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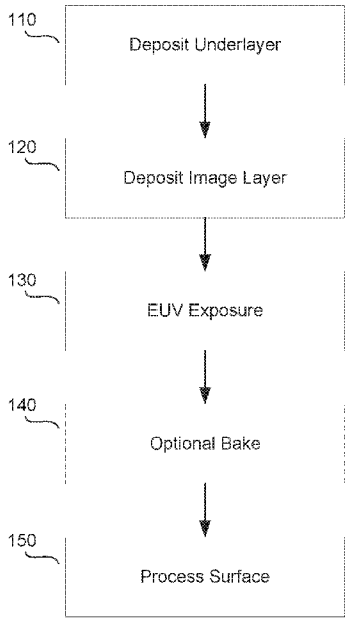
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(54) Title: METHODS FOR MAKING HARD MASKS USEFUL IN NEXT-GENERATION LITHOGRAPHY

(57) Abstract: Imaging layers on the surface of a substrate may be patterned using next generation lithographic techniques, and the resulting patterned film may be used as a lithographic mask, for example, for production of a semiconductor device.

FIG. 1



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[Continued on next page]

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METHODS FOR MAKING HARD MASKS USEFUL IN NEXT-GENERATION LITHOGRAPHY

INCORPORATION BY REFERENCE

[0001] A PCT Request Form is filed concurrently with this specification as part of the present application. Each application that the present application claims benefit of or priority to as identified in the concurrently filed PCT Request Form is incorporated by reference herein in its entirety and for all purposes.

FIELD

[0002] The present disclosure relates to systems and methods for making imaging layers on the surface of a substrate. Such imaging layers may be patterned using next generation lithographic techniques, and the resulting patterned film may be used as a lithographic mask, for example, for production of a semiconductor device.

BACKGROUND

[0003] The background description provided herein generally presents the context of the present technology. Work of the presently named inventors, to the extent it is described in this background section, as well as aspects of the description that may not otherwise qualify as prior art at the time of filing, are not admitted as prior art against the present technology.

[0004] The fabrication of semiconductor devices, such as integrated circuits, is a multi-step process involving photolithography. In general, the process includes the deposition of material on a wafer, and patterning the material through lithographic techniques to form structural features (e.g., transistors, conductors and other circuit features) of the semiconductor device. The steps of a typical photolithography process known in the art include: preparing the substrate; applying a photoresist, such as by spin coating; exposing the photoresist to light in a desired pattern, causing the exposed areas of the photoresist to become either more or less soluble in a developer solution; developing by applying a developer solution to remove either the exposed or the unexposed areas of the photoresist; and subsequent processing to create features on the areas of the substrate from which the photoresist has been removed, such as by etching or material deposition.

[0005] The evolution of semiconductor design has created the need, and has been driven by the ability, to create ever-smaller features on semiconductor substrate materials. This progression of technology has been characterized in "Moore's Law" as a doubling of the density of transistors in dense integrated circuits every two years. Indeed, chip design and manufacturing has progressed such that modern microprocessors may contain billions of transistors and other circuit features on a single chip. Individual features on such chips may be on the order of 22 nanometers (nm) or smaller, in some cases less than 10 nm.

[0006] One challenge in manufacturing devices having such small features is the ability to reliably and reproducibly create photolithographic masks having sufficient resolution. Current photolithography processes typically use 193 nm ultraviolet (UV) light to expose a photoresist. The fact that the light has a wavelength significantly greater than the desired size of the features to be produced on the

semiconductor substrate creates inherent issues. Achieving feature sizes smaller than the wavelength of the light requires use of complex resolution enhancement techniques, such as multipatterning. Thus, there is significant interest and research effort in developing so-called "next-generation lithography" techniques using e-beam radiation or shorter wavelength light, such as extreme ultraviolet (EUV) radiation having wavelengths less than 20 nm, e.g., 13.5 nm.

[0007] Next generation lithographic techniques can present challenges, however. For example, the efficacy of EUV photolithographic processes can be limited by low power output of light sources and loss of light during patterning. Traditional organic chemically amplified resists (CAR) similar to those used in 193 nm UV lithography have potential drawbacks when used in EUV lithography, particularly as they have low absorption coefficients in EUV region and the diffusion of photo-activated chemical species can result in blur or line edge roughness. Furthermore, in order to provide the etch resistance required to pattern underlying device layers, the required thickness of conventional CAR materials can result in high aspect ratios at risk of pattern collapse. Accordingly, there remains a need for improved EUV photoresist materials, having such properties as decreased thickness, greater absorbance, and greater etch resistance.

SUMMARY

[0008] The present disclosure provides methods for making imaging layers on the surface of a substrate. Such imaging layers may be patterned using next generation lithographic techniques, generally such as DUV, EUV, X-ray and e-beam, into chemically distinct regions (i.e., surface imaging). The resulting patterned film may be used, for example, as a lithographic mask for production of a semiconductor device.

[0009] In some implementations, methods in accordance with this disclosure may involve creating an imaging layer of a SnOx thin film that is terminated with alkyl groups selected such that they will undergo tin-carbon bond cleavage, such as beta-hydride elimination, upon irradiation with EUV light. In an EUV patterning step, the alkyl groups can be cleaved, leaving regions of Sn-H bonds while the unexposed surfaces remain alkyl-terminated.

[0010] In one embodiment, a method of making an imaging layer on a substrate, involves providing a substrate having a surface comprising exposed hydroxyl groups, and forming a hydrocarbyl-terminated SnO_x film as the imaging layer on the surface of the substrate, the hydrocarbyl-terminated SnO_x film having a tin-carbon bond cleavable by irradiating the imaging layer.

[0011] In some embodiments, the substrate surface may include a SnOx underlayer to the hydrocarbyl-terminated SnO_x film imaging layer. The hydroxy-terminated SnO_x underlayer on the surface of the substrate material can enhance absorption of radiation upon the irradiating of the imaging layer and generate secondary electrons from the substrate to further harvest additional EUV photons, making the EUV patterning process more sensitive and reducing the required EUV dose necessary for imaging layer exposure.

[0012] In various embodiments, the imaging layer may be deposited by an atomic layer deposition process exhibiting self-limiting characteristics. In other embodiments, the imaging layer is a thin film deposited by a (non-self-limiting) chemical vapor deposition process.

[0013] For example, the alky-substituted tin capping agent may be of the general formula

$$R_nSnX_{4-n}$$

wherein R is a $C_2 - C_{10}$ alkyl or substituted alkyl substituent. X may be any suitable leaving group readily displaced by water to form hydroxyl intermediates, which in turn react with other Sn-X functionality to create Sn-O-Sn crosslinks. In various embodiments R is branched, having multiple beta-hydrogen atoms (the maximum corresponding to a tert-butyl substituent). For example, R may be t-butyl, t-pentyl, t-hexyl, cyclohexyl, isopropyl, isobutyl, sec-butyl, n-butyl, n-pentyl, or n-hexyl or derivatives thereof, as well as analogous materials containing one or more heteroatoms, such as fluorine, chlorine, bromine, iodine, nitrogen and oxygen.

[0014] The present technology also provides methods for forming a pattern on a surface of a coated substrate made by the methods of the present technology, using EUV or other radiation. Further processing of the coated substrate may exploit chemical differences in the exposed and unexposed regions, in particular the hydrocarbyl-terminated SnO_x converted to hydrogen-terminated SnO_x in the exposed region(s) of the imaging layer. The difference in properties between exposed and unexposed areas may be exploited in subsequent processing, such as by reacting the irradiated region, the unirradiated region, or both, with one or more reagents to selectively add material to or remove material from the imaging layer.

[0015] In various embodiments, the present technology provides methods of patterning thin etch resistant hard mask layers on the surface of a substrate, comprising:

providing a substrate comprising a substrate material having a surface comprising exposed hydroxyl groups;

depositing an imaging layer on the surface, the imaging layer comprising hydrocarbyl-terminated SnO_x;

selectively irradiating the imaging layer, such that the imaging layer comprises an irradiated region wherein a hydrocarbyl-substitution on a SnO_x moiety of the hydrocarbyl-terminated imaging layer is removed and/or converted to a hydrogen-terminated SnO_x, and an unirradiated region wherein the imaging layer comprises the hydrocarbyl-terminated SnO_x; and

processing the imaging layer by reacting the irradiated region, the unirradiated region, or both, with one or more reagents to selectively deposit or remove material from the imaging layer.

[0016] The irradiating may comprise the use of DUV, EUV, X-ray or e-beam radiation. In some embodiments, the processing further comprises oxidizing the hydrogen-terminated (Sn-H) functionality in the irradiated region to form a Sn-OH hydroxy-terminated SnO_x.

[0017] Further areas of applicability of the present technology will become apparent from the detailed description, the claims and the drawings. The detailed description and specific examples are intended for purposes of illustration only and are not intended to limit the scope of the technology.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] The present technology will become more fully understood from the detailed description and the accompanying drawings, of which:

Figure 1 is a flow chart of an exemplary process of the present technology.

Figure 2 depicts the general architecture of a substrate as it is formed in an exemplary process of the present technology.

Figure 3 further depicts the general architecture of another substrate as it is formed in an exemplary process of the present technology.

Figure 4 further depicts the general architecture of another substrate as it is formed in an exemplary process of the present technology.

Figure 5 is a flow chart of an exemplary negative tone resist process of the present technology.

Figure 6 schematically depicts the general architecture of a mask as it is formed in a negative tone resist process of Figure 5.

Figures 7A-B depict with sample chemical structures the general architecture of a mask as it is formed in a negative tone resist process of Figure 5.

Figure 8 is a flow chart of an alternative exemplary negative tone resist process of the present technology.

Figure 9 depicts the general architecture of a mask as it is formed in the negative tone resist process of Figure 8.

Figure 10 is a flow chart exemplifying a process of the present technology for forming self-assembled sol gels on a substrate.

Figure 11 is a flow chart exemplifying a process of the present technology for forming self-assembled block co-polymers on a substrate.

Figure 12 is a flow chart exemplifying a process of the present technology for selective growth of metal device structures on a substrate.

Figure 13 depicts the general architecture of a substrate as metal is deposited in the process of Figure 12.

DETAILED DESCRIPTION

[0019] Reference is made herein in detail to specific embodiments of the disclosure. Examples of the specific embodiments are illustrated in the accompanying drawings. While the disclosure will be described in conjunction with these specific embodiments, it will be understood that it is not intended to limit the disclosure to such specific embodiments. On the contrary, it is intended to cover alternatives, modifications, and equivalents as may be included within the spirit and scope of the disclosure. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present disclosure. The present disclosure may be practiced without some or all of these specific details. In other instances, well known process operations have not been described in detail so as to not unnecessarily obscure the present disclosure.

[0020] As discussed above, the present disclosure provides methods for making imaging layers on semiconductor substrates, which may be patterned using EUV or other next generation lithographic techniques. In addition to EUV, which includes the standard 13.5 nm EUV wavelength currently in use and development, the radiation sources most relevant to such lithography are DUV (deep-UV), which generally refers to use of 248nm or 193nm excimer laser sources, X-ray, which formally includes EUV at the lower energy range of the X-ray range, as well as e-beam, which can cover a wide energy range. Such methods include those where a substrate, having exposed hydroxyl groups, is contacted with a hydrocarbyl-substituted tin capping agent to form a hydrocarbyl-terminated SnO_x film as the imaging layer on the surface of the substrate. In various embodiments, the imaging layer is a thin layer that may function as an adhesion layer over a substrate to facilitate selective deposition of additional materials on the substrate, such as in forming hard masks for lithographic processes. The specific methods may depend on the particular materials and applications used in the semiconductor substrate and ultimate semiconducting device. Thus, the methods described in this application are merely exemplary of the methods and materials that may be used in present technology.

