフエノールA型エポキシ樹脂（油化シエル社製、エピコート828）100部にt-ブチル錫オキサイド0.5部を加え、80℃で加熱撹拌を行い、実施例1と同様の液状シリコーン樹脂30部およびγ-メルカプトプロピルトリメトキシシラン2部、さらに水0.5部を加え、加熱撹拌を行う。得られるエポキシ樹脂組成物は、乳白色の液体であつた。25℃でのB型粘度計における粘度は20000 cps。粒子径0.5～2μ。

実施例10

ビスフエノールA型エポキシ樹脂（油化シエル社製、エピコート828）100部にt-ブチル錫オキサイド0.5部を加え、80℃で撹拌を行い、実施例1と同様の液状シリコーン樹脂30部およびγ-グリシドキシプロピルトリメトキシシラン1部を加え、6時間加熱撹拌を続ける。得られるエポキシ樹脂組成物は、乳白色の液体であつた。25℃でのB型粘度計における粘度は32000 cps。粒子径3～8μ。

実施例11

末端シラノールポリジメチルシロキサン〔I〕（p＝7）10部に、（3,3,3-トリフルオロプロピル）メチルジメトキシシラン2.5部およびt-ブチル錫オキサイド0.5部を加え、窒素雰囲気下50℃で24時間縮合反応を行う。反応の確認はメトキシ基のIR吸収の消滅で行つた。その後、

これらにビスフエノールA型エポキシ樹脂（油化シエル社製、エピコート828）100部およびγ-アミノプロピルトリエトキシシラン1.0部を加え、空気中で80℃にて6時間加熱撹拌を行う。得られるエポキシ樹脂組成物は、乳白色の液状であつた。25℃でのB型粘度計による粘度は24000 cps。粒子径0.5～2μ。

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METHOD AND COMPOSITION FOR GROWING POLYPHYLETIC METALLIC OR METALLIC COMPOUND LAYER

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Applicant(s): AIR PROD & CHEM ± (AIR PROD AND CHEM INC)

Classification: - international: ***C01B33/06; C01G25/00; C01G35/00; C23C16/00; C23C16/06; C23C16/30; C23C16/34; C23C16/40; C23C18/12; H01L21/285; H01L21/8242; H01L21/8246; H01L27/105; H01L27/108; H01L39/24;*** (IPC1-7): C01G25/00; C23C16/06; C23C16/30; H01L21/285; H01L21/8242; H01L27/105; H01L39/24

- cooperative: **C23C16/34 (EP)**; **C23C16/40 (EP)**; **C23C16/401 (EP)**; **C23C16/405 (EP)**; **C23C18/1216 (EP)**; **C23C18/1225 (EP)**; **C23C18/1254 (EP)**; **C23C18/1258 (EP)**; H01L21/02565 (EP); H01L21/02628 (EP)

Application number: JP20000212008 20000707

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Also published as: EP1067595 (A2) EP1067595 (A3) JP3576934 (B2) KR20010015186 (A) TW467963 (B) more

Abstract of JP2001081560 (A)

PROBLEM TO BE SOLVED: To provide a composition and method for growing a polyphyletic metallic or metallic compound layer on a base material. SOLUTION: This composition contains a solventless mixture of at least two kinds of metal-ligand complex precursor, in which the mixture lis in a liquid state under ambient conditions, and also, the ligands are selected from the group consisting of alkyl, alkoxide, halogen, hydrogen, amide, imide, azide ions, nitric acid radicals, cyclopentadienyl, carbonyl and fluorine, oxygen and nitrogen substituted similar products thereof. For obtaining a layer

by using the same, the composition is fed out to a growing zone area in which a base material is located, the base material is brought into contact with the composition under the growing conditions to grow a polyphyletic metallic or metallic compound layer on the base material, and the contact between the composition and the base material is selected from chemical vapor phase growth, spray thermal decomposition, a sol-gel process, spin coating and atomic layer epitaxial.

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(54)【発明の名称】多元金属化合物層の成長のための方法及び混合金属又は金属化合物層の成長のための組成物

(57)【特許請求の範囲】

【請求項１】

下記のａ）～ｄ）を含む、電子材料の基材上に酸素含有多元金属化合物層を成長させるための方法。

ａ）周囲条件において液体を構成する２種以上の金属－配位子錯体前駆物質の無溶媒の液体混合物であって、当該配位子が同一であり、且つアルキル、アルコキシド、水素、アミド、イミド、アジ化物イオン、硝酸根、シクロペンタジエニル、カルボニル、並びにそれらのフッ素、酸素及び窒素置換類似物からなる群より選ばれる、無溶媒の液体混合物を提供すること

ｂ）当該無溶媒の液体混合物を上記基材が位置している成長帯域へ送出すること

ｃ）当該基材を成長条件下で当該無溶媒の液体混合物と接触させ、この成長条件下での接触を、化学気相成長、スプレー熱分解、ゾル－ゲルプロセス、スピンコーティング及び原子層エピタキシーからなる群より選択すること

ｄ）当該無溶媒の液体混合物から当該基材上に酸素含有多元金属化合物層を成長させること

【請求項２】

下記のａ）～ｄ）を含む、電子材料の基材上に酸素含有多元金属化合物層を成長させるための方法。

ａ）周囲条件において液体を構成する２種以上の金属－配位子錯体前駆物質の無溶媒の液体混合物であって、当該配位子が同一であり、且つアルキル、アルコキシド、水素、アミ

ド、イミド、アジ化物イオン、硝酸根、シクロペンタジエニル、カルボニル、並びにそれらのフッ素、酸素及び窒素置換類似物からなる群より選ばれる、無溶媒の液体混合物を提供すること
ｂ）当該無溶媒の液体混合物を直接の液体注入によりフラッシュ蒸発帯域へ送出して当該無溶媒の液体混合物を気化させること
ｃ）当該基材を、得られた当該無溶媒の液体混合物の蒸気と成長条件下で接触させること
ｄ）当該無溶媒の液体混合物から当該基材上に酸素含有多元金属化合物層を成長させること

【請求項３】
前記周囲条件が４０℃以下且つ２０７ｋＰａ（ゲージ圧）（３０ｐｓｉｇ）以下である、請求項１又は２記載の方法。

【請求項４】
前記周囲条件が２０～３０℃且つ３４～４１ｋＰａ（ゲージ圧）（５～６ｐｓｉｇ）である、請求項１又は２記載の方法。

【請求項５】
前記基材上に前記多元金属化合物層を成長させる前に前記無溶媒混合物を酸素源と混合する、請求項１から４までのいずれか一つに記載の方法。

【請求項６】
前記酸素源を９５＋体積％の酸素、オゾン、亜酸化窒素、酸化窒素、二酸化窒素、水、過酸化水素、空気及びそれらの混合物からなる群から選ぶ、請求項５記載の方法。

【請求項７】
電子材料の基材上に多元金属化合物層を成長させるための方法であって、下記のａ）～ｄ）、すなわち、
ａ）周囲条件において液体を構成する２種以上の金属－配位子錯体前駆物質の無溶媒混合物であって、当該配位子が同一であり、且つアルキル、アルコキシド、ハロゲン、水素、アミド、イミド、アジ化物イオン、硝酸根、シクロペンタジエニル、カルボニル、並びにそれらのフッ素、酸素及び窒素置換類似物からなる群より選ばれる、無溶媒混合物を提供すること、
ｂ）当該無溶媒混合物を直接の液体注入によりフラッシュ蒸発帯域へ送出して当該無溶媒混合物を気化させること、
ｃ）当該基材を、得られた当該無溶媒混合物の蒸気と成長条件下で接触させること、
ｄ）当該無溶媒混合物から当該基材上に多元金属化合物層を成長させること、
を含み、当該基材上に当該多元金属化合物層を成長させる前に当該無溶媒混合物を窒素源と混合する、電子材料の基材上に多元金属化合物層を成長させるための方法。

【請求項８】
前記窒素源を窒素、アンモニア、ヒドラジン、アルキルヒドラジン、アジ化水素、アルキルアミン及びそれらの混合物からなる群から選ぶ、請求項７記載の方法。

【請求項９】
前記多元金属化合物層を、混合金属合金、混合金属酸化物、混合金属窒化物、混合金属炭化物、混合金属炭窒化物、混合金属酸炭窒化物、混合金属酸炭化物、混合金属硫化物、混合金属リン化物、混合金属ヒ化物、混合金属アンチモン化物、混合金属セレン化物、混合金属テルル化物及びそれらの混合物からなる群より選ぶ、請求項１から４までのいずれか一つに記載の方法。

【請求項１０】
混合金属又は金属化合物層の成長のための組成物であって、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物を含み、当該混合物が周囲条件において液体であり、且つ当該配位子が、アルキル、アルコキシド、ハロゲン、水素、アミド、イミド、アジ化物イオン、硝酸根、シクロペンタジエニル、カルボニル、並びにそれらのフッ素、酸素及び窒素置換類似物からなる群より選ばれ、当該混合物が、周囲条件において液体である第一の金属－配位子錯体前駆物質と、周囲条件において液体である第二の金属－配位子錯体前駆

物質とを含む、混合金属又は金属化合物層の成長のための組成物。
【請求項１１】
前記少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物の当該金属が、亜鉛、カドミウム、水銀、アルミニウム、ガリウム、インジウム、タリウム、スズ、鉛、アンチモン、ビスマス、リチウム、ナトリウム、カリウム、ルビジウム、セシウム、ベリリウム、マグネシウム、カルシウム、ストロンチウム、バリウム、スカンジウム、イットリウム、ランタン、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、タンタル、クロム、モリブデン、タングステン、マンガン、テクネチウム、レニウム、鉄、ルテニウム、オスミウム、コバルト、ロジウム、イリジウム、ニッケル、パラジウム、白金、銅、銀、金、ケイ素及びセリウムからなる群より個々に選ばれる、請求項１０記載の組成物。
【請求項１２】
前記少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物の当該配位子が、ジメチルアミド、ジエチルアミド、エチルメチルアミド、ブチルアミド、ジプロピルアミド、メチルプロピルアミド、エチルプロピルアミド、メトキシ、エトキシ、プロポキシ及びブトキシからなる群より選ばれる、請求項１０又は１１記載の組成物。
【請求項１３】
前記少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物が、Ｚｒ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$、Ｓｎ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$及びＴｉ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$を含む、請求項１０記載の組成物。
【請求項１４】
前記少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物が、Ｚｒ（Ｎ（ＣＨ$_3$）$_2$）$_4$、Ｓｎ（Ｎ（ＣＨ$_3$）$_2$）$_4$及びＴｉ（Ｎ（ＣＨ$_3$）$_2$）$_4$を含む、請求項１０記載の組成物。
【請求項１５】
前記少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物が、Ｚｒ（Ｏ（Ｃ$_4$Ｈ$_9$））$_4$、Ｓｎ（Ｏ（Ｃ$_4$Ｈ$_9$））$_4$及びＴｉ（Ｏ（Ｃ$_4$Ｈ$_9$））$_4$を含む、請求項１０記載の組成物。
【請求項１６】
前記少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物が、Ｔａ（Ｎ（ＣＨ$_3$）$_2$）$_5$及びＴｉ（Ｎ（ＣＨ$_3$）$_2$）$_4$を含む、請求項１０記載の組成物。
【請求項１７】
前記少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物が、Ａｌ（ＯＣＨ$_2$ＣＨ$_3$）$_3$及びＴａ（ＯＣＨ$_2$ＣＨ$_3$）$_5$を含む、請求項１０記載の組成物。
【請求項１８】
前記少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物が、ＣＨ$_3$ＣＨ$_2$Ｎ＝Ｔａ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_3$及びＴｉ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$を含む、請求項１０記載の組成物。
【請求項１９】
前記少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物が、Ｓｉ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$を含み、且つ、Ｔｉ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$、Ｚｒ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$、Ｈｆ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$、Ｖ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_3$、Ｖ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$、Ｎｂ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_3$、Ｎｂ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$、ＣＨ$_3$ＣＨ$_2$Ｎ＝Ｎｂ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_3$、ＣＨ$_3$ＣＨ$_2$Ｎ＝Ｖ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_3$、（ＣＨ$_3$ＣＨ$_2$Ｎ＝）$_2$Ｍｏ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$、（ＣＨ$_3$ＣＨ$_2$Ｎ＝）$_2$Ｗ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_4$、及びＣＨ$_3$ＣＨ$_2$Ｎ＝Ｔａ（Ｎ（ＣＨ$_2$ＣＨ$_3$）$_2$）$_3$からなる群より選ばれる金属－配位子錯体前駆物質を含む、請求項１０記載の組成物。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】

本発明は、基材上に多元金属又は金属化合物層を成長させるための組成物と方法に関する。

【０００２】

【従来の技術及び発明が解決しようとする課題】

半導体製造産業は、集積回路、記憶装置及びフラットパネルディスプレイ装置のための適切な電気デバイスを作るために半導体及び絶縁性又は誘電性基材に薄い層、プラグ、ビア及びパターンでもって金属、金属混合物及び金属化合物混合物を堆積させるのに適切な材料と堆積技術を必要としている。

【０００３】

適当な電子材料基材上に金属、金属化合物及びそれらの混合物を堆積させるための様々な方法が知られており、それらには、物理的な方法（スパッタリング、分子線エピタキシー、蒸着及びレーザーアブレーション）、合金化、そして化学気相成長（プラズマ、光又はレーザーに支援される、低圧及び高温での）が含まれる。

【０００４】

様々な多元金属酸化物が、"Advances in Processingof Ferroelectric Thin Films", L. M. Sheppard, Ceramic Bulletin, Vol. 71, No. 1, pp. 85－95（1992）、"Formation of Al_2O_3－Ta_2O_5 Double－Oxide Thin Films by Low－Pressure MOCVD and Evaluation of Their Corrosion Resistances in Acid andAlkali Solutions", Hara et al., Journal of the Electrochemical Society, 146（2）, pp. 510－516（1999）、"High Coercivity in $Sm_2Fe_{17}N_x$ Magnets", Schnitzke et al., Appl. Phys. Lett. 57（26）, pp. 2853－2855（Dec. 24, 1990）、"Investigation of Ternary Transition－Metal Nitride Systems by Reactive Cosputtering", Van Dover et al., Chem. Mater., Vol. 5, pp. 32－35（1993）、"Reactively Sputtered Ti－Si－N Films II. Diffusion Barriers for Aland Cu Metallizations on Si", Sun etal., J. Appl. Phys., 81（2）, pp. 664－671（Jan. 15, 1997）、"MOCVD Routes to Thin Metal Oxide Films for Superconducting Electronics", Schulz et al., Adv. Mater. 6, No. 10, pp. 719－730（1994）、"Compositional and Microstructural Characterization of RuO_2－TiO_2 Catalysts Synthesized by the Sol－Gel Method", Guglielmi et. al., J. Electrochem. Soc., Vol. 139, No. 6, pp. 1665－1661（June 1992）、"Enhancement of the Dielectric Constant of Ta_2O_5 Through Substitution with TiO_2", Cava et al., Nature, Vol. 377, 21, pp. 215－217（Sept. 1995）、米国特許第４０５８４３０号明細書で列挙されたものを含めて、文献で知られており、そのうちの後者の米国特許明細書には「原子層エピタキシー」として知られる成長方法も開示されている。

【０００５】

化学気相成長（ＣＶＤ）は、均一でコンフォーマルな成長をもたらす特性と高制御性の条件下で材料のアレイを成長させることができることから、近年支持を獲得している。一般的に、化学気相成長は、制御された仕方でもって高純度の材料を高速に成長させることが

できる。

【０００６】

しかし、化学気相成長には、その実施を忌避させるいくつかの欠点がある。所望の化学物質の全てが、化学気相成長で処理できるだけ十分に揮発性であるわけではない。一部の化学物質は貯蔵あるいは送出条件において固体である。一部の化学物質は適切な貯蔵と送出のためには揮発性でありすぎる。

【０００７】

化学気相成長を行うための状況は、例えば多元金属化学物質の気相成長、例として多元金属酸化物の化学気相成長におけるように、いくつかの化学物質を同時に成長（堆積）させる必要性によって更に複雑にされる。金属前駆物質がお互いどうし反応することがあり、あるいはＣＶＤのための少なくとも１種の金属前駆物質が非常に揮発性であり又は非常に不揮発性である、すなわち固体であることがある。

【０００８】

ＣＶＤのこれらの不都合を克服するために、先行技術では、固体の金属前駆物質を溶解するために、あるいはＣＶＤ用の液体の、特に粘稠な液体の、金属前駆物質を混合するために、溶媒を使用してきた。

【０００９】

米国特許第５２０４３１４号明細書には、ＣＶＤのための金属前駆物質の液体混合物あるいは溶媒混合物のフラッシュ蒸発のための孔付きの装置が開示されている。

米国特許第５８２０６６４号明細書には、ＣＶＤにとって有用である、混合金属化合物前駆物質の種々の溶媒混合物が記載されている。

【００１０】

しかし、ＣＶＤのために液体を送出するための溶媒系は、相溶性の揮発性溶媒を選定しなくてはならないので、問題がある。溶媒は、所定の流量と時間について送出される有効な化学物質の量を減少させる。より重大なことに、溶媒は、慎重な扱いを要する半導体及び電子デバイスの製造を行う敏感な反応帯域へ更に別の化学物質を導入する。そのような溶媒が存在することの不利な影響を考慮しなくてはならない。最後に、溶媒は環境及びコスト要因を代表するものである。溶媒又はその分解生成物は、利用後に再循環し、捕捉し、あるいは処理しなくてはならない。

【００１１】

国際公開第９８／４６６１７号パンフレットには、金属前駆物質と、混合β－ジケトネートから金属を成長（堆積）させる方法とが記載されている。この国際出願は、直接の液体の注入によるＣＶＤ及びそのほかの成長用に金属前駆物質を液体で送出することに関するものである。混合β－ジケトネートを使用することは、前駆物質の液体状態を増進して送出を容易にする。溶媒はこれらの液体混合物にとっての一つの選択肢である。

【００１２】

同様の開示が、"New Liquid Precursors for Chemical Vapor Deposition", Gordon et al., Mater. Res. Soc. Symp. Proc., 495, pp. 63－68（1998）と、"Liquid Compounds for CVD of Alkaline Earth Metals", Gordon et. al., MRS Meeting, April 7, 1999, San Francisco, CAに見られる。

【００１３】

金属前駆物質の送出のために適切な液体媒体を提供する先行技術の試みは、選ばれた溶媒又は混合β－ジケトネート配位子を使用して送出のための液体条件を確保することを必要とした。溶媒にあっては、汚染と除去が問題となる。混合配位子にあっては、液体なしの条件に至りかねない意図しない配位子交換が問題となる。β－ジケトネート配位子はしばしば、固体条件に通じる条件を回避するためのβ－ジケトネート置換基の調節がないと固体金属化合物に通じ、かくして意図することなく配位子交換するという結果を更に悪化させる。本発明は、確固とした成長性能のために溶媒と配位子交換の欠点を回避するため、

成長のために金属の無溶媒の共通配位子混合物を液体状態で、好ましくは直接の液体注入により使用することによって、これらの欠点を克服する。

【００１４】

【課題を解決するための手段】

本発明は、次に掲げるａ）～ｄ）を含む、電子材料の基材上に酸素含有多元金属化合物層を成長させるための方法である。

ａ）周囲条件において液体を構成する２種以上の金属－配位子錯体前駆物質の無溶媒の液体混合物を提供すること。ここで、当該配位子は同一であって、アルキル、アルコキシド、水素、アミド、イミド、アジ化物イオン、硝酸根、シクロペンタジエニル、カルボニル、並びにそれらのフッ素、酸素及び窒素置換類似物からなる群より選ばれる。

ｂ）当該無溶媒の液体混合物を、上記基材が位置している成長帯域へ送出すること。

ｃ）当該基材を成長条件下で当該無溶媒の液体混合物と接触させ、この成長条件下での接触を、化学気相成長、スプレー熱分解、ゾルーゲルプロセス、スピンコーティング及び原子層エピタキシーからなる群より選択すること。

ｄ）当該無溶媒の液体混合物から当該基材上に酸素含有多元金属化合物層を成長させること。

【００１５】

本発明は、より好ましくは、次に掲げるａ）～ｄ）を含む、電子材料の基材上に酸素含有多元金属化合物層を成長させるための方法である。

ａ）周囲条件において液体を構成する２種以上の金属－配位子錯体前駆物質の無溶媒の液体混合物を提供すること。ここで、当該前駆物質の配位子は同一であって、そしてアルキル、アルコキシド、水素、アミド、イミド、アジ化物イオン、硝酸根、シクロペンタジエニル、カルボニル、並びにそれらのフッ素、酸素及び窒素置換類似物からなる群より選ばれる。

ｂ）当該無溶媒の液体混合物を直接の液体注入によりフラッシュ蒸発帯域へ送出して当該無溶媒の液体混合物を気化させること。

ｃ）当該基材を、得られた当該無溶媒の液体混合物の蒸気と成長条件下で接触させること。

ｄ）当該無溶媒の液体混合物から当該基材上に酸素含有多元金属化合物層を成長させること。

【００１６】

好ましくは、周囲条件は４０℃以下且つ２０７ｋＰａ（ゲージ圧）（３０ｐｓｉｇ）以下である。

より好ましくは、周囲条件は２０～３０℃且つ３４～４１ｋＰａ（ゲージ圧）（５～６ｐｓｉｇ）である。

【００１７】

好ましくは、無溶媒混合物は基材上に多元金属化合物層を成長させる前に酸素源と混合される。

好ましくは、酸素源は９５＋体積％の酸素、オゾン、亜酸化窒素、酸化窒素、二酸化窒素、水、過酸化水素、空気及びそれらの混合物からなる群から選ばれる。

【００１８】

もう一つの側面において、本発明は、電子材料の基材上に多元金属化合物層を成長させるための方法であって、下記のａ）～ｄ）、すなわち、

ａ）周囲条件において液体を構成する２種以上の金属－配位子錯体前駆物質の無溶媒混合物であって、当該配位子が同一であり、且つアルキル、アルコキシド、ハロゲン、水素、アミド、イミド、アジ化物イオン、硝酸根、シクロペンタジエニル、カルボニル、並びにそれらのフッ素、酸素及び窒素置換類似物からなる群より選ばれる、無溶媒混合物を提供すること、

ｂ）当該無溶媒混合物を直接の液体注入によりフラッシュ蒸発帯域へ送出して当該無溶媒混合物を気化させること、

ｃ）当該基材を、得られた当該無溶媒混合物の蒸気と成長条件下で接触させること、
ｄ）当該無溶媒混合物から当該基材上に多元金属化合物層を成長させること、
を含み、当該基材上に当該多元金属化合物層を成長させる前に当該無溶媒混合物を窒素源と混合する、電子材料の基材上に多元金属化合物層を成長させるための方法である。
好ましくは、窒素源は窒素、アンモニア、ヒドラジン、アルキルヒドラジン、アジ化水素、アルキルアミン及びそれらの混合物からなる群から選ばれる。

【００１９】
好ましくは、無溶媒混合物から基材上に多元金属又は金属化合物層を作るための成長法は、化学気相成長、スプレー熱分解、ゾルーゲルプロセス、スピンコーティング及び原子層エピタキシーからなる群より選ばれる。

【００２０】
好ましくは、多元金属化合物層は、混合金属合金、混合金属酸化物、混合金属窒化物、混合金属炭化物、混合金属炭窒化物、混合金属酸炭窒化物、混合金属酸炭化物、混合金属硫化物、混合金属リン化物、混合金属ヒ化物、混合金属アンチモン化物、混合金属セレン化物、混合金属テルル化物及びそれらの混合物からなる群より選ばれる。

【００２１】
本発明はまた、混合金属又は金属化合物層を成長させるための組成物であって、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物を含み、当該混合物が周囲条件において液体であり、且つ当該前駆物質の配位子が、アルキル、アルコキシド、ハロゲン、水素、アミド、イミド、アジ化物イオン、硝酸根、シクロペンタジエニル、カルボニル、並びにそれらのフッ素、酸素及び窒素置換類似物からなる群より選ばれ、当該混合物は周囲条件において液体である第一の金属－配位子錯体前駆物質と、周囲条件において液体である第二の金属－配位子錯体前駆物質とを含む、混合金属又は金属化合物層の成長のための組成物である。

【００２３】
好ましくは、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物の金属は、亜鉛、カドミウム、水銀、アルミニウム、ガリウム、インジウム、タリウム、スズ、鉛、アンチモン、ビスマス、リチウム、ナトリウム、カリウム、ルビジウム、セシウム、ベリリウム、マグネシウム、カルシウム、ストロンチウム、バリウム、スカンジウム、イットリウム、ランタン、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、タンタル、クロム、モリブデン、タングステン、マンガン、テクネチウム、レニウム、鉄、ルテニウム、オスミウム、コバルト、ロジウム、イリジウム、ニッケル、パラジウム、白金、銅、銀、金、ケイ素及びセリウムからなる群より個々に選ばれる。

【００２４】
好ましくは、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物の配位子は、ジメチルアミド、ジエチルアミド、エチルメチルアミド、ブチルアミド、ジプロピルアミド、メチルプロピルアミド、エチルプロピルアミド、メトキシ、エトキシ、プロポキシ及びブトキシからなる群より選ばれる。

【００２５】
好ましくは、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物は、Ｚｒ（Ｎ（CH_2CH_3）$_2$）$_4$、Ｓｎ（Ｎ（CH_2CH_3）$_2$）$_4$及びＴｉ（Ｎ（CH_2CH_3）$_2$）$_4$を含む。
あるいはまた、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物は、Ｚｒ（Ｎ（CH_3）$_2$）$_4$、Ｓｎ（Ｎ（CH_3）$_2$）$_4$及びＴｉ（Ｎ（CH_3）$_2$）$_4$を含む。

【００２６】
更にあるいは、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物は、Ｚｒ（Ｏ（C_4H_9））$_4$、Ｓｎ（Ｏ（C_4H_9））$_4$及びＴｉ（Ｏ（C_4H_9））$_4$を含む。
更にあるいは、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物は、Ｔａ（Ｎ

（CH_3）$_2$）$_5$ 及びTi（N（CH_3）$_2$）$_4$ を含む。
更にあるいは、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物は、$CH_3CH_2N=Ta$（N（CH_2CH_3）$_2$）$_3$ 及びTi（N（CH_2CH_3）$_2$）$_4$ を含む。
更にあるいは、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物は、Al（OCH_2CH_3）$_3$ 及びTa（OCH_2CH_3）$_5$ を含む。

