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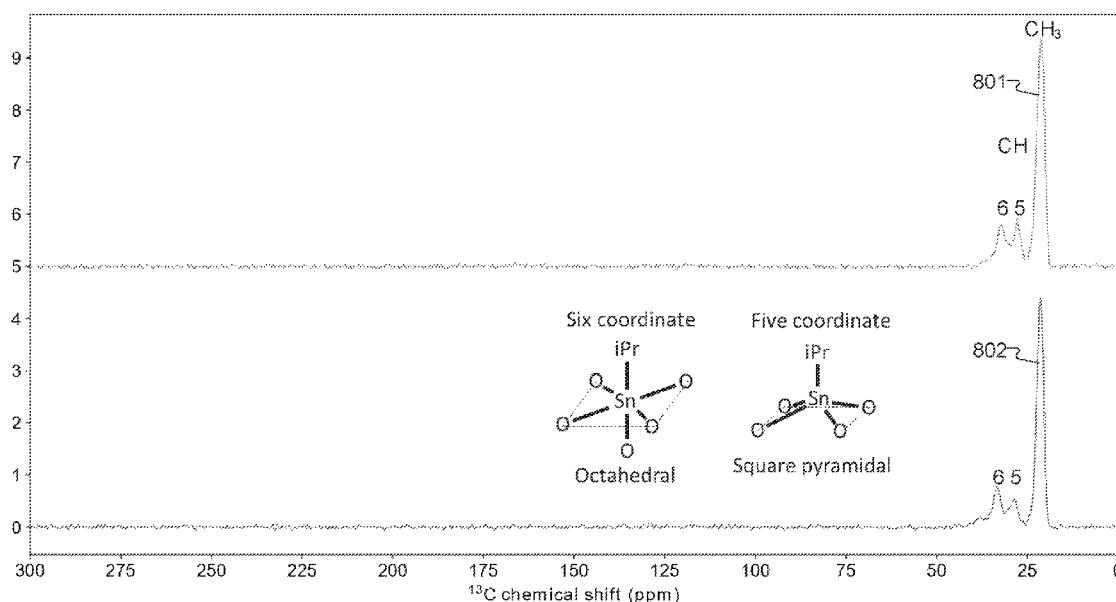


FIG. 8

(57) Abstract: The present disclosure relates to a film formed with a precursor and an organic co-reactant, as well as methods for forming and employing such films. The film can be employed as a photopatternable film or a radiation-sensitive film. In particular embodiments, the carbon content within the film can be tuned by decoupling the sources of the radiation-sensitive metal elements and the radiation-sensitive organic moieties during deposition. In non-limiting embodiments, the radiation can include extreme ultraviolet (EUV) or deep ultraviolet (DUV) radiation.



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DRY DEPOSITED PHOTORESISTS WITH ORGANIC CO-REACTANTSINCORPORATION BY REFERENCE

5 [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 their entireties and for all purposes. This application claims the benefit of U.S. Provisional Patent Application No. 62/705,854, filed July 17, 2020, which is incorporated herein by reference in its entirety.

FIELD

10 [0002] The present disclosure relates to a film formed with a precursor and an organic co-reactant, as well as methods for forming and employing such films. The film can be employed as a photopatternable film or a radiation-sensitive film. In particular embodiments, the carbon content within the film can be tuned by decoupling the sources of the radiation-sensitive metal elements and the radiation-sensitive organic moieties during deposition. In
15 non-limiting embodiments, the radiation can include extreme ultraviolet (EUV) or deep ultraviolet (DUV) radiation.

BACKGROUND

[0003] The background description provided herein is for the purpose of generally presenting the context of the present technology. Work of the presently named inventors, to
20 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 neither expressly nor impliedly admitted as prior art against the present technology.

[0004] Patterning of thin films in semiconductor processing is often an important step in the fabrication of semiconductors. Patterning involves lithography. In photolithography,
25 such as 193 nm photolithography, patterns are printed by emitting photons from a photon source onto a mask and printing the pattern onto a photosensitive photoresist, thereby causing a chemical reaction in the photoresist that, after development, removes certain portions of the photoresist to form the pattern.

[0005] Advanced technology nodes (as defined by the International Technology Roadmap
30 for Semiconductors) include nodes 22 nm, 16 nm, and beyond. In the 16 nm node, for

example, the width of a typical via or line in a Damascene structure is typically no greater than about 30 nm. Scaling of features on advanced semiconductor integrated circuits (ICs) and other devices is driving lithography to improve resolution.

[0006] Extreme ultraviolet (EUV) lithography can extend lithography technology by moving to smaller imaging source wavelengths than would be achievable with other photolithography methods. EUV light sources at approximately 10-20 nm, or 11-14 nm wavelength, for example 13.5 nm wavelength, can be used for leading-edge lithography tools, also referred to as scanners. EUV radiation is strongly absorbed in a wide range of solid and fluid materials including quartz and water vapor, and so operates in a vacuum.

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SUMMARY

[0007] The present disclosure relates to use of an organic co-reactant with a precursor to provide a patterning radiation-sensitive film. For instance, the precursor can be an organometallic compound that can be deposited to provide a metal-containing photoresist, and the organic co-reactant can be employed to react with the precursor during deposition.

15 Such a reaction can provide a modified precursor, which can possess a radiation-responsive organic moiety provided by the organic co-reactant and a radiation-sensitive metal center provided by the precursor. In non-limiting embodiments, the radiation can include extreme ultraviolet (EUV) or deep ultraviolet (DUV) radiation.

[0008] In some embodiments, use of carbon-containing co-reactants (or organic co-reactants) can expand the library of film compositions and enable tuning of the film of its various properties (e.g., mechanical properties of the film, optical properties such as patterning radiation sensitivity, and/or patterning performance). Such organic co-reactants can be used during the deposition process to decouple the density of radiation-sensitive elements from the density of radiation-responsive organic moieties in the film, which can
25 allow tuning of the ratio of radiation-sensitive metal to radiation-responsive organic moieties that might lead to improved patterning radiation sensitivity and/or improved resultant patterning quality. Non-limiting deposition processes include chemical vapor deposition (CVD), as well as atomic layer deposition (ALD), molecular layer deposition (MLD), and plasma-enhanced forms thereof.

30 [0009] Furthermore, the organic co-reactant can be selected to instill other beneficial properties to the film. In one instance, the selected organic co-reactant can introduce a ligand

to a metal center of the precursor, in which the introduced ligand is highly soluble to a positive tone developer upon exposure to patterning radiation. An illustrative ligand includes a bivalent oxalyl ligand located between metal centers, which provides a resilient film in radiation unexposed areas (e.g., EUV or DUV unexposed areas) but results in a removable film in radiation exposed areas (e.g., EUV or DUV exposed areas). In this way, the organic co-reactant can provide a positive tone resist. In another instance, the introduced ligand includes a polymerizable moiety (e.g., alkenylene, alkynylene, or epoxy) located between metal centers, which can undergo photopolymerization in radiation exposed areas. In this way, the organic co-reactant provides an enhanced negative tone resist.