Substrates

[0021] Substrates useful in the methods of the present technology may include any material construct suitable for lithographic processing, particularly for the production of integrated circuits and other semiconducting devices. In some embodiments, substrates are silicon wafers. Substrates may be silicon wafers upon which features have been created ("underlying topographical features"), having an irregular surface topography. (As referred to herein, the "surface" is a surface onto which a film of the present technology is to be deposited or that is to be exposed to EUV during processing.) Such underlying topographical features may include regions in which material has been removed (e.g., by etching) or regions in which materials have been added (e.g., by deposition) during processing prior to conducting a method of this technology. Such prior processing may include methods of this technology or other processing methods in an iterative process by which two or more layers of features are formed on the substrate.

[0022] In some embodiments, the substrate is a hard mask, which is used in lithographic etching of an underlying semiconductor material. The hard mask may comprise any of a variety of materials, including amorphous carbon (a-C), SnO_x, SiO_2, SiO_xN_y, SiO_xC, Si_3N_4, TiO_2, TiN, W, W-doped C, WO_x, HfO_2, ZrO_2, and Al_2O_3. For example, the substrate may preferably comprise SnO_x, such as SnO_2. In various embodiments, the layer may be from 1 nm to 100 nm thick, or from 2 nm to 10 nm thick.

[0023] In various embodiments, the substrate comprises exposed hydroxyl groups on its surface. In general, the surface may be any surface that comprises, or has been treated to produce, an exposed hydroxyl surface. (As referred to herein, "surface" means a portion of the substrate which defines the boundary between the substrate and another material or lack thereof (e.g., a gas, coating or vacuum), and may be, in various embodiments, available for exposure to radiation or reaction with components in the other material.) Thus, methods may include "providing" such a substrate, wherein the substrate having exposed hydroxyl groups is obtained as a starting material apart from the methods of the present

technology, or produced as part of a single process comprising formation of hydroxyl groups on a substrate followed by contacting the surface with a hydroxyl-substituted tin capping agent, as noted above and described further below. For example, such hydroxyl groups may be formed on the surface of the substrate by surface treatment of a substrate using oxygen plasma, water plasma, or ozone.

[0024] In some embodiments, a substrate comprising exposed hydroxyl groups comprises a surface layer or film comprising hydroxyl-terminated SnO_x. For example, the substrate may comprise amorphous carbon having a surface of hydroxyl-terminated SnO_x. Without limiting the mechanism, function or utility of present technology, it is believed that the hydroxyl-terminated SnO_x layer may offer benefits such as improved adhesion of materials deposited on the surface of the substrate and enhanced absorption of EUV (or other radiation) during patterning. Sensitivity to EUV or other irradiation and resolution may be dependent on the properties of the SnO_x layer, such as thickness, density and short range charge transfer characteristics. In various embodiments, the SnO_x layer has a thickness of from 0.1 nm to 20 nm, or from 0.2 nm to 10 nm, or from 0.5 nm to 5 nm.

[0025] In some embodiments, the hydroxyl-terminated SnO_x layer is deposited on the surface of the substrate by vapor deposition. In such methods, the deposition comprises reacting $Sn\text{-}X_n$ with an oxygen-containing counter-reactant, wherein X is a ligand such as dialkylamido, (e.g., dimethylamido, methylethylamido, and diethylamido), alcohol (e.g., t-butoxy, and isopropoxy), halogen (e.g., F, Cl, Br, and I), or other organic substituent (e.g., acetylacetone, N2,N3-di-tertbutyl-butane-2,3-diamido). For example, $Sn\text{-}X_n$ may be $SnCl_4$, SnI_4, or $Sn(NR_2)_4$ wherein R is = methyl or ethyl, or $Sn(t\text{-}BuO)_4$. In some embodiments, multiple types of ligands are present. The oxygen-containing counter-reactant may be selected from the group consisting of water, hydrogen peroxide, formic acid, alcohols, oxygen, ozone, and combinations thereof.

[0026] Suitable vapor deposition processes include chemical vapor deposition (CVD), atomic layer deposition (ALD), plasma-enhanced chemical vapor deposition (PECVD), or plasma-enhanced atomic layer deposition (PEALD). In some embodiments, the deposition is ALD, in a cyclical process of depositing the $Sn\text{-}X_n$ and depositing the oxygen-containing counter-reactant. In some embodiments, the deposition is CVD, by simultaneously flowing the $Sn\text{-}X_n$ and the oxygen-containing counter-reactant. Materials and processes among those useful herein for depositing SnO_x layers are described in Nazarov et al., Atomic Layer Deposition of Tin Dioxide Nanofilms: A Review, 40 Rev. Adv. Mater. Sci 262 (2015).

[0027] In an exemplary continuous CVD process, two or more gas streams, in separate inlet paths, of $Sn\text{-}X_n$ and source of oxygen-containing counter-reactant are introduced to the deposition chamber of a CVD apparatus, where they mix and react in the gas phase, to form the SnO_x coating on the substrate. The streams may be introduced, for example, using a dual plenum showerhead. The apparatus is configured so that the streams of $Sn\text{-}X_n$ and source of oxygen-containing counter-reactant are mixed in the chamber, allowing the $Sn\text{-}X_n$ and source of oxygen-containing counter-reactant to react to form the SnO_x layer. The CVD process is generally conducted at reduced pressures, such as from 0.1 Torr to 10 Torr. In some embodiments, the process is conducted at from 1 – 2 Torr. The temperature of the

substrate is preferably below the temperature of the reactant streams. For example, the substrate temperature may be from 0 °C to 250 °C, or from ambient temperature (e.g., 23 °C) to 150 °C.

[0028] A SnO_x substrate may also be deposited by an ALD process. For example, the $Sn\text{-}X_n$ and oxygen-containing counter-reactant are introduced at separate times. The precursors react on the surface, forming up to a monolayer of material at a time for each pulse. This may allow excellent control over the uniformity of film thickness across the surface. The ALD process is generally conducted at reduced pressures, such as from 0.1 Torr to 10 Torr. In some embodiments, the process is conducted from 1 – 2 Torr. The substrate temperature may be from 0 °C to 250 °C, or from ambient temperature (e.g., 23 °C) to 150 °C. The process may be a thermal process or, preferably, a plasma-assisted deposition.

Tin Capping Agent

[0029] Hydrocarbyl-substituted tin capping agents useful herein include substituents that undergo tin-carbon bond cleavage upon irradiating of the imaging layer. Such cleavage may be homolytic. In some embodiments, the cleavage may occur by beta-hydride elimination to release an alkene fragment, leaving behind a hydrogen atom bonded to the tin atom that originally bore the alkyl substituent.

[0030] The specific tin capping agent may be selected depending on the intended lithographic process, i.e., the specific irradiation that is to be used. Further, the hydrocarbyl-substituted tin capping agent may be selected so as to serve as a barrier to subsequent deposition of materials onto the substrate. Thus, in some embodiments, the hydrocarbyl-substituted tin capping agent is an atomic layer deposition blocking agent to prevent the attachment or growth of soluble metal oxide precursors from solutions brought into contact with the surface.

[0031] In various embodiments, the hydrocarbyl-substituted tin capping agent is alkyl-substituted, such as an agent of the following general formula:

$$R_nSnX_m$$

wherein R is a $C_2 – C_{10}$ alkyl or substituted alkyl having a beta-hydrogen, X is a suitable leaving group upon reaction with an hydroxyl group of the exposed hydroxyl groups, and, in various embodiments, n = 1 – 3, and m = 4 – n. For example, R may be t-butyl, t-pentyl, t-hexyl, cyclohexyl, isopropyl, isobutyl, sec-butyl, n-butyl, n-pentyl, or n-hexyl or derivatives thereof having a heteroatom substituent in the beta position. Suitable heteroatoms include halogen (F, Cl, Br, or I), or oxygen (-OH or -OR). X may be dialkylamido, (e.g., dimethylamido, methylethylamido, or diethylamido), an alcohol (e.g. t-butoxy, isopropoxy), halogen (e.g., F, Cl, Br, or I), or another organic ligand. Examples of hydrocarbyl-substituted tin capping agents include t-butyltris(dimethylamino)tin, n-butyltris(dimethylamino)tin, t-butyltris(diethylamino)tin, di(t-butyl)di(dimethylamino)tin, secbutyltris(dimethylamino)tin, n-pentyltris(dimethylamino)tin, isobutyltris(dimethylamino)tin, isopropyltris(dimethylamino)tin, t-butyltris(t-butoxy)tin, n-butyl(tris(t-butoxy)tin, or isopropyltris(t-butoxy)tin.

Method of Making an Imaging Layer

[0032] In various aspects, methods of the present technology comprise:

providing the substrate having the surface, wherein the surface comprises exposed hydroxyl groups; and

contacting the surface with an hydrocarbyl-substituted tin capping agent, to form a hydrocarbyl-terminated SnO_x film as the imaging layer on the surface of the substrate.

[0033] In general, contacting the surface with the hydrocarbyl-substituted tin capping agent may be performed using any suitable technique, preferably so as to create a uniform distribution of the capping agent on the surface. Such methods include vapor deposition techniques such as ALD and CVD. Water may also be dosed to aid in the reaction of the capping agent with the exposed hydroxyl groups of the substrate. Such methods may employ repeated applications of the capping agent and water to form a surface sufficiently statured with the hydrocarbyl-substituted tin capping functionality. Exposure to additional alky-based reagents, such as alky thiols, may be used to form a surface having an increased level of hydrocarbyl substituents on the surface of the substrate.

[0034] In an exemplary continuous CVD process, two or more gas streams, in separate inlet paths, of $R_nSn\text{-}X_m$ and source of oxygen-containing counter-reactant are introduced to the deposition chamber of a CVD apparatus, where they mix, react in the gas phase, and condense to form the SnO_x coating on the substrate. The streams may be introduced, for example, using dual-plenum showerhead. The apparatus is configured so that the streams of of $R_nSn\text{-}X_m$ and source of oxygen-containing counter-reactant are mixed in the chamber, allowing the $R_nSn\text{-}X_m$ and source of oxygen-containing counter-reactant to react to form the SnO_x layer. The CVD process is generally conducted at reduced pressures, such as from 0.1 Torr to 10 Torr. In some embodiments, the process is conducted at from 1 – 2 Torr. The temperature of the substrate is preferably below the temperature of the reactant streams. For example, the substrate temperature may be from 0 °C to 250 °C, or from ambient temperature (e.g., 23 °C) to 150 °C.

[0035] A SnO_x imaging layer may also be deposited by an ALD process. In this case, the $R_nSn\text{-}X_m$ and oxygen-containing counter-reactant are introduced at separate times, representing an ALD cycle. The precursors react on a surface, forming up to a monolayer of material at a time for each ALD cycle. This allows for excellent control over the film thickness uniformity across the wafer. The ALD process is generally conducted at reduced pressures, such as from 0.1 Torr to 10 Torr. In some embodiments, the process is conducted from 1-2 Torr. The substrate temperature may be from 0 °C to 250 °C, or from ambient temperature (e.g., 23 °C) to 150 °C. The process will be a thermal-driven process. The film is not expected to grow significantly after the first cycle and subsequent cycling is designed to further saturate the surface with R terminated Sn.

Patterning

[0036] The present technology also provides methods wherein the imaging layer is patterned by exposing a region of the imaging layer to irradiation, such as EUV, DUV or e-beam. In such patterning, the radiation is focused on one or more regions of the imaging layer. The exposure is typically performed such that imaging layer film comprises one or more regions that are not exposed to the radiation. The resulting imaging layer may comprise a plurality of exposed and unexposed regions, creating a pattern consistent with the creation of transistor or other features of a semiconductor device,

formed by addition or removal of material from the substrate in subsequent processing of the substrate. EUV, DUV and e-beam radiation methods and equipment among useful herein include methods and equipment known in the art.