【００２７】

好ましくは、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物は、Si（N（CH_2CH_3）$_2$）$_4$ を含み、且つ、Ti（N（CH_2CH_3）$_2$）$_4$、Zr（N（CH_2CH_3）$_2$）$_4$、Hf（N（CH_2CH_3）$_2$）$_4$、V（N（CH_2CH_3）$_2$）$_5$、V（N（CH_2CH_3）$_2$）$_4$、Nb（N（CH_2CH_3）$_2$）$_5$、Nb（N（CH_2CH_3）$_2$）$_4$、$CH_3CH_2N=Nb$（N（CH_2CH_3）$_2$）$_3$、$CH_3CH_2N=V$（N（CH_2CH_3）$_2$）$_3$、（$CH_3CH_2N=$）$_2$W（N（CH_2CH_3）$_2$）$_2$、（$CH_3CH_2N=$）$_2$Mo（N（CH_2CH_3）$_2$）$_2$ 及び$CH_3CH_2N=Ta$（N（CH_2CH_3）$_2$）$_3$ からなる群より選ばれる金属－配位子錯体前駆物質を含む。

【００２８】

【発明の実施の形態】

多成分金属含有材料、例えば混合金属酸化物や窒化物等は、各個々の金属酸化物／窒化物成分にはない独特の物理的性質を有することがよくある。例えば、一部の混合金属酸化物は、高誘電率材料、強誘電体、高温超伝導体、触媒及び耐腐食性コーティング用に使用することができる。また、一部の混合金属窒化物は、良好な拡散バリア特性、超伝導及び磁気特性を示す。

【００２９】

電子産業では、集積回路（ＩＣ）デバイスの大きさがどんどん小さくなるにつれて、化学気相成長（ＣＶＤ）により成長させた薄膜は種々の非平坦面におけるコンフォーマルカバレージに関して物理気相成長（ＰＶＤ）法よりも有利であることを証明している。一般に、前駆物質の送出における容易さと再現性のために、ＣＶＤ用途向けには液体の前駆物質の方が好まれる。ＣＶＤ処理で使用される普通の前駆物質送出方法には、蒸気の抜き出し、キャリヤガスでのバブリング、霧滴（エーロゾル又はスプレー）での送出、そして直接の液体注入（ＤＬＩ）が含まれる。ＤＬＩは、供給元コンテナにおけるのと同じ比率の構成成分を反応器へ送出するので、多成分の送出にとって特に好ましい方法である。ＤＬＩには、前駆物質を室温で保管しそして送出しようとする必要量のみを加熱するという、従って前駆物質の保存寿命を向上させるという、追加の利点がある。

【００３０】

本発明においては、ＣＶＤ用途におけるＤＬＩを含めて、前駆物質分散送出法のために使用することができる新しい液体前駆物質混合物組成が開示される。揮発性の成分は、
１）それらが化学的に相容性であり、従って不揮発性のポリマー種又は多核種が生成されないように、
２）金属上での配位子交換のため又は配位子間反応のために沈降物が生じないように、すなわち全ての前駆物質について同一の配位子が使用される（すなわちホモレプチック（homoleptic）であり、本発明について言えば、（ＲＮ）＝ＭはＭ（NR_2）と同じであると見なされる）ように、
３）混合物が低粘度と熱安定性を維持するように、そして
４）不所望の酸化還元化学反応（例えば、$M^{+1}+M'^{+3}\rightarrow M^{+2}+M'^{+2}$）が起こらないように、
選ばれる。

【００３１】

液体混合物は、液体の金属－配位子錯体を直接混合するか、あるいは液体の金属－配位子

錯体（１種又は複数種）中に固体の金属－配位子錯体（１種又は複数種）を溶解させて、調製することができる。これらの系では、前駆物質混合物を溶解又は希釈し得られた混合物の全体を液相とするのに、溶媒は必要でなくあるいは求められない。有機溶媒を使用する広い範囲のＣＶＤ前駆物質溶液が、以前は薄膜の成長のための前駆物質として使用されていた。本発明の新しい無溶媒の前駆物質混合物は、ＣＶＤ処理後に集めるべき余計な揮発性有機媒体がないので、排気中のＣＶＤ流出物を除去する負担を軽減する。その上、ここに記載された液体混合物では溶媒を使用しないので、大きな処理量の金属含有蒸気をＣＶＤ反応器へ送出することができる。こうして、これらの新しい液体前駆物質混合物を使用するＣＶＤの全体プロセスは、従来技術の説明で述べた前駆物質溶液の液体注入による送出よりも環境に優しく且つ原価効率的である。

【００３２】

ＣＶＤ又はＭＯＣＶＤ（有機金属ＣＶＤ）のほかに、本発明の液体混合物は、原子層エピタキシー、スピンコーティング、スプレー熱分解及びゾルーゲルプロセスで処理することができる。原子層エピタキシーでは、ほぼ単層の前駆物質分子が表面に吸着される。この第一の前駆物質層の上に第二の反応物を投入し、続いてこの第二の反応物と既に表面にある第一の反応物とを反応させる。この交互の手順を繰り返して、原子の厚さに近い層でもって所望の厚さの元素又は化合物を提供する。基材の温度を制御して不所望の成長（堆積）を避けることができる。スピンコーティングでは、液体媒体を回転している基材上へ分配して、加熱又は反応等の作用により乾燥させる。スプレー熱分解では、霧滴（エーロゾル）を作り続いて前駆物質を熱的に又は光の作用で分解させる。ゾルーゲルプロセスでは、前駆物質の加水分解と縮合を行い、前駆物質は回転、浸漬又は吹き付けにより目標の基材上に付着させる。得られたアモルファスの膜を比較的低温（５００～８００℃）でアニールし、結晶化と緻密化を行う。ＤＬＩを使用するＣＶＤでは、無溶媒混合物を周囲条件で貯蔵器から液体の状態でフラッシュ蒸発帯域へ送出し、そこで無溶媒混合物を金属－配位子錯体前駆物質の気化温度、典型的に１００～５００℃まで素早く加熱する。これらは、反応室のような成長帯域において起こる様々な成長プロセスについてそれぞれの成長条件を構成する。

【００３３】

多成分前駆物質は、金属アルキル、金属アルコキシド、金属ハロゲン化物、金属水素化物、金属アミド、金属イミド、金属アジ化物、金属硝酸塩、金属シクロペンタジエニル、金属カルボニル、及びそれらのフッ素、酸素及び窒素置換類似物からなる群より選ばれるが、それらに限定はされない。好ましくは、少なくとも２種の金属－配位子錯体前駆物質の無溶媒混合物の配位子は、ジメチルアミド、ジエチルアミド、エチルメチルアミド、ブチルアミド、ジプロピルアミド、メチルプロピルアミド、エチルプロピルアミド、メトキシ、エトキシ、プロポキシ及びブトキシからなる群より選ばれる。可能性のある従来技術の配位子交換の問題を回避するために、同じであるか共通の配位子、ホモレプチック配位子を使用することが重要である。好ましくは、ホモレプチック配位子は単座配位子である。

【００３４】

金属配位子前駆物質の金属は、亜鉛、カドミウム、水銀、アルミニウム、ガリウム、インジウム、タリウム、スズ、鉛、アンチモン、ビスマス、リチウム、ナトリウム、カリウム、ルビジウム、セシウム、ベリリウム、マグネシウム、カルシウム、ストロンチウム、バリウム、スカンジウム、イットリウム、ランタン、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、タンタル、クロム、モリブデン、タングステン、マンガン、テクネチウム、レニウム、鉄、ルテニウム、オスミウム、コバルト、ロジウム、イリジウム、ニッケル、パラジウム、白金、銅、銀、金、ケイ素及びセリウムのうちの１種又は２種以上でよい。

【００３５】

２種以上の金属－配位子前駆物質の無溶媒混合物が液体でなければならない周囲条件は、一般に４０℃以下且つ２０７ｋＰａ（ゲージ圧）（３０ｐｓｉｇ）未満として定義される。好ましくは、液相の送出のための周囲条件は２０～３０℃且つ３４～４１ｋＰａ（ゲー

ジ圧）（５～６ｐｓｉｇ）である。

【００３６】

適切に選ばれた前駆物質は、酸化剤又は窒素含有反応物の存在下においては、混合金属酸化物、窒化物及び酸窒化物のいずれかをもたらす。そのほかに、適切な前駆物質混合物とＣＶＤ条件を使用して、混合金属合金、炭化物、炭窒化物、酸炭化物、酸炭窒化物、硫化物、リン化物、ヒ化物、アンチモン化物、セレン化物及びテルル化物を成長させることも可能である。酸化剤又は窒素含有反応物には、９５＋体積％の酸素、オゾン、水、過酸化水素、亜酸化窒素、酸化窒素、二酸化窒素、空気、窒素ガス、アンモニア、ヒドラジン、アルキルヒドラジン、アルキルアミン及びそれらの混合物が含まれるが、酸化剤又は窒素含有反応物はそれらには限定されない。

【００３７】

熱ＣＶＤに加えて、上記の前駆物質は、プラズマ、レーザー又は光に支援されるＣＶＤ成長、周知の成長手法のために、あるいは原子層エピタキシーにより、利用することができよう。更に、液体混合物前駆物質の適切な選択は、膜のゾルーゲルプロセス、スプレー熱分解及びスピンコーティングにも当てはめることができる。

【００３８】

少なくとも２種の金属－配位子錯体前駆物質の典型例の無溶媒混合物は、$Zr(N(CH_2CH_3)_2)_4$ と$Sn(N(CH_2CH_3)_2)_4$ と$Ti(N(CH_2CH_3)_2)_4$、又は$Zr(N(CH_3)_2)_4$ と$Sn(N(CH_3)_2)_4$ と$Ti(N(CH_3)_2)_4$、又は$Zr(O(C_4H_9))_4$ と$Sn(O(C_4H_9))_4$ と$Ti(O(C_4H_9))_4$、又は$Ta(N(CH_3)_2)_5$ と$Ti(N(CH_3)_2)_4$、又は$CH_3CH_2N{=}Ta(N(CH_2CH_3)_2)_3$ と$Ti(N(CH_2CH_3)_2)_4$、又は$Al(OCH_2CH_3)_3$ と$Ta(OCH_2CH_3)_5$、又は$Si(N(CH_2CH_3)_2)_4$ と、次の群、すなわち$Ti(N(CH_2CH_3)_2)_4$、$Zr(N(CH_2CH_3)_2)_4$、$Hf(N(CH_2CH_3)_2)_4$、$V(N(CH_2CH_3)_2)_5$、$V(N(CH_2CH_3)_2)_4$、$Nb(N(CH_2CH_3)_2)_5$、$Nb(N(CH_2CH_3)_2)_4$、$CH_3CH_2N{=}Nb(N(CH_2CH_3)_2)_3$、$CH_3CH_2N{=}V(N(CH_2CH_3)_2)_3$、$(CH_3CH_2N{=})_2W(N(CH_2CH_3)_2)_2$、$(CH_3CH_2N{=})_2Mo(N(CH_2CH_3)_2)_2$ 及び$CH_3CH_2N{=}Ta(N(CH_2CH_3)_2)_3$ からなる群より選ばれる金属－配位子錯体前駆物質、を含む。

【００３９】

【実施例】

次に、前駆物質と成長（堆積）のいくつかの比限定の例でもって、本発明を説明することにする。

【００４０】

（例１）

この例は$Zr-Sn-Ti-O_x$ 前駆物質を説明する。

１９．０ｇ（０．０５モル）の$Zr(N(CH_2CH_3)_2)_4$、２０．４ｇ（０．０５モル）の$Sn(N(CH_2CH_3)_2)_4$、及び５０．５ｇ（０．１５モル）の$Ti(N(CH_2CH_3)_2)_4$ を、不活性雰囲気下に室温で混合して、黄－オレンジ色の透明な液体混合物を得た。この混合物を１１０～１２０℃の加熱浴温度範囲において減圧下で蒸留した。これはＤＬＩ送出のために有用であることを示す。

【００４１】

（例２）

この例は$Ti-Ta-O_x$ を説明する。

$Ti-Ta-O_x$ のための金属－配位子錯体前駆物質の無溶媒液体混合物は、例１におけるのと同じやり方でもって$Ti(N(CH_3)_2)_5$（液体）に溶かしたＴａ（

$N(CH_3)_2)_5$（固体）から作ることができる。

【００４２】

（例３）

この例は$Ti-Ta-O_x$を説明する。

$Ti-Ta-O_x$のための金属－配位子錯体前駆物質の無溶媒液体混合物は、例１におけるのと同じやり方でもって$Ti(N(CH_2CH_3)_2)_4$に混合した$CH_3CH_2N=Ta(N(CH_2CH_3)_2)_3$から作ることができる。

【００４３】

（例４）

この例はAlをドープしたTaO_xを説明する。

AlをドープしたTaO_xのための金属－配位子錯体前駆物質の無溶媒液体混合物は、例１におけるのと同じやり方でもって$Al(OCH_2CH_3)_3$（固体）と$Ta(OCH_2CH_3)_5$（液体）の混合物から作ることができる。

【００４４】

（例５）

この例はＭ－Ｓｉ－Ｍを説明する。

Ｍ－Ｓｉ－Ｍのための金属－配位子錯体前駆物質の無溶媒液体混合物は、例１におけるのと同じやり方でもって、（ａ）$Si(N(CH_2CH_3)_2)_4$（液体）と（ｂ）$M(N(CH_2CH_3)_2)_x$（この式中のＭ＝Ｔｉ、Ｚｒ、Ｈｆ、Ｖ、Ｎｂであり、ｘ＝４又は５である）、あるいは（ｃ）$(R-N=)_x M'(N(CH_2CH_3)_2)_y$（この式中のＭ'＝Ｔａ、Ｎｂ、Ｗ、Ｍｏであり、Ｒ＝C_1～C_5アルキルであり、Ｍ'＝Ｔａ又はＮｂの場合ｘ＝１且つｙ＝３、Ｍ'＝Ｗ又はＭｏの場合ｘ＝ｙ＝２である）（全て液体）の混合物から作ることができる。

【００４５】

（例６）

この例はＣＶＤによる混合金属化合物の成長を説明する。

１００ｓｃｃｍの酸素流とともに１２０ｓｃｃｍのヘリウムスイープガスを使用して、気化温度が１１０℃の直接液体注入装置の、混合金属化合物膜の成長のため２４０～３００℃に保持したウエハー基材ターゲット上へ、$Zr(N(CH_2CH_3)_2)_4$、$Sn(N(CH_2CH_3)_2)_4$及び$Ti(N(CH_2CH_3)_2)_4$の金属－配位子錯体前駆物質の溶媒混合物を０．０６ｍｌ／ｍｉｎで送出した。成長は１０～３０ｎｍ（１００～３００オングストローム）／ｍｉｎであった。反応器の反応室圧力は２７０Ｐａ（２Ｔｏｒｒ）であった。これらの条件下でＣＶＤにより前駆物質混合物から成長させた膜のエネルギー分散性Ｘ線分析から、成長した膜中にＺｒ、Ｓｎ及びＴｉ金属が取り込まれることが証明された。

【００４６】

金属前駆物質を送出するための適切な液体媒体を提供するという以前の試みは、送出のために液体条件を確保するのに、選ばれた溶媒又は混合β－ジケトネート配位子の使用を必要とした。溶媒は費用を追加することになり、そして相溶性のために適切な選定をするという問題、且つまた汚染と使用後の除去という問題を引き起こす。液相での送出の目標を解決するための無溶媒の試みは、β－ジケトネート配位子を必要としたが、これらでは非液体条件に至りかねない意図しない配位子交換が問題となる。固体条件に通じる条件を回避するためにβ－ジケトネート置換基を操作しなければ、β－ジケトネート配位子はしばしば固体の金属化合物をもたらし、そうして意図しない配位子交換の結果を一層悪化させる。本発明は、ばらつきのない成長性能のために溶媒とβ－ジケトネート配位子交換の欠点を避けるため、好ましくは直接の液体注入による金属の混合物の成長用の液体状態の金属－配位子錯体において、無溶媒の、非β－ジケトネートの、単一又は共通配位子を使用することによって、これらの欠点を克服することを示した。

【００４７】

本発明はいくつかの好ましい態様に関して説明されてはいるが、本発明の完全な範囲は特

許請求の範囲の記載から確認されるべきものである。

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MANUFACTURING METHOD FOR METAL OR METAL OXIDE FINE PATTERN

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Abstract of JP2003218118 (A)

PROBLEM TO BE SOLVED: To provide a manufacturing method for a metal or a metal oxide fine pattern capable of forming a metal pattern. ;SOLUTION: The method includes the steps of (a) forming a thin film on a substrate by coating it with an organometallic compound, (b) removing the film of the organometallic compound of the unexposed part with solvent, after decomposing the organometallic compound by exposure with masks to induce difference in solubility between exposed and unexposed parts and (c) forming a metal or metal oxide pattern reducing or oxidizing the exposed part. ;COPYRIGHT: (C)2003,JPO

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最終頁に続く

(54)【発明の名称】　金属または金属酸化物微細パターンの製造方法

(57)【要約】
【課題】　金属パターン形成可能な金属または金属酸化物微細パターンの製造方法を提供すること。
【解決手段】　（ａ）有機金属化合物を基板上にコートして薄膜を形成する段階と、（ｂ）マスクを用いた露光によって前記有機金属化合物を分解させて露光部と非露光部との溶解度差を誘発させた後、溶媒を用いて前記非露光部の有機金属化合物薄膜を除去する段階と、（ｃ）前記露光部を還元または酸化処理して金属または金属酸化物パターンを形成する段階とを含む。

【特許請求の範囲】

【請求項１】　（ａ）有機金属化合物を基板上にコートして薄膜を形成する段階と、

（ｂ）マスクを用いた露光により前記有機金属化合物を分解させて露光部と非露光部との溶解度差を誘発させた後、溶媒を用いて前記非露光部の有機金属化合物薄膜を除去する段階と、

（ｃ）前記露光部を還元または酸化処理し、金属または金属酸化物パターンを形成する段階とを含む金属パターンの形成方法。

【請求項２】　前記有機金属化合物が下記化学式１で表わされることを特徴とする請求項１記載の金属パターンの形成方法。

【化１】

$$M_mL_nX_p \quad (1)$$

（式中、Ｍは遷移金属、ランタノイドまたは主族元素であり、Ｌは配位子、Ｘは１～３個の陰イオン性配位子をそれぞれ示し、ｍは１～１０の整数であって、ｍが２以上であれば、それぞれのＭは互いに異なっていてもよく、ｎは０～６０の整数であり、ｎが２以上であれば、それぞれのＬは互いに異なっていてもよく、金属が２つ以上の場合には金属と金属を連結する配位子としても作用することができ、ｐは０～６０の整数であって、ｐが２以上であれば、それぞれのＸは互いに異なっていてもよい、ただし、ｎとｐとの少なくとも一方は０ではない。）

【請求項３】　前記（ａ）段階において、前記有機金属化合物をニトリル系溶媒、脂肪族系炭化水素溶媒、芳香族系炭化水素溶媒、ケトン系溶媒、エーテル系溶媒、アセテート系溶媒、アルコール系溶媒、シリコン溶媒、またはこれらの混合物に溶解させてコートすることを特徴とする請求項１記載の金属パターンの形成方法。

【請求項４】　前記基板は無機物、有機物、または無機物と有機物との複合体であることを特徴とする請求項１記載の金属パターンの形成方法。

【請求項５】　前記（ａ）段階において、薄膜形成がスピンコート法、ロールコート法、ディップコート法、スプレーコート法、フローコート法またはスクリーンプリント法によって行われることを特徴とする請求項１記載の金属パターンの形成方法。

【請求項６】　前記（ｂ）段階が真空雰囲気下、または、空気、酸素、水素、窒素、アルゴン、もしくはこれらの混合ガス雰囲気下で行われることを特徴とする請求項１記載の金属パターンの形成方法。

【請求項７】　前記（ｂ）段階は常温または有機金属化合物の熱分解が起こらない範囲の温度である１０～８０℃で行われることを特徴とする請求項１記載の金属パターンの形成方法。

【請求項８】　前記（ｂ）段階の露光時に光源として紫外線（ＵＶ）を使用することを特徴とする請求項１記載の金属パターンの形成方法。

【請求項９】　前記（ｂ）段階において、溶媒としてニトリル系溶媒、脂肪族系炭化水素溶媒、芳香族系炭化水素溶媒、ケトン系溶媒、エーテル系溶媒、アセテート系溶媒、アルコール系溶媒、シリコン溶媒、無機溶媒、またはこれらの混合物を使用することを特徴とする請求項１記載の金属パターンの形成方法。

【請求項１０】　前記（ｃ）段階で還元または酸化処理が気相または液相反応によって行われることを特徴とする請求項１記載の金属パターンの形成方法。

【請求項１１】　前記還元処理がヒドラジン類、シラン類、アミン類及び金属水素化物類からなる群より選ばれた還元剤を使用して行われることを特徴とする請求項１記載の金属パターンの形成方法。

【請求項１２】　前記酸化処理がＮ－オキサイド類、ペルオキシド類、過安息香酸、オゾン、酸素、過酸化水素、硫酸及び硝酸からなる群より選ばれた有機または無機酸化剤によって行われることを特徴とする請求項１記載の金属パターンの形成方法。

【請求項１３】　前記（ｃ）段階が真空雰囲気または空気、酸素、水素、窒素、アルゴンもしくはこれらの混合ガス雰囲気で行われることを特徴とする請求項１記載の金属パターンの形成方法。

【請求項１４】　前記（ｃ）段階の後、３０～１０００℃の温度範囲で熱処理する段階をさらに含むことを特徴とする請求項１記載の金属パターンの形成方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、金属または金属酸化物微細パターンの製造方法に関し、より詳細には、光反応により露光部の溶解度と非露光部の溶解度とを異ならせた後、溶媒を用いて現像し、所望のパターン形成後、酸化または還元のような化学的反応によって純粋な金属または金属酸化物に転換させる、より速くて効率的な金属パターンの形成方法に関する。

【０００２】

【従来の技術】基板上に異なる電気的特性を有する材料を用いて薄膜のパターンを形成することにより、各種電子素子に適用することができる。電子素子を製造する工程において、現行の技術は結晶化されたシリコンウェーハに様々な電子的性質を有する物質を塗布して製造している。既存の金属パターン形成方法の例を挙げると、金属有機物をＣＶＤ法またはＡＬＤ法を用いてシリコンまたはガラス基板上にフィルムを形成した後、その上に感光性樹脂をスピンコート法で塗布し、光リソグラフィ法によってパターンを形成した後、別途のエッチング工程によって感光性樹脂を除去する方法がある。また、他の方法としては、プラズマ蒸着法、スパッタ法、電気メッキ法などにより基板上に金属膜を形成し、その上に感光

性樹脂を塗布した後、光を用いたパターン形成工程及びエッチング工程によって金属パターンを得る方法がある。

【０００３】前述した従来の方法はいずれも高温、高真空装置を必要とし、感光性樹脂を用いてパターンを形成する工程、及び感光性樹脂を除去するエッチング工程が必ず伴う。このような工程は一般的に多数の工程を含むため、高いコストがかかるという欠点がある。通常、各段階は、基板の表面上に感光性樹脂工程を適用した後、光、Ｘ線または電子線を照射することにより、選択領域の性質を変化させ、露光または非露光されたフォトレジスト部分を除去し、化学処理または蒸着を行う工程からなる。このような工程を数回繰返し行って最終的なパターンを形成する際、分解能の低下が欠点として指摘されている。さらに、このような工程では蒸着された物質の表面が平坦でないため、平坦化工程がさらに必要となるという欠点も含んでいる。

【０００４】これまでは、主に物理的な方法で金属を蒸着して使用することが広く用いられていたが、高い温度で金属蒸気が基質に溶け込んで生成する層が、素子の機能を妨害して性能を低下させるという欠点がある。これからは半導体工程ではより微細化されたパターンが要求され、且つ低抵抗配線が要求されると考えられるため、最近は銅配線に対する研究が活発に行われている。しかし、銅の場合、現在使用しているアルミニウムより抵抗が低いという利点があるが、シリコン基板に拡散するという欠点によって商用化が困難であるという難点がある。銀の場合、銅より抵抗が低く且つ電子移動性も小さいため、次世代配線材料として注目を浴びている。

【０００５】また、この頃に入り活発な研究が行われているフレキシブルディスプレイ、またはＴＦＴ－ＬＣＤ分野は追求する妙味があり、さらには大画面を実現するために高品質のゲート絶縁膜と低抵抗ソース／ドレーン電極領域形成技術が非常に重要である。即ち、低温で比抵抗の低い配線を使用することが重要であり、半導体工程で言及したように、コスト削減には工程の単純化が必要である。

【０００６】一方、光反応を利用しない金属パターン形成方法も提案されてきた。例えば、有機金属化合物薄膜層に電子ビームを照射して金属パターンを形成する方法が開示されているが、これは光反応によるものではない（特許文献１）。また、基板に金属有機物インクを塗布した後、レーザで加熱して熱分解反応によって金属パターンを得る方法が開示されているが、この方法では基板が高温に露出され、金属以外の物質の蒸着は許容されない（特許文献２）。

【０００７】一方、光に敏感な有機化合物が金属に配位結合して合成された有機化合物を基板上にコートした後、感光性樹脂塗布工程を経ることなく、直ちに光を照射してパターンを得る方法が開示されている（特許文献３）。前記特許文献において、有機配位子化合物としては、アセチルアセトナート、ジアルキルジチオカーバメイト、カルボキシレート、ピリジン、アミン、ジアミン、アルシン、ジアルシン、ホスフィン、ジホスフィン、アレンまたはアルコキシ配位子を使用し、ここにオキサレート、ハロゲン、水素、ヒドロキシ、シアノ、カルボニル、ニトロ、ニトレート、ニトロキシル、エチレン、アセチレン、チオシアネート、イソチオシアネート、水、アジド、カーボネイト、アミン、チオカルボニルからなる群より選ばれる１種の配位子または２種以上の配位子を結合させて有機金属化合物を合成した。前記特許文献３によれば、そのように合成された有機金属化合物を基板上に塗布した後、パターン形成したマスクに光を通過させると、光が直接有機金属化合物と反応し、金属に配位された有機配位子が分解されて脱離し、残っている金属は周囲の金属原子または大気中の酸素と反応して金属酸化膜パターンを形成する。ところが、前記方法は、配位子の殆どを光反応によって脱離させて金属または金属酸化膜を作るため、リガンド汚れ(ligand contamination)が残り、形成された酸化膜の電気伝導度を向上させるために、水素と窒素との混合ガスを流しながら、２００℃以上の高温で３０分から数時間に亘って還元処理及び表面熱処理過程を行わなければならないという問題点がある。また、この方法に使用された有機金属化合物は、立体的障害の比較的大きい配位子から構成されており、光照射によって分解する配位子の空間が大きいため、金属膜の膜厚の収縮率が増加する。その結果、前記方法による金属パターン形成の際、金属膜の収縮率が７５～９０％に至って金属膜の亀裂とひび割れが発生するという問題点がある。