10 **[0010]** Accordingly, in a first aspect, the present disclosure encompasses a stack including: a semiconductor substrate having a top surface, and a patterning radiation-sensitive film disposed on the top surface of the semiconductor substrate. In some embodiments, the film includes a radiation-absorbing unit (e.g., a radiation-sensitive element) and a radiation-sensitive carbon-containing unit from an organic co-reactant (e.g., a radiation-responsive organic moiety, such as any described herein). In particular embodiments, the radiation-sensitive carbon-containing unit is a bound ligand formed as a reaction product between the radiation-absorbing unit (e.g., in an initial precursor) and the organic co-reactant. Non-limiting examples of radiation-absorbing units include a metal or a metalloid (e.g., tin (Sn), tellurium (Te), hafnium (Hf), and zirconium (Zr), or a combination thereof). In other
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embodiments, the radiation-sensitive carbon-containing unit is selected from the group of alkenylene moieties, alkynylene moieties, carbonyl moieties, and dicarbonyl moieties, or a combination thereof.

[0011] In some embodiments, the EUV-sensitive film includes a vertical gradient characterized by a change in EUV absorbance. In particular embodiments, the vertical
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gradient includes an increase in EUV absorbance, in which a bottom portion of the film in proximity to the substrate has a higher EUV absorbance than a top portion of the film. In other embodiments, the vertical gradient includes a decrease in carbon content, in which a bottom portion of the film in proximity to the substrate has a lower carbon content than a top portion of the film. In yet other embodiments, the vertical gradient includes an increase in
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carbon content, in which a bottom portion of the film in proximity to the substrate has a higher carbon content than a top portion of the film.

[0012] In some embodiments, the stack includes a photoresist layer having the radiation-absorbing unit and the radiation-sensitive carbon-containing unit. In other embodiments, the

stack includes a capping layer (e.g., which can include a radiation-absorbing unit and a radiation-sensitive carbon-containing unit).

[0013] In a second aspect, the present disclosure features a method of forming a film. In some embodiments, the method includes providing an initial precursor in the presence of an organic co-reactant to provide a modified precursor; and depositing the modified precursor on a surface of a substrate to provide a patterning radiation-sensitive film. In other embodiments, the initial precursor includes an organometallic compound having one or more ligands, wherein the organic co-reactant replaces at least one of the ligand(s) to provide a modified precursor.

[0014] In some embodiments, the modified precursor is characterized by an increase in EUV absorption or an increase in an EUV absorption cross-section, as compared to the initial precursor. In other embodiments, the modified precursor includes an increased or a decreased carbon content, as compared to the initial precursor.

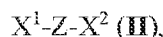
[0015] In some embodiments, said providing further includes providing a molar ratio of the initial precursor to the organic co-reactant of from about 1000:1 to about 1:4. In particular embodiments, such providing can include delivering the initial precursor in vapor form and the organic co-reactant in vapor form to a chamber including the semiconductor substrate.

[0016] In some embodiments, the initial precursor includes a structure having formula (I):



wherein: M is a metal or a metalloid (e.g., any herein); each R is, independently, halo, optionally substituted alkyl, optionally substituted aryl, optionally substituted amino, optionally substituted alkoxy, or L; each L is, independently, is a ligand, ion, or other moiety that is reactive with an organic co-reactant or a counter-reactant, in which R and L with M, taken together, can optionally form a heterocyclyl group or in which R and L, taken together, can optionally form a heterocyclyl group; $a \geq 1$ (e.g., a is 1, 2, or 3); $b \geq 1$ (e.g., b is 1, 2, 3, 4, 5, or 6); and $c \geq 1$ (e.g., c is 1, 2, 3, 4, 5, 6). In particular embodiments, each R is L, and/or M is tin (Sn), such as Sn(IV) or Sn(II). In some embodiments, each L is, independently, H, halo, optionally substituted alkyl, optionally substituted aryl, optionally substituted amino, optionally substituted bis(trialkylsilyl)amino, optionally substituted trialkylsilyl, or optionally substituted alkoxy (e.g., any L described herein).

[0017] In some embodiments, the organic co-reactant includes one or more polymerizable moieties, alkynyl moieties, dicarbonyl moieties, carbonyl moieties, or haloalkyl moieties. In other embodiments, the organic co-reactant includes a structure having formula (II):



5 wherein: each of X^1 and X^2 is, independently, a leaving group (e.g., halo, H, hydroxyl, optionally substituted alkyl, optionally substituted haloalkyl, optionally substituted heteroalkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted alkoxy, or optionally substituted aryl); and Z is carbonyl, dicarbonyl, optionally substituted alkylene (e.g., optionally substituted C_{1-3} alkylene or optionally substituted C_{1-2} alkylene), optionally substituted haloalkylene, optionally substituted alkenylene, or optionally substituted alkynylene.

[0018] In particular embodiments, Z is carbonyl. In further embodiments, at least one of X^1 and X^2 is H (e.g., as in an aldehyde, such as in $H-C(O)-X^2$). In further embodiments, both of X^1 and X^2 is selected from the group of optionally substituted alkyl, optionally substituted haloalkyl, optionally substituted heteroalkyl, optionally substituted alkenyl, optionally substituted alkynyl, or optionally substituted aryl (e.g., as in a ketone). In further
15 embodiments, at least one of X^1 and X^2 is halo (e.g., as in a carbonyl halide, such as in $F-C(O)-X^2$, $Cl-C(O)-X^2$, $Br-C(O)-X^2$, or $I-C(O)-X^2$). In further embodiments, at least one of X^1 and X^2 is hydroxyl (e.g., as in a carboxylic acid, such as in $HO-C(O)-X^2$).

20 [0019] In some embodiments, said providing includes providing the initial precursor and the organic co-reactant in vapor form. In other embodiments, said providing further includes providing a counter-reactant (e.g., any described herein, such as an oxygen-containing counter-reactant, including O_2 , O_3 , water, a peroxide, hydrogen peroxide, oxygen plasma, water plasma, an alcohol, a dihydroxy alcohol, a polyhydroxy alcohol, a fluorinated
25 dihydroxy alcohol, a fluorinated polyhydroxy alcohol, a fluorinated glycol, formic acid, and other sources of hydroxyl moieties, as well as combinations thereof). In particular embodiments, reactivity of the counter-reactant can be comparable to that of the organic co-reactant, thereby ensuring that the organic co-reactant will react sufficiently with the initial precursor to incorporate the organic ligand into the deposited film. For instance, if the
30 counter-reactant is significantly more reactive (with the initial precursor) than the organic co-reactant (with the initial precursor), then reaction conditions may favor incorporation of the counter-reactant rather than the organic co-reactant into the deposited film. In other embodiments, the counter-reactant is not water, not a peroxide, or not a plasma. In yet other

embodiments, the organic co-reactant is provided with the initial precursor in an initial operation, and then the counter-reactant is provided in a subsequent operation. Further details are provided herein.

5 **[0020]** In a third aspect, the present disclosure encompasses a method of employing a capping layer. In some embodiments, the method includes: providing a substrate including a photoresist layer disposed on a top surface of the substrate; providing an initial precursor in the presence of an organic co-reactant to provide a modified precursor; and depositing the modified precursor on a surface of the photoresist layer to provide the capping layer. In other
10 embodiments, the initial precursor includes an organometallic compound having one or more ligands (e.g., having at least one ligand), and the organic co-reactant replaces at least one of the ligand(s) to provide the modified precursor. In other embodiments, the capping layer is a patterning radiation-sensitive film or includes patterning radiation-transparent region(s). In yet other embodiments, the capping layer reduces off-gassing of one or more metal species present in the photoresist layer.