[0037] In particular, areas of the imaging layer are created through patterning that have altered physical or chemical properties relative to unexposed areas. In particular, in various embodiments, the hydrocarbyl-terminated SnO_x present on the surface is be converted to hydrogen-terminated SnO_x in the exposed region(s) of the imaging layer, particularly when the exposure is performed in a vacuum using EUV. However, removing exposed imaging layers from vacuum into air, or the controlled introduction of oxygen, ozone, H_2O_2 or water, can result in the oxidation of surface Sn-H into Sn-OH The difference in properties between exposed and unexposed areas may be exploited in subsequent processing, such as by reacting the irradiated region, the unirradiated region, or both, with one or more reagents to selectively add material to or remove material from the imaging layer.

[0038] Accordingly, in various embodiments, the present technology provides methods of making a lithographic hard mask on the surface of a substrate, comprising:

providing a substrate comprising a substrate material having a surface comprising exposed hydroxyl groups;

depositing an imaging layer on the surface, the imaging layer comprising hydrocarbyl-terminated SnO_x;

selectively irradiating the imaging layer, such that the imaging layer comprises an irradiated region wherein the hydrocarbyl-terminated SnO_x of the imaging layer has been converted to hydrogen-terminated SnO_x, and an unirradiated region wherein the imaging layer comprises the hydrocarbyl-terminated SnO_x; and

processing the imaging layer by reacting the irradiated region, the unirradiated region, or both, with one or more reagents to selectively add material to or remove material from the imaging layer.

In various embodiments, the substrate material comprises amorphous carbon or SnO_x.

[0039] Optionally, the imaging layer is heated or "baked" so as to remove excess moisture and drive the Sn-O-Sn cross-linking. For example, the sample can be baked at conditions so the R-Sn bonds will not be significantly cleaved, such as between 50 °C and 200 °C for 5 min. or between 70 °C and 150 °C for 2 min.

Lithographic Processing

[0040] As noted above, the subsequent processing of the imaging layer, following irradiation, will depend on the substrate materials and the desired features of the semiconducting device made using the substrate. For example, features may be created on the substrate by various lithographic techniques, such as using spin-coat application of films which become selectively soluble in liquid developers in either exposed (positive tone) or unexposed (negative tone) areas defined by a patterned exposure tool.

[0041] Lithographic methods of the present technology are generally depicted in the process flow of Figure 1. As shown, a substrate is formed by depositing a hydroxy-terminated SnO_x "underlayer" on a

substrate material (110). The hydroxy-terminated SnO_x underlayer on the surface of the substrate can enhance absorption of radiation upon the irradiating of the imaging layer and generate secondary electrons from the substrate to further harvest additional EUV photons, making the EUV patterning process more sensitive and reducing the required EUV dose necessary for imaging layer exposure.

[0042] An imaging layer is then formed by depositing the surface with a hydrocarbyl-substituted tin capping agent, to form a hydrocarbyl-terminated SnO_x film on the surface of the substrate (120). The substrate is then exposed to radiation, (e.g., using EUV) (130), and, optionally, baked (140). The imaging layer surface is then processed (150). Figure 2 depicts schematically and with sample chemical structures the general architecture of a substrate as it is formed in such a process. Figure 3 depicts a specific instance of such a process, wherein the imaging layer is formed from the hydrocarbyl-substituted tin capping agent t-butyl$Sn(N(CH_3)_2)_3$. Figure 4 depicts an alternative for an active (EUV release) PR adhesion imaging layer formed from the tin capping agent is n-$BuSn(OtBu)_3$.

[0043] In some methods, the processing comprises oxidizing the hydrogen-terminated SnO_x in the irradiated region to form a hydroxy-terminated SnO_x. The oxidizing may comprise exposing the irradiated region to oxygen or water. In some methods, subsequent processing comprises removing the hydroxy-terminated SnO_x in the irradiated region to expose and etch underlying substrate material. The etching may be performed by treating the patterned film with dilute aqueous hydrofluoric acid or alternatively dilute aqueous tetramethylammonium hydroxide (TMAH). Processing may further comprise etching of an underlying substrate layer using oxygen plasma.

[0044] In some embodiments, processing further comprises depositing a metal oxide, which may be operable as a hard mask, on the hydroxy-terminated SnO_x of the irradiated region. Such hard mask material may comprise a metal oxide selected from the group consisting of SnO_2, SiO_2, TiO_2, WO_x, HfO_2, ZrO_2, Ta_2O_5, Nb_2O_5, B_2O_3, GeO_2, ZnO, V_2O_5, and Al_2O_3. The deposition may be performed, for example, by ALD.

[0045] In some methods of the present technology, the hydrocarbyl-terminated SnO_x of the unirradiated region is removed by hydrogen or methane plasma to expose the underlying amorphous carbon layer. Processing may further comprise etching of the underlying substrate material using oxygen plasma.

[0046] Without limiting the mechanism, function or utility of present technology, it is believed that, in some embodiments, lithographic methods of the present technology offer benefits over methods among those known in the art, such as avoiding the need to apply and remove wet resist formulations (e.g., avoiding scumming and pattern distortion), simplifying processes such as developing exposed substrates under vacuum in a continuous process following EUV or other irradiation, reducing pattern collapse through use of very thin metal oxide structures, improving line edge roughness, and offering the ability to tune hardmask chemistry to the specific substrate and semiconductor device design.

Additional Embodiments

[0047] As noted above, specific post-imaging methods and applications of the present technology may involve any of a variety of materials and processes depending on the substrate and desired device design.

The processing of the imaging layer may depend on the substrate materials and the desired features of the semiconducting device to be made using the substrate. For example, features may be created on the substrate by various standard lithographic techniques, typically involving the application of films which become selectively soluble in developers in either exposed (positive tone) or unexposed (negative tone) areas defined by a patterned exposure tool. Processing may also include making lithographic masks comprising directed self-assembled (DSA) block co-polymers (BCP), directed self-assembly of sol-gels, and selective deposition of material (e.g., metal or metal oxide) by atomic layer deposition or chemical vapor deposition.

[0048] For example, in some embodiments, processing of the imaging layer and substrate creates a positive tone mask. Such methods may include:

selectively irradiating regions of an imaging layer of a substrate made by methods of the present technology;

oxidizing hydrogen-terminated SnO_x in the irradiated region to form a hydroxy-terminated SnO_x, such as reacting the irradiated regions with air or water;

contacting the irradiated regions with dilute aqueous hydrofluoric acid (HF) or dilute aqueous tetramethylammonium hydroxide (TMAH) to etch the exposed hydroxyl-terminated surface, exposing the underlying substrate material (e.g., amorphous carbon); and

etching the exposed underlayer with oxygen plasma.

[0049] In some embodiments, processing of the imaging layer and substrate creates a negative tone resist. For example, such methods may include:

selectively irradiating regions of an imaging layer of a substrate made by methods of the present technology;

oxidizing hydrogen-terminated SnO_x in the irradiated region to form a hydroxy-terminated SnO_x, such as reacting the irradiated regions with air or water;

selectively depositing, such as by ALD, a metal oxide hard mask on the hydroxyl-terminated regions;

removing the unexposed regions (i.e., regions having hydrocarbyl-terminate SnO_x) of the substrate, such as using an H_2, CH_4 or BCl_3-based plasma, to expose the underlying substrate (e.g., amorphous carbon); and

etching the exposed underlying substrate with oxygen plasma.

[0050] Elements of one such process are depicted in a process flow in Figure 5. Figures 6, and 7A-B depict the general architecture of a mask as it is formed (staring from the hydroxylation of the exposed surface) in one such negative tone resist process schematically and with sample chemical structures, respectively.

[0051] The elements of an alternative negative tone resist process are depicted in Figure 8. In this process, the hydrogen-terminated SnO_x in the irradiated region is not oxidized. Rather, a metal or metal oxide hard mask is deposited, such as by ALD, on the Sn-H surface of the irradiated region. General methods and conditions for ALD deposition of metals on hydride surfaces include those described in

Kwon, et. al., *Substrate Selectivity of (^{t}Bu-Allyl)Co(CO)$_3$ during Thermal Atomic Layer Deposition of Cobalt*, 24 Chem. Mater. 1025 (2012), and *Lemaire, et. al., Understanding inherent substrate selectivity during atomic layer deposition: Effect of surface preparation, hydroxyl density, and metal oxide composition on nucleation mechanisms during tungsten ALD*, 146 J. Chem. Phys. 052811 (2017). In such a process, the substrate may be maintained under vacuum from irradiation through the deposition of ALD, simplifying material handling procedures during the process and potentially offering efficiencies in manufacturing. Figure 9 depicts the general architecture of a mask as it is formed in an alternative negative tone resist process.

[0052] In some embodiments, processing of the imaging layer and substrate employs negative tone patterning. For example, such methods may include:

selectively irradiating regions of an imaging layer of a substrate made by methods of the present technology;

oxidizing hydrogen-terminated SnO_x in the irradiated region to form a hydroxy-terminated SnO_x, such as reacting the irradiated regions with air or water;

selectively depositing solution of a metal sol-gel oxide (e.g., spin-coated tetraethylorthosilicate at pH 2 with nitric acid) on the hydroxyl-terminated regions to form a metal oxide etch mask on the irradiated regions;

removing (e.g., by rinsing) unreacted sol-gel solution;

removing the unexposed regions (i.e., regions having hydrocarbyl-terminated SnO_x) of the substrate, such as using a hydrogen or methane plasma, to expose the underlying substrate (e.g., amorphous carbon); and

etching the exposed underlying substrate with oxygen plasma.

[0053] Materials and methods for making sol-gels are described in Hench, et al., *The Sol-Gel Process*, 90 Chem. Rev. 33 (1990), and Lu, et. al., *Continuous formation of supported cubic and hexagonal mesoporous films by sol-gel dip-coating*, 389 Nature 364 (1997). Elements of such a process are depicted in the process flow of Figure 10.

[0054] In some embodiments, processing of the imaging layer and substrate comprises deposition and self-assembly of block co-polymers to pattern hydrophilic and hydrophobic regions of the imaging surface, to create a hard mask. For example, such methods for creating hard masks may include:

selectively irradiating regions of an imaging layer of a substrate made by methods of the present technology;

oxidizing hydrogen-terminated SnO_x in the irradiated region to form a hydroxy-terminated SnO_x, such as reacting the irradiated regions with air or water;

coating the surface with a block co-polymer reactants;

annealing the surface, to create an assembled block co-polymer;

selectively removing a substituent of the block co-polymer to form the mask; and

etching the exposed underlayer with oxygen plasma.

[0055] In some embodiments, a hydrophilic metal oxide may be deposited on hydrophilic regions of the imaging surface (i.e., the irradiated regions), prior to coating with the block co-polymer reactants, to create topography that guides self-assembly of the block co-polymers. Materials and methods for making self-assembled block co-polymers are described in Hamley, *Nanostructure fabrication using block copolymers*, 14 Nanotechnology R39 (2003). Elements of such a process are depicted in the process flow of Figure 11. This approach can reduce the size of features and potentially reduce defects associated with BCP self-assembly.

[0056] The present technology also provides methods for selective growth of electroless metal device structures, such as for hard masks, on a substrate. For example, the surface may be exposed to aqueous solutions of oxidizing metal ions (such as Pd^{+2} salts) to selectively deposit catalytic Pd "seed" atom layers for subsequent selective growth of conductive cobalt, nickel or copper features by electroless deposition (ELD). In other embodiments, exposed "deprotected" areas of a thin tin-based imaging layer, which are no longer hydrophobic, may be selectively etched away by brief exposure to an aqueous acid etchant such a concentrated HF or solutions of oxalic acid.