【０００８】

【特許文献１】特開昭６２－２６３９７３号公報

【特許文献２】米国特許第５，０６４，６８４号明細書

【特許文献３】米国特許第５，５３４，３１２号明細書

【０００９】

【発明が解決しようとする課題】本発明は、かかる従来の技術の問題点を解決するためのもので、その目的は光反応によって露光部の溶解度と非露光部との溶解度差を誘発させた後、現像して所望のパターン形成後、酸化または還元のような化学的反応により、純粋な金属または金属酸化物に転換する、より速くて効率的な金属パターンの形成方法を提供する。

【００１０】

【課題を解決するための手段】上記目的を達成するために、本発明は、（ａ）有機金属化合物を基板上にコートして薄膜を形成する段階と、（ｂ）マスクを用いた露光により前記有機金属化合物を分解させて露光部と非露光部の溶解度差を誘発させた後、溶媒を用いて前記非露光部との有機金属化合物薄膜を除去する段階と、（ｃ）前記露光部を還元または酸化処理し、金属または金属酸化

物パターンを形成する段階とを含む金属パターンの形成方法を提供する。

【００１１】

【発明の実施の形態】以下、本発明をより詳細に説明する。

【００１２】本発明で使用される有機金属化合物は下記化学式１で表示される。

【００１３】

【化２】

$$M_mL_nX_p \quad (1)$$

【００１４】式中、Mは遷移金属、ランタノイドまたは主族元素であり、Lは配位子、Xは１～３価の陰イオン性配位子をそれぞれ示し、mは１～１０の整数であって、mが２以上であれば、それぞれのMは互いに異なっていてもよく、nは０～６０の整数であり、nが２以上であれば、それぞれのLは互いに異なっていてもよく、金属が２つ以上の場合には金属と金属を連結する配位子としても作用することができ、pは０～６０の整数であって、pが２以上であれば、それぞれのXは互いに異なっていてもよい。ただし、nとpとの少なくとも一方は０ではない。

【００１５】前記有機金属化合物中の配位子の数は金属の種類とその酸化数によって変化し、金属１個当り０～６個まで結合することができる。また、前記陰イオン性配位子の数も、金属１個当り０～６個まで結合することが可能である。

【００１６】前記有機金属化合物を構成する金属Mは、好ましくはＣｏ、Ａｇ、Ａｕ、Ｃｕ、Ｐｄ、Ｎｉ、Ｐｔ、Ｚｎ及びＣｄからなる群より選ばれる９～１２族の後遷移金属、或いはＡｌのような主族元素である。

【００１７】Lは金属Mに結合した配位子であって、Ｎ、Ｐ、Ａｓ、Ｏ、Ｓ、Ｓｅ、Ｔｅのような供与原子を有する有機配位子であり、好ましくは炭素数が２０以下の有機配位子である。具体的には、アセチルアセトナート、アセテート、β－ケトイミネート、β－ジイミネート、β－ケトエステル、ジアルキルジチオカーバメイト、カルボキシレート、オキサレート、ハロゲン、水素、ヒドロキシ、シアノ、ニトロ、ニトレート、ニトロキシル、アジド、カルボネイト、チオシアネート、イソチオシアネート、アルコキシまたはその誘導体などで例示される陰イオン性配位子、ピリジン、アミン、ジアミン、アルシン、ジアルシン、ホスフィン、ジホスフィン、アレン、カルボニル、イミダゾリリデン、エチレン、アセチレン、水、チオカルボニル、チオエーテルまたはこれらの誘導体などで例示される中性配位子を使用することができる。

【００１８】Xは陰イオン性配位子であり、前記有機金属化合物を全体的に中性に合わせる役割を果たし、金属Mに配位されていても、配位されていなくてもよい。Xが陰イオンである状態での具体例としては、ハロゲンイオン、水酸化物イオン（OH^-）、シアン化物イオン（CN^-）、亜硝酸イオン（NO_2^-）、硝酸イオン（NO_3-）、次亜硝酸イオン（NO^-）、アジ化物イオン（N_3^-）、チオシアン酸イオン、イソチオシアン酸イオン、テトラアルキルボレートイオン（BR_4^-、Ｒ＝Ｍｅ、ＥｔまたはＰｈ）、テトラハロボレートイオン（BX_4^-、Ｘ＝ＦまたはＢｒ）、ヘキサフルオロホスフェートイオン（PF_6^-）、トリフレートイオン（$CF_3SO_3^-$）、トシルイオン（Ts^-）、硫酸イオン（SO_4^{2-}）、炭酸イオン（CO_3^{2-}）などを例として挙げることができる。

【００１９】本発明において金属パターンの形成に用いられる基板の材質は、本発明の目的を阻害しない限り特に制限されず、シリコンまたはガラスのような無機物からなる基板、プラスチックのような有機物からなる基板、または無機物と有機物との複合体からなる基板などを使用することができる。

【００２０】本発明では、有機金属化合物を適当な有機溶媒に溶かしてこれを基板にコートし、有機金属化合物薄膜を形成する。その具体的なコーティング方法としては、スピンコート法、ロールコート法、ディップコート法、スプレーコート法、フローコート法またはスクリーンプリント法などを用いることが好ましく、これに制限されるものではない。この中でも、最も好ましい塗布方法はスピンコート法である。この際、使用される有機溶媒としては、特別に制限されるものではないが、アセトニトリル、プロピオニトリル、ペンタンニトリル、ヘキサンニトリル、ヘプタンニトニル、イソブチルニトリルなどのニトリル系溶媒、ヘキサン、ヘプタン、オクタン、ドデカンなどの脂肪族系炭化水素溶媒、アニソール、メシチレン、キシレンなどの芳香族系炭化水素溶媒、メチルイソブチルケトン、１－メチル－２－ピロリジノン、シクロヘキサノン、アセトンなどのケトン系溶媒、テトラヒドロフラン、ジイソブチルエーテル、イソプロピルエーテルなどのエーテル系溶媒、酢酸エチル、酢酸ブチル、プロピレングリコールメチルエーテルアセテート(propylene glycol methyl ether acetate)などのアセテート系溶媒、イソプロピルアルコール、ブチルアルコール、ヘキシルアルコール、オクチルアルコールなどのアルコール系溶媒、テトラエトキシシラン（ＴＥＯＳ）、テトラメトキシシラン（ＴＭＯＳ）などのシリコン系溶媒、またはこれらの混合物を用いることが好ましい。

【００２１】このような方法で形成された有機金属化合物の薄膜をフォトマスクを用いて露光し、有機金属化合物を分解させて露光部と非露光部との溶解度差を誘発させる。即ち、露光された部位の化合物は、元の化合物とは異なる化合物に変わるが、ＥＭＲ(electromagnetic radiation)によって、金属原子に結合されている配位子

が脱離すると、金属化合物が不安定になり、分解が加速し、金属、或いは雰囲気によっては金属酸化物に変わる。

【００２２】有機金属化合物の、前記光化学反応機構は、金属と配位子によって異なるが、一般的に次のような４つ、即ち金属から配位子への電荷移動、配位子から金属への電荷移動、ｄ軌道-ｄ軌道励起状態(d-d excitation state)及び分子内電荷移動の作用により、まず金属と配位子との結合が不安定になり、この結合が切れながら分解が起こると考えられる。このようなＥＭＲに使用される光源は制限されるものではないが、紫外線（ＵＶ）光を使用することが最も好ましい。

【００２３】本発明の重要な特徴は、有機金属化合物が光によって完全分解され、ほぼ純粋な金属または金属酸化物になるまで露光を行うのではなく、現像時に露光された部分が溶媒に溶け込んで一緒に出ない時まで露光することにより、露光時間を最小限に短縮することができることにある。露光時間の短縮は生産性の増加に繋がるので、通常、露光時間が短いほど良い。

【００２４】前記露光工程後、非露光部はコーティング時に用いた前記有機溶媒または他の溶媒を用いて溶解することができ、露光部は溶解せず残り、パターンを得ることができる。現像溶媒も前記有機溶媒を使用し、或いはテトラメチルアンモニウムヒドロキシド（ＴＭＡＨ）のような半導体工程で用いられる無機溶媒を使用しても構わず、互いに異なる溶媒を交互に使用してもよい。使用可能な有機溶媒の具体例については、コーティングに際して使用される溶媒として例示した通りであるので、ここでは記載を省略する。

【００２５】前記露光及び現像工程は、状況に応じて、真空雰囲気下、または、空気、酸素、水素、窒素、アルゴンもしくはこれらの混合ガス雰囲気下で行われることが好ましい。前記露光及び現像工程は、常温または有機金属化合物の熱分解が起こらない範囲の温度１０～８０℃で行われることが好ましい。

【００２６】現像後に確保されたパターンの組成を化学反応によって所望の金属または金属酸化物に変換することができる。この際、純粋な金属を得るために還元反応、金属酸化物を得るためには酸化反応を行う。前記還元または酸化反応は、真空雰囲気下または空気、酸素、水素、窒素、アルゴンもしくはこれらの混合ガス雰囲気下で行うことができる。

【００２７】還元剤としては有機または無機還元剤を使用することができ、好ましくは有機還元剤としてはヒドラジン類、シラン類、アミン類またはその誘導体などを使用することができる。無機還元剤としては$NaBH_4$、$LiAlH_4$などのような金属水素化物(metal hydride)を使用することができる。これら有機および無機還元剤は溶媒に溶解して使用し、或いはそれ自体使用することができる。

【００２８】酸化剤としては有機または無機酸化剤を使用することができ、好ましくはトリメチルアミンＮ－オキサイド、ピリジンＮ－オキサイドなどのＮ－オキサイド類、ビス（トリメチルシリル）ペルオキサイドなどのペルオキサイド類、過安息香酸、オゾンまたは酸素などの有機酸化剤や過酸化水素、硫酸、硝酸のような無機酸化剤などを使用する。

【００２９】前記還元または酸化処理は、気相または液相反応により、基質との反応を行うことができる。

【００３０】このような還元または酸化反応の完了後に形成されたパターンをさらに３０～１０００℃の温度範囲で熱処理し、金属パターンの基板との接着性を増加させることができる。従来の方法によれば、特に基板がプラスチックの場合には、基板の性質が熱によって変わるので熱処理が不可能である。これに対し、本発明では既に純粋な金属パターンを得ることができるので、基板の性質が変わらない温度範囲で、熱処理が可能であるという利点を有する。

【００３１】より具体的に本発明によって金属銀パターンを得る方法を、下記に示すように例を挙げて説明する。

【００３２】銀の塩を有機配位子と反応させて溶解度の良い有機銀化合物を作り、ニトリルまたはアルコール系の溶媒に溶かして基板上にスピンコートする。マスクを用いて露光する際、配位子によって露光時間が異なるが、殆どの有機配位子が３０分以上で脱離することが赤外線分光法で確認することができた。しかし、同じ化合物の場合でも、約１０分程経過すると、有機溶媒に対する溶解度は画然と差がつくので、直ちに現像を行っても、露光部分はパターンを形成して基板上に残る。さらに有機還元剤を用いて化学反応を起こすと、数十秒内に反応が完結し、光反応のみで得たパターンと比較して、一層純粋な銀のパターンを得ることができる。同様に、純粋な金属酸化物を得るために有機酸化剤を用いると、一層短時間内に反応を終わらせることができる。

【００３３】

【実施例】以下、実施例によって本発明をより詳細に説明する。下記実施例は説明するための例示に過ぎず、本発明を制限するものではない。

【００３４】製造例１：$Ag(NH_2Pr)_n(NO_3)$混合物（ｎ＝１、２、３及び４）の合成

全ての化合物を合成する際、シュレンク技術またはグローブボックス技術を用いて水分または酸素雰囲気を排除した窒素雰囲気下で行った。

【００３５】５０ｍＬの丸底シュレンクフラスコに$AgNO_3$（３．４ｇ、２０．０ｍｍｏｌ）を１５ｍＬのアセトニトリルに溶かした後、プロピルアミン（１．２ｇ、２０．３ｍｍｏｌ）をシリンジで滴加した。常温で約１時間攪拌しつつ反応させた後、０．２μｍの薄膜フィルタで沪過し、その後光を遮断し、減圧下で３～４時間に亘

って溶媒を全て除去した。光を遮断した状態で溶媒を蒸発させる間にも、化合物が不安定であって黒色の銀金属が析出することを観察できた。銀とプロピルアミンとの反応比が１：１の場合には、化合物自体が２～３時間経過すると分解し始め、分解された銀粒子が化合物の分解を加速化させるものと予測される。従って、やや過量のプロピルアミンを用いて再び反応させてみた。

【００３６】５０mLの丸底シュレンクフラスコに$AgNO_3$（３.４g、２０.０mmol）を１５mLのアセトニトリルに溶かした後、プロピルアミン（３.６g、６０.９mmol）をシリンジで滴加した。常温で約１時間撹拌しつつ反応させた後、０.２mmの薄膜フィルタで沪過し、その減圧下で過量のアミンと溶媒を全て除去した。前記１：１の場合より非常に安定な状態で存在できる反応物を得ることができた。また、溶媒を完全に除去して無色のオイルが得られた。質量スペクトル分析の結果、プロピルアミンが１～４個まで結合されている化合物が存在することを確認した。元素分析結果は銀金属とプロピルアミンが１：１.２の比率であった。これは実際銀金属とプロピルアミンが１：１で結合した化合物が主要生成物であることを示唆しているが、その化合物自体では不安定であると推測される。出発物質の反応比を１：１及び１：３として反応させて得た各化合物の^{1}H-NMRスペクトル結果は同一であり、純粋なプロピルアミンとは異なり、全ての水素の共鳴位置が少しずつ高い磁場側へ移動した。

【００３７】^{1}H-NMR(CD_3CN, ppm): 2.68 {t, 2H, N-CH_2)}, 1.49 {m, 2H, CH_2CH_3}, 0.90 {t, 3H, CH_2CH_3}

実施例１～１１：アミン配位子及び溶媒変化による還元反応の影響

前記製造例１で合成した化合物、及び配位子として各種アミンを使用して前記製造例１と同様の方法で合成した化合物をニトリルまたはアルコール溶媒にそれぞれ溶かしてスピンコートして光反応させ、還元反応性を調べた。この際、基板はガラスを使用し、光源はOriel Co.社の２００W製品の広帯域紫外線を使用した。そして、マスクを介して露光し、パターンを形成させた後、上述のものと同じ溶媒を用いて現像した。それぞれの化合物毎に光反応性に差異があったが、３０秒間の還元工程では殆ど非常に大きい反応性を見せた。その結果を表１に示す。

【００３８】実施例１～３は製造例１で製造された化合物の溶媒の変化による光反応性の差異を示すものであるが、アセトニトリル、プロピオニトリルのようなニトリル系溶媒とイソプロピルアルコールのようなアルコール系溶媒では安定性及びコーティング性に優れた。従って、アミン配位子を変化させた金属化合物（実施例４～１１）ではニトリル系溶媒を使用した。

【００３９】

【表１】

実施例	化合物*	溶媒[1]	光反応時間（分）[2]	還元剤（モル濃度/秒）	比抵抗[3]（μΩcm）
1	$Ag(H_2NPr)_x(NO_3)$	CH_3CN	5	ヒドラジン（0.1/30）	15～20
2	$Ag(H_2NPr)_x(NO_3)$	CH_3CH_2CN	5	ヒドラジン（0.1/30）	20～30
3	$Ag(H_2NPr)_x(NO_3)$	IPA	5	ヒドラジン（0.1/30）	15～20
4	$Ag(H_2NBu)_n(NO_3)$	CH_3CN	5	ヒドラジン（0.1/30）	15～20
5	$Ag(C_2H_5CH(NH_2)CH_3)_2(NO_3)$	CH_3CN	10	ヒドラジン（0.1/30）	40～200
6	$Ag(aniline)_2(NO_3)$	CH_3CN	10	ヒドラジン（0.1/30）	～2000
7	$Ag(TMEDA)_2(NO_3)$	CH_3CN	1	ヒドラジン（0.1/30）	～100
8	$Ag(t\text{-}BuNH_2)_2(NO_3)$	CH_3CN	5	ヒドラジン（0.1/30）	20～30
9	$Ag(Py)_2(NO_3)$	CH_3CN	10	ヒドラジン（0.1/30）	～300
10	$Ag(NH_2C_5H_4OH)_2(NO_3)$	CH_3CN	10	ヒドラジン（0.1/30）	～100
11	$Ag(NH(C_2H_4OH)_2)_2(NO_3)$	C_2H_5OH	5	ヒドラジン（0.1/30）	20～30

【００４０】１）溶媒はコーティング溶媒を意味し、光反応後に現像溶媒として同じ溶媒を使用した。

【００４１】２）光反応時間は現像時に露光部位がほぼ脱離されない時まで露光を行う時間を意味し、この時間が短いほど光感度に優れる。

【００４２】３）比抵抗値は４端子プローブで測定した値である。

【００４３】*Pr=プロピル基、IPA=イソプロピルアルコール、Bu=ブチル基、TMEDA=テトラメチルエチレンジアミン、Py=ピリジン

光反応後にヒドラジン／アセトニトリル０.１M溶液下で還元反応させた結果、常温、常圧、空気雰囲気下で純粋な金属（銀）パターンを得ることができた。コーティング溶媒によっては光反応性及び還元反応性に差が殆ど

なかったが、アミン配位子の種類によっては若干の差異があることが分った。即ち、アミンが空間的に大きいか或いは炭素数が多ければ、光反応時間も長くなり、還元反応も遅く起こることを確認した。本還元反応は還元剤を気状にして行っても類似の様相を見せた。

製造例2：$Ag(NH_2Pr)_n(NO_3)$混合物（n＝1、2、3及び4）の合成

50mLの丸底シュレンクフラスコに$AgNO_3$（3.08g、20.0mmol）を15mLのアセトニトリルに溶かした後、プロピルアミン（3.6g、60.9mmol）をシリンジで滴加した。常温で約1時間攪拌しつつ反応させた後、0.2μmの薄膜フィルタで沪過し、その後減圧下で過量のアミンと溶媒を全て除去した。溶媒を完全に除去して透明な黄色のオイルが得られた。^{1}H-NMRスペクトル結果は製造例1による化合物と似ていた。

【0044】^{1}H-NMR(CD_3CN, ppm): 2.68 [t, 2H, N-CH_2)], 1.49 [m, 2H, CH_2CH_3], 0.90 [t, 3H, CH_2CH_3]

実施例12～20：陰イオン性配位子または配位子変化による還元反応の影響

製造例2で合成した化合物、及び配位子と陰イオン性配位子を変化させながら製造例1と同様の方法で合成した化合物をニトリルまたはアルコール溶媒に溶かしスピンコートして光反応させ、還元反応性を調べた。この際、基板はガラスを使用し、光源はOriel Co.社の200W製品の広帯域紫外線を使用した。そして、マスクを介して露光してパターンを形成させた後、同じ溶媒を用いて現像した。それぞれの化合物毎に光反応性に大きい差を示した。さらに、還元工程でも陰イオン性配位子の差異によって反応性が大きく異なることが分った。その結果を表2に示す。

【0045】

【表2】

実施例	化合物*	溶媒[1]	光反応時間(分)[2]	還元剤(モル濃度/秒)	比抵抗[3](μΩcm)
12	$Ag(H_2NPr)_n(NO_3)$	CH_3CN	3	ヒドラジン(0.01/10)	15～20
13	$Ag(H_2NPr)_n(NO_3)$	CH_3CH_2CN	3	ヒドラジン(0.01/10)	20～30
14	$Ag(H_2NPr)_n(NO_3)$	IPA	3	ヒドラジン(0.01/10)	15～20
15	$Ag(H_2NBu)_2(NO_3)$	CH_3CN	3	ヒドラジン(0.01/30)	15～20
16	$Ag(H_2NPr)_n(BF_4)$	CH_3CN	10	ヒドラジン(0.01/30)	～3000
17	$Ag(H_2NPr)$(Acac)	CH_3CN	30	ヒドラジン(0.01/30)	
18	$Ag(H_2NPr)$(DBM)	CH_3CN	30	ヒドラジン(0.01/30)	
19	$Ag(H_2NPr)$(Ac)	CH_3CN	30	ヒドラジン(0.01/30)	
20	$Ag(H_2NPr)_2(N_3)$	CH_3CN	30	ヒドラジン(0.01/30)	

【0046】1）溶媒はコーティング溶媒を意味し、光反応後に現像溶媒として同じ溶媒を使用した。

【0047】2）光反応時間は現像時に露光部位がほぼ脱離しなくなるまで露光を行う時間を意味し、この時間が短いほど光感度に優れる。

【0048】3）比抵抗値は4端子プローブで測定した値である。

【0049】*Acac=アセチルアセトネート、IPA=イソプロピルアルコール、Bu=ブチル基、DBM=ジベンゾイルメタン、Ac=アセテート

実施例12～14は製造例2で合成した化合物の溶媒変化による光反応性の差異を示すものであるが、アセトニトリル、プロピオニトリル及びイソプロピルアルコールのいずれにおいても光反応性に優れており、還元剤の濃度を低くしても（ヒドラジン／アセトニトリル0.01M溶液）還元がよく発生して純粋な金属のパターンを得ることができた。

【0050】即ち、製造例1による$Ag(NH_2Pr)_n(NO_3)$化合物よりも製造例2による$Ag(NH_2Pr)_n(NO_3)$が光反応性に優れ且つ溶解度も良いため、現像時に解像度の良いパターンを得られた。また$Ag(NH_2Pr)_n(NO_3)$を用いて陰イオン性配位子Xまたは配位子Lを変化させながら光反応性と還元反応性を調べた。陰イオン性配位子X がBF_4^-である実施例16は、光反応性は多少劣るが、ガラス基板に対する接着力は非常に増加した。実施例17～20は光反応性が$Ag(NH_2Pr)_n(NO_3)$または$Ag(NH_2Pr)_n(NO_3)$化合物よりも非常に遅く、測定の結果、金属パターンの比抵抗値もメガオーム水準であったが、伝導性のある金属（銀）パターンが得られたことを確認した。

実施例21～27:金属種類及び還元剤の変化による還元反応の影響

有機金属化合物を、金属の種類及び還元剤の種類を変化させつつ光反応性及び還元反応性を調べた。この際、基

板はガラスを使用し、光源はOriel Co.社の２００Ｗ製品の広帯域紫外線を使用した。そして、マスクを介して露光し、薄膜を形成させた後、還元反応を試みた。その結果を表３に示す。

【００５１】

【表３】

実施例	化合物	溶媒[1]	光反応時間(分)[2]	還元剤（モル濃度/秒）	比抵抗[3]（μΩcm）
21	$Ag(H_2NPr)_n(NO_3)$	CH_3CN	5	$LiAlH_4$/THF (0.1/30)	30～40
22	$Ag(H_2NPr)_n(NO_3)$	CH_3CN	3	$LiAlH_4$/THF (0.1/30)	20～30
23	$Ag(H_2NPr)_n(NO_3)$	CH_3CN	3	$(MeO)_3SiH$ (0.5/30)	200～220
24	$Cu(H_2NPr)_n(NO_3)_2$	CH_3CN	30	ヒドラジン (0.1/30)	-
25	$Au(H_2NPr)_n(CN)$	CH_3CN	30	ヒドラジン (0.01/30)	20～30
26	$Au(H_2NPr)_n(Cl)$	CH_3CN	30	ヒドラジン (0.01/30)	-
27	$Co(Acac)_2$	CH_3CN	30	ヒドラジン (0.01/30)	-

【００５２】１）溶媒とはコーティング溶媒を意味し、光反応後に現像溶媒として同じ溶媒を使用した。

【００５３】２）光反応時間は最大３０分とし、光感度に優れる場合は時間を短くし還元反応性を調べた。

【００５４】３）比抵抗値は４端子プローブで測定した。

【００５５】実施例２１～２３は還元剤としてＬｉＡｌH_4とトリメトキシシランを用いた場合であるが、ヒドラジンを用いた場合より還元反応性がやや劣っている。

【００５６】実施離２４～２７は銀以外の金属、即ち銅、金、コバルト化合物の光反応性及び還元反応性を実験したものである。銅及びコバルト化合物の光反応性は銀または金化合物に比べて低かった。測定の結果、比抵抗値も３～４メガオーム水準であったが、伝導性のある金属（銀）パターンが得られたことを確認した。実施例２５の$Au(H_2NPr)_nCN$化合物の場合には銀の如きヒドラジン条件で還元反応がよく起こり、２０～３０μΩｃｍの非常に低い比抵抗値を示した。

【００５７】

【発明の効果】本発明によれば、既存の物理的蒸着方法ではなく、簡単なコーティング方法を用いて有機金属化合物薄膜を形成させた後、感光性樹脂を使用せず露光及び酸化剤または還元剤を処理する化学反応を用いて短時間内に効率よく純粋な金属または金属酸化物パターンを得る方法を提供することができる。

フロントページの続き

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TIN OXIDE FILM FORMER, TIN OXIDE FILM FORMATION METHOD USING IT, AND TIN OXIDE FILM FORMED BY IT

Inventor(s): OKADA TAKAYUKI; SASAOKA SHINICHI ± (OKADA TAKAYUKI, ; SASAOKA SHINICHI)

Applicant(s): NITTO KASEI CO LTD ± (NITTO KASEI CO LTD)

Classification: **- international:** ***C01G19/02; H01B13/00; H01B5/14***
- cooperative:

Application number: JP20060270898 20061002 Global Dossier

Priority number (s): JP20060270898 20061002

Abstract of JP2008091215 (A)

PROBLEM TO BE SOLVED: To provide a tin oxide film former capable of forming a tin oxide film at low temperatures. ;SOLUTION: This tin oxide film former contains at least one kind out of organic tin compounds comprising: (1) a compound formed of one tin atom bonded to (p) organic groups each having a double bond at the [beta]-position (when p is 2-4, the organic groups are identical or different from one another), any one kind within (m) halogen atoms, hydroxyl groups, alkoxy groups and acyloxy groups, and any one kind within (n) halogen atoms, hydroxyl groups, alkoxy groups and acyloxy groups (p is an integer of 1-4, m and n are each an integer of 0-3, and p+m+n=4); (2) a compound formed of one tin atom bonded to two organic groups each having a double bond at the [beta]-position, and an oxygen atom bonded by one double bond; and (3) a compound formed of one tin atom bonded to one organic group having a double bond at the [beta]-position, an oxygen atom bonded by one double bond, and one hydroxyl group; wherein the organic groups in (1), (2) and (3) are identical or different from one another. ;COPYRIGHT: (C)2008,JPO&INPIT

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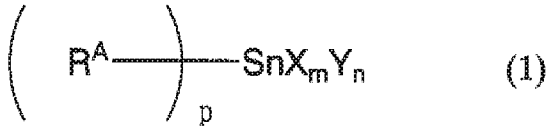
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最終頁に続く