15 **[0021]** In some embodiments, the method further includes (e.g., after said depositing): patterning the photoresist layer by an EUV exposure, thereby providing an exposed film having EUV exposed areas and EUV unexposed areas. In some embodiments, the photoresist layer underlies the capping layer. In other embodiments, the EUV radiation has a wavelength in the range of about 10 nm to about 20 nm in a vacuum ambient.

20 **[0022]** In other embodiments, the method further includes (e.g., after said patterning): developing the exposed film, thereby removing the EUV exposed areas or EUV unexposed areas to provide a pattern. In particular embodiments, the method is for removing EUV exposed areas, thereby providing a pattern within a positive tone resist film. In other
25 embodiments, the method is for removing EUV unexposed areas, thereby providing a pattern within a negative tone resist.

30 **[0023]** In a fourth aspect, the present disclosure features a method of employing a resist. In some embodiments, the method includes: providing an initial precursor in the presence of an organic co-reactant to provide a modified precursor; depositing the modified precursor on a surface of a substrate to provide a patterning radiation-sensitive film as a resist film; patterning the resist film by exposure to patterning radiation, thereby providing an exposed film having radiation exposed areas and radiation unexposed areas; and developing the exposed film. In other embodiments, said developing includes removing the radiation

exposed areas to provide a pattern within a positive tone resist film. In yet other embodiments, said developing includes removing the radiation unexposed areas to provide a pattern within a negative tone resist.

5 [0024] In particular embodiments, the initial precursor includes an organometallic compound having one or more ligands (e.g., at least one ligand). In further embodiments, the organic co-reactant replaces at least some significant, detectable percentage of one ligand to provide the modified precursor. In other embodiments, the organic co-reactant replaces at least one of the ligand(s) of the initial precursor to provide the modified precursor. In some
10 embodiments, the detectable percentage is from about at least 0.1%, 0.5%, 1%, or 3%, as well as from 0.1% to 5%.

[0025] In some embodiments, the patterning radiation includes an EUV exposure having a wavelength in the range of about 10 nm to about 20 nm in a vacuum ambient. In further embodiments, said patterning includes a release of carbon dioxide and/or carbon monoxide from the exposed film.

15 [0026] In some embodiments, the method includes post-exposure baking of the exposed film in the optional presence of includes an oxygen-containing agent, water vapor, and/or carbon dioxide. In other embodiments, the method includes said developing in the presence of an oxygen-containing agent, water vapor, and/or carbon dioxide.

[0027] In some embodiments, said patterning further includes photopolymerization
20 occurring within the exposed film. In particular embodiments, the organic co-reactant and/or the film includes a photopolymerizable moiety. In further embodiments, the photopolymerizable moiety includes optionally substituted alkenylene, optionally substituted alkynylene, or optionally substituted epoxy (e.g., optionally substituted oxiranyl).

[0028] In a fifth aspect, the present disclosure features an apparatus for forming a resist
25 film. In some embodiments, the apparatus includes: a deposition module; a patterning module; a development module; and a controller including one or more memory devices, one or more processors, and system control software coded with instructions including machine-readable instructions.

[0029] In some embodiments, the deposition module includes a chamber for depositing a
30 patterning radiation-sensitive film (e.g., an EUV-sensitive film). In other embodiments, the patterning module includes a photolithography tool with a source of sub-300 nm wavelength radiation (e.g., in which the source can be a source of sub-30 nm wavelength radiation). In

yet other embodiments, the development module includes a chamber for developing the resist film.

5 **[0030]** In further embodiments, the instructions include machine-readable instructions for (e.g., in the deposition module) causing deposition of a modified precursor on a top surface of a semiconductor substrate. In some embodiments, such deposition can form the patterning radiation-sensitive film as a resist film, in which an initial precursor is provided in the presence of an organic co-reactant to provide the modified precursor. In other embodiments, such deposition can include causing a change of a molar ratio of the initial precursor and the organic co-reactant to provide a further modified precursor to form the patterning radiation-sensitive film.

10 **[0031]** In some embodiments, the instructions include machine-readable instructions for (e.g., in the patterning module) causing patterning of the resist film with sub-300 nm resolution (e.g., or with sub-30 nm resolution) directly by patterning radiation exposure (e.g., by EUV exposure), thereby forming an exposed film having radiation exposed areas and radiation unexposed areas. In other embodiments, the exposed film has EUV exposed areas and EUV unexposed areas. In yet other embodiments, the instructions include machine-readable instructions for (e.g., in the development module) causing development of the exposed film to remove the radiation exposed areas or the radiation unexposed areas to provide a pattern within the resist film. In particular embodiments, the machine-readable instructions include instructions for causing removal of the EUV exposed areas or the EUV unexposed areas.

15 **[0032]** In any embodiment herein, the patterning radiation-sensitive film includes an extreme ultraviolet (EUV)-sensitive film, a deep-ultraviolet (DUV)-sensitive film, a photoresist film, or a photopatternable film.

20 **[0033]** In any embodiment herein, the patterning radiation-sensitive film includes a plurality of polymerizable moieties (e.g., photopolymerizable moieties), alkenylene moieties, alkynylene moieties, carbonyl moieties, or dicarbonyl moieties.

25 **[0034]** In any embodiment herein, the patterning radiation-sensitive film includes an organometallic material or an organometal oxide material.

30 **[0035]** In any embodiment herein, the initial precursor includes a structure having formula (I), (Ia), (III), (IV), (V), (VI), (VII), or (VIII), as described herein.

[0036] In any embodiment herein, a single initial precursor is employed with one or more organic co-reactants. In other embodiments, two, three, four, or more different initial precursors are employed within one or more organic co-reactants.

5 [0037] In any embodiment herein, the organic co-reactant includes a structure having formula (II), (IIa), (IIb), (IIc), (IId), or (IIf), as described herein.

[0038] In any embodiment herein, the organic co-reactant has a vapor pressure of from about 0.1 mTorr to 350 Torr (e.g., 0.1 mTorr to 50 mTorr, 0.5 mTorr to 100 mTorr, 0.1 mTorr to 200 Torr, 0.1 mTorr to 300 Torr, 0.5 mTorr to 200 Torr, 0.5 mTorr to 300 Torr, 0.5 mTorr to 350 Torr, such as at room temperature of about 20°C to 25°C).

10 [0039] In any embodiment herein, the modified precursor includes the use of a chalcogenide precursor or an oxygen-containing counter-reactant.

[0040] In any embodiment herein, a single initial precursor is employed with a single organic co-reactant. In other embodiments, a single initial precursor is employed with two, three, four, or more different organic co-reactants. In yet other embodiments, two or more
15 different initial precursors are employed with two or more different organic co-reactants.

[0041] In any embodiment herein, a molar ratio of the initial precursor to the organic co-reactant of from about 1000:1 to about 1:4 (e.g., about 1000:1 to 1:4, 100:1 to 10:1, 50:1 to 1:4, etc.).

[0042] In any embodiment herein, depositing includes depositing the modified precursor in
20 vapor form. In other embodiments, said depositing includes providing an initial precursor, an organic co-reactant, and/or a counter-reactant in vapor form. In particular embodiments, said depositing includes chemical vapor deposition (CVD), atomic layer deposition (ALD), or molecular layer deposition (MLD). Additional details follow.