[0057] For example, such methods comprise:

selectively irradiating regions of an imaging layer of substrate made by methods of the present technology;

selectively depositing a palladium (Pd) activation layer on the exposed regions (i.e., regions having Sn-H surface moieties) of the substrate; and

depositing, by electroless deposition, a metal, e.g., cobalt, on the Pd activation layer.

[0058] In various embodiments, the deposited metal is a late transition metal, such as cobalt, nickel, copper, or mixtures thereof. Without limiting the mechanism, function or utility of present technology, it is believed that, in some embodiments, such methods may provide a simple additive patterning approach for depositing metal features on a substrate only where such features are needed, in contrast to subtractive technologies known in the art that involve blanket deposition of metal followed by patterned removal. Elements of such a process are depicted in the process flow of Figure 12 and illustrated in Figure 13.

Conclusion

[0059] Methods for making imaging layers on the surface of a substrate that may be patterned using next generation lithographic techniques into chemically distinct regions (i.e., surface imaging). The resulting patterned film may be used, for example, as a lithographic mask for production of a semiconductor device.

[0060] It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art. Although various details have been omitted for clarity's sake, various design alternatives may be implemented. Therefore, the present examples are to be considered as illustrative and not restrictive, and the disclosure is not to be limited to the details given herein but may be modified within the scope of the disclosure and the appended claims.

CLAIMS

What is claimed is:

1. A method of making an imaging layer on a substrate, the method comprising:

providing a substrate having a surface comprising exposed hydroxyl groups; and

forming a hydrocarbyl-terminated SnO_x film as an imaging layer on the surface of the substrate, the hydrocarbyl-terminated SnO_x film having a tin-carbon bond cleavable by irradiating the imaging layer.

2. The method of claim 1, wherein the forming the hydrocarbyl-terminated SnOx film imaging layer comprises contacting the surface of the substrate with a hydrocarbyl-substituted tin capping agent that undergoes tin-carbon bond cleavage upon the irradiating of the imaging layer.

3. The method of claim 1, wherein the hydrocarbyl-substituted tin capping agent acts as a blocking agent to prevent the attachment or growth of soluble metal oxide precursors from solutions brought into contact with the surface.

4. The method of any of claims 1 – 3, wherein the hydrocarbyl-substituted tin capping agent is of the formula

$$R_nSnX_{4-n}$$

wherein R is a $C_2 – C_{10}$ alkyl or substituted alkyl comprising a beta-hydrogen, X is a leaving group upon reaction with a hydroxyl group of the exposed hydroxyl groups, and n=1 - 3.

5. The method of claim 4, wherein R is selected from the group consisting of t-butyl, t-pentyl, t-hexyl, cyclohexyl, isopropyl, isobutyl, sec-butyl, n-butyl, n-pentyl, n-hexyl, and derivatives thereof having a heteroatom substituent in the beta position.

6. The method of either of claims 4 or 5, wherein X is selected from the group consisting of dialkylamido, (e.g., dimethylamido, methylethylamido, or diethylamido), alcohol (e.g. t-butoxy, isopropoxy), and halogen (e.g., F, Cl, Br, or I).

7. The method of claim 2, wherein the hydrocarbyl-substituted tin capping agent is selected from the group consisting of t-butyltris(dimethylamino)tin, n-butyltris(dimethylamino)tin, t-butyltris(diethylamino)tin, isopropyltris(dimethylamino)tin, t-butyltris(t-butoxy)tin, n-butyl(tris(t-butoxy)tin, di(t-butyl)di(dimethylamino)tin, secbutyltris(dimethylamino)tin, n-pentyltris(dimethylamino)tin, isobutyltris(dimethylamino)tin, isopropyltris(dimethylamino)tin, t-butyltris(t-butoxy)tin, n-butyl(tris(t-butoxy)tin, and isopropyltris(t-butoxy)tin.

8. The method according to any one of the preceding claims, wherein the substrate comprises amorphous carbon (a-C), SnO_x, SiO_2, SiO_xN_y, SiO_xC, Si_3N_4, TiO_2, TiN, W, W-doped C, WO_x, HfO_2, ZrO_2, Al_2O_3 or Bi_2O_3.

9. The method according to any one of claims 1 – 8, wherein the providing comprises forming a hydroxyl-terminated SnO_x layer on the surface of the substrate material.

10. The method according to claim 9, wherein the forming comprises depositing a hydroxyl-terminated SnO_x layer on the surface by vapor deposition.

11. The method of claim 10, wherein the depositing comprises reaction of $Sn\text{-}X_n$ with an oxygen-containing counter-reactant, wherein X is dialkylamido, (e.g., dimethylamido, methylethylamido, diethylamido), alcohols (t-butoxy, isopropoxy), or halogen (e.g., F, Cl, Br, and I).

12. The method of claim 11, wherein $Sn\text{-}X_n$ is $SnCl_4$, SnI_4, or $Sn(NR_2)_4$ wherein R is methyl or ethyl, or $Sn(t\text{-}BuO)_4$.

13. The method of either of claims 11 or 12, wherein the oxygen-containing counter-reactant is selected from the group consisting of water, hydrogen peroxide, formic acid, alcohols, oxygen, ozone, oxygen plasma, water plasma, and combinations thereof.

14. The method according to any one of claims 10 – 13, wherein the vapor deposition is chemical vapor deposition (CVD), atomic layer deposition (ALD), plasma-enhanced chemical vapor deposition (PECVD), or plasma-enhanced atomic layer deposition (PEALD).

15. The method according to any one of claims 10 – 14, wherein the depositing is an ALD cyclical process of depositing the $Sn\text{-}X_n$ and depositing the oxygen-containing counter-reactant.

16. The method according to any one of claims 10 – 14, wherein the depositing is a CVD process comprising simultaneously depositing the $Sn\text{-}X_n$ and the oxygen-containing counter-reactant.

17. The method according to any one of the preceding claims, wherein the imaging layer has a thickness of from 0.5 nm to 5 nm.

18. The method according to any one of the preceding claims, wherein the substrate comprises underlying topographical features.

19. The method according to any one of the preceding claims, further comprising the irradiating of the imaging layer to form at least one exposed region wherein the hydrocarbyl-terminated SnO_x is converted to hydrogen-terminated SnO_x in the exposed region.

20. The method according to claim 19, wherein the irradiating comprises the use of DUV, EUV, X-ray or e-beam radiation.

21. The method according to claim 19, wherein the hydroxy-terminated SnO_x layer on the surface of the substrate material enhances absorption of radiation upon the irradiating of the imaging layer.

22. The method according to any one of the preceding claims, wherein the irradiating comprises the use of EUV radiation.

23. A method of making a lithographic hard mask on the surface of a substrate, comprising:

providing a substrate comprising a substrate material having a surface comprising exposed hydroxyl groups;

depositing an imaging layer on the surface, the imaging layer comprising hydrocarbyl-terminated SnO_x;

selectively irradiating the imaging layer, such that the imaging layer comprises an irradiated region wherein a hydrocarbyl-substitution on a SnO_x moiety of the hydrocarbyl-terminated imaging layer is removed and/or converted to a hydrogen-terminated SnO_x, and an unirradiated region wherein the imaging layer comprises the hydrocarbyl-terminated SnO_x; and

processing the imaging layer by reacting the irradiated region, the unirradiated region, or both, with one or more reagents to selectively add material to or remove material from the imaging layer.

24. The method of claim 23, wherein the providing comprises depositing a hydroxyl-terminated SnO_x layer on the surface of the substrate material by vapor deposition.

25. The method of claim 23, wherein the depositing the hydrocarbyl-terminated SnOx film imaging layer comprises contacting the surface of the substrate with a hydrocarbyl-substituted tin capping agent that undergoes tin-carbon bond cleavage upon the irradiating of the imaging layer.

26. The method of claim 25, wherein the hydrocarbyl-substituted tin capping agent is of the formula

$$R_nSnX_{4-n}$$

wherein R is a $C_2 - C_{10}$ alkyl or substituted alkyl having a beta-hydrogen, X is a suitable leaving group upon reaction with an hydroxyl group of the exposed hydroxyl groups, and n=1 – 3.

27. The method of claim 26, wherein the hydrocarbyl-substituted tin capping agent is t-butyltris(dimethylamino)tin, n-butyltris(dimethylamino)tin, t-butyltris(diethylamino)tin, isopropyltris(dimethylamino)tin, and t-butyltris(t-butoxy)tin, or n-butyl(tris(t-butoxy)tin.

28. The method according to any one of claims 23 – 27, wherein the irradiating comprises the use of DUV, EUV, X-ray or e-beam radiation.

29. The method according to claim 28, wherein the irradiating comprises the use of EUV radiation.

30. The method of claim 23, wherein the hydrocarbyl-substitution on the SnO_x moiety of the hydrocarbyl-terminated imaging layer is converted to a hydrogen-terminated SnO_x by beta-hydride elimination.

31. The method according to any one of claims 23 - 30, wherein the processing comprises oxidizing the hydrogen-terminated SnO_x in the irradiated region to form a hydroxy-terminated SnO_x.

32. The method of claim 31, wherein the oxidizing comprises exposing the irradiated region to oxygen or water.

33. The method of claim 31, wherein the processing comprises removing the hydroxy-terminated SnO_x in the irradiated region to expose the underlying substrate material, and wherein underlying substrate material comprises amorphous carbon.

34. The method of claim 33, wherein the removing comprises treating the irradiated region to dilute hydrofluoric acid or dilute aqueous tetramethylammonium hydroxide (TMAH).

35. The method of claim 33, wherein the processing further comprises etching of the underlying amorphous carbon substrate material using oxygen plasma.

36. The method of claim 31, wherein the processing further comprises depositing a metal oxide hard mask on the hydroxy-terminated SnO_x of the irradiated region.

37. The method of claim 36, wherein the metal oxide hard mask comprises a metal oxide selected from the group consisting of SnO_x, SiO_2, SiO_xN_y, SiO_xC, TiO_2, WO_x, HfO_2, ZrO_2, Al_2O_3 and Bi_2O_3.

38. The method of claim 23, further comprising selective deposition of a metal layer by atomic layer deposition solely on the hydrogen-terminated SnO_x areas generated by selectively irradiating the imaging layer.

39. The method according to claim 23, wherein the hydrocarbyl-terminated SnO_x of the unirradiated region is removed by hydrogen or methane plasma to expose the underlying substrate material, and wherein underlying substrate material comprises amorphous carbon.

40. The method of claim 39, wherein the processing further comprises etching of the underlying substrate using an oxygen plasma.