(54)【発明の名称】酸化錫膜形成剤、該酸化錫膜形成剤を用いる酸化錫膜形成方法、及び該形成方法により形成される酸化錫膜

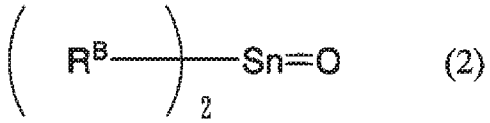
(57)【要約】　（修正有）
【課題】低温で酸化錫膜を形成することができる酸化錫膜形成剤を提供する。
【解決手段】（１）ｐ個のβ位に二重結合を有する有機基（ｐが２～４の場合有機基は同じでも異ってもよい）とｍ個のハロゲン原子、水酸基、アルコキシ基又はアシルオキシ基のうちいずれか１種及びｎ個のハロゲン原子、水酸基、アルコキシ基又はアシルオキシ基のうちいずれか１種と結合した１個の錫原子よりなる化合物（ｐは１～４、ｍ及びｎは０～３の整数を示し、ｐ＋ｍ＋ｎ＝４である）（２）２個のβ位に二重結合を有する有機基及び１個の二重結合で結ばれた酸素原子と結合した１個の錫原子よりなる化合物（３）１個のβ位に二重結合を有する有機基と１個の二重結合で結ばれた酸素原子及び１個の水酸基と結合した１個の錫原子よりなる化合物（（１），（２），（３）中の有機基はそれぞれ同一または異なる）の有機錫化合物を少なくとも１種含有する酸化錫形成剤。
【選択図】なし

【特許請求の範囲】
【請求項1】
下記一般式（１）：
【化1】



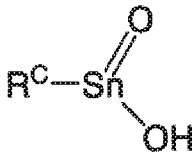
(1)

下記一般式（２）：
【化2】



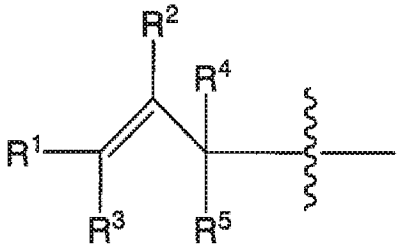
(2)

並びに、下記一般式（３）：
【化3】



(3)

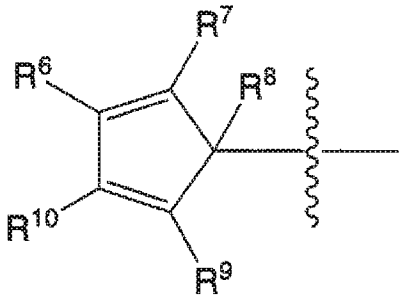
（一般式（１）、（２）及び（３）中、R^A、R^B及びR^Cは、それぞれ同一又は異なって、β位に二重結合を有する有機基を示し、ｐが２～４の整数の場合、R^Aは、同一又は異なっていてもよく、Ｘ及びＹは、それぞれ同一又は異なって、ハロゲン原子、水酸基、アルコキシ基又はアシルオキシ基を示し、ｐは１～４の整数を示し、ｍ及びｎは０～３の整数を示し、ｐ＋ｍ＋ｎ＝４である。）
で表される有機錫化合物を少なくとも１種含有する酸化錫膜形成剤。
【請求項2】
前記有機基が、下記一般式（４）
【化4】



(4)

（式中、R^1、R^2、R^3、R^4及びR^5は、同一又は異なって、水素原子又は炭素数１～１２の炭化水素基を示す。）
の炭化水素基、或いは、下記一般式（５）：

【化5】



(5)

（式中、Ｒ６、Ｒ７、Ｒ８、Ｒ９及びＲ１０は、同一又は異なって、水素原子又は炭素数１～１２の炭化水素基を示す。）
の炭化水素基である請求項１に記載の酸化錫膜形成剤。
【請求項3】
請求項１又は２に記載の酸化錫膜形成剤を含む溶液を基材に塗布した後、２００℃以下で熱処理することを特徴とする酸化錫膜形成方法。
【請求項4】
請求項３に記載の酸化錫膜形成方法により形成される酸化錫膜。
【発明の詳細な説明】
【技術分野】
【0001】
本発明は、酸化錫膜形成剤、該酸化錫膜形成剤を用いる酸化錫膜形成方法、及び該形成方法により形成される酸化錫膜に関する。
【背景技術】
【0002】
酸化錫薄膜は、電子デバイスの電極、光学膜等の様々な用途に使用される。このような用途に用いられる酸化錫薄膜には、一般的に透明性が高く、かつ電気特性が均一であることが求められている。従来より、酸化錫薄膜の基板としてはガラス基板が通常使用されている。
【0003】
近年、酸化錫薄膜が多用されるプラズマディスプレイや液晶ディスプレイの分野、太陽電池の分野等において、デバイスの大型化に伴い、酸化錫薄膜の大面積化が要求されている。
【0004】
しかし、酸化錫薄膜の基板としてガラス基板を使用する場合、酸化錫薄膜の大面積化に伴い重量増加、価格増加等の問題がある。そこで、酸化錫薄膜をプラスチック基板上に堆積することにより、安価で軽いディスプレイ、赤外線反射膜、タッチパネル等の開発が積極的に取り組まれている。
【0005】
一方、酸化錫薄膜の形成方法として、上記膜特性の安定性及び透明性を確保するため、従来からイオンビーム法、スパッタリング法等の物理的方法が用いられている。
【0006】
しかし、これらの手法を用いて大画面のデバイスを得るためには、より大型で且つ精密な高真空加工装置が必要となる。かかる装置を用いる場合、高い加工エネルギーが必要となるためランニングコストが高くなる。また、膜形成工程が複雑化することにより該工程に必要とされる種々の装置を設置するための広い敷地面積を要するという問題がある。しかも、高真空加工装置は非常に高価である。
【0007】
上記観点から、特に大画面かつ高性能な酸化錫薄膜を得るために、上述した物理的方法

を用いたプロセスに代わる新しい酸化錫薄膜の形成プロセスの検討が行われている。

【0008】

その代替方法として最も有望視されているのが、薄膜形成の際に複雑な装置や工程が不要な熱分解法である。

【0009】

熱分解法としては、基板上に、錫化合物、特にアルキル錫化合物やカルボン酸錫塩などを含む塗布液を塗布して薄膜を形成し、これを熱分解して酸化錫薄膜を形成する方法が一般的である。

【0010】

アルキル錫化合物やカルボン酸錫塩などを塗布して酸化錫薄膜を形成する方法として、例えば、ジブチル錫ジアセテートを含む塗布液、又はテトラブチル錫を含む塗布液を基板上に塗布して薄膜を形成し、これを焼成する方法が開示されている（特許文献１参照）。また、カルボン酸錫塩を含む塗布液、或いはカルボン酸錫塩と塩化パラジウム又は塩化白金酸とを含む塗布液を基板上に塗布して薄膜を形成し、これを焼成する方法も開示されている（特許文献２参照）。

【0011】

しかしながら、上記のようなアルキル錫化合物やカルボン酸錫塩などを塗布して酸化錫薄膜を形成する方法は、有機基と錫原子との結合を切るのに高い温度を要し、酸化錫薄膜に有機成分が残存しないように、さらに、高温で後焼成する必要がある。そのため、基材に相当な熱的負荷がかかる。よって、この方法を採用する場合、使用できる基材が、ガラスやポリイミド、ポリアリレート等の耐熱性の良いポリマー素材からなる基材に限定されるという問題がある。

【0012】

この問題を解消する方法として、テトラブチル錫又は塩化第二錫を含む塗布液に熱分解促進剤として過酸化水素を使用することにより分解温度の低温化を図る方法が開示されているが（特許文献３）、この方法でも分解温度は３００℃程度であり、使用できる基材が未だ限定されている。

【0013】

よって、酸化錫薄膜の大面積化に伴い、汎用のポリマー素材の基板に対して熱分解法により酸化錫薄膜を形成する際に、さらに低温で分解する錫化合物からなる酸化錫膜形成剤の開発が切望されている。

【特許文献1】特開平７－３３０３３６号公報

【特許文献2】特開昭６０－８１７０４号公報

【特許文献3】特開２００２－１４６５３６号公報

【発明の開示】

【発明が解決しようとする課題】

【0014】

本発明は、低温で酸化錫膜を形成することができる酸化錫膜形成剤を提供することを主な目的とする。

【課題を解決するための手段】

【0015】

発明者らは、上記目的を達成するために鋭意研究を重ねた結果、特定の有機錫化合物を含有する酸化錫膜形成剤が上記目的を達成できることを見出し、本発明を完成するに至った。

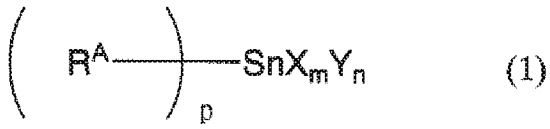
【0016】

すなわち、本発明は下記の酸化錫膜形成剤に係る。

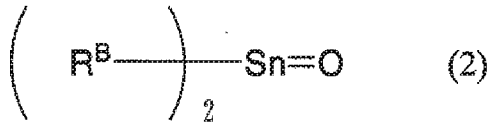
１．　下記一般式（１）：

【0017】

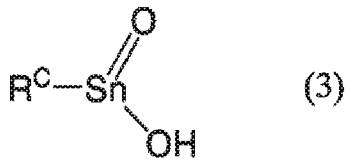
【化1】



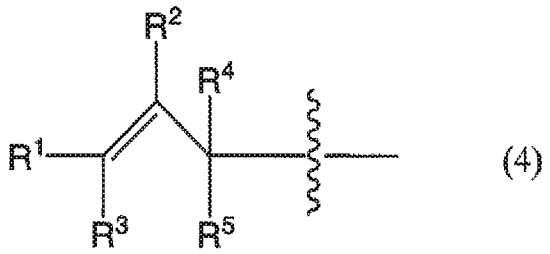
【0018】
下記一般式（２）：
【0019】
【化2】



【0020】
並びに、下記一般式（３）：
【0021】
【化3】



【0022】
（一般式（１）、（２）及び（３）中、R^A、R^B及びR^Cは、それぞれ同一又は異なって、β位に二重結合を有する有機基を示し、ｐが２～４の整数の場合、R^Aは、同一又は異なっていてもよく、Ｘ及びＹは、それぞれ同一又は異なって、ハロゲン原子、水酸基、アルコキシ基又はアシルオキシ基を示し、ｐは１～４の整数を示し、ｍ及びｎは０～３の整数を示し、ｐ＋ｍ＋ｎ＝４である。）
で表される有機錫化合物を少なくとも１種含有する酸化錫膜形成剤。
２．　前記有機基が、下記一般式（４）：
【0023】
【化4】

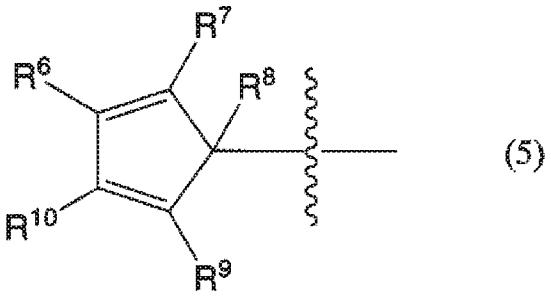


【0024】
（式中、R^1、R^2、R^3、R^4及びR^5は、同一又は異なって、水素原子又は炭素数１～１２の炭化水素基を示す。）

の炭化水素基、或いは、下記一般式（５）：

【0025】

【化5】



(5)

【0026】

（式中、Ｒ^{6}、Ｒ^{7}、Ｒ^{8}、Ｒ^{9}及びＲ^{10}は、同一又は異なって、水素原子又は炭素数１～１２の炭化水素基を示す。）

の炭化水素基である上記項１に記載の酸化錫膜形成剤。

３．　上記項１又は２に記載の酸化錫膜形成剤を含む溶液を基材に塗布した後、２００℃以下で熱処理することを特徴とする酸化錫膜形成方法。

４．　上記項３に記載の酸化錫膜形成方法により形成される酸化錫膜。

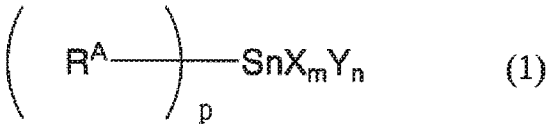
【0027】

酸化錫膜形成剤

本発明の酸化錫膜形成剤は、一般式（１）：

【0028】

【化6】



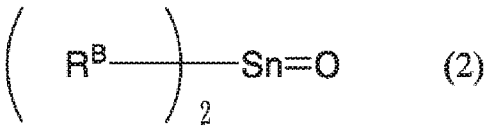
(1)

【0029】

一般式（２）：

【0030】

【化7】



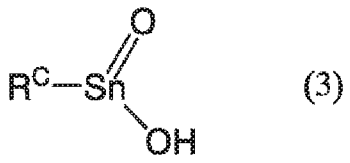
(2)

【0031】

並びに、一般式（３）：

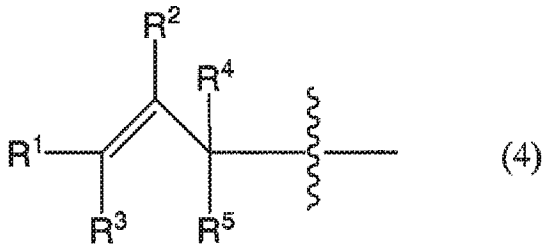
【0032】

【化8】



(3)

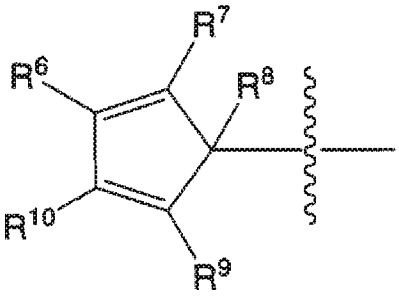
【0033】
（一般式（１）、（２）及び（３）中、R^A、R^B及びR^Cは、それぞれ同一又は異なって、β位に二重結合を有する有機基を示し、ｐが２～４の場合、R^Aは、同一又は異なっていてもよく、Ｘ及びＹは、それぞれ同一又は異なって、ハロゲン原子、水酸基、アルコキシ基又はアシルオキシ基を示し、ｐは１～４の整数を示し、ｍ及びｎは０～３の整数を示し、ｐ＋ｍ＋ｎ＝４である。）
で表される有機錫化合物を少なくとも１種含有する。
【0034】
本発明の酸化錫膜形成剤は、有機錫化合物を含有する。特に、本発明において、前記有機錫化合物は、錫原子に、β位に二重結合を有する有機基が結合してなるものである。本発明の酸化錫膜形成剤を用いて酸化錫膜を形成する際、低い温度（２００℃以下）で有機成分を分解・除去することができる。
【0035】
本発明の酸化錫膜形成剤は、一般式（１）、（２）及び（３）で表される有機錫化合物を、任意の割合で混合して使用できる。
【0036】
β位に二重結合を有する有機基としては、特に限定されないが、主に、下記一般式（４）：
【0037】
【化9】



(4)

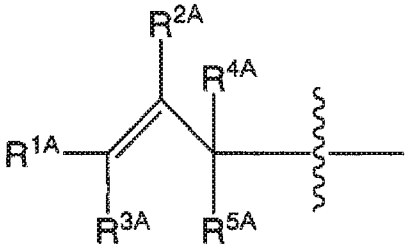
【0038】
（式中、R^1、R^2、R^3、R^4及びR^5は、同一又は異なって、水素原子又は炭素数１～１２の炭化水素基を示す。）
の炭化水素基、或いは、下記一般式（５）：
【0039】

【化10】



(5)

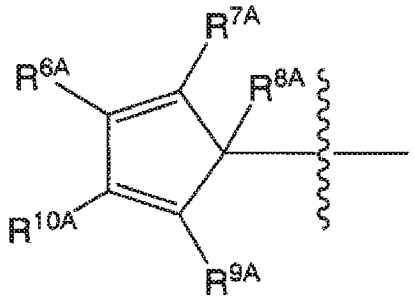
【0040】
（式中、R^6、R^7、R^8、R^9及びR^{10}は、同一又は異なって、水素原子又は炭素数１～１２の炭化水素基を示す。）
の炭化水素基を挙げることができる。
【0041】
以下、β位に二重結合を有する有機基について、上記一般式（４）又は（５）の有機基を代表例として本発明の酸化錫膜形成剤、酸化錫膜形成方法及び酸化錫膜について具体的に説明する。
なお、本発明では、上記有機錫化合物そのものを酸化錫膜形成剤としてもよいし、上記有機錫化合物及び公知の添加剤からなる混合物を酸化錫膜形成剤としてもよい。公知の添加剤としては、例えば、トリフルオロ酢酸、フッ化アンモニウム、フッ化水素、三塩化アンチモン、三フッ化アンチモン、トリエトキシアンチモン、オクチル酸アンチモン等が挙げられる。
【0042】
一般式（１）で表される有機錫化合物
上記一般式（１）で表される有機錫化合物中、R^Aは、下記一般式（４Ａ）又は（５Ａ）のβ位に二重結合を有する有機基を示し、R^Aを２以上含む場合、同一又は異なっていてもよい。
【0043】
【化11】



(4A)

【0044】

【化12】



(5A)

【0045】

一般式（４Ａ）中、Ｒ１Ａ、Ｒ２Ａ、Ｒ３Ａ、Ｒ４Ａ及びＲ５Ａは、同一又は異なって、水素原子又は炭素数１～１２の炭化水素基を示す。炭化水素基としては、直鎖若しくは分岐鎖若しくは環状のアルキル基、アルケニル基、又はアリール基が挙げられる。

【0046】

特に、Ｒ１Ａ、Ｒ２Ａ、Ｒ３Ａ、Ｒ４Ａ及びＲ５Ａとしては、水素原子、炭素原子数１～６の直鎖若しくは分岐鎖若しくは環状のアルキル基、アルケニル基、又はアリール基が好ましい。炭素原子数１～６の直鎖、分岐鎖又は環状のアルキル基或いはアルケニル基及びアリール基としては、例えば、メチル基、エチル基、ｎ－プロピル基、ｉｓｏ－プロピル基、ｎ－ブチル基、ｉｓｏ－ブチル基、ｔｅｒｔ－ブチル基、ビニル基、アリル基、イソプロペニル基、ブテニル基、フェニル基、シクロヘキシル基等が挙げられる。

【0047】

本発明においては、Ｒ４Ａ及びＲ５Ａは、水素原子であることが好ましい。

【0048】

一般式（５Ａ）中、Ｒ６Ａ、Ｒ７Ａ、Ｒ８Ａ、Ｒ９Ａ及びＲ１０Ａは、同一又は異なって、水素原子又は炭素数１～１２の炭化水素基を示す。炭化水素基としては、直鎖若しくは分岐鎖若しくは環状のアルキル基、アルケニル基、又はアリール基が挙げられる。

【0049】

Ｒ６Ａ、Ｒ７Ａ、Ｒ８Ａ、Ｒ９Ａ及びＲ１０Ａとしては、特に、水素原子、炭素原子数１～６の直鎖若しくは分岐鎖若しくは環状のアルキル基、アルケニル基、又はアリール基が好ましく、水素原子がより好ましい。炭素原子数１～６の直鎖、分岐鎖又は環状のアルキル基或いはアルケニル基及びアリール基としては、メチル基、エチル基、ｎ－プロピル基、ｉｓｏ－プロピル基、ｎ－ブチル基、ｉｓｏ－ブチル基、ｔｅｒｔ－ブチル基、ビニル基、アリル基、イソプロペニル基、ブテニル基、フェニル基、シクロヘキシル基等が挙げられる。

【0050】

一般式（１）中、Ｘ及びＹは、それぞれ同一又は異なって、ハロゲン原子、水酸基、アルコキシ基又はアシルオキシ基を示す。

【0051】

ハロゲン原子としては、フッ素原子、塩素原子、臭素原子又はヨウ素原子が挙げられる。この中でも、特に塩素原子が好ましい。

【0052】

アルコキシ基としては、例えばメトキシ基、エトキシ基、ｎ－プロポキシ基、ｉｓｏ－プロポキシ基、ｎ－ブトキシ基、ｉｓｏ－ブトキシ基、ｔｅｒｔ－ブトキシ基、２－エチルヘキシルオキシ基、ｎ－オクチルオキシ基、シクロヘキシルオキシ基、フェノキシ基等が挙げられる。

【0053】

アシルオキシ基としては、アセトキシ基、プロパノイルオキシ酸残基、ピバロイルオキシ基、ヘキサノイルオキシ基、オクタノイルオキシ基、ベンゾイルオキシ基等が挙げられ

る。この中でも、特にアセトキシ基及びピバロイルオキシ基が好ましい。

【0054】

一般式（１）中、ｐは１～４の整数を示し、ｍ及びｎは０～３の整数を示す。また、ｐ、ｍ及びｎは、ｐ＋ｍ＋ｎ＝４の条件を満たすものである。

【0055】

一般式（１）で表される有機錫化合物の具体例を下記１）～１１）に示す。

【0056】

１）ｍ＝０、ｎ＝０のとき、すなわち、$(R^A)_4Sn$の場合

ａ）R^Aが一般式（４Ａ）で表される有機基の場合

例えば、テトラアリル錫、テトラメタリル錫、テトラクロチル錫、テトラプレニル錫等が挙げられる。

【0057】

ｂ）R^Aが一般式（５Ａ）で表される有機基の場合

例えば、テトラシクロペンタジエニル錫、テトラキス（ペンタメチルシクロペンタジエニル）錫、テトラキス（２，５－ジメチルシクロペンタジエニル）錫等が挙げられる。

【0058】

２）ｍ＝１、Ｘ＝ハロゲン原子、ｎ＝０、又は、ｍ＝０、ｎ＝１、Ｙ＝ハロゲン原子のとき、すなわち、$(R^A)_3SnD$（式中、Ｄは、上記ハロゲン原子として例示したものと同様）の場合

ａ）R^Aが一般式（４Ａ）で表される有機基の場合

例えば、トリアリル錫クロライド、トリメタリル錫クロライド、トリクロチル錫クロライド、トリプレニル錫クロライド、トリアリル錫ブロマイド、トリメタリル錫ブロマイド、トリクロチル錫ブロマイド、トリプレニル錫ブロマイド等が挙げられる。

【0059】

ｂ）R^Aが一般式（５Ａ）で表される有機基の場合

例えば、トリシクロペンタジエニル錫クロライド、トリシクロペンタジエニル錫ブロマイド等が挙げられる。

【0060】

３）ｍ＝１、Ｘ＝アルコキシ基、ｎ＝０、又は、ｍ＝０、ｎ＝１、Ｙ＝アルコキシ基のとき、すなわち、$(R^A)_3SnOR^D$（式中、R^Dは、炭素原子数１～６の直鎖または分岐鎖または環状のアルキル基、アルケニル基あるいはアリール基を示す）の場合

ａ）R^Aが一般式（４Ａ）で表される有機基の場合

例えば、トリアリル錫メトキシド、トリメタリル錫メトキシド、トリクロチル錫メトキシド、トリプレニル錫メトキシド、トリアリル錫エトキシド、トリメクリル錫エトキシド、トリクロチル錫エトキシド、トリプレニル錫エトキシド、トリアリル錫ｎ－プロポキシド、トリメクリル錫ｎ－プロポキシド、トリクロチル錫ｎ－プロポキシド、トリプレニル錫ｎ－プロポキシド、トリアリル錫ｉｓｏ－プロポキシド、トリメタリル錫ｉｓｏ－プロポキシド、トリクロチル錫ｉｓｏ－プロポキシド、トリプレニル錫ｉｓｏ－プロポキシド、トリアリル錫ｎ－ブトキシド、トリメタリル錫ｎ－ブトキシド、トリクロチル錫ｎ－ブトキシド、トリプレニル錫ｎ－ブトキシド、トリアリル錫ｔｅｒｔ－ブトキシド、トリメタリル錫ｔｅｒｔ－ブトキシド、トリクロチル錫ｔｅｒｔ－ブトキシド、トリプレニル錫ｔｅｒｔ－ブトキシド、トリアリル錫フェノキシド、トリメタリル錫フェノキシド、トリクロチル錫フェノキシド、トリプレニル錫フェノキシド等が挙げられる。

【0061】

ｂ）R^Aが一般式（５Ａ）で表される有機基の場合

例えば、トリシクロペンタジエニル錫メトキシド、トリシクロペンタジエニル錫エトキシド、トリシクロペンタジエニル錫ｎ－プロポキシド、トリシクロペンタジエニル錫ｉｓｏ－プロポキシド、トリシクロペンタジエニル錫ｎ－ブトキシド、トリシクロペンタジエニル錫ｔｅｒｔ－ブトキシド、トリシクロペンタジエニル錫フェノキシド等が挙げられる。

【0062】
４）ｍ＝１、Ｘ＝アシルオキシ基、ｎ＝０、又は、ｍ＝０、ｎ＝１、Ｙ＝アシルオキシ基のとき、すなわち、$(R^A)_3SnOCOR^E$（式中、R^Eは、水素原子、炭素原子数１～１８の直鎖または分岐鎖または環状のアルキル基、アルケニル基あるいはアリール基を示す）の場合
ａ）R^Aが一般式（４Ａ）で表される有機基の場合
トリアリル錫フォルメート、トリメタリル錫フォルメート、トリクロチル錫フォルメート、トリプレニル錫フォルメート、トリアリル錫アセテート、トリメタリル錫アセテート、トリクロチル錫アセテート、トリプレニル錫アセテート、トリアリル錫プロピオネート、トリメタリル錫プロピオネート、トリクロチル錫プロピオネート、トリプレニル錫プロピオネート、トリアリル錫ブチレート、トリメタリル錫ブチレート、トリクロチル錫ブチレート、トリプレニル錫ブチレート、トリアリル錫ピバレート、トリメタリル錫ピバレート、トリクロチル錫ピバレート、トリプレニル錫ピバレート、トリアリル錫オクテート、トリメタリル錫オクテート、トリクロチル錫オクテート、トリプレニル錫オクテート、トリアリル錫ラウレート、トリメタリル錫ラウレート、トリクロチル錫ラウレート、トリプレニル錫ラウレート、トリアリル錫ベンゾエート、トリメタリル錫ベンゾエート、トリクロチル錫ベンゾエート、トリプレニル錫ベンゾエート等が挙げられる。
【0063】
ｂ）R^Aが一般式（５Ａ）で表される有機基の場合
例えば、トリシクロペンタジエニル錫フォルメート、トリシクロペンタジエニル錫アセテート、トリシクロペンタジエニル錫プロピオネート、トリシクロペンタジエニル錫ブチレート、トリシクロペンタジエニル錫ピバレート、トリシクロペンタジエニル錫オクテート、トリシクロペンタジエニル錫ラウレート、トリシクロペンタジエニル錫ベンゾエート等が挙げられる。
【0064】
５）ｍ＝０～２、Ｘ＝ハロゲン原子、ｎ＝０～２、Ｙ＝ハロゲン原子（ただし、ｍ＋ｎ＝２）のとき、すなわち、$(R^A)_2SnD_2$（式中、Ｄは上記と同じで、同一又は異なっていてもよい）の場合
ａ）R^Aが一般式（４Ａ）で表される有機基の場合
例えば、ジアリル錫ジクロライド、ジメタリル錫ジクロライド、ジクロチル錫ジクロライド、ジプレニル錫ジクロライド、ジアリル錫ジブロマイド、ジメタリル錫ジブロマイド、ジクロチル錫ジブロマイド、ジプレニル錫ジブロマイド等が挙げられる。この中で、ジメタリル錫ジクロライド及びジプレニル錫ジクロライドは新規化合物である。
【0065】
ｂ）R^Aが一般式（５Ａ）で表される有機基の場合
例えば、ジシクロペンタジエニル錫ジクロライド、ジシクロペンタジエニル錫ジブロマイド等が挙げられる。
【0066】
６）ｍ＝０～２、Ｘ＝アルコキシ基、ｎ＝０～２、Ｙ＝アルコキシ基（ただし、ｍ＋ｎ＝２）のとき、すなわち、$(R^A)_2Sn(OR^D)_2$（式中、R^Dは上記と同じで、同一又は異なっていてもよい）の場合
ａ）R^Aが一般式（４Ａ）で表される有機基の場合
例えば、ジアリル錫ジメトキシド、ジメタリル錫ジメトキシド、ジクロチル錫ジメトキシド、ジプレニル錫ジメトキシド、ジアリル錫ジエトキシド、ジメタリル錫ジエトキシド、ジクロチル錫ジエトキシド、ジプレニル錫ジエトキシド、ジアリル錫ジｎ－プロポキシド、ジメタリル錫ジｎ－プロポキシド、ジクロチル錫ジｎ－プロポキシド、ジプレニル錫ジｎ－プロポキシド、ジアリル錫ジｉｓｏ－プロポキシド、ジメタリル錫ジｉｓｏ－プロポキシド、ジクロチル錫ジｉｓｏ－プロポキシド、ジプレニル錫ジｉｓｏ－プロポキシド、ジアリル錫ジｎ－ブトキシド、ジメタリル錫ジｎ－ブトキシド、ジクロチル錫ジｎ－ブトキシド、ジプレニル錫ジｎ－ブトキシド、ジアリル錫ジｔｅｒｔ－ブトキシド、ジメタ