Definitions

25 [0043] By “alkenyl” is meant an optionally substituted C₂₋₂₄ alkyl group having one or more double bonds. The alkenyl group can be cyclic (e.g., C₃₋₂₄ cycloalkenyl) or acyclic. The alkenyl group can also be substituted or unsubstituted. For example, the alkenyl group can be substituted with one or more substitution groups, as described herein for alkyl.

[0044] By “alkenylene” is meant a multivalent (e.g., bivalent) form of an alkenyl group,
30 which is an optionally substituted C₂₋₂₄ alkyl group having one or more double bonds. The alkenylene group can be cyclic (e.g., C₃₋₂₄ cycloalkenyl) or acyclic. The alkenylene group

can be substituted or unsubstituted. For example, the alkenylene group can be substituted with one or more substitution groups, as described herein for alkyl. Exemplary, non-limiting alkenylene groups include -CH=CH- or -CH=CHCH₂-.

5 [0045] By “alkoxy” is meant -OR, where R is an optionally substituted alkyl group, as described herein. Exemplary alkoxy groups include methoxy, ethoxy, butoxy, trihaloalkoxy, such as trifluoromethoxy, etc. The alkoxy group can be substituted or unsubstituted. For example, the alkoxy group can be substituted with one or more substitution groups, as described herein for alkyl. Exemplary unsubstituted alkoxy groups include C₁₋₃, C₁₋₆, C₁₋₁₂, C₁₋₁₆, C₁₋₁₈, C₁₋₂₀, or C₁₋₂₄ alkoxy groups.

10 [0046] By “alkyl” and the prefix “alk” is meant a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl (Me), ethyl (Et), n-propyl (n-Pr), isopropyl (*i*-Pr), cyclopropyl, n-butyl (n-Bu), isobutyl (*i*-Bu), *s*-butyl (*s*-Bu), *t*-butyl (*t*-Bu), cyclobutyl, n-pentyl, isopentyl, *s*-pentyl, neopentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, eicosyl, tetracosyl, and the like. The alkyl group can be
15 cyclic (e.g., C₃₋₂₄ cycloalkyl) or acyclic. The alkyl group can be branched or unbranched. The alkyl group can also be substituted or unsubstituted. For example, the alkyl group can include haloalkyl, in which the alkyl group is substituted by one or more halo groups, as described herein. In another example, the alkyl group can be substituted with one, two, three or, in the case of alkyl groups of two carbons or more, four substituents independently
20 selected from the group consisting of: (1) C₁₋₆ alkoxy (e.g., -O-Ak, wherein Ak is optionally substituted C₁₋₆ alkyl); (2) amino (e.g., -NR^{N1}R^{N2}, where each of R^{N1} and R^{N2} is, independently, H or optionally substituted alkyl, or R^{N1} and R^{N2}, taken together with the nitrogen atom to which each are attached, form a heterocyclyl group); (3) aryl; (4) arylalkoxy (e.g., -O-Lk-Ar, wherein Lk is a bivalent form of optionally substituted alkyl and Ar is
25 optionally substituted aryl); (5) aryloyl (e.g., -C(O)-Ar, wherein Ar is optionally substituted aryl); (6) cyano (e.g., -CN); (7) carboxyaldehyde (e.g., -C(O)H); (8) carboxyl (e.g., -CO₂H); (9) C₃₋₈ cycloalkyl (e.g., a monovalent saturated or unsaturated non-aromatic cyclic C₃₋₈ hydrocarbon group); (10) halo (e.g., F, Cl, Br, or I); (11) heterocyclyl (e.g., a 5-, 6- or 7-membered ring, unless otherwise specified, containing one, two, three, or four non-carbon
30 heteroatoms, such as nitrogen, oxygen, phosphorous, sulfur, or halo); (12) heterocyclyoxy (e.g., -O-Het, wherein Het is heterocyclyl, as described herein); (13) heterocyclyoil (e.g., -C(O)-Het, wherein Het is heterocyclyl, as described herein); (14) hydroxyl (e.g., -OH); (15) N-protected amino; (16) nitro (e.g., -NO₂); (17) oxo (e.g., =O); (18) -CO₂R^A, where R^A is

selected from the group consisting of (a) C₁₋₆ alkyl, (b) C₄₋₁₈ aryl, and (c) (C₄₋₁₈ aryl) C₁₋₆ alkyl (e.g., -Lk-Ar, wherein Lk is a bivalent form of optionally substituted alkyl group and Ar is optionally substituted aryl); (19) -C(O)NR^BR^C, where each of R^B and R^C is, independently, selected from the group consisting of (a) hydrogen, (b) C₁₋₆ alkyl, (c) C₄₋₁₈ aryl, and (d) (C₄₋₁₈ aryl) C₁₋₆ alkyl (e.g., -Lk-Ar, wherein Lk is a bivalent form of optionally substituted alkyl group and Ar is optionally substituted aryl); and (20) -NR^GR^H, where each of R^G and R^H is, independently, selected from the group consisting of (a) hydrogen, (b) an N-protecting group, (c) C₁₋₆ alkyl, (d) C₂₋₆ alkenyl (e.g., optionally substituted alkyl having one or more double bonds), (e) C₂₋₆ alkynyl (e.g., optionally substituted alkyl having one or more triple bonds), (f) C₄₋₁₈ aryl, (g) (C₄₋₁₈ aryl) C₁₋₆ alkyl (e.g., Lk-Ar, wherein Lk is a bivalent form of optionally substituted alkyl group and Ar is optionally substituted aryl), (h) C₃₋₈ cycloalkyl, and (i) (C₃₋₈ cycloalkyl) C₁₋₆ alkyl (e.g., -Lk-Cy, wherein Lk is a bivalent form of optionally substituted alkyl group and Cy is optionally substituted cycloalkyl, as described herein), wherein in one embodiment no two groups are bound to the nitrogen atom through a carbonyl group. The alkyl group can be a primary, secondary, or tertiary alkyl group substituted with one or more substituents (e.g., one or more halo, oxo, or alkoxy). In some embodiments, the unsubstituted alkyl group is a C₁₋₂, C₁₋₃, C₁₋₆, C₁₋₁₂, C₁₋₁₆, C₁₋₁₈, C₁₋₂₀, or C₁₋₂₄ alkyl group.

[0047] By “alkylene” is meant a multivalent (e.g., bivalent) form of an alkyl group, as described herein. Exemplary alkylene groups include methylene, ethylene, propylene, butylene, etc. In some embodiments, the alkylene group is a C₁₋₃, C₁₋₆, C₁₋₁₂, C₁₋₁₆, C₁₋₁₈, C₁₋₂₀, C₁₋₂₄, C₂₋₃, C₂₋₆, C₂₋₁₂, C₂₋₁₆, C₂₋₁₈, C₂₋₂₀, or C₂₋₂₄ alkylene group. The alkylene group can be branched or unbranched. The alkylene group can also be substituted or unsubstituted. For example, the alkylene group can be substituted with one or more substitution groups, as described herein for alkyl.

[0048] By “alkyleneoxy” is meant an alkylene group, as defined herein, attached to the parent molecular group through an oxygen atom.