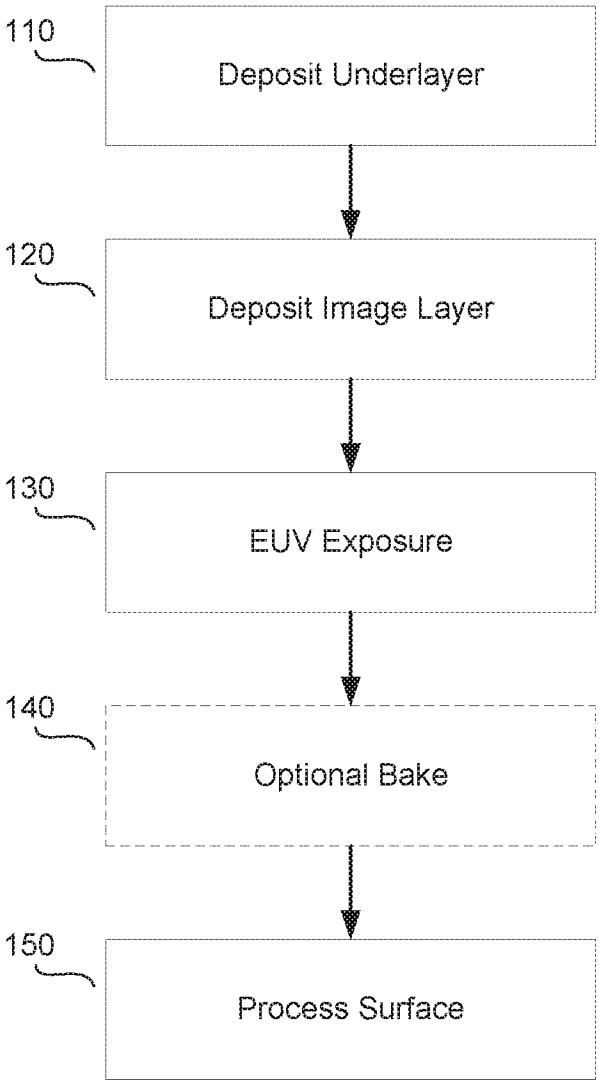
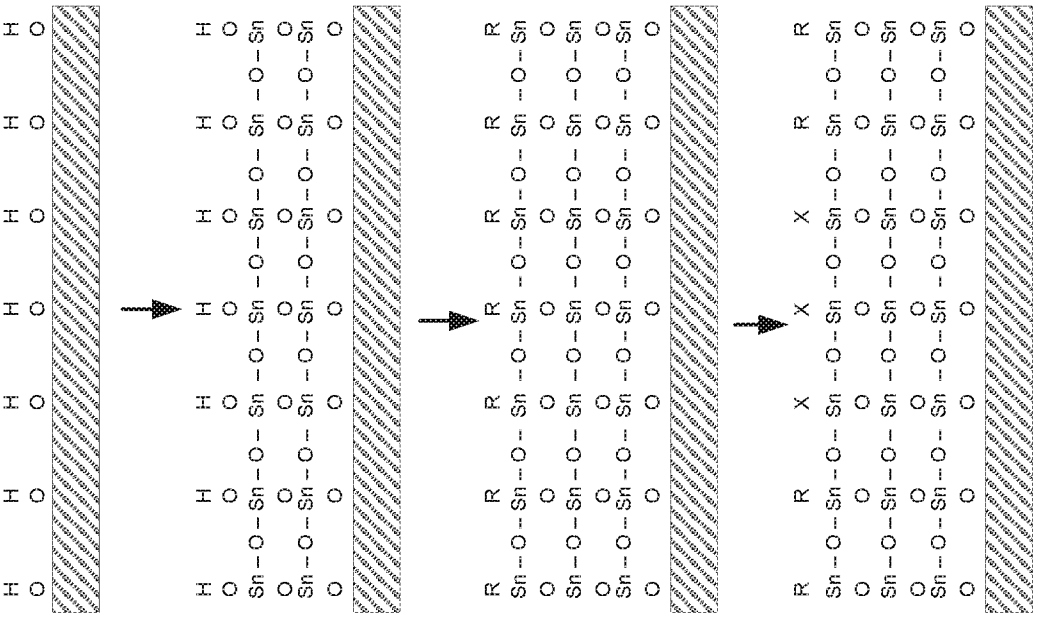

110
Deposit Underlayer
120
Deposit Image Layer
130
EUV Exposure
140
Optional Bake
150
Process Surface

FIG. 1



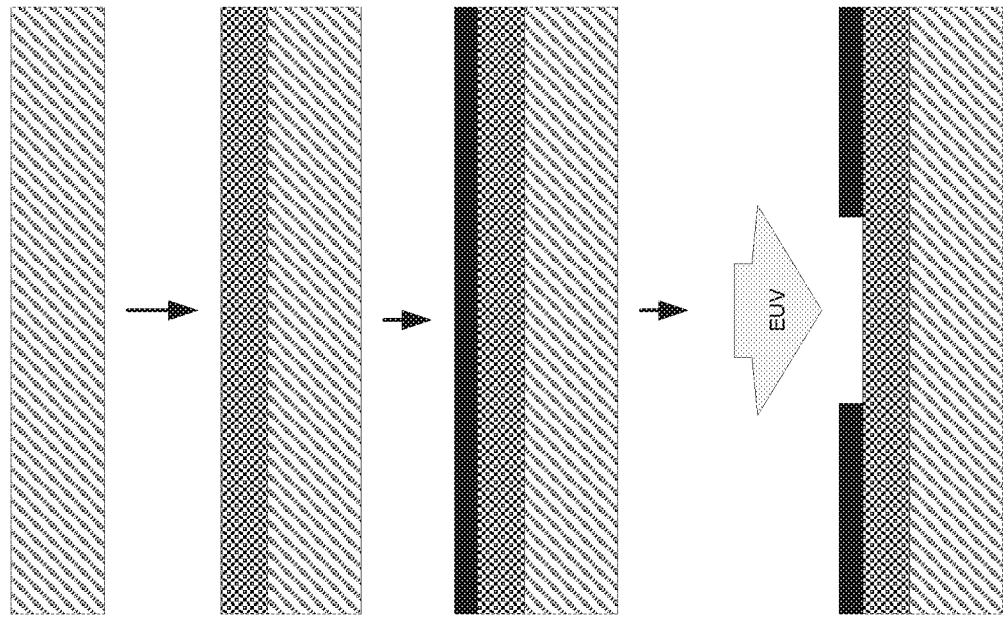


FIG. 2

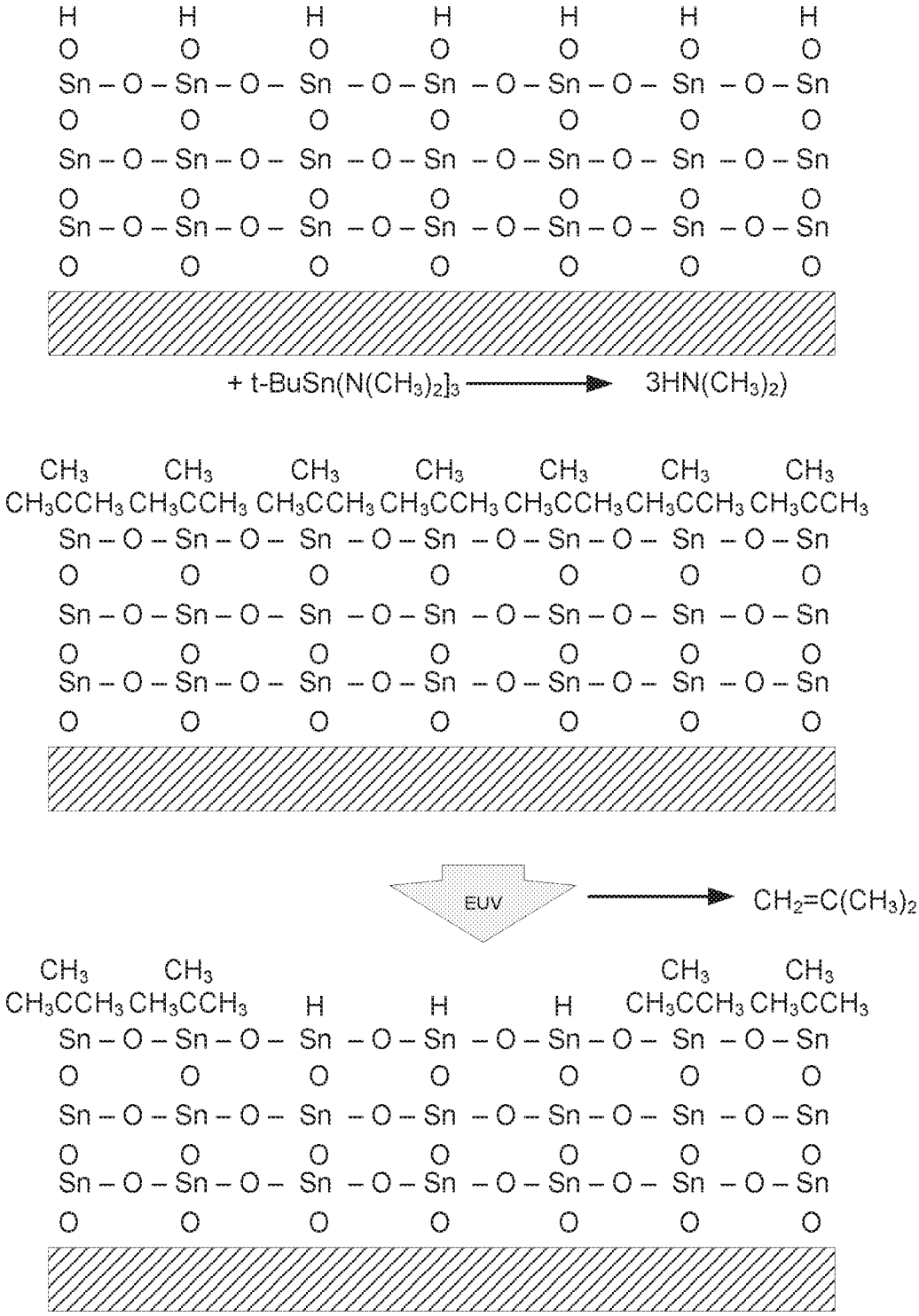


FIG. 3

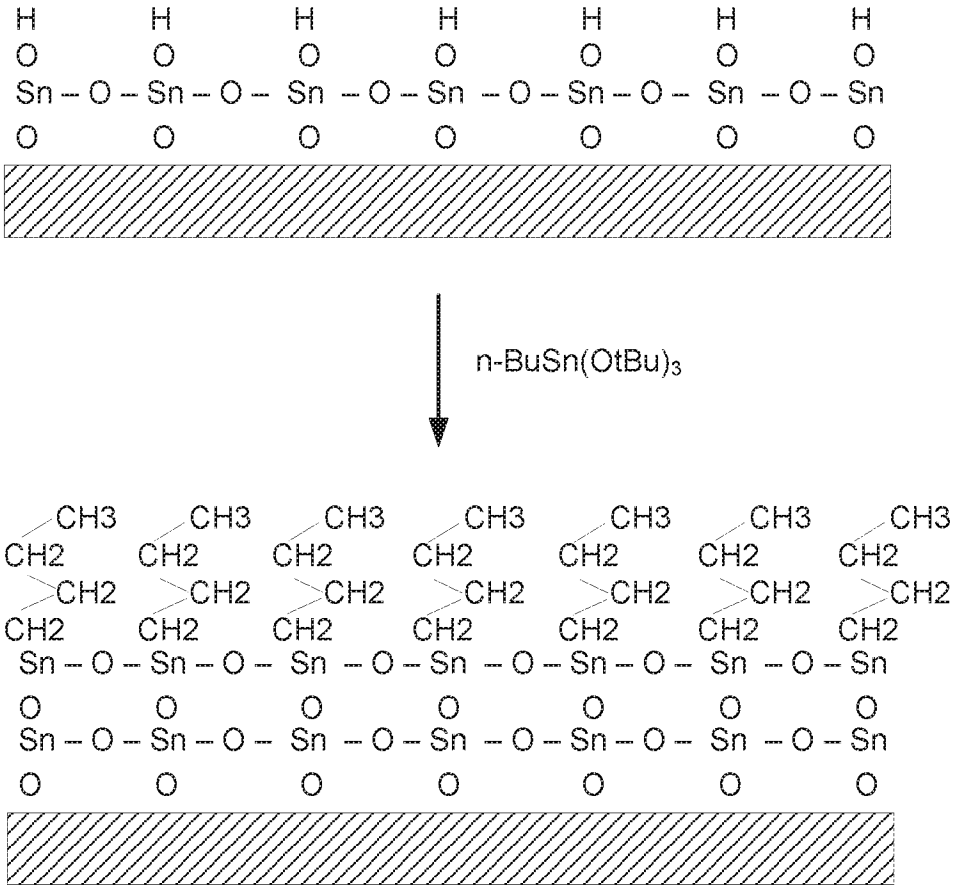

H H H H H H H
O O O O O O O
Sn – O – Sn – O – Sn – O – Sn – O – Sn – O – Sn – O – Sn
O O O O O O O
n-BuSn(OtBu)3
CH3 CH3 CH3 CH3 CH3 CH3 CH3
CH2 CH2 CH2 CH2 CH2 CH2 CH2
CH2 CH2 CH2 CH2 CH2 CH2 CH2
CH2 CH2 CH2 CH2 CH2 CH2 CH2
Sn – O – Sn – O – Sn – O – Sn – O – Sn – O – Sn – O – Sn
O O O O O O O
Sn – O – Sn – O – Sn – O – Sn – O – Sn – O – Sn – O – Sn
O O O O O O O