リル錫ジｔｅｒｔ－ブトキシド、ジクロチル錫ジｔｅｒｔ－ブトキシド、ジプレニル錫ジｔｅｒｔ－ブトキシド、ジアリル錫ジフェノキシド、ジメタリル錫ジフェノキシド、ジクロチル錫ジフェノキシド、ジプレニル錫ジフェノキシド等が挙げられる。この中で、ジメタリル錫ジメトキシド、ジクロチル錫ジメトキシド、ジプレニル錫ジメトキシド、ジアリル錫ジエトキシド、ジアリル錫ジｎ－ブトキシド、ジメタリル錫ジｎ－ブトキシド、ジクロチル錫ジｎ－ブトキシド及びジプレニル錫ジｎ－ブトキシドは新規化合物である。

【0067】

ｂ）R^Aが一般式（５Ａ）で表される有機基の場合

例えば、ジシクロペンタジエニル錫ジメトキシド、ジシクロペンタジエニル錫ジエトキシド、ジシクロペンタジエニル錫ジｎ－プロポキシド、ジシクロペンタジエニル錫ジｉｓｏ－プロポキシド、ジシクロペンタジエニル錫ジｎ－ブトキシド、ジシクロペンタジエニル錫ジｔｅｒｔ－ブトキシド、ジシクロペンタジエニル錫ジフェノキシド等が挙げられる。この中で、ジシクロペンタジエニル錫ジメトキシド及びジシクロペンタジエニル錫ジｎ－ブトキシドは新規化合物である。

【0068】

７）ｍ＝０～２、Ｘ＝アシルオキシ基、ｎ＝０～２、Ｙ＝アシルオキシ基（ただし、ｍ＋ｎ＝２）のとき、すなわち、$(R^A)_2Sn(OCOR^E)_2$（式中、R^Eは、上記と同じで、同一又は異なっていてもよい）の場合

ａ）R^Aが一般式（４Ａ）で表される有機基の場合

例えば、ジアリル錫ジフォルメート、ジメタリル錫ジフォルメート、ジクロチル錫ジフォルメート、ジプレニル錫ジフォルメート、ジアリル錫ジアセテート、ジメタリル錫ジアセテート、ジクロチル錫ジアセテート、ジプレニル錫ジアセテート、ジアリル錫ジプロピオネート、ジメタリル錫ジプロピオネート、ジクロチル錫ジプロピオネート、ジプレニル錫ジプロピオネート、ジアリル錫ジブチレート、ジメタリル錫ジブチレート、ジクロチル錫ジブチレート、ジプレニル錫ジブチレート、ジアリル錫ジピバレート、ジメタリル錫ジピバレート、ジクロチル錫ジピバレート、ジプレニル錫ジピバレート、ジアリル錫ジオクテート、ジメタリル錫ジオクテート、ジクロチル錫ジオクテート、ジプレニル錫ジオクテート、ジアリル錫ジラウレート、ジメタリル錫ジラウレート、ジクロチル錫ジラウレート、ジプレニル錫ジラウレート、ジアリル錫ジベンゾエート、ジメタリル錫ジベンゾエート、ジクロチル錫ジベンゾエート、ジプレニル錫ジベンゾエート等が挙げられる。この中で、ジアリル錫ジフォルメート、ジメタリル錫ジフォルメート、ジクロチル錫ジフォルメート、ジプレニル錫ジフォルメート、ジアリル錫ジアセテート、ジメタリル錫ジアセテート、ジクロチル錫ジアセテート、ジプレニル錫ジアセテート、ジアリル錫ジピバレート、ジメタリル錫ジピバレート、ジクロチル錫ジピバレート、ジプレニル錫ジピバレート、ジメタリル錫ジオクテート、ジクロチル錫ジオクテート及びジプレニル錫ジオクテートは新規化合物である。

【0069】

ｂ）R^Aが一般式（５Ａ）で表される有機基の場合

例えば、ジシクロペンタジエニル錫ジフォルメート、ジシクロペンタジエニル錫ジアセテート、ジシクロペンタジエニル錫ジプロピオネート、ジシクロペンタジエニル錫ジブチレート、ジシクロペンタジエニル錫ジピバレート、ジシクロペンタジエニル錫ジオクテート、ジシクロペンタジエニル錫ジラウレート、ジシクロペンタジエニル錫ジベンゾエート等が挙げられる。この中で、ジシクロペンタジエニル錫ジフォルメート、ジシクロペンタジエニル錫ジピバレート及びジシクロペンタジエニル錫ジオクテートは新規化合物である。

【0070】

８）ｍ＝１、Ｘ＝水酸基、ｎ＝１、Ｙ＝ハロゲン原子、又は、ｍ＝１、Ｘ＝ハロゲン原子基、ｎ＝１、Ｙ＝水酸基のとき、すなわち、$(R^A)_2SnDOH$（式中、Ｄは上記と同じ）の場合

ａ）R^Aが一般式（４Ａ）で表される有機基の場合

例えば、ヒドロキシジアリル錫クロライド、ヒドロキシジメタリル錫クロライド、ヒドロキシジクロチル錫クロライド、ヒドロキシジプレニル錫クロライド等が挙げられる。この中で、ヒドロキシジメタリル錫クロライド、ヒドロキシジクロチル錫クロライド及びヒドロキシジプレニル錫クロライドは新規化合物である。

【0071】

ｂ）R^Aが一般式（５Ａ）で表される有機基の場合

例えば、ヒドロキシジシクロペンタジエニル錫クロライド、ヒドロキシビス（ペンタメチルシクロペンタジエニル）錫クロライド、ヒドロキシビス（２，５－ジメチルシクロペンタジエニル）錫クロライド等が挙げられる。

【0072】

９）ｍ、ｎ＝０～３、Ｘ、Ｙ＝ハロゲン原子（ただし、ｍ＋ｎ＝３）のとき、すなわち、（R^A）SnD_3（式中、Ｄは上記と同じ）の場合

ａ）R^Aが一般式（４Ａ）で表される有機基の場合

例えば、モノアリル錫トリクロライド、モノメタリル錫トリクロライド、モノクロチル錫トリクロライド、モノプレニル錫トリクロライド、モノアリル錫トリブロマイド、モノメタリル錫トリブロマイド、モノクロチル錫トリブロマイド、モノプレニル錫トリブロマイド等が挙げられる。この中で、モノプレニル錫トリクロライドは新規化合物である。

【0073】

ｂ）R^Aが一般式（５Ａ）で表される有機基の場合

例えば、モノシクロペンタジエニル錫トリクロライド、モノシクロペンタジエニル錫トリブロマイド等が挙げられる。

【0074】

１０）ｍ、ｎ＝０～３、Ｘ、Ｙ＝アルコキシ基（ただし、ｍ＋ｎ＝３）のとき、すなわち、（R^A）$Sn(OR^D)_3$（式中、R^Dは上記と同じで、同一又は異なっていてもよい）の場合

ａ）R^Aが一般式（４Ａ）で表される有機基の場合

例えば、モノアリル錫トリメトキシド、モノメタリル錫トリメトキシド、モノクロチル錫トリメトキシド、モノプレニル錫トリメトキシド、モノアリル錫トリエトキシド、モノメタリル錫トリエトキシド、モノクロチル錫トリエトキシド、モノプレニル錫トリエトキシド、モノアリル錫トリｎ－プロポキシド、モノメタリル錫トリｎ－プロポキシド、モノクロチル錫トリｎ－プロポキシド、モノプレニル錫トリｎ－プロポキシド、モノアリル錫トリｉｓｏ－プロポキシド、モノメタリル錫トリｉｓｏ－プロポキシド、モノクロチル錫トリｉｓｏ－プロポキシド、モノプレニル錫トリｉｓｏ－プロポキシド、モノアリル錫トリｎ－ブトキシド、モノメタリル錫トリｎ－ブトキシド、モノクロチル錫トリｎ－ブトキシド、モノプレニル錫トリｎ－ブトキシド、モノアリル錫トリｔｅｒｔ－ブトキシド、モノメタリル錫トリｔｅｒｔ－ブトキシド、モノクロチル錫トリｔｅｒｔ－ブトキシド、モノプレニル錫トリｔｅｒｔ－ブトキシド、モノアリル錫トリフェノキシド、モノメタリル錫トリフェノキシド、モノクロチル錫トリフェノキシド、モノプレニル錫トリフェノキシド等が挙げられる。この中で、モノアリル錫トリメトキシド、モノメタリル錫トリメトキシド、モノクロチル錫トリメトキシド、モノプレニル錫トリメトキシド、モノアリル錫トリｎ－ブトキシド、モノメタリル錫トリｎ－ブトキシド、モノクロチル錫トリｎ－ブトキシド及びモノプレニル錫トリｎ－ブトキシドは新規化合物である。

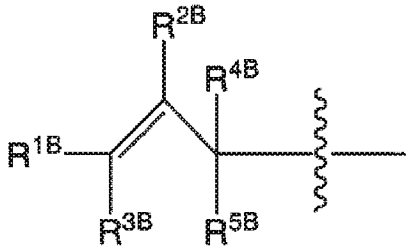
【0075】

ｂ）R^Aが一般式（５Ａ）で表される有機基の場合

例えば、モノシクロペンタジエニル錫トリメトキシド、モノシクロペンタジエニル錫トリエトキシド、モノシクロペンタジエニル錫トリｎ－プロポキシド、モノシクロペンタジエニル錫トリｉｓｏ－プロポキシド、モノシクロペンタジエニル錫トリｎ－ブトキシド、モノシクロペンタジエニル錫トリｔｅｒｔ－ブトキシド、モノシクロペンタジエニル錫トリフェノキシド等が挙げられる。この中で、モノシクロペンタジエニル錫トリメトキシド及びモノシクロペンタジエニル錫トリｎ－ブトキシドは新規化合物である。

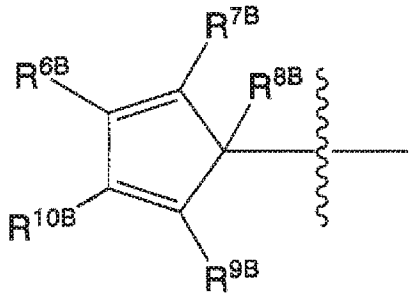
【0076】
１１）ｍ、ｎ＝０～３、Ｘ、Ｙ＝アシルオキシ基（ただし、ｍ＋ｎ＝３）のとき、すなわち、（R^A）Ｓｎ（ＯＣＯＲ^B）$_3$（式中、R^Bは、上記と同じで、同一又は異なっていてもよい）の場合
ａ）R^Aが一般式（４Ａ）で表される有機基の場合
例えば、モノアリル錫トリフォルメート、モノメタリル錫トリフォルメート、モノクロチル錫トリフォルメート、モノプレニル錫トリフォルメート、モノアリル錫トリアセテート、モノメタリル錫トリアセテート、モノクロチル錫トリアセテート、モノプレニル錫トリアセテート、モノアリル錫トリプロピオネート、モノメタリル錫トリプロピオネート、モノクロチル錫トリプロピオネート、モノプレニル錫トリプロピオネート、モノアリル錫トリブチレート、モノメタリル錫トリブチレート、モノクロチル錫トリブチレート、モノプレニル錫トリブチレート、モノアリル錫トリピバレート、モノメタリル錫トリピバレート、モノクロチル錫トリピバレート、モノプレニル錫トリピバレート、モノアリル錫トリオクテート、モノメタリル錫トリオクテート、モノクロチル錫トリオクテート、モノプレニル錫トリオクテート、モノアリル錫トリラウレート、モノメタリル錫トリラウレート、モノクロチル錫トリラウレート、モノプレニル錫トリラウレート、モノアリル錫トリベンゾエート、モノメタリル錫トリベンゾエート、モノクロチル錫トリベンゾエート、モノプレニル錫トリベンゾエート等が挙げられる。この中で、モノアリル錫トリフォルメート、モノメタリル錫トリフォルメート、モノクロチル錫トリフォルメート、モノプレニル錫トリフォルメート、モノアリル錫トリアセテート、モノメタリル錫トリアセテート、モノクロチル錫トリアセテート、モノプレニル錫トリアセテート、モノアリル錫トリピバレート、モノメタリル錫トリピバレート、モノクロチル錫トリピバレート、モノプレニル錫トリピバレート、モノアリル錫トリオクテート、モノメタリル錫トリオクテート、モノクロチル錫トリオクテート及びモノプレニル錫トリオクテートは新規化合物である。
【0077】
ｂ）R^Aが一般式（５Ａ）で表される有機基の場合
例えば、モノシクロペンタジエニル錫トリフォルメート、モノシクロペンタジエニル錫トリアセテート、モノシクロペンタジエニル錫トリプロピオネート、モノシクロペンタジエニル錫トリブチレート、モノシクロペンタジエニル錫トリピバレート、モノシクロペンタジエニル錫トリオクテート、モノシクロペンタジエニル錫トリラウレート、モノシクロペンタジエニル錫トリベンゾエート等が挙げられる。この中で、モノシクロペンタジエニル錫トリフォルメート、モノシクロペンタジエニル錫トリアセテート、モノシクロペンタジエニル錫トリピバレート及びモノシクロペンタジエニル錫トリオクテートは新規化合物である。
【0078】
特に、本発明において、一般式（１）で表される有機錫化合物としては、上記１）、５）７）、８）、９）及び１１）の場合が好ましい。
【0079】
一般式（１）で表される有機錫化合物は、任意の方法で製造することができる。
【0080】
例えば、テトラ有機錫（例えば上記１））は、R^Aに対応するグリニヤール試薬を調製し、これを四塩化錫と反応させる方法、R^Aに対応する有機リチウム化合物と四塩化錫とを反応させる方法等により合成することができる。
【0081】
トリ有機錫クロライド、ジ有機錫ジクロライド、モノ有機錫トリクロライド等の有機錫塩化物（例えば上記２）、５）、９））は、テトラオルガノ錫を四塩化錫と任意の割合で再分配反応させることにより合成することができる。
【0082】
有機錫水酸化物（例えば上記８））は、有機錫塩化物をアルカリ水溶液で加水分解することにより合成することができる。

【0083】
有機錫アルコキサイド（例えば上記３）、６）、１０））は、有機錫塩化物と金属アルコキサイドとを反応させ、金属塩化物を除去することにより合成することができる。
【0084】
有機錫カルボキシレート（例えば上記４）、７）、１１））は、有機錫塩化物とカルボン酸とをアミン存在下で反応させる方法、有機錫アルコキサイドとカルボン酸とを反応させる方法（脱アルコール反応）、有機錫水酸化物とカルボン酸とを反応させる方法（脱水縮合反応）、有機錫水酸化物とカルボン酸無水物とを反応させる方法等により合成することができる。
【0085】
一般式（２）で表される有機錫化合物
上記一般式（２）で表される有機錫化合物中、R^Bは、下記一般式（４Ｂ）又は（５Ｂ）のβ位に二重結合を有する有機基を示す。
【0086】
【化13】



(4B)

【0087】
【化14】



(5B)

【0088】
一般式（４Ｂ）中、R^{1B}、R^{2B}、R^{3B}、R^{4B}及びR^{5B}は、上記R^{1A}、R^{2A}、R^{3A}、R^{4A}及びR^{5A}と同様である。特に、本発明においては、R^{4B}及びR^{5B}が、水素原子であることが好ましい。
【0089】
一般式（５Ｂ）中、R^{6B}、R^{7B}、R^{8B}、R^{9B}及びR^{10B}は、上記R^{6A}、R^{7A}、R^{8A}、R^{9A}及びR^{10A}と同様である。特に、本発明においては、R^{6B}、R^{7B}、R^{8B}、R^{9B}及びR^{10B}は、水素原子、炭素原子数１～６の直鎖若しくは分岐鎖若しくは環状のアルキル基、アルケニル基、又はアリール基が好ましく、水素原子がより好ましい。炭素原子数１～６の直鎖若しくは分岐鎖若しくは環状のアルキル基、アルケニル基、又はアリール基としては、上記例示のものが挙げられる。
一般式（２）で表される有機錫化合物としては、例えばジアリル錫オキサイド、ジメタリル錫オキサイド、ジクロチル錫オキサイド、ジプレニル錫オキサイド、ジシクロペンタジエニル錫オキサイド等が挙げられる。この中で、ジメタリル錫オキサイド、ジクロチル錫

オキサイド、ジプレニル錫オキサイド及びジシクロペンタジエニル錫オキサイドは新規化合物である。

【0090】

一般式（２）で表される有機錫化合物は、任意の方法で製造することができる。

【0091】

例えば、R^Bに対応するグリニヤール試薬を調製し、これを四塩化錫と反応させることによりテトラ有機錫を合成し、次いでテトラ有機錫と四塩化錫とを１対１で再分配反応させることにより対応するジ有機錫ジクロライドを合成し、さらにジ有機錫ジクロライドをアルカリ水溶液で加水分解することにより合成することができる。

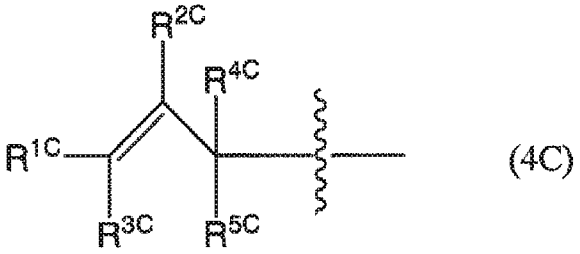
【0092】

一般式（３）で表される有機錫化合物

上記一般式（３）で表される有機錫化合物中、R^Cは、下記一般式（４Ｃ）又は（５Ｃ）のβ位に二重結合を有する有機基を示す。

【0093】

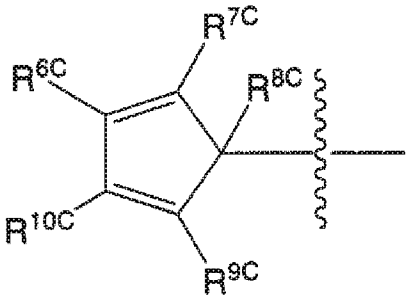
【化15】



(4C)

【0094】

【化16】



(5C)

【0095】

一般式（４Ｃ）中、R^{1C}、R^{2C}、R^{3C}、R^{4C}及びR^{5C}は、上記R^{1A}、R^{2A}、R^{3A}、R^{4A}及びR^{5A}と同様である。特に、本発明においては、R^{4C}及びR^{5C}が、水素原子であることが好ましい。

【0096】

一般式（５Ｃ）中、R^{6C}、R^{7C}、R^{8C}、R^{9C}及びR^{10C}は、上記R^{6A}、R^{7A}、R^{8A}、R^{9A}及びR^{10A}と同様である。特に、本発明においては、R^{6C}、R^{7C}、R^{8C}、R^{9C}及びR^{10C}は、水素原子、炭素原子数１～６の直鎖若しくは分岐鎖若しくは環状のアルキル基、アルケニル基、又はアリール基が好ましく、水素原子がより好ましい。炭素原子数１～６の直鎖若しくは分岐鎖若しくは環状のアルキル基、アルケニル基、又はアリール基としては、上記例示のものが挙げられる。

一般式（３）で表される有機錫化合物としては、例えば、アリル錫酸、メタリル錫酸、クロチル錫酸、プレニル錫酸、シクロペンタジエニル錫酸等が挙げられる。なお、アリル錫酸、メタリル錫酸、クロチル錫酸、プレニル錫酸及びシクロペンタジエニル錫酸は新規化合物である。

【0097】

一般式（３）で表される有機錫化合物は、任意の方法で製造することができる。

【0098】

例えば、R^{6}に対応するグリニヤール試薬を調製し、これを四塩化錫と反応させることによりテトラ有機錫を合成し、次いでテトラ有機錫と四塩化錫とを１対３で再分配反応させることにより対応するモノ有機錫トリクロライドを合成し、さらにモノ有機錫トリクロライドをアルカリ水溶液で加水分解することにより合成することができる。

上記一般式（１）（２）（３）で表される有機錫化合物は、従来の有機錫化合物に比べ分解温度が低い。特に、２００℃という低温で熱分解させた場合においても、有機成分は実質的に残存しない。このような有機錫化合物は、液晶表示素子、タッチパネル等の各種エレクトロニクス素子や薄膜太陽電池に好適に用いられる透明導電膜等の酸化錫膜形成剤として有用である。

【0099】

酸化錫膜形成方法

本発明の酸化錫膜形成方法は、前記酸化錫膜形成剤を含む溶液を基材に塗布した後、２００℃以下で熱処理することを特徴とする。

【0100】

特に、本発明の酸化錫膜形成方法では、前記酸化錫膜形成剤を用いることにより、２００℃以下という低温下で熱分解反応を行う場合においても有機成分が実質的に残存せず、好適に酸化錫膜を形成させることができる。そのため、本発明の酸化錫膜形成方法によれば、様々な基材（特に熱に弱い基材）に対して、熱分解法により酸化錫膜を形成させることができる。

【0101】

前記溶液は、本発明の酸化錫膜形成剤を溶媒に溶解ないし分散させることにより調製できる。使用する溶媒は、酸化錫膜形成剤に含まれる有機錫化合物の種類等に応じて適宜設定すればよい。例えば、メタノール、エタノール、プロパノール、ブタノール、トルエン、アセトン、酢酸エチル等を使用できる。これらは、１種又は２種以上で用いることができる。

【0102】

溶液中の酸化錫膜形成剤の含有量は、１０～９０重量％が好ましい。酸化錫膜形成剤の含有量がかかる範囲の場合、厚み３０００ｎｍ以下の酸化錫薄膜を好適に製造できる。

【0103】

溶液中には、通常の塗料に用いられる添加剤を含んでいてもよい。そのような添加剤としては、例えば、トリフルオロ酢酸、フッ化アンモニウム、フッ化水素、三塩化アンチモン、三フッ化アンチモン、トリエトキシアンチモン、オクチル酸アンチモン等が挙げられる。これらは、１種又は２種以上で用いてもよい。

【0104】

基材としては、プラスチック、ガラス等が挙げられる。この中でも、特に、軽量であること、低コストであること等の観点から、プラスチックが好ましい。

【0105】

塗布方法としては、特に限定されず、公知の方法を適宜採用すればよい。例えば、ハケ塗り法、スプレー法、ディッピング法、フローコート法、スピンコート法等が挙げられる。これらは、１種又は２種以上を併用して行ってもよい。

【0106】

前記溶液を塗布した後、２００℃以下、好ましくは９０～２００℃で熱処理を行う。熱処理温度が９０℃未満の場合、得られる酸化錫膜中に、有機成分が残存するおそれがある。また、熱処理温度が２００℃を超える場合、基材の種類によっては、基材が破損してしまうおそれがある。

【0107】

昇温速度は、通常、毎分５～２０℃程度であればよい。

【0108】

熱処理時間は、熱処理温度、基材の種類等に応じて適宜設定すればよく、通常、０．５～１時間程度であればよい。

【0109】

熱処理は、大気中（空気中）、酸化性雰囲気中、又は、窒素ガス、アルゴンガス等の不活性ガス雰囲気中で行えばよい。特に、大気中（空気中）又は酸化性雰囲気中で熱処理を行うことが好ましい。

【0110】

なお、塗布後、上記加熱処理に先立って、塗布物を乾燥させてもよい。

【0111】

本発明の酸化錫膜形成方法によれば、低コストで、且つ、狭い敷地内で好適に大面積の酸化錫膜を形成させることができる。

【0112】

酸化錫膜

本発明の酸化錫膜は、上記酸化錫膜形成方法により形成される。

【0113】

本発明の酸化錫膜の厚みは、特に限定されず、目的とする用途に応じて適宜設定すればよい。例えば、厚みが３０００ｎｍ以下、好ましくは１０～２０００ｎｍの場合、液晶表示素子やタッチパネル等の各種エレクトロニクス素子や薄膜太陽電池に用いられる透明導電膜等として有効である。

【0114】

本発明の酸化錫膜は、有機成分を実質的に含有していないため、透明性及び耐久性が高く、且つ、電気特性が均一である。

【発明の効果】

【0115】

本発明の酸化錫膜形成剤によれば、熱分解法により酸化錫膜を形成する際、２００℃以下という低い温度で有機成分を分解・除去することができる。そのため、様々な基材、特に、プラスチック等の熱に弱い基材に対しても、熱分解法により酸化錫膜を形成させることが可能となる。

【0116】

本発明の酸化錫膜形成剤によれば、熱分解法により酸化錫膜を形成する際、低い温度（２００℃以下）で有機成分を分解・除去することができる。

【0117】

本発明の酸化錫膜形成方法は、低い温度（２００℃以下）で熱分解反応を行うため、基材に熱的負荷をあまりかけることなく、様々な基材（特に熱に弱い基材）に対して酸化錫膜を好適に形成させることができる。