[0049] By “alkynyl” is meant an optionally substituted C₂₋₂₄ alkyl group having one or more triple bonds. The alkynyl group can be cyclic or acyclic and is exemplified by ethynyl, 1-propynyl, and the like. The alkynyl group can also be substituted or unsubstituted. For example, the alkynyl group can be substituted with one or more substitution groups, as described herein for alkyl.

[0050] By “alkynylene” is meant a multivalent (e.g., bivalent) form of an alkynyl group, which is an optionally substituted C₂₋₂₄ alkyl group having one or more triple bonds. The alkynylene group can be cyclic or acyclic. The alkynylene group can be substituted or unsubstituted. For example, the alkynylene group can be substituted with one or more substitution groups, as described herein for alkyl. Exemplary, non-limiting alkynylene groups include -C≡C- or -C≡CCH₂-.

[0051] By “amino” is meant -NR^{N1}R^{N2}, where each of R^{N1} and R^{N2} is, independently, H, optionally substituted alkyl, or optionally substituted aryl, or R^{N1} and R^{N2}, taken together with the nitrogen atom to which each are attached, form a heterocyclyl group, as defined herein.

[0052] By “aminoalkyl” is meant an alkyl group, as defined herein, substituted by an amino group, as defined herein.

[0053] By “aminoaryl” is meant an aryl group, as defined herein, substituted by an amino group, as defined herein.

[0054] By “aryl” is meant a group that contains any carbon-based aromatic group including, but not limited to, phenyl, benzyl, anthracenyl, anthryl, benzocyclobutenyl, benzocyclooctenyl, biphenyl, chrysenyl, dihydroindenyl, fluoranthenyl, indacenyl, indenyl, naphthyl, phenanthryl, phenoxybenzyl, picenyl, pyrenyl, terphenyl, and the like, including fused benzo-C₄₋₈ cycloalkyl radicals (e.g., as defined herein) such as, for instance, indanyl, tetrahydronaphthyl, fluorenyl, and the like. The term aryl also includes heteroaryl, which is defined as a group that contains an aromatic group that has at least one heteroatom incorporated within the ring of the aromatic group. Examples of heteroatoms include, but are not limited to, nitrogen, oxygen, sulfur, and phosphorus. Likewise, the term non-heteroaryl, which is also included in the term aryl, defines a group that contains an aromatic group that does not contain a heteroatom. The aryl group can be substituted or unsubstituted. The aryl group can be substituted with one, two, three, four, or five substituents, such as any described herein for alkyl.

[0055] By “carbonyl” is meant a -C(O)- group, which can also be represented as >C=O. A carbonyl group can be present in various compounds, such as in aldehydes, ketones, carbonyl halides, or carboxylic acids. By aldehyde is meant -C(O)H or a compound including such a group. An example of an aldehyde can include R¹C(O)H, in which R¹ is selected from alkyl, alkenyl, alkynyl, haloalkyl, heteroalkyl, aryl, as defined herein, or any combination thereof.

By ketone is meant $-C(O)R$ or a compound including such a group, where R is selected from alkyl, haloalkyl, heteroalkyl, alkenyl, alkynyl, aryl, as defined herein, or any combination thereof. An example of a ketone can include $R^1C(O)R$, in which each of R and R^1 is, independently, selected from alkyl, haloalkyl, heteroalkyl, alkenyl, alkynyl, aryl, as defined
 5 herein, or any combination thereof. By carbonyl halide is meant $-C(O)X$ or a compound including such a group, where X is halo. An example of a carbonyl halide can include $R^1C(O)X$, in which R^1 is selected from alkyl, haloalkyl, heteroalkyl, alkenyl, alkynyl, aryl, as defined herein, or any combination thereof. By carboxylic acid is meant $-C(O)OH$ or a compound including such a group. An example of a carboxylic acid can include $R^1C(O)OH$,
 10 in which R^1 is selected from alkyl, haloalkyl, heteroalkyl, alkenyl, alkynyl, aryl, as defined herein, or any combination thereof. Non-limiting examples of aldehydes, ketones, carbonyl halides, and carboxylic acids include acetaldehyde, acetone, butanone, acetyl halide ($CH_3-C(O)-X$, in which X is halo), acetic acid, and the like. In yet another example, non-limiting carbonyl moieties include $R^{C1}-C(O)-R^{C2}$, in which each of R^{C1} and R^{C2} is, independently, H,
 15 halo, hydroxyl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted haloalkyl, optionally substituted alkoxy, optionally substituted heteroalkyl, optionally substituted aryl, a leaving group (e.g., any described herein), or a combination thereof.

[0056] By “cycloalkyl” is meant a monovalent saturated or unsaturated non-aromatic or aromatic cyclic hydrocarbon group of from three to eight carbons, unless otherwise specified,
 20 and is exemplified by cyclopropyl, cyclobutyl, cyclopentyl, cyclopentadienyl, cyclohexyl, cycloheptyl, bicyclo[2.2.1]heptyl, and the like. The cycloalkyl group can also be substituted or unsubstituted. For example, the cycloalkyl group can be substituted with one or more groups including those described herein for alkyl.

[0057] By “dicarbonyl” is meant any moiety or compound including two carbonyl groups, as defined herein. Non-limiting dicarbonyl moieties include 1,2-dicarbonyl (e.g., $R^{C1}-C(O)-C(O)R^{C2}$, in which each of R^{C1} and R^{C2} is, independently, H, optionally substituted alkyl, halo, optionally substituted alkoxy, hydroxyl, or a leaving group); 1,3-dicarbonyl (e.g., $R^{C1}-C(O)-C(R^{1a}R^{2a})-C(O)R^{C2}$, in which each of R^{C1} and R^{C2} is, independently, H, optionally
 30 substituted alkyl, halo, optionally substituted alkoxy, hydroxyl, or a leaving group and in which each of R^{1a} and R^{2a} is, independently, H or an optional substituent provided for alkyl, as defined herein); and 1,4-dicarbonyl (e.g., $R^{C1}-C(O)-C(R^{1a}R^{2a})-C(R^{3a}R^{4a})-C(O)R^{C2}$, in which each of R^{C1} and R^{C2} is, independently, H, optionally substituted alkyl, halo, optionally

substituted alkoxy, hydroxyl, or a leaving group and in which each of R^{1a}, R^{2a}, R^{3a}, and R^{4a} is, independently, H or an optional substituent provided for alkyl, as defined herein).

[0058] By “halo” is meant F, Cl, Br, or I.

[0059] By “haloalkyl” is meant an alkyl group, as defined herein, substituted with one or
5 more halo.

[0060] By “haloalkylene” is meant an alkylene group, as defined herein, substituted with one or more halo.

[0061] By “heteroalkyl” is meant an alkyl group, as defined herein, substituted with one or more heteroatoms (e.g., independently selected from the group consisting of nitrogen,
10 oxygen, phosphorous, sulfur, selenium, or halo).

[0062] By “heteroalkylene” is meant an alkylene group, as defined herein, substituted with one or more heteroatoms (e.g., independently selected from the group consisting of nitrogen, oxygen, phosphorous, sulfur, selenium, or halo).