FIG. 4

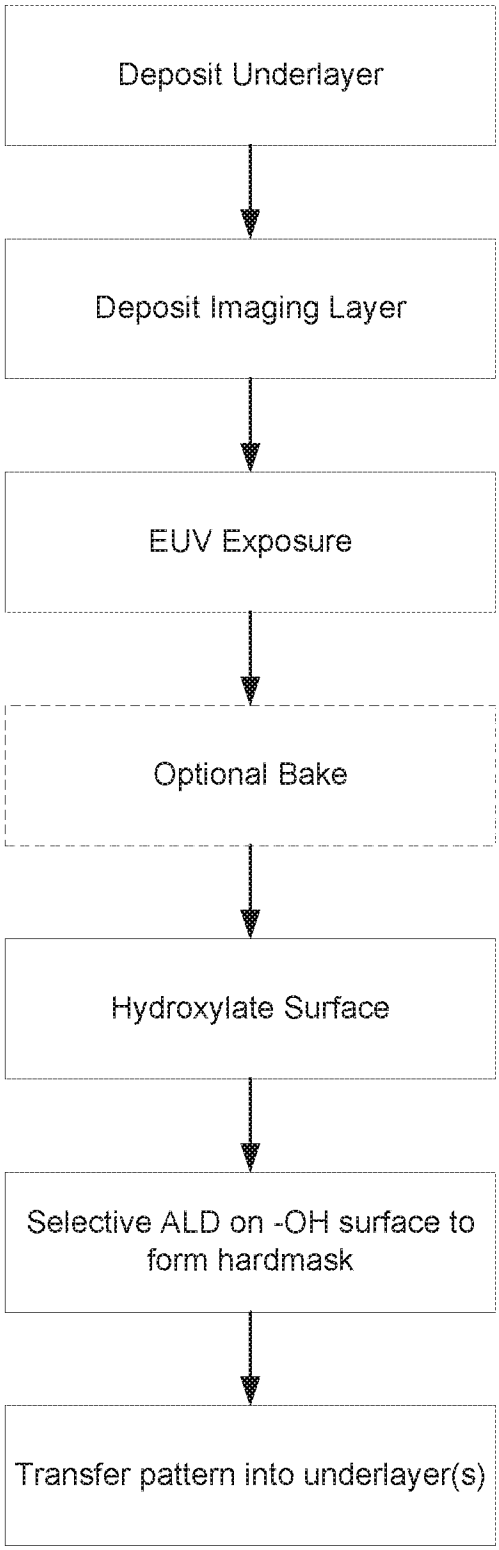

Deposit Underlayer
Deposit Imaging Layer
EUV Exposure
Optional Bake
Hydroxylate Surface
Selective ALD on -OH surface to form hardmask
Transfer pattern into underlayer(s)