本発明の酸化錫膜は、有機成分を実質的に含有していないため、透明性及び耐久性が高く、且つ、電気特性が均一である。よって、本発明の酸化錫膜は、液晶表示素子やタッチパネル等の各種エレクトロニクス素子や薄膜太陽電池に用いられる透明導電膜等として有効である。

【発明を実施するための最良の形態】

【0118】

以下に製造例、実施例及び比較例を示し、本発明をより詳細に説明する。ただし、本発明は、製造例、実施例及び比較例に限定されるものではない。

【0119】

製造例１　「アリルマグネシウムクロライドの製造」

温度計、還流冷却器及び撹拌機を備えた１０００ｍｌの四つ口フラスコに窒素気流下で、マグネシウム３８．１２ｇ（１．５７ｍｏｌ）及びＴＨＦ６００ｍｌを仕込み、０～５℃に保持しつつ、アリルクロライド１００．００ｇ（１．３１ｍｏｌ）及びＴＨＦ１００ｍｌをあらかじめ混合した溶液を滴下した。滴下終了後、０～５℃で１時間反応を熟成させることにより、アリルマグネシウムクロライドＴＨＦ溶液（グリニヤール試薬Ａ）７５０

．５８ｇを得た。

【0120】

製造例２　「メタリルマグネシウムクロライドの製造」

アリルクロライドの代わりにメタリルクロライド１１８．６２ｇ（１．３１ｍｏｌ）を用いた以外は製造例１と同様の方法に従って、メタリルマグネシウムクロライドＴＨＦ溶液（グリニヤール試薬Ｂ）７７０．８５ｇを得た。

【0121】

製造例３　「クロチルマグネシウムクロライドの製造」

アリルクロライドの代わりにクロチルクロライド１１８．６２ｇ（１．３１ｍｏｌ）を用いた以外は製造例１と同様の方法に従って、クロチルマグネシウムクロライドＴＨＦ溶液（グリニヤール試薬Ｃ）７７０．８５ｇを得た。

【0122】

製造例４　「プレニルマグネシウムブロマイドの製造」

１０００ｍｌの四つ口フラスコの代わりに２０００ｍｌの四つ口フラスコを用い、さらに、アリルクロライドの代わりにプレニルブロマイド１９５．２３ｇ（１．３１ｍｏｌ）を用いた以外は製造例１と同様の方法に従って、プレニルマグネシウムブロマイドＴＨＦ溶液（グリニヤール試薬Ｄ）１０８８．４６ｇを得た。

【0123】

製造例５　「テトラアリル錫の製造」

温度計、還流冷却器及び攪拌機を備えた１０００ｍｌの四つ口フラスコに窒素気流下、製造例１で得られたグリニヤール試薬Ａ５５９．５１ｇ（０．８８ｍｏｌ）を仕込み、１５～２５℃に保持しつつ、四塩化錫５０．００ｇ（０．１９ｍｏｌ）及びトルエン１００ｍｌをあらかじめ混合した溶液を滴下した。滴下終了後、１５～２５℃で３時間反応を熟成させた。１５～２５℃で、生成する塩化マグネシウムが溶解するまで飽和アンモニウムクロライド水溶液を加え、静置した後、分液し上層と下層とを分離した。下層をトルエン１００ｍｌで２回抽出し、抽出液と分離した上層とを合わせた後、無水硫酸ナトリウムを加え脱水させた。無水硫酸ナトリウムを沪過除去した後、沪液を濃縮し、粗錫化合物Ａ５４．３１ｇを得た。次いで、この粗錫化合物Ａを減圧蒸留することにより精製し、錫化合物Ａ５０．５１ｇを得た。純度は９９．５％であった（ＧＣにて確認）。この錫化合物Ａは、ＦＴ－ＩＲによるアリル基由来の吸収ピーク（３０７８ｃｍ$^{-1}$、１６２２ｃｍ$^{-1}$、８８３ｃｍ$^{-1}$）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝２４３）、且つ、下記の元素分析の結果からテトラアリル錫であることがわかった。

【0124】

【表1】

	Ｃ（％）	Ｈ（％）	Ｓｎ（％）
測定値	５１．０	７．０	４２．０
理論値	５０．９	７．１	４２．０

【0125】

製造例６　「テトラメタリル錫の製造」

グリニヤール試薬Ａの代わりに製造例２で得られたグリニヤール試薬Ｂ５８８．７６ｇ（０．８８ｍｏｌ）を用いた以外は製造例５と同様の方法に従って、錫化合物Ｂを６３．７８ｇ得た。純度は９９．４％であった（ＧＣにて確認）。この錫化合物Ｂは、ＦＴ－ＩＲによるメタリル基由来の吸収ピーク（３０７４ｃｍ$^{-1}$、１６２９ｃｍ$^{-1}$、８６４ｃｍ$^{-1}$）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝２８４）、且つ、下記の元素分析の結果からテトラメタリル錫であることがわかった。

【0126】

【表2】

	Ｃ（％）	Ｈ（％）	Ｓｎ（％）
測定値	５６．７	８．４	３４．９
理論値	５６．７	８．３	３５．０

【0127】

製造例７　「テトラクロチル錫の製造」

グリニヤール試薬Ａの代わりに製造例３で得られたグリニヤール試薬Ｃ７０６．５１ｇ（０．８８ｍｏｌ）を用いた以外は製造例５と同様の方法に従って、錫化合物Ｃを６３．７８ｇ得た。純度は９９．０％であった（ＧＣにて確認）。この錫化合物Ｃは、ＦＴ－ＩＲによるクロチル基由来の吸収ピーク（３０１４ｃｍ$^{-1}$、１６３９ｃｍ$^{-1}$、９００ｃｍ$^{-1}$）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝２８４）、且つ、下記の元素分析の結果からテトラクロチル錫であることがわかった。

【0128】

【表3】

	Ｃ（％）	Ｈ（％）	Ｓｎ（％）
測定値	５６．６	８．２	３５．２
理論値	５６．７	８．３	３５．０

【0129】

製造例８　「テトラプレニル錫の製造」

１０００ｍｌの四つ口フラスコの代わりに２０００ｍｌの四つ口フラスコを用い、さらに、グリニヤール試薬Ａの代わりに製造例４で得られたグリニヤール試薬Ｄ８８２．８５ｇ（０．８８ｍｏｌ）を用いた以外は製造例５と同様の方法に従って、錫化合物Ｄを６８．２７ｇ得た。純度は９９．０％であった（ＧＣにて確認）。この錫化合物Ｄは、ＦＴ－ＩＲによるプレニル基由来の吸収ピーク（２９６４ｃｍ$^{-1}$、１６６０ｃｍ$^{-1}$、８４４ｃｍ$^{-1}$）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝３２６）、且つ、下記の元素分析の結果からテトラプレニル錫であることがわかった。

【0130】

【表4】

	Ｃ（％）	Ｈ（％）	Ｓｎ（％）
測定値	６０．９	９．３	２９．８
理論値	６０．８	９．２	３０．０

【0131】

製造例９　「テトラシクロペンタジエニル錫の製造」

温度計、還流冷却器及び撹拌機を備えた１０００ｍｌの四つ口フラスコに窒素気流下で、シクロペンタジエニルリチウム６５．５６ｇ（０．９１ｍｏｌ）及びトルエン２００ｍｌを仕込み、１５～２５℃に保持しつつ、四塩化錫５０．００ｇ（０．１９ｍｏｌ）及びトルエン１００ｍｌをあらかじめ混合した溶液を滴下した。滴下終了後、１５～２５℃で３時間反応を熟成させた。１５～２５℃で水１００ｍｌを加え撹拌し、静置した後、分液し上層と下層とを分離した。上層に２％硫酸水溶液１００ｍｌを加え撹拌し、静置した後、分液し上層と下層とを分離した。さらに、その上層に水１００ｍｌを加え撹拌し、静置した後、分液し上層と下層とを分離する作業を下層が中性になるまで繰り返した。分離した上層に無水硫酸ナトリウムを加え脱水した。無水硫酸ナトリウムを沪過除去した後、沪液を濃縮し、粗錫化合物Ｅ７２．００ｇを得た。次いでこれを減圧蒸留することにより精製し、錫化合物Ｅ５７．６０ｇを得た。純度は９９．０％であった（ＧＣにて確認）。こ

の錫化合物Ｅは、ＦＴ－ＩＲによるシクロペンタジエニル基由来の吸収ピーク（３０７８ｃｍ$^{-1}$、１６２２ｃｍ$^{-1}$、８８３ｃｍ$^{-1}$）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝３７９）、且つ、下記の元素分析の結果からテトラシクロペンタジエニル錫であることがわかった。

【0132】

【表5】

	Ｃ（％）	Ｈ（％）	Ｓｎ（％）
測定値	６３．４	５．３	３１．３
理論値	６３．４	５．３	３１．３

【0133】

製造例１０　「ジアリル錫ジクロライドの製造」

温度計、還流冷却器及び撹拌機を備えた１００ｍｌの四つ口フラスコに窒素気流下で、製造例５で得られたテトラアリル錫４３．６８ｇ（０．１５ｍｏｌ）を仕込み、４０～５０℃に保持しつつ、四塩化錫４０．００ｇ（０．１５ｍｏｌ）を滴下した。滴下終了後、１５～２５℃で３０分間反応を熟成させることにより、粗錫化合物Ｆ８３．４５ｇを得た。次いで、この粗錫化合物Ｆを蒸留することにより精製し、錫化合物Ｆ７０．００ｇを得た。純度は９５．５％であった（ＧＣにて確認）。この錫化合物Ｆは、ＦＴ－ＩＲによるアリル基由来の吸収ピーク（３０７８ｃｍ$^{-1}$、１６２２ｃｍ$^{-1}$、８８３ｃｍ$^{-1}$）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝２３０）、且つ、下記の元素分析の結果からジアリル錫ジクロライドであることがわかった。

【0134】

【表6】

	Ｃ（％）	Ｈ（％）	Ｃｌ（％）	Ｓｎ（％）
測定値	２６．３	３．８	２６．１	４３．８
理論値	２６．５	３．７	２６．１	４３．７

【0135】

製造例１１　「ジメタリル錫ジクロライドの製造」

テトラアリル錫の代わりに製造例６で得られたテトラメタリル錫５２．３４ｇ（０．１５ｍｏｌ）を用いた以外は製造例１０と同様の方法に従って、錫化合物Ｇを７７．００ｇ得た。純度は９６．１％であった（ＧＣにて確認）。この錫化合物Ｇは、ＦＴ－ＩＲによるメタリル基由来の吸収ピーク（３０７４ｃｍ$^{-1}$、１６２９ｃｍ$^{-1}$、８６４ｃｍ$^{-1}$）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝２４５）、且つ、下記の元素分析の結果からジメタリル錫ジクロライドであることがわかった。

【0136】

【表7】

	Ｃ（％）	Ｈ（％）	Ｃｌ（％）	Ｓｎ（％）
測定値	３２．０	４．７	２３．５	３９．８
理論値	３２．０	４．７	２３．７	３９．６

【0137】

製造例１２　「ジクロチル錫ジクロライドの製造」

テトラアリル錫の代わりに製造例７で得られたテトラクロチル錫５２．３４ｇ（０．１５ｍｏｌ）を用いた以外は製造例１０と同様の方法に従って、錫化合物Ｈを７７．００ｇ得た。純度は９６．１％であった（ＧＣにて確認）。この錫化合物Ｈは、ＦＴ－ＩＲによるクロチル基由来の吸収ピーク（３０１４ｃｍ$^{-1}$、１６３９ｃｍ$^{-1}$、９００ｃｍ$^{-1}$

）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝２４５）、且つ、下記の元素分析の結果からジクロチル錫ジクロライドであることがわかった。

【0138】

【表8】

	Ｃ（％）	Ｈ（％）	Ｃｌ（％）	Ｓｎ（％）
測定値	３２．０	４．７	２３．５	３９．８
理論値	３２．０	４．７	２３．７	３９．６

【0139】

製造例１３　「ジプレニル錫ジクロライドの製造」

テトラアリル錫の代わりに製造例８で得られたテトラプレニル錫６１．２９ｇ（０．１５ｍｏｌ）を用いた以外は製造例１０と同様の方法に従って、錫化合物Ｉを８０．５４ｇ得た。純度は９５．０％であった（ＧＣにて確認）。この錫化合物Ｉは、ＦＴ－ＩＲによるプレニル基由来の吸収ピーク（２９６４ｃｍ$^{-1}$、１６６０ｃｍ$^{-1}$、８４４ｃｍ$^{-1}$）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝２５９）、且つ、下記の元素分析の結果からジプレニル錫ジクロライドであることがわかった。

【0140】

【表9】

	Ｃ（％）	Ｈ（％）	Ｃｌ（％）	Ｓｎ（％）
測定値	４１．０	６．１	１２．１	４０．８
理論値	４１．１	６．２	１２．１	４０．６

【0141】

製造例１４　「ジシクロペンタジエニル錫ジクロライドの製造」

テトラアリル錫の代わりに製造例９で得られたテトラシクロペンタジエニル錫５６．８６ｇ（０．１５ｍｏｌ）を用いた以外は製造例１０と同様の方法に従って、錫化合物Ｊを７６．７５ｇ得た。純度は９７．０％であった（ＧＣにて確認）。この錫化合物Ｊは、ＦＴ－ＩＲによるシクロペンタジエニル基由来の吸収ピーク（３０７４ｃｍ$^{-1}$、１６２９ｃｍ$^{-1}$、８６４ｃｍ$^{-1}$）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝３２０）、且つ、下記の元素分析の結果からジシクロペンタジエニル錫ジクロライドであることがわかった。

【0142】

【表10】

	Ｃ（％）	Ｈ（％）	Ｃｌ（％）	Ｓｎ（％）
測定値	３７．５	３．０	２２．３	３７．２
理論値	３７．６	３．１	２２．２	３７．１

【0143】

製造例１５　「ジアリル錫オキサイドの製造」

温度計、還流冷却器及び撹拌機を備えた３００ｍｌの四つ口フラスコに窒素気流下で、製造例１０で得られたジアリル錫ジクロライド４０．００ｇ（０．１５ｍｏｌ）を仕込み、２０～４０℃に保持しつつ、１０％水酸化ナトリウム水溶液１７６．８８ｇ（０．４４ｍｏｌ）を滴下した。滴下終了後、２０～４０℃で３時間反応を熟成させた。生成した白色不溶物を沪別し、沪液が中性になるまで水洗を行った。この白色固形物をロータリーエバポレーターにて減圧乾燥することにより錫化合物Ｋを１６．００ｇ得た。この錫化合物Ｋは、ＦＴ－ＩＲによるアリル基由来の吸収ピーク（３０７８ｃｍ$^{-1}$、１６２４ｃｍ$^{-}$

$^{-1}$、８８９ｃｍ$^{-1}$）、Ｓｎ－Ｏ－Ｓｎ由来の吸収ピーク（４３０ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からジアリル錫オキサイドであることがわかった。

【0144】

【表11】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	３３．０	４．６	７．６	５４．８
理論値	３３．２	４．７	７．４	５４．７

【0145】

製造例１６　「ジメタリル錫オキサイドの製造」

ジアリル錫ジクロライドの代わりに製造例１１で得られたジメタリル錫ジクロライド４４．９５ｇ（０．１５ｍｏｌ）を用いた以外は製造例１５と同様の方法に従って、錫化合物Ｌを１８．３６ｇ得た。この錫化合物Ｌは、ＦＴ－ＩＲによるメタリル基由来の吸収ピーク（３０７４ｃｍ$^{-1}$、１６２９ｃｍ$^{-1}$、８６４ｃｍ$^{-1}$）、Ｓｎ－Ｏ－Ｓｎ由来の吸収ピーク（４３０ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からジメタリル錫オキサイドであることがわかった。

【0146】

【表12】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	３９．１	５．９	６．５	４８．５
理論値	３９．２	５．８	６．５	４８．５

【0147】

製造例１７　「ジクロチル錫オキサイドの製造」

ジアリル錫ジクロライドの代わりに製造例１２で得られたジクロチル錫ジクロライド４４．９５ｇ（０．１５ｍｏｌ）を用いた以外は製造例１５と同様の方法に従って、錫化合物Ｍを１８．３６ｇ得た。この錫化合物Ｍは、ＦＴ－ＩＲによるクロチル基由来の吸収ピーク（３０１４ｃｍ$^{-1}$、１６３９ｃｍ$^{-1}$、９００ｃｍ$^{-1}$）、Ｓｎ－Ｏ－Ｓｎ由来の吸収ピーク（４２９ｃｍ$^{-1}$）、且つ、下記の元素分析の結果よりジクロチル錫オキサイドであることがわかった。

【0148】

【表13】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	３９．３	５．９	６．４	４８．４
理論値	３９．２	５．８	６．５	４８．５

【0149】

製造例１８　「ジプレニル錫オキサイドの製造」

ジアリル錫ジクロライドの代わりに製造例１３で得られたジプレニル錫ジクロライド４９．１８ｇ（０．１５ｍｏｌ）を用いた以外は製造例１５と同様の方法に従って、錫化合物Ｎを３２．７６ｇ得た。この錫化合物Ｎは、ＦＴ－ＩＲによるプレニル基由来の吸収ピーク（２９６４ｃｍ$^{-1}$、１６６０ｃｍ$^{-1}$、８４４ｃｍ$^{-1}$）、Ｓｎ－Ｏ－Ｓｎ由来の吸収ピーク（４２８ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からジプレニル錫オキサイドであることがわかった。

【0150】

【表14】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	４３．９	６．５	５．９	４３．７
理論値	４４．０	６．６	５．９	４３．５

【0151】

製造例１９　「ジシクロペンタジエニル錫オキサイドの製造」

ジアリル錫ジクロライドの代わりに製造例１４で得られたジシクロペンタジエニル錫ジクロライド４７．９７ｇ（０．１５ｍｏｌ）を用いた以外は製造例１５と同様の方法に従って、錫化合物Ｏを３１．７９ｇ得た。この錫化合物Ｏは、ＦＴ－ＩＲによるシクロペンタジエニル基由来の吸収ピーク（３０７４ｃｍ$^{-1}$、１６２９ｃｍ$^{-1}$、８６４ｃｍ$^{-1}$）、Ｓｎ－Ｏ－Ｓｎ由来の吸収ピーク（４３０ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からジシクロペンタジエニル錫オキサイドであることがわかった。

【0152】

【表15】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	４５．３	３．８	６．０	４４．９
理論値	４５．３	３．８	６．１	４４．８

【0153】

製造例２０　「ヒドロキシシクロヘキシル錫クロライドの製造」

１０％水酸化ナトリウム水溶液の滴下量を６０．００ｇ（０．１５ｍｏｌ）にした以外は製造例１５と同様の方法に従って、錫化合物Ｐを３７．９８ｇ得た。この錫化合物Ｐは、ＦＴ－ＩＲによるクロヘキシル基由来の吸収ピーク（３０１４ｃｍ$^{-1}$、１６３９ｃｍ$^{-1}$、９００ｃｍ$^{-1}$）、Ｓｎ－Ｏ－Ｈ由来の吸収ピーク（５３０ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からヒドロキシシクロヘキシル錫クロライドであることがわかった。

【0154】

【表16】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｃｌ（％）	Ｓｎ（％）
測定値	３４．１	５．４	５．６	１２．７	４２．２
理論値	３４．１	５．４	５．７	１２．６	４２．２

【0155】

製造例２１　「ジアリル錫ジアセテートの製造」

温度計、還流冷却器及び撹拌機を備えた５００ｍｌの四つ口フラスコに窒素気流下で、製造例３で得られたジアリル錫クロライド５４．３５ｇ（０．２０ｍｏｌ）、酢酸２４．０２ｇ（０．４０ｍｌ）、及びベンゼン１５０ｍｌを仕込み、２０～３０℃に保持しつつ、トリエチルアミン４０．４７ｇ（０．４０ｍｏｌ）を滴下した。滴下終了後、２０～３０℃で３時間反応を熟成させた。生成した白色不溶物を沪別し、沪液を濃縮することにより錫化合物Ｑを６２．５１ｇ得た。この錫化合物Ｑは、ＦＴ－ＩＲによるアリル基由来の吸収ピーク（３０７８ｃｍ$^{-1}$、１６２２ｃｍ$^{-1}$、８９８ｃｍ$^{-1}$）、錫カルボニル由来の吸収ピーク（１５６６ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からジアリル錫ジアセテートであることがわかった。

【0156】

【表17】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	３７．７	５．０	２０．０	３７．３
理論値	３７．７	５．０	２０．１	３７．２

【0157】

製造例２２　「ジアリル錫ジピバレートの製造」

酢酸の代わりにピバリン酸４０．８５ｇ（０．４０ｍｏｌ）を用いた以外は製造例２１と同様の方法に従って、錫化合物Ｒを７９．０１ｇ得た。この錫化合物Ｒは、ＦＴ－ＩＲによるアリル基由来の吸収ピーク（３０８２ｃｍ$^{-1}$、１６２７ｃｍ$^{-1}$、８９８ｃｍ$^{-1}$）、錫カルボニル由来の吸収（１５７７ｃｍ$^{-1}$）ピーク、且つ、下記の元素分析の結果からジアリル錫ジピバレートであることがわかった。

【0158】

【表18】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	４７．６	６．９	１６．０	２９．５
理論値	４７．７	７．０	１５．９	２９．４

【0159】

製造例２３　「ジメタリル錫ジアセテートの製造」

ジアリル錫ジクロライドの代わりに製造例１１で得られたジメタリル錫ジクロライド５９．９６ｇ（０．２０ｍｏｌ）を用いた以外は製造例２１と同様の方法に従って、錫化合物Ｓを６８．０１ｇ得た。この錫化合物Ｓは、ＦＴ－ＩＲによるメタリル基由来の吸収ピーク（３０７４ｃｍ$^{-1}$、１６２９ｃｍ$^{-1}$、８６４ｃｍ$^{-1}$）、錫カルボニル由来の吸収ピーク（１５６６ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からジメタリル錫ジアセテートであることがわかった。

【0160】

【表19】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	４５．３	５．４	１７．３	３２．０
理論値	４５．３	５．４	１７．３	３２．０

【0161】

製造例２４　「ジメタリル錫ジピバレートの製造」

ジアリル錫ジクロライドの代わりに製造例１１で得られたジメタリル錫ジクロライド５９．９６ｇ（０．２０ｍｏｌ）を用い、さらに、酢酸の代わりにピバリン酸４０．８５ｇ（０．４０ｍｏｌ）を用いた以外は製造例２１と同様の方法に従って、錫化合物Ｔを８４．５１ｇ得た。この錫化合物Ｔは、ＦＴ－ＩＲによるメタリル基由来の吸収ピーク（３０７４ｃｍ$^{-1}$、１６２９ｃｍ$^{-1}$、８６４ｃｍ$^{-1}$）、錫カルボニル由来の吸収ピーク（１５７７ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からジメタリル錫ジピバレートであることがわかった。

【0162】

【表20】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	５０．２	７．４	１５．０	２７．４
理論値	５０．１	７．５	１４．９	２７．５

【0163】

製造例２５　「モノアリル錫トリクロライドの製造」

温度計、還流冷却器及び攪拌機を備えた５００ｍｌの四つ口フラスコに窒素気流下で、製造例５で得られたテトラアリル錫５６．８８ｇ（０．２０ｍｏｌ）を仕込み、４０～５０℃に保持しつつ、四塩化錫１５６．３１ｇ（０．６０ｍｏｌ）を滴下した。滴下終了後、１５～２５℃で３０分間反応を熟成させることにより粗錫化合物Ｕ２１２．９０ｇを得た。次いで、得られた粗錫化合物Ｕを蒸留することにより精製し、錫化合物Ｕ１９１．６１ｇを得た。純度は９９．５％であった（ＧＣにて確認）。この錫化合物Ｕは、ＦＴ－ＩＲによるアリル基由来の吸収ピーク（３０７８ｃｍ$^{-1}$、１６２２ｃｍ$^{-1}$、８８３ｃｍ$^{-1}$）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝２６６）、且つ、下記の元素分析の結果からモノアリル錫トリクロライドであることがわかった。

【0164】

【表21】

	Ｃ（％）	Ｈ（％）	Ｃｌ（％）	Ｓｎ（％）
測定値	１３．５	１．９	４０．１	４４．５
理論値	１３．５	１．９	４０．０	４４．６

【0165】

製造例２６　「モノメタリル錫トリクロライドの製造」

テトラアリル錫の代わりに製造例６で得られたテトラメタリル錫６７．８２ｇ（０．２０ｍｏｌ）を用いた以外は製造例２５と同様の方法に従って、錫化合物Ｖを２０１．７２ｇ得た。純度は９９．０％であった（ＧＣにて確認）。この錫化合物Ｖは、ＦＴ－ＩＲによるメタリル基由来の吸収ピーク（３０７４ｃｍ$^{-1}$、１６２９ｃｍ$^{-1}$、８６４ｃｍ$^{-1}$）、ＧＣ－ＭＳによる分子イオンピーク（ｍ/ｚ＝２８０）、且つ、下記の元素分析の結果からモノメタリル錫トリクロライドであることがわかった。

【0166】

【表22】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	１７．２	２．５	３８．０	４２．３
理論値	１７．１	２．５	３８．０	４２．４

【0167】

製造例２７　「モノアリル錫オキサイドの製造」

温度計、還流冷却器及び攪拌機を備えた２０００ｍｌの四つ口フラスコに窒素気流下で、製造例２５で得られたモノアリル錫トリクロライド５３．２３ｇ（０．２０ｍｏｌ）を仕込み、２０～４０℃に保持しつつ、１０％水酸化ナトリウム水溶液３６０ｇ（０．９０ｍｏｌ）を滴下した。滴下終了後、２０～４０℃で３時間反応を熟成させた。次いで、得られた反応液に５％塩酸６５６．２８ｇ（０．９０ｍｏｌ）を添加することによりｐＨを５に調整し、生成した白色不溶物を沪別し、沪液が中性になるまで水洗を行った。この白色固形物をロータリーエバポレーターにて減圧乾燥することにより錫化合物Ｗを３４．７０ｇ得た。この錫化合物ＷはＦＴ－ＩＲによるアリル基由来の吸収ピーク（３０７８ｃｍ$^{-1}$、１６２４ｃｍ$^{-1}$、８８９ｃｍ$^{-1}$）、Ｓｎ－Ｏ－Ｓｎ由来の吸収ピーク（４３０

ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からモノアリル錫オキサイドであることがわかった。

【0168】

【表23】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	１８．６	３．０	１６．７	６１．７
理論値	１８．７	３．１	１６．６	６１．６

【0169】

製造例２８　「モノメタリル錫オキサイドの製造」

モノアリル錫トリクロライドの代わりに製造例２６で得られたモノメタリル錫トリクロライド５６．０３ｇ（０．２０ｍｏｌ）を用いた以外は製造例２７と同様の方法に従って、錫化合物Ｘを３７．２２ｇ得た。この錫化合物Ｘは、ＦＴ－ＩＲによるメタリル基由来の吸収ピーク（３０７４ｃｍ$^{-1}$、１６２９ｃｍ$^{-1}$、８６４ｃｍ$^{-1}$）、Ｓｎ－Ｏ－Ｓｎ由来の吸収ピーク（４３０ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からモノメタリル錫オキサイドであることがわかった。