[0063] By “heterocyclyl” is meant a 3-, 4-, 5-, 6- or 7-membered ring (e.g., a 5-, 6- or 7-
15 membered ring), unless otherwise specified, containing one, two, three, or four non-carbon heteroatoms (e.g., independently selected from the group consisting of nitrogen, oxygen, phosphorous, sulfur, selenium, or halo). The 3-membered ring has zero to one double bonds, the 4- and 5-membered ring has zero to two double bonds, and the 6- and 7-membered rings have zero to three double bonds. The term “heterocyclyl” also includes bicyclic, tricyclic and
20 tetracyclic groups in which any of the above heterocyclic rings is fused to one, two, or three rings independently selected from the group consisting of an aryl ring, a cyclohexane ring, a cyclohexene ring, a cyclopentane ring, a cyclopentene ring, and another monocyclic heterocyclic ring, such as indolyl, quinolyl, isoquinolyl, tetrahydroquinolyl, benzofuryl, benzothienyl and the like. Heterocyclics include acridinyl, adenyl, alloxazinyl,
25 azaadamantanyl, azabenzimidazolyl, azabicyclononyl, azacycloheptyl, azacyclooctyl, azacyclononyl, azahypoxanthinyl, azaindazolyl, azaindolyl, azecinyl, azepanyl, azepinyl, azetidiny, azetyl, aziridinyl, azirinyl, azocanyl, azocinyl, azonanyl, benzimidazolyl, benzisothiazolyl, benzisoxazolyl, benzodiazepinyl, benzodiazocinyl, benzodihydrofuryl, benzodioxepinyl, benzodioxinyl, benzodioxanyl, benzodioxocinyl, benzodioxolyl,
30 benzodithiopyranyl, benzodithiopyranyl, benzodioxocinyl, benzofuranyl, benzophenazinyl, benzopyranonyl, benzopyranyl, benzopyrenyl, benzopyronyl, benzoquinoliny, benzoquinoliziny, benzothiadiazepinyl, benzothiadiazolyl, benzothiazepinyl,

- benzothiazocinyl, benzothiazolyl, benzothienyl, benzothiophenyl, benzothiazinonyl, benzothiazinyl, benzothiopyranyl, benzothiopyronyl, benzotriazepinyl, benzotriazinonyl, benzotriazinyl, benzotriazolyl, benzoxathiinyl, benzotrioxepinyl, benzoxadiazepinyl, benzoxathiazepinyl, benzoxathiepinyl, benzoxathiocinyl, benzoxazepinyl, benzoxazinyl, 5 benzoxazocinyl, benzoxazolinonyl, benzoxazolinyl, benzoxazolyl, benzylsultamyl, benzylsultimyl, bipyrazinyl, bipyridinyl, carbazolyl (e.g., 4H-carbazolyl), carbolinyl (e.g., β -carbolinyl), chromanonyl, chromanyl, chromenyl, cinnolinyl, coumarinyl, cytdinyl, cytosinyl, decahydroisoquinolinyl, decahydroquinolinyl, diazabicyclooctyl, diazetyl, diaziridinethionyl, diaziridinonyl, diaziridinyl, diazirinyl, dibenzisoquinolinyl, dibenzoacridinyl, 10 dibenzocarbazolyl, dibenzofuranyl, dibenzophenazinyl, dibenzopyranonyl, dibenzopyronyl (xanthonyl), dibenzoquinoxaliny, dibenzothiazepinyl, dibenzothiepinyl, dibenzothiophenyl, dibenzoxepinyl, dihydroazepinyl, dihydroazetyl, dihydrofuranyl, dihydrofuryl, dihydroisoquinolinyl, dihydropyranyl, dihydropyridinyl, dihydroppyridyl, dihydroquinolinyl, dihydrothienyl, dihydroindolyl, dioxanyl, dioxazinyl, dioxindolyl, dioxiranyl, dioxenyl, 15 dioxinyl, dioxobenzofuranyl, dioxolyl, dioxotetrahydrofuranyl, dioxothiomorpholinyl, dithianyl, dithiazolyl, dithienyl, dithiinyl, furanyl, furazanyl, furoyl, furyl, guaninyl, homopiperazinyl, homopiperidinyl, hypoxanthinyl, hydantoinyl, imidazolidinyl, imidazoliny, imidazolyl, indazolyl (e.g., 1H-indazolyl), indolenyl, indolinyl, indoliziny, indolyl (e.g., 1H-indolyl or 3H-indolyl), isatinyl, isatyl, isobenzofuranyl, isochromanyl, 20 isochromenyl, isoindazolyl, isoindolinyl, isoindolyl, isopyrazolonyl, isopyrazolyl, isoxazolidinyl, isoxazolyl, isoquinolinyl, isoquinolinyl, isothiazolidinyl, isothiazolyl, morpholinyl, naphthindazolyl, naphthindolyl, naphthiridinyl, naphthopyranyl, naphthothiazolyl, naphthothioxolyl, naphthotriazolyl, naphthoxindolyl, naphthyridinyl, octahydroisoquinolinyl, oxabicycloheptyl, oxauracil, oxadiazolyl, oxazinyl, oxaziridinyl, 25 oxazolidinyl, oxazolidonyl, oxazolinyl, oxazolonyl, oxazolyl, oxepanyl, oxetanonyl, oxetanyl, oxetyl, oxtenayl, oxindolyl, oxiranyl, oxobenzoisothiazolyl, oxochromenyl, oxoisoquinolinyl, oxoquinolinyl, oxothiolanyl, phenanthridinyl, phenanthrolinyl, phenazinyl, phenothiazinyl, phenothienyl (benzothiofuranyl), phenoxathiinyl, phenoxazinyl, phthalazinyl, phthalazonyl, phthalidyl, phthalimidinyl, piperazinyl, piperidinyl, piperidonyl (e.g., 4- 30 piperidonyl), pteridinyl, purinyl, pyranyl, pyrazinyl, pyrazolidinyl, pyrazolinyl, pyrazolopyrimidinyl, pyrazolyl, pyridazinyl, pyridinyl, pyridopyrazinyl, pyridopyrimidinyl, pyridyl, pyrimidinyl, pyrimidyl, pyronyl, pyrrolidinyl, pyrrolidonyl (e.g., 2-pyrrolidonyl), pyrrolinyl, pyrrolizidinyl, pyrrolyl (e.g., 2H-pyrrolyl), pyrylium, quinazolinyl, quinolinyl, quinoliziny (e.g., 4H-quinoliziny), quinoxaliny, quinuclidinyl, selenazinyl, selenazolyl,