FIG. 5

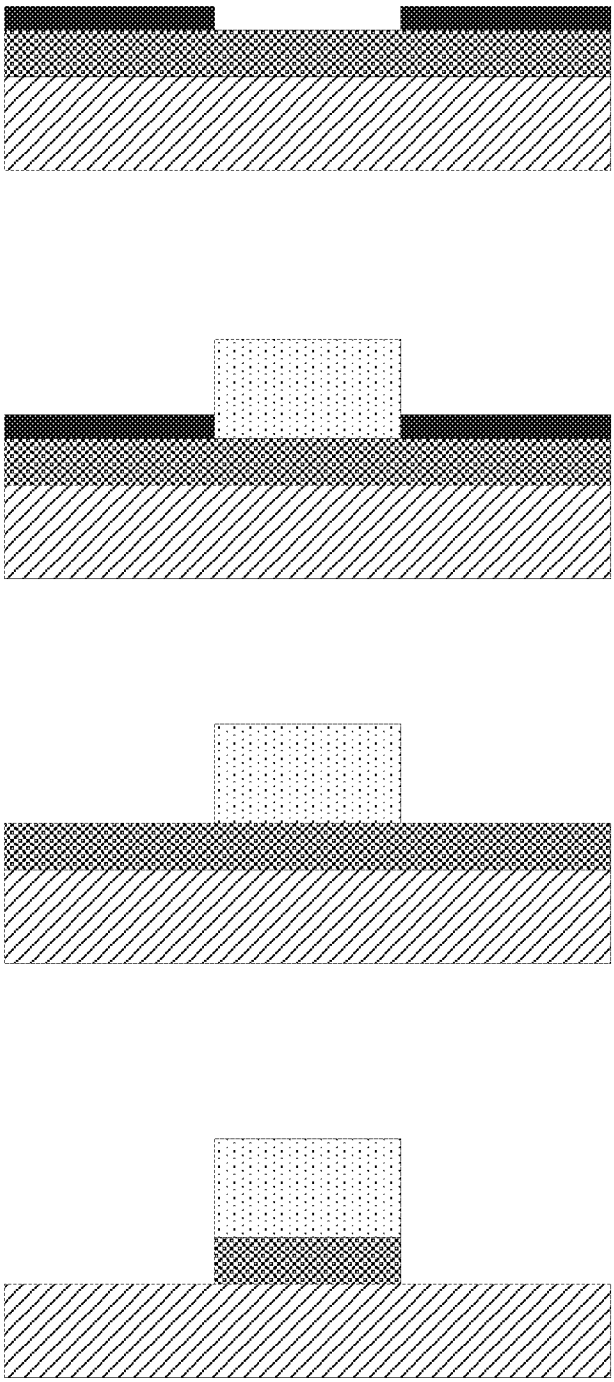


FIG. 6

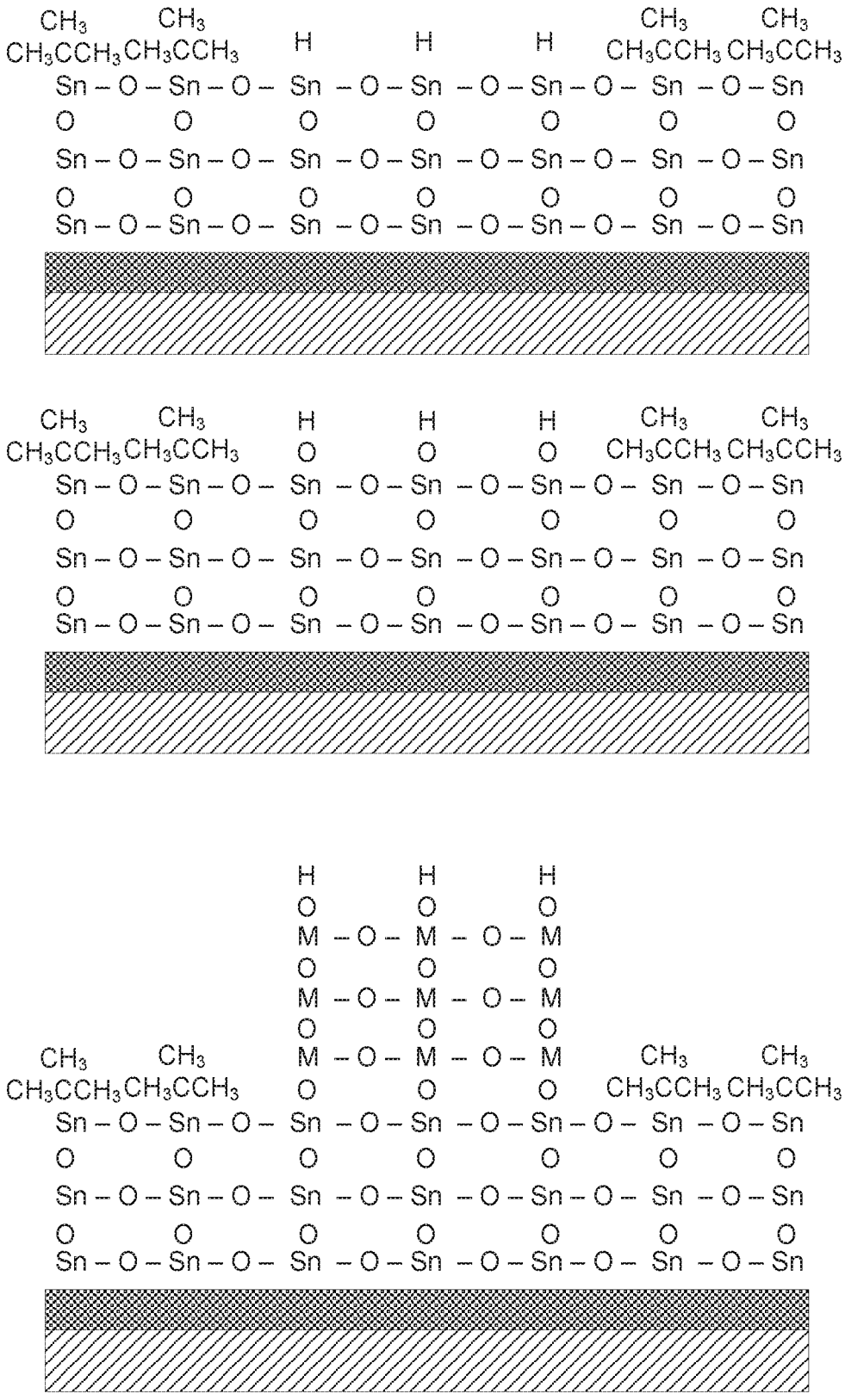


FIG. 7A

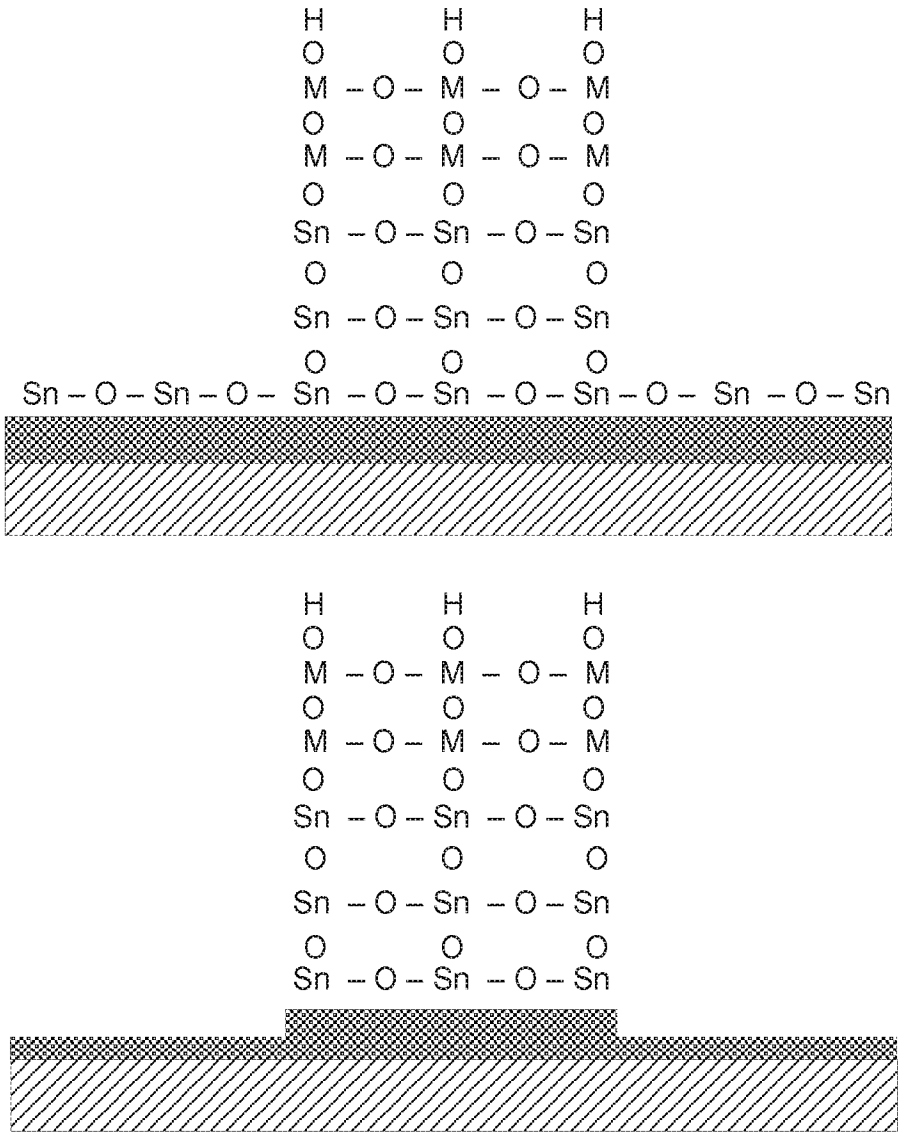

H H H
O O O
M – O – M – O – M
O O O
M – O – M – O – M
O O O
Sn – O – Sn – O – Sn
O O O
Sn – O – Sn – O – Sn
O O O
Sn – O – Sn – O – Sn – O – Sn – O – Sn – O – Sn
H H H
O O O
M – O – M – O – M
O O O
M – O – M – O – M
O O O
Sn – O – Sn – O – Sn
O O O
Sn – O – Sn – O – Sn
O O O
Sn – O – Sn – O – Sn

FIG. 7B

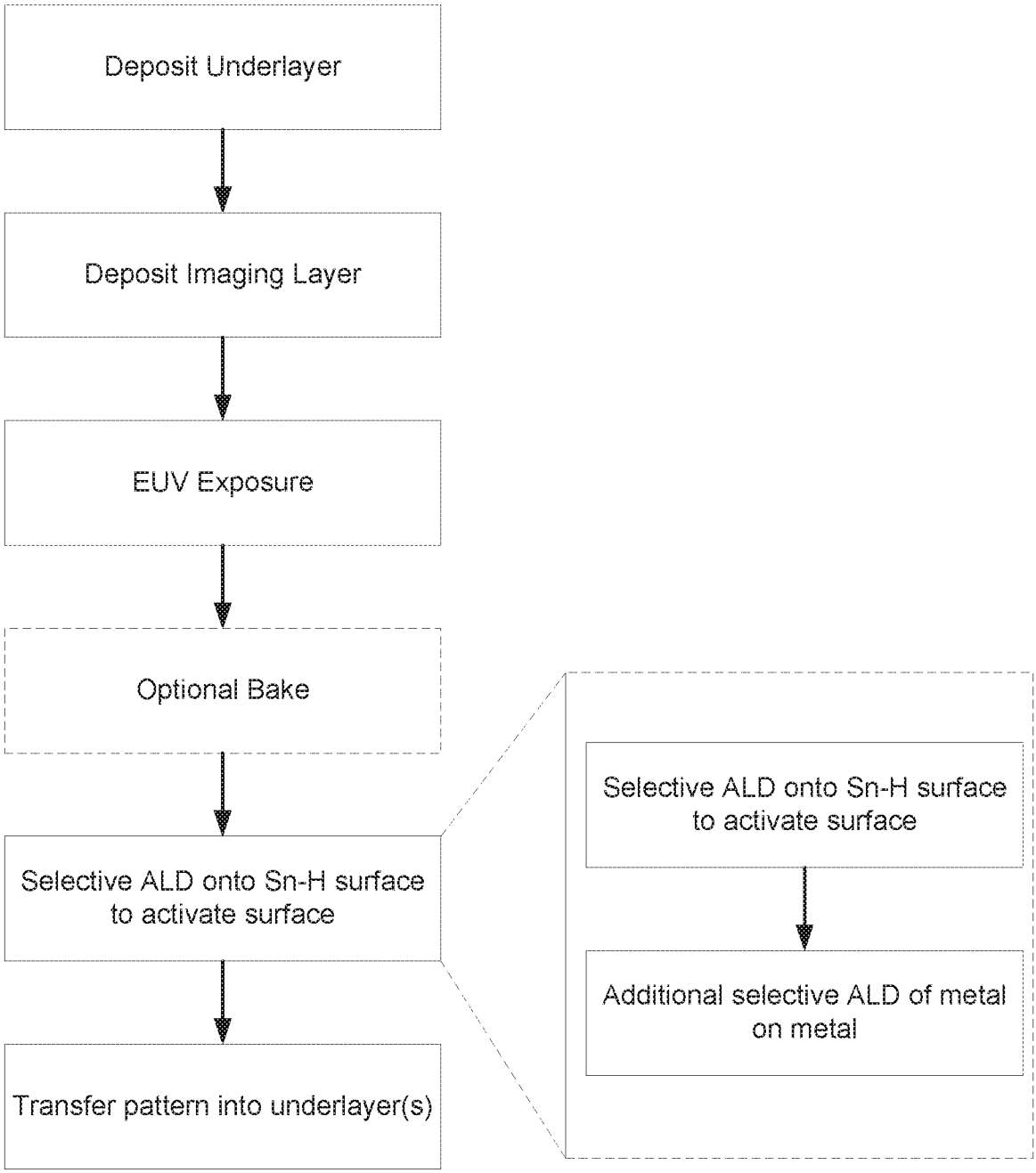

Deposit Underlayer
Deposit Imaging Layer
EUV Exposure
Optional Bake
Selective ALD onto Sn-H surface to activate surface
Transfer pattern into underlayer(s)
Selective ALD onto Sn-H surface to activate surface
Additional selective ALD of metal on metal

FIG. 8

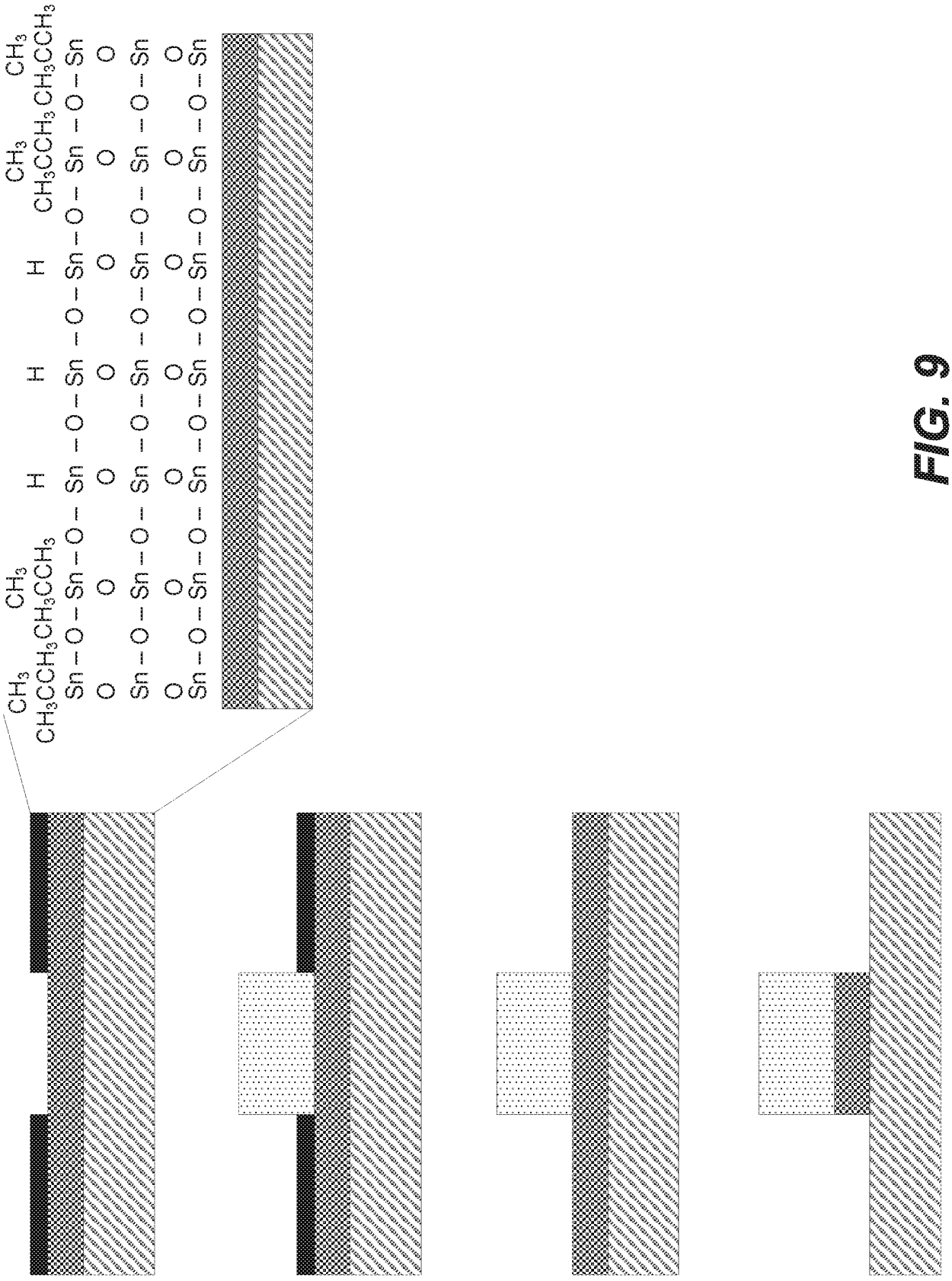

CH3 CH3 CH3 CH3
CH3CCH3CH3CCH3 H H H CH3CCH3CH3CCH3
Sn – O – Sn – O – Sn – O – Sn – O – Sn – O – Sn
O O O O O O
Sn – O – Sn – O – Sn – O – Sn – O – Sn – O – Sn
O O O O O O
Sn – O – Sn – O – Sn – O – Sn – O – Sn – O – Sn