【0170】

【表24】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	２３．２	３．９	１５．４	５７．５
理論値	２３．２	３．９	１５．５	５７．４

【0171】

製造例２９　「モノアリル錫トリアセテートの製造」

温度計、還流冷却器及び撹拌機を備えた５００ｍｌの四つ口フラスコに窒素気流下で、製造例２５で得られたモノアリル錫トリクロライド２６．６１ｇ（０．１０ｍｏｌ）、酢酸１８．０２ｇ（０．３０ｍｌ）、及びベンゼン１５０ｍｌを仕込み、２０～３０℃に保持しつつ、トリエチルアミン３０．３６ｇ（０．３０ｍｏｌ）を滴下した。滴下終了後、２０～３０℃で３時間反応を熟成させた。生成した白色不溶物を沪別し、沪液を濃縮することにより錫化合物Ｙを３３．６９ｇ得た。この錫化合物Ｙは、ＦＴ－ＩＲによるアリル基由来の吸収ピーク（３０７８ｃｍ$^{-1}$、１６２２ｃｍ$^{-1}$、８９８ｃｍ$^{-1}$）、錫カルボニル由来の吸収ピーク（１５６６ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からモノアリル錫トリアセテートであることを確認した。

【0172】

【表25】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	３２．０	４．３	２８．６	３５．１
理論値	３２．１	４．２	２８．５	３５．２

【0173】

製造例３０　「モノメタリル錫トリアセテートの製造」

モノアリル錫トリクロライドの代わりに製造例２６で得られたモノメタリル錫トリクロライド２８．０２ｇ（０．１０ｍｏｌ）を用いた以外は製造例２９と同様の方法に従って、錫化合物Ｚを３３．３３ｇ得た。この錫化合物Ｚは、ＦＴ－ＩＲによるメタリル基由来の吸収ピーク（３０７４ｃｍ$^{-1}$、１６２９ｃｍ$^{-1}$、８６４ｃｍ$^{-1}$）、錫カルボニル由来の吸収ピーク（１５６６ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からモノメタリル錫トリアセテートであることがわかった。

【0174】
【表26】

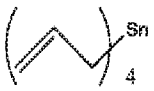
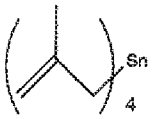
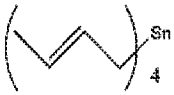
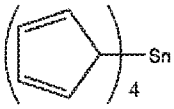
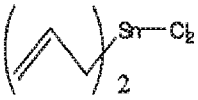
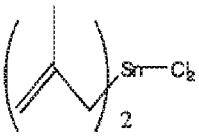
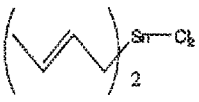
	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	３４．０	４．６	２７．５	３３．９
理論値	３４．２	４．６	２７．４	３３．８

【0175】
製造例３１　「ジメチル錫オキサイドの製造」
ジアリル錫ジクロライドの代わりにジメチル錫ジクロライド（東京化成工業株式会社）３２．９４ｇ（０．１５ｍｏｌ）を用いた以外は製造例１５と同様の方法に従って、錫化合物ａを２２．２４ｇ得た。この錫化合物ａはＦＴ－ＩＲによるメチル基由来の吸収ピーク（２９８９ｃｍ$^{-1}$、２９２０ｃｍ$^{-1}$）、Ｓｎ－Ｏ－Ｓｎ由来の吸収ピーク（４２８ｃｍ$^{-1}$）、且つ、下記の元素分析の結果からジメチル錫オキサイドであることがわかった。
【0176】
【表27】

	Ｃ（％）	Ｈ（％）	Ｏ（％）	Ｓｎ（％）
測定値	１４．６	３．７	９．８	７１．９
理論値	１４．６	３．７	９．７	７２．０

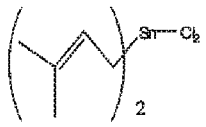
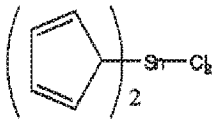
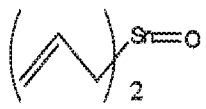
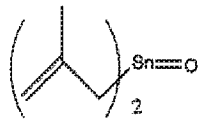
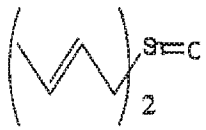
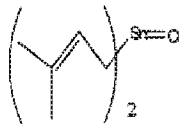
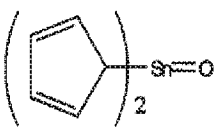
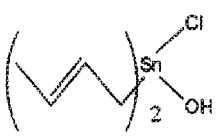
【0177】
実施例１～２６及び比較例１～４　「熱分解性確認試験」
製造例５～３０で得られた錫化合物Ａ～Ｚ（実施例１～２６）と従来の錫化合物（比較例１～４）の分解温度を示差熱熱重量同時測定（ＴＧ／ＤＴＡ）により測定した。なお、比較例１では、製造例３１で得られた錫化合物ａ、比較例２では、ジブチル錫オキサイド（ＤＢＴＯ）（日東化成株式会社製）、比較例３では、ジオクチル錫オキサイド（ＤＯＴＯ）（日東化成株式会社製）及び比較例４では、ビス（２－エチルヘキサン酸）錫（製品名「ネオスタンＵ－２８」日東化成株式会社製）を用いた。
【0178】
また、測定は以下の条件で行った。
【0179】
測定装置：Ｓｅｉｋｏ　Ｉｎｓｔｒｕｍｅｎｔｓ　ＳＳＣ／５２００
測定条件：
測定温度　５０～２００℃、昇温速度　１０℃／分、測定雰囲気　空気
ＴＧ／ＤＴＡ終了後の残渣のＩＲを測定することにより、有機成分の有無を分析した。
【0180】
結果を表２８～３１に示す。
【0181】

【表28】

	化合物	分解温度 開始～終了	ＩＲ測定結果	
			有機成分 C-H (2958cm^{-1})	Sn-O-Sn (500～700cm^{-1})
実施例１	錫化合物Ａ 	113～165℃	無し	有り
実施例２	錫化合物Ｂ 	138～190℃	無し	有り
実施例３	錫化合物Ｃ 	153～199℃	無し	有り
実施例４	錫化合物Ｄ 	160～191℃	無し	有り
実施例５	錫化合物Ｅ 	165～198℃	無し	有り
実施例６	錫化合物Ｆ 	100～155℃	無し	有り
実施例７	錫化合物Ｇ 	106～160℃	無し	有り
実施例８	錫化合物Ｈ 	133～179℃	無し	有り

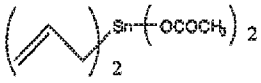
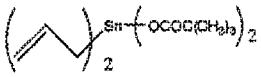
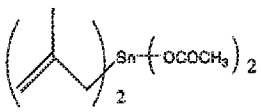
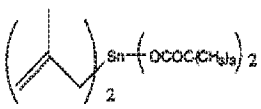
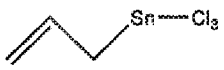
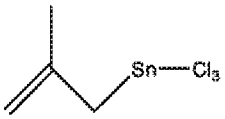
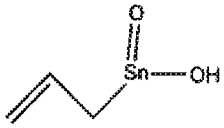
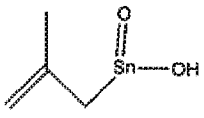
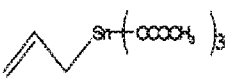
【0182】

【表29】

	化合物	分解温度 開始～終了	ＩＲ測定結果	
			有機成分 C-H ($2958cm^{-1}$)	Sn-O-Sn ($500～700cm^{-1}$)
実施例９	錫化合物Ｉ 	143～185℃	無し	有り
実施例１０	錫化合物Ｊ 	152～195℃	無し	有り
実施例１１	錫化合物Ｋ 	90～162℃	無し	有り
実施例１２	錫化合物Ｌ 	100～181℃	無し	有り
実施例１３	錫化合物Ｍ 	154～179℃	無し	有り
実施例１４	錫化合物Ｎ 	165～193℃	無し	有り
実施例１５	錫化合物Ｏ 	168～199℃	無し	有り
実施例１６	錫化合物Ｐ 	155～189℃	無し	有り

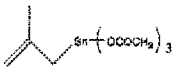
【0183】

【表30】

	化合物	分解温度 開始～終了	ＩＲ測定結果	
			有機成分 C-H ($2958cm^{-1}$)	Sn-O-Sn ($500～700cm^{-1}$)
実施例１７	錫化合物Q 	100～177℃	無し	有り
実施例１８	錫化合物R 	146～190℃	無し	有り
実施例１９	錫化合物S 	113～183℃	無し	有り
実施例２０	錫化合物T 	160～196℃	無し	有り
実施例２１	錫化合物U 	94～166℃	無し	有り
実施例２２	錫化合物V 	108～164℃	無し	有り
実施例２３	錫化合物W 	89～152℃	無し	有り
実施例２４	錫化合物X 	115～181℃	無し	有り
実施例２５	錫化合物Y 	103～170℃	無し	有り

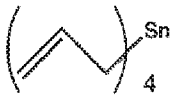
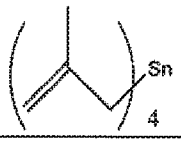
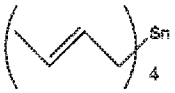
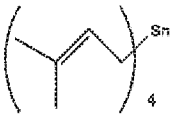
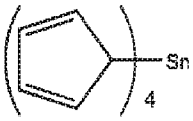
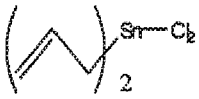
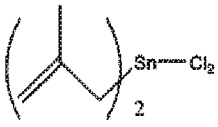
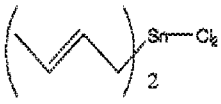
【0184】

【表31】

	化合物	分解温度 開始～終了	ＩＲ測定結果	
			有機成分 C-H ($2958cm^{-1}$)	Sn-O-Sn ($500～700cm^{-1}$)
実施例２６	錫化合物Ｚ 	118～187℃	無し	有り
比較例１	錫化合物ａ Me_2SnO	＊１	有り	有り
比較例２	ＤＢＴＯ Bu_2SnO	＊１	有り	有り
比較例３	ＤＯＴＯ Oct_2SnO	＊１	有り	有り
比較例４	ネオスタンU-28 $(C_7H_{15}COO)_2Sn$	＊１	有り	無し

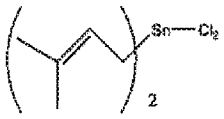
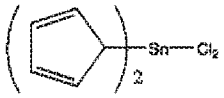
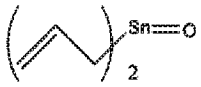
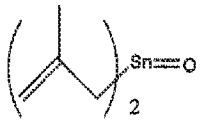
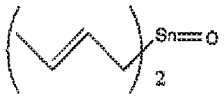
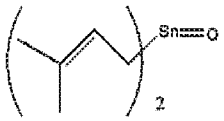
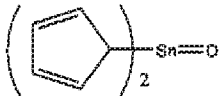
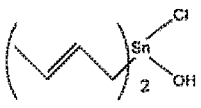
【0185】
＊１：２００℃では、徐々に重量減少がみられ恒量とならず、分解温度は特定できなかった。
表２８～３１から明らかなように、従来の錫化合物を用いた比較例１～４では有機成分が分解せず残存しているのに対し、本発明の酸化錫薄膜原料である特定の錫化合物を用いた実施例１～２６では、２００℃以下の温度で分解し無機化していることがわかる。
【0186】
実施例２７～５２および比較例５～８　「酸化錫薄膜の形成確認試験」
製造例５～３０で得られた錫化合物Ａ～Ｚ並びに上記錫化合物ａ、ＤＢＴＯ、ＤＯＴＯ及びネオスタンＵ－２８（比較例５～８）をエタノールに溶解し１０％溶液を調製した。このとき、錫化合物Ｋ、Ｌ、Ｍ、Ｎ、Ｏ、Ｗ、Ｘおよび従来の錫化合物ａ、ＤＢＴＯ、ＤＯＴＯはエタノールに対する溶解度が低いため、７０℃に加温しホモジナイザーにて撹拌し均一溶液とした。これらの溶液をスピンコーターを用いてガラス基板上に塗布し、乾燥させた。次いで、毎分１０℃の昇温速度で２００℃まで昇温し、２００℃で１５分間焼成し酸化錫薄膜を得た。
【0187】
得られた酸化錫膜の状態を目視にて観察した。薄膜がムラ無く、均一かつ平滑である場合を○、ムラが有り、ブツ、白濁が生じている場合を×とした。
【0188】
さらに薄膜表面の顕微ＩＲを測定することにより有機成分の有無を分析した。
【0189】
結果を表３２～３５に示す。
【0190】

【表32】

	化合物	薄膜状態	ＩＲ測定結果	
			有機成分 C-H ($2958cm^{-1}$)	Sn-O-Sn ($500\sim700cm^{-1}$)
実施例２７	錫化合物Ａ 	○	無し	有り
実施例２８	錫化合物Ｂ 	○	無し	有り
実施例２９	錫化合物Ｃ 	○	無し	有り
実施例３０	錫化合物Ｄ 	○	無し	有り
実施例３１	錫化合物Ｅ 	○	無し	有り
実施例３２	錫化合物Ｆ 	○	無し	有り
実施例３３	錫化合物Ｇ 	○	無し	有り
実施例３４	錫化合物Ｈ 	○	無し	有り

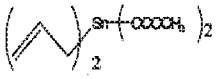
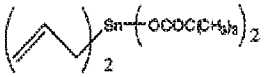
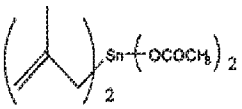
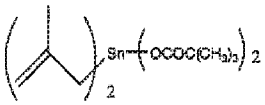
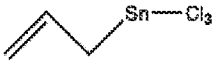
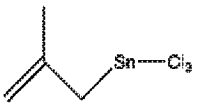
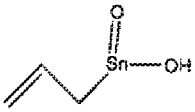
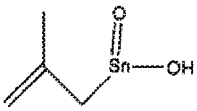
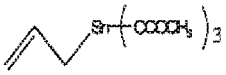
【0191】

【表33】

	化合物	薄膜状態	ＩＲ測定結果	
			有機成分 C-H (2958cm^{-1})	Sn-O-Sn (500～700cm^{-1})
実施例３５	錫化合物Ｉ 	○	無し	有り
実施例３６	錫化合物Ｊ 	○	無し	有り
実施例３７	錫化合物Ｋ 	○	無し	有り
実施例３８	錫化合物Ｌ 	○	無し	有り
実施例３９	錫化合物Ｍ 	○	無し	有り
実施例４０	錫化合物Ｎ 	○	無し	有り
実施例４１	錫化合物Ｏ 	○	無し	有り
実施例４２	錫化合物Ｐ 	○	無し	有り

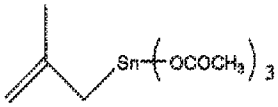
【0192】

【表34】

	化合物	薄膜状態	ＩＲ測定結果	
			有機成分 C-H ($2958cm^{-1}$)	Sn-O-Sn ($500\sim700cm^{-1}$)
実施例４３	錫化合物Q 	○	無し	有り
実施例４４	錫化合物R 	○	無し	有り
実施例４５	錫化合物S 	○	無し	有り
実施例４６	錫化合物T 	○	無し	有り
実施例４７	錫化合物U 	○	無し	有り
実施例４８	錫化合物V 	○	無し	有り
実施例４９	錫化合物W 	○	無し	有り
実施例５０	錫化合物X 	○	無し	有り
実施例５１	錫化合物Y 	○	無し	有り

【0193】

【表35】

	化合物	薄膜状態	ＩＲ測定結果	
			有機成分 C-H (2958cm^{-1})	Sn-O-Sn (500～700cm^{-1})
実施例５２	錫化合物Ｚ 	○	無し	有り
比較例５	錫化合物ａ Me_2SnO	×	有り	有り
比較例６	ＤＢＴＯ Bu_2SnO	×	有り	有り
比較例７	ＤＯＴＯ Oct_2SnO	×	有り	有り
比較例８	ﾈｵｽﾀﾝ U-28 $(C_7H_{15}COO)_2Sn$	×	有り	無し

【0194】

表３２～３５から明らかなように、実施例２７～５２は、従来の錫化合物を用いた比較例５～８に比べ、薄膜の状態が良いことがわかる。また顕微ＩＲの結果から、比較例５～８では有機成分が分解せず残存しているのに対し、実施例２７～５２では完全に有機成分が分解して無機化していることがわかる。すなわち２００℃という低温下での熱分解により酸化錫薄膜が形成されたことがわかる。

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Resin composition comprising catalyst precursor for electroless plating to form electromagnetic wave shielding layer, methods for forming metal patterns using the resin composition and metal patterns formed by the methods

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Disclosed is a resin composition which comprises a catalyst precursor for electroless plating to form an electromagnetic wave shielding layer. The resin composition comprises an organic polymer resin, a polyfunctional monomer having an ethylenically unsaturated bond, a photoinitiator, a sliver organic complex precursor as a catalyst precursor, and an organic solvent. Further disclosed are methods for forming metal patterns using the resin composition and metal patterns formed by the methods. The methods comprise forming a pattern, reducing the pattern, and electroless plating the reduced pattern. A patterned layer of the catalyst formed using the resin composition is highly adhesive, a loss of the catalyst during a wet process is substantially prevented, and an increase in plating rate leads to the formation of a uniform, fine metal pattern after electroless plating. Electromagnetic wave shielding materials comprising the metal pattern can be used in the formation of films for shielding electromagnetic waves.

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Resin composition comprising catalyst precursor for electroless plating to form electromagnetic wave shielding layer, methods for forming metal patterns using the resin composition and metal patterns formed by the methods

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Abstract of TW200801799 (A)

Disclosed is a resin composition which comprises a catalyst precursor for electroless plating to form an electromagnetic wave shielding layer. The resin composition comprises an organic polymer resin, a polyfunctional monomer having an ethylenically unsaturated bond, a photoinitiator, a sliver organic complex precursor as a catalyst precursor, and an organic solvent. Further disclosed are methods for forming metal patterns using the resin composition and metal patterns formed by the methods. The methods comprise forming a pattern, reducing the pattern, and electroless plating the reduced pattern. A patterned layer of the catalyst formed using the resin composition is highly adhesive, a loss of the catalyst during a wet process is substantially prevented, and an increase in plating rate leads to the formation of a uniform, fine metal pattern after electroless plating. Electromagnetic wave shielding materials comprising the metal pattern can be used in the formation of films for shielding electromagnetic waves.

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(54)【発明の名称】電磁波遮蔽層の製造時に無電解メッキに対する触媒前駆体樹脂組成物、これを用いた金属パターンの形成方法及びこれにより製造された金属パターン

(57)【要約】
本発明は、電磁波遮蔽層の形成時に無電解メッキ用触媒前駆体を含む樹脂組成物に関するもので、本発明の触媒前駆体樹脂組成物は有機高分子樹脂と、エチレン性不飽和結合を有する多官能モノマーと、光開始剤と、銀イオン有機錯化物前駆体及び有機溶媒を含んでなり、金属パターンの形成方法は本発明の触媒前駆体樹脂組成物を用いてパターンを形成し、還元及び無電解メッキすることにより形成される。本発明による樹脂組成物を用いて金属パターンを形成する場合、形成された触媒パターン層の接着性に優れて、現像またはメッキ工程のような湿潤工程中の触媒遺失が少なく、蒸着速度が向上され無電解メッキ後に均一で微細な金属パターンに形成されることができる。また、本発明により形成された金属パターンを有する電磁波遮蔽材は電磁波遮蔽膜の形成に適合に用いることができる。
【選択図】図１

【特許請求の範囲】
【請求項1】
（ａ）有機高分子樹脂と、（ｂ）エチレン性不飽和結合を有する多官能モノマーと、（ｃ）光開始剤と、（ｄ）銀イオン有機錯化物前駆体及び（ｅ）有機溶媒を含んでなる電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項2】
前記有機高分子樹脂は、カルボキシル基含有モノマー及びカルボキシル基含有モノマーと共重合が可能な不飽和二重結合含有モノマーの共重合体であることを特徴とする請求項１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項3】
前記カルボキシル基含有モノマーは、アクリル酸、メタクリル酸、クロトン酸、イタコン酸、マレイン酸、フマル酸、モノメチルマレイン酸、イソプレンスルホン酸、スチレンスルホン酸及び５－ノルボルネン－２－カルボキシル酸で構成されるグループから選ばれた少なくとも１種以上であることを特徴とする請求項２に記載の電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項4】
前記有機高分子樹脂は、重量平均分子量が２，０００～３０，０００であることを特徴とする請求項１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項5】
前記有機高分子樹脂は、酸価が９０～７００ｍｇＫＯＨ／ｇであることを特徴とする請求項１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項6】
前記エチレン性不飽和結合を有する多官能モノマーは、エチレングリコールジアクリレート、エチレングリコールジメタクリレート、エチレン基の数が２～１４であるポリエチレングリコールジアクリレート、またはポリエチレングリコールジメタクリレート、トリメチロールプロパントリアクリレート、トリメチロールプロパントリメタクリレート、ペンタエリトリトールトリアクリレート、ペンタエリトリトールトリメタクリレート、ペンタエリトリトールテトラアクリレート、ペンタエリトリトールテトラメタクリレート、プロピレン基の数が２～１４であるプロピレングリコールジアクリレート、またはプロピレングリコールジメタクリレート、ジペンタエリトリトールペンタアクリレート、ジペンタエリトリトールペンタメタクリレート、ジペンタエリトリトールヘキサアクリレート、ジペンタエリトリトールヘキサメタクリレート等の多価アルコールをα，β－不飽和カルボキシル酸でエステル化して得られる化合物と、トリメチロールプロパントリグリシジルエーテルアクリル酸付加物、ビスフェノールＡジグリシジルエーテルアクリル酸付加物等のグリシジル基を含有する化合物にアクリル酸またはメタクリル酸を付加して得られる化合物と、β－ヒドロキシエチルアクリレートまたはβ－ヒドロキシエチルメタクリレートのフタル酸エステル、β－ヒドロキシエチルアクリレートまたはβ－ヒドロキシエチルメタクリレートのトルエンジイソシアネート付加物等の水酸化基及びエチレン性不飽和結合を有する化合物とマルチ（ｍｕｌｔｉ）－カルボキシル酸のエステル化合物または水酸化基及びエチレン性不飽和結合を有する化合物のマルチ（ｍｕｌｔｉ）－ポリイソシアネート付加物で構成されるグループから選ばれた少なくとも１種以上であることを特徴とする請求項１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項7】
前記エチレン性不飽和結合を有する多官能モノマーは、エチレン性不飽和結合を有する官能基数が3以上であることを特徴とする請求項６に記載の電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項8】
前記エチレン性不飽和結合を有する多官能モノマーは前記有機高分子樹脂　１００重量部に対して２０～１５０重量部で配合されることを特徴とする請求項１に記載の電磁波遮

蔽用触媒前駆体樹脂組成物。
【請求項9】
前記光開始剤は、アセトフェノン類、ベンゾフェノン類、ミッヒラー（Ｍｉｃｈｌｅｒ）ベンゾイルベンゾエイト、α－アミルオキシムエステル、チオキサントン類及びトリアジン類で構成されるグループから選ばれた少なくとも１種以上であることを特徴とする請求項１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項10】
前記光開始剤は、前記有機高分子樹脂１００重量部に対して１～２５重量部で用いられることを特徴とする請求項１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項11】
前記銀イオン有機錯化物前駆体は、銀アセテート系、銀スルホネート系、β－カルボニルケトン系シルバー（Ｉ）錯化物及びβ－カルボニルエステル系シルバー（Ｉ）錯化物で構成されるグループから選ばれた少なくとも１種以上であることを特徴とする請求項１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項12】
前記銀イオン有機錯化物前駆体は銀アセテート、銀ラクテート、銀ミリステート、銀シトレート、銀ベンゾエート、銀フェニルアセテート、銀シクロヘキサンブチレート、銀パラトルエンスルホネート、銀オキサレート、銀マロネート、銀サクシネート、銀アジペート、シルバー（Ｉ）アセチルアセトネート、３－クロロ－２，４－ペンタンジオネートシルバー（Ｉ）錯化物、３，５－ヘプタンジオネートシルバー（Ｉ）錯化物、２－アセチルシクロヘキサノネートシルバー（Ｉ）錯化物、３－エチル－２，４－ペンタジオネートシルバー（Ｉ）錯化物、ベンゾイルアセトンシルバー（Ｉ）錯化物、ジベンゾイルメタンシルバー（Ｉ）錯化物、２，２，６，６－テトラメチルヘプタンジエンシルバー（Ｉ）錯化物、エチルアセトアセテートシルバー（Ｉ）錯化物、メチルアセトアセテートシルバー（Ｉ）錯化物、イソプロピルアセトアセテートシルバー（Ｉ）錯化物及びｔｅｒｔ－アリールブチルアセトアセテートシルバー（Ｉ）錯化物で構成されるグループから選ばれた少なくとも１種以上であることを特徴とする請求項１１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項13】
前記銀イオン有機錯化物前駆体は、フルオロ化された銀イオン有機錯化物であることを特徴とする請求項１１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。
【請求項14】
前記フルオロ化された銀イオン有機錯化物前駆体は、銀（Ｉ）フルオロサルフェイト、銀（Ｉ）トリフルオロアセテート、銀（Ｉ）トリフルオロメタンサルフェイト、銀（Ｉ）ペンタフルオロプロピオネート、銀（Ｉ）ヘプタフルオロブチラート、１，５－シクロオクタジエン－ヘキサフルオロアセチルアセトネートシルバー（Ｉ）錯化物、１，１，１－トリフルオロ－２，４－ペンタジオネートシルバー（Ｉ）錯化物、５，５－ジメチル－１，１，１－トリフルオロ－２，４－ヘキサンジオネートシルバー（Ｉ）錯化物、１－（４－メトキシフェニル）－４，４，４－トリフルオロブタンジオネートシルバー（Ｉ）錯化物、５，５，６，６，７，７，８，８，９，９，１０，１０，１１，１１，１２，１２，１２－ヘプタデカフルオロデカン－２，４－ジオネートシルバー（Ｉ）錯化物、１，１，１，２，２，３，３－ヘプタフルオロ-７，７－ジメチル－４，６－オクタンジオネートシルバー（Ｉ）錯化物、１，１，１，３，５，５，５－ヘプタフルオロペンタン－２，４－ジオネートシルバー（Ｉ）錯化物、１，１，１，５，５，５－ヘキサフルオロペンタン－２，４－ジオネートシルバー（Ｉ）錯化物、５，５，６，６，７，７，８，８，８－ノナフルオロオクタン－２，４－ジオネートシルバー（Ｉ）錯化物、５Ｈ，５Ｈ－ペルフルオロノナン－４，６－ジオネートシルバー（Ｉ）錯化物、６Ｈ，６Ｈ－ペルフルオロ-ウンデカン－５，７－ジオネートシルバー（Ｉ）錯化物、８Ｈ，８Ｈ－ペルフルオロペンタデカン－７，８－ジオネートシルバー（Ｉ）錯化物、６Ｈ，６Ｈ－ペルフルオロウンデカン－５，７－ジオネートシルバー（Ｉ）錯化物、１－フェニル－２Ｈ，２Ｈ－ペルフルオ