- selenophenyl, succinimidyl, sulfolanyl, tetrahydrofuranyl, tetrahydrofuryl, tetrahydroisoquinolanyl, tetrahydroisoquinolyl, tetrahydropyridinyl, tetrahydropyridyl (piperidyl), tetrahydropyranyl, tetrahydropyryl, tetrahydroquinolanyl, tetrahydroquinolyl, tetrahydrothienyl, tetrahydrothiophenyl, tetrazinyl, tetrazolyl, thiadiazinyl (e.g., 6H-1,2,5-thiadiazinyl or 2H,6H-1,5,2-dithiazinyl), thiadiazolyl, thianthrenyl, thianyl, thianaphthenyl, thiazepinyl, thiazinyl, thiazolidinedionyl, thiazolidinyl, thiazolyl, thienyl, thiepanyl, thiepinyl, thietanyl, thietyl, thiiranyl, thiocanyl, thiochromanonyl, thiochromanyl, thiochromenyl, thiodiazinyl, thiodiazolyl, thioindoxyl, thiomorpholinyl, thiophenyl, thiopyranyl, thiopyryl, thiotriazolyl, thiourazolyl, thioxanyl, thioxolyl, thymidinyl, thyminyl, triazinyl, triazolyl, trithianyl, urazinyl, urazolyl, uretidinyl, uretinyl, uricyl, uridinyl, xanthenyl, xanthinyl, xanthionyl, and the like, as well as modified forms thereof (e.g., including one or more oxo and/or amino) and salts thereof. The heterocyclyl group can be substituted or unsubstituted. For example, the heterocyclyl group can be substituted with one or more substitution groups, as described herein for aryl.
- 15 [0064] By “hydroxyl” is meant -OH.
- [0065] By “imino” is meant -NR-, in which R can be H or optionally substituted alkyl.
- [0066] By “oxo” is meant an =O group.
- [0067] By “oxy” is meant -O-.
- [0068] As used herein, the term “about” means +/-10% of any recited value. As used
- 20 herein, this term modifies any recited value, range of values, or endpoints of one or more ranges.
- [0069] As used herein, the terms “top,” “bottom,” “upper,” “lower,” “above,” and “below” are used to provide a relative relationship between structures. The use of these terms does not indicate or require that a particular structure must be located at a particular location in the
- 25 apparatus.
- [0070] Other features and advantages of the invention will be apparent from the following description and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

- [0071] FIG. 1A-1H presents schematic diagrams of illustrative deposited films, in which
- 30 organic moieties can provide additional EUV reactivity. Provided are non-limiting films including (A, C, E, F) an ethynyl-derived ligand as the organic moiety, (B, D, G) an oxalyl-

derived ligand as the organic moiety, or (H) a labile alkyl ligand as the organic moiety. X can be H, another alkyl group, a metal atom (e.g., a Sn atom), a labile ligand, or a leaving group (e.g., any described herein).

5 [0072] FIG. 2A-2C presents schematic diagrams of illustrative stacks. Provided are (A) a stack including a film 202 deposited with a modified precursor, (B) another stack including a film 212 having differing carbon content in regions 212a, 212b by controlling the amount of the initial precursor and organic co-reactant; and (C) yet another stack including a film 223 deposited with a modified precursor, in which the film 223 is a capping layer disposed above a photoresist layer 222.

10 [0073] FIG. 3A-3C presents schematic illustrations and diagrams of non-limiting methods that employ an initial precursor and an organic co-reactant. Provided are (A) a first method 300 to provide either a positive tone resist (path i) or a negative tone resist (path ii); (B) a second method 320 to provide a capping layer 333; and (C) a block diagram of an illustrative method 350.

15 [0074] FIG. 4 presents a schematic illustration of an embodiment of a process station 400 for dry development.

[0075] FIG. 5 presents a schematic illustration of an embodiment of a multi-station processing tool 500.

20 [0076] FIG. 6 presents a schematic illustration of an embodiment of an inductively coupled plasma apparatus 600.

[0077] FIG. 7 presents a schematic illustration of an embodiment of a semiconductor process cluster tool architecture 700.

[0078] FIG. 8 presents solid state ¹³C-NMR spectra of a first film 801 (formed without an organic co-reactant) and a second film 802 (formed with an organic co-reactant).

25 [0079] FIG. 9 presents graphs showing use of water 901 or 2-heptanone 902 for developing non-limiting films after EUV exposure.

[0080] FIG. 10 presents line/space patterns for various exposed and developed films.

DETAILED DESCRIPTION

30 [0081] This disclosure relates generally to the field of semiconductor processing. In particular, the disclosure is directed to the use of one or more initial precursors in

combination with one or more organic co-reactants, thereby providing modified precursors for deposition. Such modified precursors can include the metal centers of the initial precursor and the organic moieties of the organic co-reactant. In this way, the chemical, physical, and/or optical properties of the deposited film can be controlled by controlling the extent of reaction between the initial precursor and the organic co-reactant, by selecting the appropriate combination of moieties and ligand present in the precursor and co-reactant, and/or by determining the desired amount of precursor and co-reactant to introduce during deposition.

[0082] 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.

[0083] EUV lithography makes use of EUV resists that are patterned to form masks for use in etching underlying layers. EUV resists may be polymer-based chemically amplified resists (CARs) produced by liquid-based spin-on techniques. An alternative to CARs is directly photopatternable metal oxide-containing films, such as those available from Inpria Corp. (Corvallis, OR), and described, for example, in U.S. Pat. Pub. Nos. US 2017/0102612, US 2016/0216606, and US 2016/0116839, incorporated by reference herein at least for their disclosure of photopatternable metal oxide-containing films. Such films may be produced by spin-on techniques or dry vapor-deposited. The metal oxide-containing film can be patterned directly (i.e., without the use of a separate photoresist) by EUV exposure in a vacuum ambient providing sub-30 nm patterning resolution, for example as described in U.S. Pat. No. 9,996,004, issued June 12, 2018 and titled EUV PHOTOPATTERNING OF VAPOR-DEPOSITED METAL OXIDE-CONTAINING HARDMASKS, and/or in International Appl. No. PCT/US19/31618, published as International Pub. No. WO 2019/217749, filed May 9, 2019, and titled METHODS FOR MAKING EUV PATTERNABLE HARD MASKS, the disclosures of which at least relating to the composition, deposition, and patterning of directly

photopatternable metal oxide films to form EUV resist masks is incorporated by reference herein. Generally, the patterning involves exposure of the EUV resist with EUV radiation to form a photo pattern in the resist, followed by development to remove a portion of the resist according to the photo pattern to form the mask.

5 **[0084]** Directly photopatternable EUV or DUV resists may be composed of or contain metals and/or metal oxides mixed within organic components. The metals/metal oxides are highly promising in that they can enhance the EUV or DUV photon adsorption, generate secondary electrons, and/or show increased etch selectivity to an underlying film stack and device layers. Up to date, these resists have been developed using a wet (solvent) approach,
10 which requires the wafer to move to the track, where it is exposed to developing solvent, dried, and then baked. Without wishing to be limited by mechanism, this wet development step does not only limit productivity but can also lead to line collapse due to surface tension effects during the evaporation of solvent between fine features. Yet in some instance, wet development may be useful or preferred, so any of the films herein can be employed with wet
15 development (see, e.g., **FIG. 9** here). Indeed, in some instances, it may be beneficial for films that can be developed using wet development, dry development, or both wet and dry development.

[0085] Generally, resists can be employed as a positive tone resist or a negative tone resist by controlling the chemistry of the resist and/or the solubility or reactivity of the developer.
20 It would be beneficial to have a EUV or DUV resist that can serve as either a negative tone resist or a positive tone resist.

Modified precursors

[0086] The present disclosure relates to use of initial precursor(s) in the presence of organic co-reactant(s) to generate a modified precursor, which in turn is immediately deposited to
25 form a patterning radiation-sensitive film (e.g., an EUV-sensitive film). This film, in turn, can serve as an EUV resist or a capping layer, as further described herein. In particular embodiments, the modified precursor is generated and deposited *in situ*, e.g., generation occurs within the chamber for deposition.

[0087] The modified precursor can be a reaction product that is formed between the initial
30 precursor and the organic co-reactant, in which the reaction product can then be deposited to form a film. Such reactions and depositions can be conducted in vapor form. In particular

embodiments, the film can include one or more ligands (e.g., labile ligands) that can be removed, cleaved, or cross-linked by radiation (e.g., EUV or DUV radiation).