FIG. 9

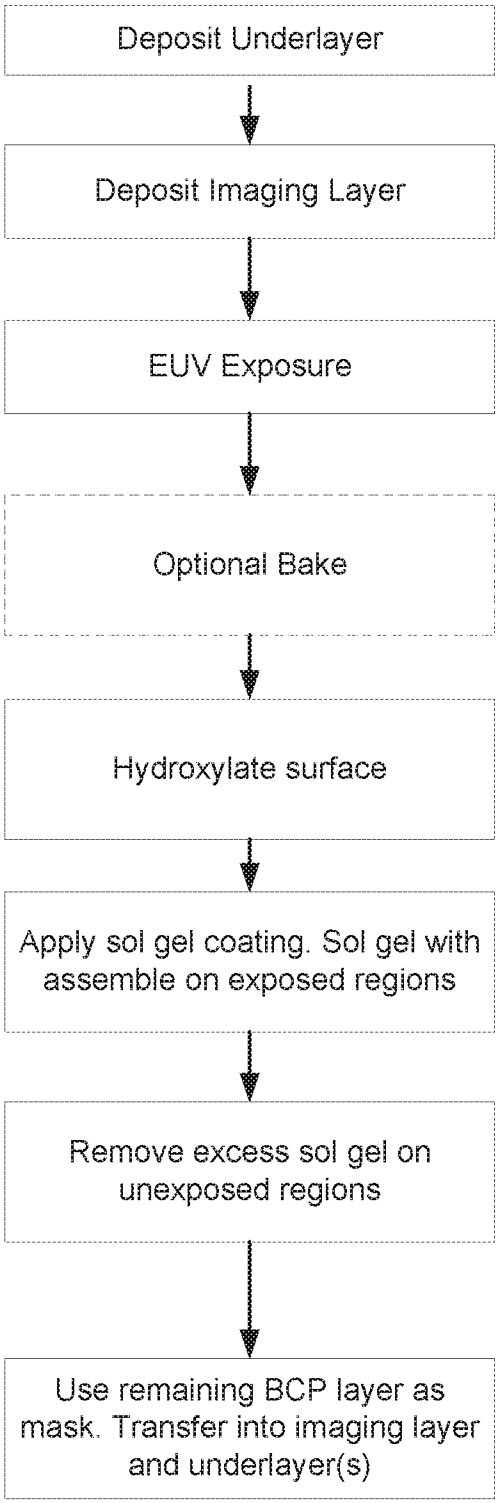

Deposit Underlayer
Deposit Imaging Layer
EUV Exposure
Optional Bake
Hydroxylate surface
Apply sol gel coating. Sol gel with assemble on exposed regions
Remove excess sol gel on unexposed regions
Use remaining BCP layer as mask. Transfer into imaging layer and underlayer(s)

FIG. 10

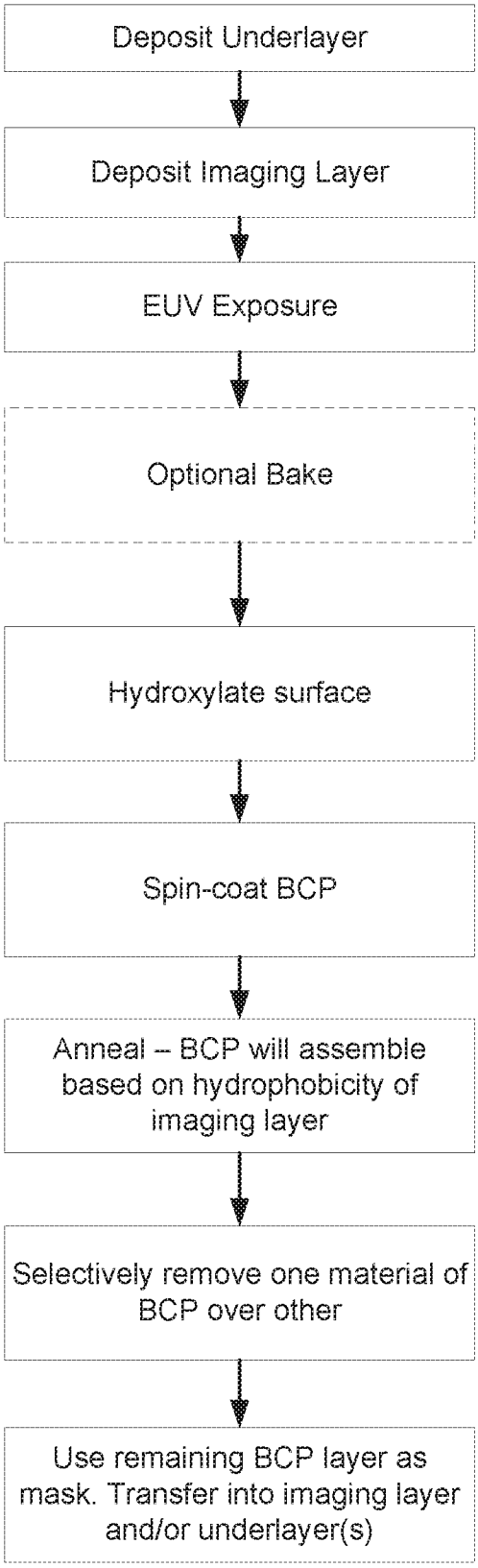

Deposit Underlayer
Deposit Imaging Layer
EUV Exposure
Optional Bake
Hydroxylate surface
Spin-coat BCP
Anneal – BCP will assemble based on hydrophobicity of imaging layer
Selectively remove one material of BCP over other
Use remaining BCP layer as mask. Transfer into imaging layer and/or underlayer(s)

FIG. 11

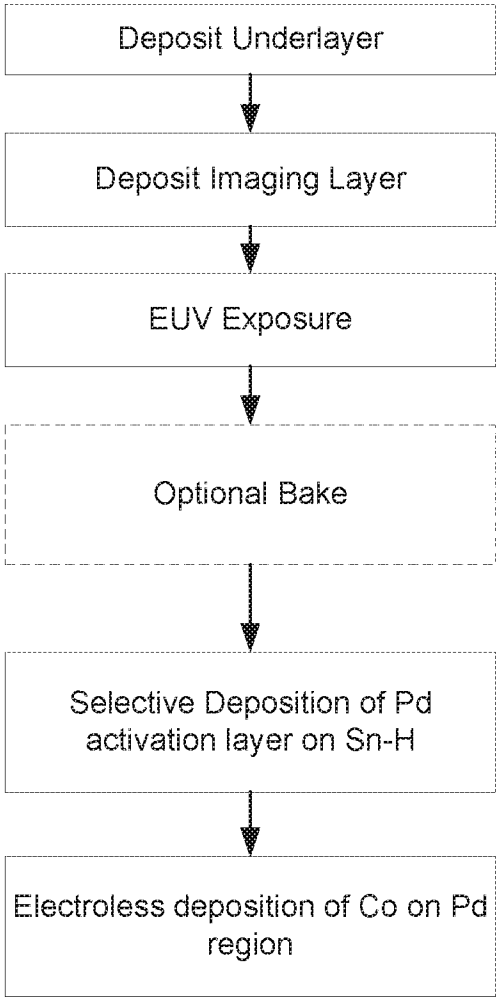

Deposit Underlayer
Deposit Imaging Layer
EUV Exposure
Optional Bake
Selective Deposition of Pd activation layer on Sn-H
Electroless deposition of Co on Pd region

FIG. 12

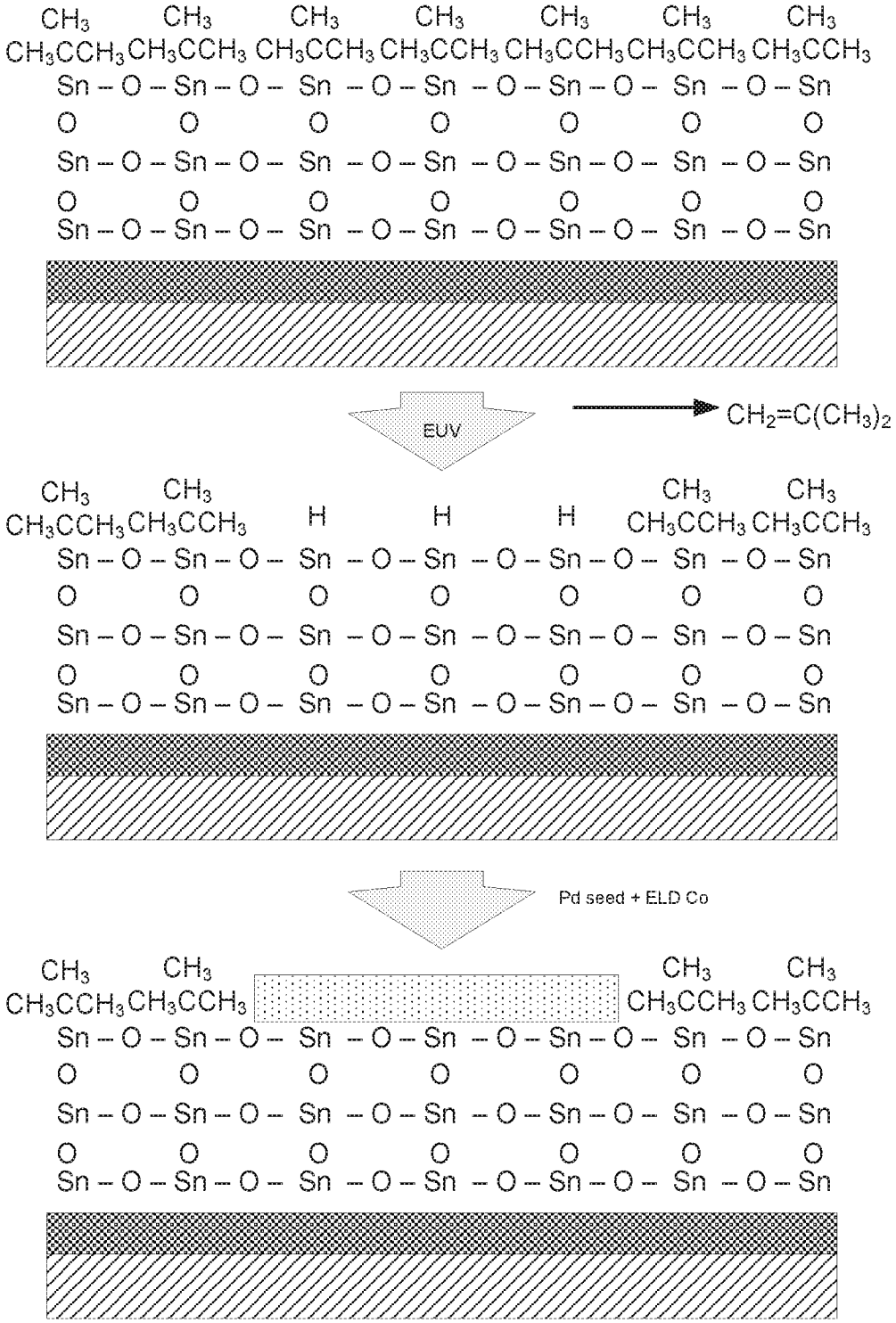


FIG. 13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/060742

A. CLASSIFICATION OF SUBJECT MATTER

G03F 7/004(2006.01)i, G03F 7/11(2006.01)i, G03F 7/20(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)
G03F 7/004; C09D 7/12; G02B 5/20; G03F 7/32; H01L 21/02; H01L 21/033; G03F 7/11; G03F 7/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: hydrocarbyl, tin oxide, hydroxyl, hardmask

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2017-0102612 A1 (INPRIA CORPORATION) 13 April 2017 paragraphs [0028]-[0089] and figures 1-2	1-40
A	US 2016-0116839 A1 (INPRIA CORPORATION) 28 April 2016 paragraphs [0074]-[0116] and figures 1-6	1-40
A	US 2018-0012759 A1 (LAM RESEARCH CORPORATION) 11 January 2018 paragraphs [0029]-[0061] and figures 1-8	1-40
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A	WO 2011-081151 A1 (ASAHI GLASS COMPANY, LIMITED et al.) 07 July 2011 paragraphs [0023]-[0055]	1-40

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

☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 April 2020 (10.04.2020)	**10 April 2020 (10.04.2020)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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