ロヘキサン－１，３－ジオネートシルバー（Ｉ）錯化物、１－フェニル－２Ｈ，２Ｈ－ペルフルオロウンデカン－１，３－ジオネートシルバー（Ｉ）錯化物、５，６，６，６－テトラフルオロ－５－（ヘプタフルオロプロポキシ）ヘキサン－２，４－ジオネートシルバー（Ｉ）錯化物、１，１，５，５－テトラフルオロペンタン－２，４ ジオネートシルバー（Ｉ）錯化物、５，５，６，６，７，７，８，８，９，９，９－ウンデカンフルオロ－ノナン－２，４－ジオネートシルバー（Ｉ）錯化物、エチル－３－クロロ－４，４，４－トリフルオロアセトアセテートシルバー（Ｉ）錯化物、エチル－４，４－ジフルオロアセトアセテートシルバー（Ｉ）錯化物、エチル－４，４，４－トリフルオロアセトアセテートシルバー（Ｉ）錯化物、イソプロピル－４，４，４－トリフルオロアセトアセテートシルバー（Ｉ）錯化物、メチル－４，４，５，５，５－ペンタフルオロ－３－オキソペンタノネートシルバー（Ｉ）錯化物、エチル－４，４，５，５，５－ペンタフルオロ－３－オキソ-ペンタノネートシルバー（Ｉ）錯化物及び１，１，１，５，５，６，６，６－オクタフルオロ－２，４－ヘキサンジオネートシルバー（Ｉ）錯化物で構成されるグループから選ばれた少なくとも１種であることを特徴とする請求項１３に記載の電磁波遮蔽用触媒前駆体樹脂組成物。

【請求項15】

前記銀イオン有機錯化物前駆体は、触媒前駆体樹脂組成物中の全体有機固形分１００重量部に２～８０重量部で添加されることを特徴とする請求項１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。

【請求項16】

前記有機溶媒は、メタノール、エタノール、ｎ－プロパノール、イソプロパノール、エチレングリコール、またはプロピレングリコールのようなアルコール類と、アセトン、メチルエチルケトン、シクロヘキサノン、またはｎ－メチル－２－ピロリドンのようなケトン類と、トルエン、キシレン、またはテトラメチルベンゼンのような芳香族炭化水素類と、セロソルブ、メチルセロソルブ、エチルセロソルブ、３－メトキシプロピルアセテート、プロピレングリコールモノメチルエテール、プロピレングリコールエチルエテール、ジプロピレングリコールモノメチルエテール、またはジプロピレングリコールエチルエテールのようなグリコールエテール類と、エチルアセテート、ブチルアセテート、セロソルブアセテート、エチルセロソルブアセテート、ブチルセロソルブアセテート、プロピレングリコールモノメチルエテールアセテート、またはプロピレングリコールエチルエテールアセテートのようなアセテート類で構成されるグループから選ばれた少なくとも１種以上であることを特徴とする請求項１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。

【請求項17】

前記有機高分子樹脂と光開始剤の混合量１００重量部に対して光増感剤を１０重量部以下でさらに含むことを特徴とする請求項１に記載の電磁波遮蔽用触媒前駆体樹脂組成物。

【請求項18】

前記光増感剤は、ｎ－ブチルアミン、トリエチルアミンまたはトリ－ｎ－ブチルホスフィンで構成されるグループから選ばれた少なくとも１種以上であることを特徴とする請求項１７に記載の電磁波遮蔽用触媒前駆体樹脂組成物。

【請求項19】

（ａ）請求項１項の触媒前駆体樹脂組成物を基材にコーティングする段階と、

（ｂ）前記コーティングされた組成物を露光及び現像して触媒パターン層を形成する段階と、

（ｃ）前記触媒パターン層を還元させる段階と、

（ｄ）前記還元された触媒パターン層を無電解メッキする段階と、

を含んでなる金属パターンの形成方法。

【請求項20】

（ａ）請求項１項の触媒前駆体樹脂組成物を用いて基材上に触媒パターン層を形成する段階と、

（ｂ）前記形成された触媒パターン層を還元させる段階と、

（ｃ）前記還元された触媒パターン層を無電解メッキする段階と、
を含んでなる金属パターンの形成方法。
【請求項21】
前記触媒パターンの形成は、オフセットプリンティング、インクジェットプリンティング、インプリントまたはスクリーンプリンティングで行うことを特徴とする請求項２０に記載の金属パターンの形成方法。
【請求項22】
前記基材は、ガラス、ポリカーボネート、アクリル樹脂、ＰＥＴ、ＴＡＣ（Ｔｒｉ－ａｃｅｔｙｌ　ｃｅｌｌｕｌｏｓｅ）、ポリ塩化ビニル樹脂、ポリアミド樹脂及びポリイミド樹脂のようなプラスチックシートまたはプラスチックフィルムで構成されるグループから選ばれた１種であることを特徴とする請求項１９または請求項２０に記載の金属パターンの形成方法。
【請求項23】
前記還元段階は、水素化ホウ素ナトリウムまたはアスコルビン酸還元剤で行われることを特徴とする請求項１９または請求項２０に記載の金属パターンの形成方法。
【請求項24】
前記還元段階は、ＵＶ露光及び／または熱を適用して行われることを特徴とする請求項１９または請求項２０に記載の金属パターンの形成方法。
【請求項25】
前記無電解メッキは、銅メッキまたは銀メッキで行われることを特徴とする請求項１９または請求項２０に記載の金属パターンの形成方法。
【請求項26】
前記銅メッキは、硫酸銅のような金属イオン塩、ホルマリンのような還元剤及びＥＤＴＡのような安定化剤を含むメッキ液を用いて行われることを特徴とする請求項２５に記載の金属パターンの形成方法。
【請求項27】
（ａ）請求項１項の触媒前駆体樹脂組成物を基材にコーティングする段階と、
（ｂ）前記コーティングされた組成物を露光及び現像して触媒パターン層を形成する段階と、
（ｃ）前記触媒パターン層を還元させる段階と、
（ｄ）前記還元された触媒パターン層を無電解メッキする段階と、
を含んでなる方法で形成された金属パターン。
【請求項28】
（ａ）請求項１項の触媒前駆体樹脂組成物を用いて基材上に触媒パターン層を形成する段階と、
（ｂ）前記形成された触媒パターン層を還元させる段階と、
（ｃ）前記還元された触媒パターン層を無電解メッキする段階と、
を含んでなる方法で形成された金属パターン。
【請求項29】
請求項２７項または２８項の金属パターンを含む電磁波遮蔽材。
【発明の詳細な説明】
【技術分野】
【0001】
本発明は、電磁波遮蔽層の形成時に無電解メッキに対する触媒前駆体樹脂組成物、これを用いた金属パターンの形成方法及びこれにより形成された金属パターンに関するものである。より詳細には銀イオン有機錯化物前駆体を含む触媒前駆体樹脂組成物、これを用いた微細な金属パターンの形成方法及びこれにより形成された金属パターンに関するもので、これにより提供される金属パターンはＣＲＴ、ＰＤＰ、液晶、ＥＬ等のディスプレイの前面から発生する電磁波遮蔽膜や軟性回路基板の配線の形成に適合に使用されることができる。
【背景技術】

【0002】
最近、多様な方式のディスプレイが常用化されながら、このようなディスプレイから発生する電磁気的なノイズ（Ｎｏｉｓｅ）の妨害現象（Ｅｌｅｃｔｒｏｎｍａｇｎｅｔｉｃ Ｉｎｔｅｒｆｅｒｅｎｃｅ：ＥＭＩ）による人体への有害性及び機器の誤作動等が大きな問題点として浮かび上がっている。このような問題を解決するためにディスプレイの前面に導電性の遮蔽（Ｓｈｉｅｌｄｉｎｇ）膜を形成して電磁波の進行方向を歪曲させてから接地して放出させる方法が用いられている。
【0003】
ＣＲＴ、ＰＤＰ等のディスプレイの前面から発生する電磁波ノイズの遮蔽方法として、透明な基材上に金属または金属酸化物を蒸着して薄い導電性の膜を形成する方法が知られているが、このような方法は透明性を提供するために膜を薄く蒸着しなければならず、このような場合には導電層の表面抵抗が非常に大きくなるため、十分な電磁波遮蔽の効果が得られない。
【0004】
上記のような方法の他にもスクリーンプリンティング、オフセットプリンティング等のプリンティング方式で導電性ペーストをパターンするか、これを再び無電解メッキ処理して電磁波遮蔽膜を形成することが報告されているが、このような場合には、印刷回路の精密度に限界があり、凹凸部分に導電性物質が染み込む等の問題がある。
【0005】
また、写真現像方法で金属層を形成しメッキまたは無電解メッキ処理する方法が提示されているが、写真現像方法は複数の層が必要で、工程が複雑であるという短所がある。金属触媒を感光性樹脂と混合してコーティングし現像してから無電解メッキまたは電解メッキを行うことが報告されているが、これは主に触媒に高価のＰｄを用いて微細パターンの形成及び無電解メッキ時の問題点等を解決する方法を具体的に提示していない。また、無電解メッキを行う場合、蒸着特性は向上されるが、強塩基水溶液におけるパターン着脱等による問題に対しては解決方案を具体的に提示していない。
【発明の開示】
【発明が解決しようとする課題】
【0006】
これに、本発明は上記のような従来技術の問題点を解決するためのもので、本発明の目的は高価のＰｄ触媒を用いず、還元転位のために熱力学的に酸化に安定的であるため扱いやすく、現像、無電解メッキ等の湿式工程時に触媒の遺失が少なく、接着性及び蒸着性に優れた触媒前駆体樹脂組成物を提供することである。
【0007】
本発明の他の目的は、上記触媒前駆体樹脂組成物を用いた金属パターンの形成方法を提供することである。
【0008】
本発明のさらに他の目的は、上記のように提供される金属パターン及びこれを含む電磁波遮蔽材を提供することである。
【課題を解決するための手段】
【0009】
本発明の第１見地によると、
（ａ）有機高分子樹脂と、
（ｂ）エチレン性不飽和結合を有する多官能モノマーと、
（ｃ）光開始剤と、
（ｄ）銀イオン有機錯化物前駆体と、
（ｅ）有機溶媒と、
を含んでなる電磁波遮蔽用触媒前駆体樹脂組成物が提供される。
【0010】
本発明の第２見地によると、

（ａ）本発明の触媒前駆体樹脂組成物を基材にコーティングする段階と、
（ｂ）上記コーティングされた組成物を露光及び現像して触媒パターン層を形成する段階と、
（ｃ）上記触媒パターン層を還元させる段階と、
（ｄ）上記還元された触媒パターン層上に無電解メッキする段階と、
を含んでなる金属パターンの形成方法が提供される。

【0011】

本発明の第３見地によると、
（ａ）上記触媒前駆体樹脂組成物を用いてプリンティング法で基材に触媒パターン層を形成する段階と、
（ｂ）上記形成された触媒パターン層を還元させる段階と、
（ｃ）上記還元された触媒パターン層上に無電解メッキする段階と、
を含んでなる金属パターンの形成方法が提供される。

【0012】

本発明の第４見地によると、
（ａ）本発明の触媒前駆体樹脂組成物を基材にコーティングする段階と、
（ｂ）上記コーティングされた組成物を露光及び現像して触媒パターン層を形成する段階と、
（ｃ）上記触媒パターン層を還元させる段階と、
（ｄ）上記還元された触媒パターン層を無電解メッキする段階と、
を含んでなる方法で形成された金属パターンが提供される。

【0013】

本発明の第５見地によると、
（ａ）本発明の触媒前駆体樹脂組成物を用いて基材上に触媒パターン層を形成する段階と、
（ｂ）上記形成された触媒パターン層を還元させる段階と、
（ｃ）上記還元された触媒パターン層を無電解メッキする段階と、
を含んでなる方法で形成された金属パターンが提供される。

【0014】

本発明の第６見地によると、
上記本発明の方法で形成された金属パターンを含む電磁波遮蔽材が提供される。

【発明の効果】

【0015】

本発明による銀イオン有機錯化物含有樹脂組成物を金属パターンの製造に用いることにより形成された触媒膜の接着性に優れ、現像またはメッキ工程のような湿潤工程中の触媒遺失が少なく、メッキ速度が向上され無電解メッキ後に均一で微細な金属パターンに形成される。また、本発明による触媒前駆体樹脂組成物及び方法で製造された金属パターンを含む電磁波遮蔽材はＣＲＴ、ＰＤＰ、液晶、ＥＬ等のディスプレイの前面から発生する電磁波遮蔽膜や軟性回路基板の配線の形成に適合に用いることができる。

【発明を実施するための最良の形態】

【0016】

以下、本発明に対してより詳細に説明する。

【0017】

本発明者らは、工程が単純で、ラインの幅が２０μｍ以下の微細な金属パターンの製造方法を研究したところ、銀イオン有機錯化物前駆体を含有する樹脂組成物を使用して触媒パターンを形成する場合、金属粒子の使用による樹脂組成物の安定性を解決し、現像またはメッキ工程のような湿潤工程中の銀触媒の遺失が減り、触媒パターン層の接着性、耐化学性、蒸着速度等が向上され無電解メッキ後に均一な微細金属パターンの形成が可能であることを発見し本発明の完成に至った。

【0018】

本発明の一具現において、本発明による触媒前駆体樹脂組成物は有機高分子樹脂と、エチレン性不飽和結合を有する多官能モノマーと、光開始剤と、銀イオン有機錯化物前駆体及び有機溶媒を含んでなることができる。

【0019】

本発明の触媒前駆体樹脂組成物を構成する有機高分子樹脂は、銀触媒を安定化させ、触媒の現像性を制御する。一般的に触媒の含量が多いと無電解メッキ時にメッキ速度は速くなるが、安定性及び現像性が落ちるという問題がある。

【0020】

無電解メッキに対する触媒として十分な銀イオン有機錯化物前駆体を含有しながらも触媒の安定性及び現像性を考慮して本発明は有機高分子樹脂として、カルボキシル基を含むモノマー及びこれと共重合が可能なモノマーの共重合体を用いることができる。これに限定するものではないが、本発明に用いられる有機高分子樹脂はカルボキシル基を含むモノマーとこれと共重合が可能なモノマーを３：７乃至９：１重量比で含むことができる。上記有機高分子樹脂においてカルボキシル基を含むモノマーとこれと共重合が可能なモノマーに対する重量比が３：７未満であると触媒との相溶性が低下し、アルカリ現像液の溶解度が低くて現像不良になりやすく、カルボキシル基を含むモノマーとこれと共重合が可能なモノマーに対する重量比が９：１を超えると溶解度が高すぎて微細パターンの触媒層を形成することが困難である。

【0021】

上記カルボキシル基を有するモノマーとしては、不飽和カルボキシル酸で例えば、アクリル酸、メタアクリル酸、クロトン酸、イタコン酸、マレイン酸、フマル酸、モノメチルマレイン酸、イソプレンスルホン酸、スチレンスルホン酸及び５－ノルボルネン－２－カルボキシル酸で構成されるグループから選ばれた少なくとも１種以上を用いることができる。上記カルボキシル基を有するモノマーは単独、或いは２以上の混合物で用いることができる。

【0022】

カルボキシル基を含有したモノマーと共重合が可能なモノマーとしては、特にこれに限定はしないが、不飽和二重結合を有する化合物を用いることができ、好ましくは金属触媒との混和性（ｃｏｍｐａｔｉｂｉｌｉｔｙ）の側面で芳香族官能基がないものを用いることができる。これに限定するものではないが、具体的にはメチルメタクリレート、エチル２－メチルアクリレート、イソブチル２－メチルアクリレート及びヘキシル２－メチルアクリレートで構成されるグループから選ばれた少なくとも１種を用いることができる。カルボキシル基含有モノマーと共重合が可能なモノマーは単独で、或いは２種以上の混合物で用いることができる。

【0023】

一方、好ましくは触媒形成層と基材の接着力を向上させ、熱硬化を考慮し上記共重合体にエポキシを有するエチレン性不飽和化合物が付加された有機高分子樹脂、より好ましくはエポキシ基とヒドロキシ基を有するエチレン性不飽和化合物が付加された有機高分子樹脂を用いることができる。

【0024】

上記有機高分子樹脂は、重量平均分子量が２，０００～３０，０００、好ましくは３，０００～１５，０００であることが微細触媒パターン層の形成に好ましく用いられる。有機高分子樹脂の重量平均分子量が２，０００未満の場合には、現像時に接着特性が低下し微細パターンの触媒層の形成が困難で、重量平均分子量が３０，０００を超える場合には、現像液の溶解度が低下し現像が行われない可能性が高い。

【0025】

また、上記有機高分子樹脂は酸価が９０～７００ｍｇＫＯＨ／ｇ、好ましくは３００～５７０ｍｇＫＯＨ／ｇであることが微細触媒パターン層の触媒層の形成に好ましく用いられる。上記有機高分子樹脂の酸価が９０ｍｇＫＯＨ／ｇ未満の場合には触媒との相溶性が低下し、アルカリ現像液の溶解度が低くて現像不良になりやすく、酸価が７００ｍｇＫＯ

Ｈ／ｇを超える場合には、溶解度が高すぎて微細パターンの触媒層を形成することが困難である。

【0026】

本発明の触媒前駆体樹脂組成物を構成するエチレン性不飽和結合含有多官能モノマーは、光硬化の促進及び現像性を向上させ無電解メッキ時に触媒パターン層の接着性、耐化学性等を向上させるために用いる。上記エチレン性不飽和結合含有多官能モノマーはこれに限定するものではないが、例えば、エチレングリコールジアクリレート、エチレングリコールジメタクリレート、エチレン基の数が２～１４であるポリエチレングリコールジアクリレートまたはポリエチレングリコールジメタクリレート、トリメチロールプロパントリアクリレート、トリメチロールプロパントリメタクリレート、ペンタエリトリトールトリアクリレート、ペンタエリトリトールトリメタクリレート、ペンタエリトリトールテトラアクリレート、ペンタエリトリトールテトラメタクリレート、プロピレン基の数が２～１４であるプロピレングリコールジアクリレートまたはプロピレングリコールジメタクリレート、ジペンタエリトリトールペンタアクリレート、ジペンタエリトリトールペンタメタクリレート、ジペンタエリトリトールヘキサアクリレート、ジペンタエリトリトールヘキサメタクリレート等の多価アルコールとα，β－不飽和カルボキシル酸をエステル化して得られる化合物と、トリメチロールプロパントリグリシジルエテールアクリル酸付加物、ビスフェノールＡジグリシジルエテールアクリル酸付加物等のグリシジル基を含有する化合物にアクリル酸またはメタアクリル酸を付加して得られる化合物と、β－ヒドロキシエチルアクリレートまたはβ－ヒドロキシエチルメタクリレートのフタル酸エステル、β－ヒドロキシエチルアクリレートまたはβ－ヒドロキシエチルメタクリレートのトルエンジイソシアネート付加物等の水酸化基及びエチレン性不飽和結合を有する化合物とマルチ（ｍｕｌｔｉ）－カルボキシル酸のエステル化合物または水酸化基及びエチレン性不飽和結合を有する化合物のマルチ（ｍｕｌｔｉ）－イソシアネート付加物等を挙げることができる。上記エチレン性不飽和結合含有多官能モノマーは単独で、或いは２種以上の混合物で用いることができる。

【0027】

上記エチレン性不飽和結合含有多官能基のモノマーは、エチレン性不飽和結合を有する官能基数が３以上であることが微細触媒パターンの形状と無電解メッキ時に耐化学性及び接着特性の側面においてより好ましい。

【0028】

上記エチレン性不飽和結合含有多官能基のモノマーの含量は上記有機高分子樹脂１００重量部に対して２０～１５０重量部であることができる。多官能基モノマーの含量が２０重量部未満であると十分な硬化が行われず、微細パターンを形成することが困難で、無電解メッキ時に溶解及び剥離等の不良が発生することがある。１５０重量部を超えるとコーティング性が減少し、内部まで均一に硬化されず微細触媒パターンを形成することが困難である。

【0029】

本発明の触媒前駆体樹脂組成物を構成する光開始剤の種類は、特に制限されないが、例えば、光重合開始剤にアセトフェノン類、ベンゾフェノン類、ミッヒラー（Ｍｉｃｈｌｅｒ）ベンゾイルベンゾエイト、α－アミルオキシムエステル、チオキサントン類及びトリアジン類で構成されるグループから選ばれた少なくとも１種の光開始剤を単独で、或いは共に用いることができる。

【0030】

アセトフェノン類の例としては、これに限定するものではないが、２－ベンジル－２（ジメチルアミノ）－１－［４－（４－モルホリニル）フェニル］－１－ブタノン）（（２－Ｂｅｎｚｙｌ－２（ｄｉｍｅｔｈｙｌａｍｉｎｏ）－１－［４－（４－ｍｏｒｐｈｏｌｉｎｙｌ）ｐｈｅｎｙｌ］－１－ｂｕｔａｎｏｎｅ、ＩＲＧＡＣＵＲＥ　３６９）、α，α－ジメトキシ－α－フェニルアセトフェノン（α，α－ｄｉｍｅｔｈｏｘｙ－α－ｐｈｅｎｙｌａｃｅｔｏｐｈｅｏｎｅ、ＩＲＧＡＣＵＲＥ　６５１）、ＩＲＧＡＣＵＲＥ　１

３００（ＩＲＧＡＣＵＲＥ　３６９（３０ｗｔ％）＋ＩＲＧＡＣＵＲＥ　６５１（７０ｗｔ％））、１－ベンゾイルシクロ－ヘキサノール（１－Ｂｅｎｚｏｙｌｃｙｃｌｏ－ｈｅｘａｎｏｌ）、２，２'-ジメトキシ－２－フェニル-アセトフェノン（２，２'－Ｄｉｍｅｔｈｏｘｙ－２－ｐｈｅｎｙｌ－ａｃｅｔｏｐｈｅｎｏｎｅ、ＤＭＰＡ）、２，２－ジエトキシアセトフェノン（２，２－ｄｉｅｔｈｏｘｙａｃｅｔｏｐｈｅｎｏｎｅ、ＤＥＡＰ）、４－メチルメルカプト-α，
α－ジメチル-モルホリノアセトフェノン（４－Ｍｅｔｈｙｌｍｅｒｃａｐｔｏ－α，α－ｄｉｍｅｔｈｙｌ－ｍｏｒｐｈｏｌｉｎｏ　ａｃｅｔｏｐｈｅｎｏｎｅ）を含むことができる。上記ベンゾフェノン類としては、これに限定するものではないが、１－フェニル－１，２－プロパンジオン－２－０－ベンゾイルオキシム（１－Ｐｈｅｎｙｌ－１，２－Ｐｒｏｐａｎｅｄｉｏｎｅ－２－Ｏ-ｂｅｎｚｏｙｌｏｘｉｍｅ、ＰＰＯ）、エタノン、１－［９－エチル－６－（２－メチルベンゾイル）－９Ｈ－カルバゾール－３－イル］－１－Ｏ－アセチルオキシム（Ｅｔｈａｎｏｎｅ、１－［９－ｅｔｈｙｌ－６－（２－Ｍｅｔｈｙｌｂｅｎｚｏｙｌ）－９Ｈ－ｃａｒｂａｚｏｌ－３－ｙｌ］－１－（Ｏ－ａｃｅｔｙｌｏｘｉｍｅ）（ＣＧＩ２４２）を含むことができる。上記チオキサントン類としてはこれに限定するものではないが、２－クロロチオ－キサンタン（２－Ｃｈｌｏｒｏｔｈｉｏ－ｘａｎｔｈａｎｅ）及び２－イソプロピルチオキサンタン（２－ｉｓｏｐｒｏｐｙｌｔｈｉｏｘａｎｔｈａｎｅ）を含むことができる。上記トリアジン類としてはこれに限定するものではないが、３－｛４－［２，４－ビス（トリクロロメチル）－ｓ－トリアジン－６－イル］フェニルチオ｝プロピオン酸（ＴＰＡ）を含むことができる。

【0031】

この際、上記光開始剤の配合量は、上記有機高分子樹脂１００重量部に対して１乃至２５重量部、好ましくは５～２０重量部である。光開始剤配合量が１重量部未満であると触媒パターン層が形成されないので好ましくなく、２５重量部を超えるとパターンの正確性が低下するため、好ましくない。

【0032】

また必要に応じて、光増感剤が上記有機高分子樹脂と光開始剤の混合量１００重量部に対して１０重量部以下、好ましくは０．１乃至１０重量部で使用されることができる。光増感剤添加量が１０重量部を超えるとパターンの正確性が低下するという点で好ましくない。

【0033】

光増感剤としてはこれに限定するものではないが、例えば、ｎ－ブチルアミン、トリエチルアミン及びトリ－ｎ－ブチルホスフィンで構成されるグループから選ばれた少なくとも１種以上が単独で、或いは２種以上の混合物で用いることができる。

【0034】

本発明の触媒前駆体樹脂組成物を構成する銀イオン有機錯化物前駆体は銀触媒前駆体として上記樹脂組成物に配合され、電磁波遮蔽層の製造時に触媒に還元され無電解メッキに対する触媒として作用する。触媒の安定性、現像及び無電解メッキのような湿潤工程における触媒遺失、接着特性、無電解時のメッキ特性及び製造費用の側面で銀イオン有機錯化物前駆体が最も好ましい。触媒として銀粒子を用いる場合には組成物内に均一に分散させることが困難で、凝集が発生しやすいため組成物内に界面活性剤のような安定剤を添加しなければならず、過量に用いる場合には現像性が落ち微細触媒層の形成が困難で、また、触媒層の接着特性が低下することがある。また、無機銀塩は水溶液に溶解され現像や無電解メッキ時に遺失されることができ、触媒層の接着特性が低下する可能性があるため、無電解メッキのメッキ特性が落ちる可能性がある。

【0035】

次いで、本発明のように銀イオン有機錯化物前駆体を用いる場合、安定性、接着性、蒸着性が無機銀塩より優れることを発見し、より好ましくはフルオロ化銀イオン有機錯化物前駆体を用いる。銀イオン有機錯化物前駆体に比べてフルオロ化銀イオン有機錯化物前駆体は有機高分子樹脂及び有機溶媒との混和性（ｃｏｍｐａｔｉｂｉｌｉｔｙ）に優れるた