[0088] The initial precursor can include any precursor (e.g., described herein) that provides a patternable film that is sensitive to radiation (or a patterning radiation-sensitive film or a photopatternable film). Such radiation can include EUV radiation or DUV radiation that is provided by irradiating through a patterned mask, thereby being a patterning radiation. The film itself can be altered by being exposed to such radiation, such that the film is radiation-sensitive. In particular embodiments, the initial precursor is an organometallic compound, which includes at least one metal center and at least one ligand that can react with the organic co-reactant. In this way, the organic moiety from the co-reactant reacts with or displaces the ligand from the metal center, thereby attaching that organic moiety as a bound ligand to the metal center. The organic moiety, itself, can enhance EUV/DUV sensitivity of the film (e.g., by increasing EUV/DUV absorptivity) or enhance contrast selectivity during development (e.g., by increasing porosity of a film). Furthermore, the organic moiety can be reactive in the presence of patterning radiation, such as by undergoing removal or elimination from the metal center or by reacting or polymerizing with other moieties within the film.

[0089] The initial precursor can have any useful number and type of ligand(s). As discussed herein, at least one ligand reacts with the organic co-reactant. A ligand can also be characterized by its ability to react in the presence of a counter-reactant or in the presence of patterning radiation. For instance, the initial precursor can include a ligand that reacts with a counter-reactant, which can introduce linkages between metal centers (e.g., an -O- linkage). Such a ligand (e.g., dialkylamino groups or alkoxy groups) could, in some instances, also react with an organic co-reactant. In another instance, the initial precursor can include a ligand that eliminates in the presence of patterning radiation. Such a ligand can include branched or linear alkyl groups having a beta-hydrogen.

[0090] The initial precursor can be any useful metal-containing precursor, such as an organometallic agent, a metal halide, or a capping agent (e.g., as described herein). In a non-limiting instance, the initial precursor includes a structure having formula (I):



wherein:

M is a metal;

each R is, independently, halo, optionally substituted alkyl, optionally substituted aryl, optionally substituted amino, optionally substituted alkoxy, or L;

each L is, independently, is a ligand, ion, or other moiety that is reactive with the organic co-reactant or a counter-reactant, in which R and L with M, taken together, can optionally form a heterocyclyl group or in which R and L, taken together, can optionally form a heterocyclyl group;

$a \geq 1$; $b \geq 1$; and $c \geq 1$.

[0091] In some embodiments, each ligand within the initial precursor can be one that is reactive with an organic co-reactant or a counter-reactant. In one instance, the initial precursor includes a structure having formula (I), in which each R is, independently, L. In another instance, the initial precursor includes a structure having formula (Ia):



wherein:

M is a metal;

each L is, independently, is a ligand, ion, or other moiety that is reactive with the organic co-reactant or a counter-reactant, in which two L, taken together, can optionally form a heterocyclyl group;

$a \geq 1$; and $c \geq 1$.

In particular embodiments of formula (Ia), a is 1. In further embodiments, c is 2, 3, or 4.

[0092] For any formula herein, M can be a metal with a high patterning radiation absorption cross-section (e.g., an EUV absorption cross-section that is equal to or greater than $1 \times 10^7 \text{ cm}^2/\text{mol}$). In some embodiments, M is tin (Sn), tellurium (Te), bismuth (Bi), antimony (Sb), hafnium (Hf), or zirconium (Zr). In further embodiments, M is Sn, a is 1, and c is 4 in formula (I) or (Ia). In other embodiments, M is Sn, a is 1, and c is 2 in formula (I) or (Ia).

In particular embodiments, M is Sn(II) (e.g., in formula (I) or (Ia)), thereby providing an initial precursor that is a Sn(II)-based compound. In other embodiments, M is Sn(IV) (e.g., in formula (I) or (Ia)), thereby providing an initial precursor that is a Sn(IV)-based compound.

[0093] For any formula herein, each L is, independently, H, halo, optionally substituted alkyl, optionally substituted aryl, optionally substituted amino, optionally substituted bis(trialkylsilyl)amino, optionally substituted trialkylsilyl, or optionally substituted alkoxy (e.g., $-\text{OR}^1$, in which R^1 can be alkyl). In some embodiments, the optionally substituted amino is $-\text{NR}^1\text{R}^2$, in which each R^1 and R^2 is, independently, H or alkyl; or in which R^1 and

R^2 , taken together with the nitrogen atom to which each are attached, form a heterocyclyl group, as defined herein. In other embodiments, the optionally substituted bis(trialkylsilyl) amino is $-N(SiR^1R^2R^3)_2$, in which each R^1 , R^2 , and R^3 is, independently, alkyl. In yet other embodiments, the optionally substituted trialkylsilyl is $-SiR^1R^2R^3$, in which each R^1 , R^2 , and R^3 is, independently, alkyl.

[0094] In other embodiments, the formula includes a first L that is $-NR^1R^2$ and a second L that is $-NR^1R^2$, in which each R^1 and R^2 is, independently, H or alkyl; or in which R^1 from a first L and R^1 from a second L, taken together with the nitrogen atom and the metal atom to which each are attached, form a heterocyclyl group, as defined herein. In yet other embodiments, the formula includes a first L that is $-OR^1$ and a second L that is $-OR^1$, in which each R^1 is, independently, H or alkyl; or in which R^1 from a first L and R^1 from a second L, taken together with the oxygen atom and the metal atom to which each are attached, form a heterocyclyl group, as defined herein.

[0095] In some embodiments, at least one of L or R is optionally substituted alkyl (e.g., in formula (I) or (Ia)). Non-limiting alkyl groups include, e.g., C_nH_{2n+1} , where n is 1, 2, 3, or greater, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, or t-butyl. In various embodiments, L or R has at least one beta-hydrogen or beta-fluorine. In particular, the initial precursor can be tetramethyl tin ($SnMe_4$), tetraethyl tin ($SnEt_4$), t-butyl tellurium hydride ($Te(t-Bu)(H)$), dimethyl tellurium ($TeMe_2$), di(t-butyl) tellurium ($Te(t-Bu)_2$), or di(isopropyl)tellurium ($Te(i-Pr)_2$).

[0096] In some embodiments, each L or at least one L is halo (e.g., in formula (I) or (Ia)). In particular, the initial precursor can be a metal halide. Non-limiting metal halides include $SnBr_4$, $SnCl_4$, SnI_4 , and $SbCl_3$.

[0097] In some embodiments, each L or at least one L can include a nitrogen atom. In particular embodiments, one or more L can be optionally substituted amino or optionally substituted bis(trialkylsilyl)amino (e.g., in formula (I) or (Ia)). Non-limiting L substituents can include, e.g., $-NMe_2$, $-NEt_2$, $-NMeEt$, $-N(t-Bu)-[CHCH_3]_2-N(t-Bu)-$ (tbba), $-N(SiMe_3)_2$, and $-N(SiEt_3)_2$. Non-limiting initial precursors can include, e.g., $Sn(NMe_2)_4$, $Sn(NEt_2)_4$, $Sn(i-Pr)(NMe_2)_3$, $Sn(n-Bu)(NMe_2)_3$, $Sn(s-Bu)(NMe_2)_3$, $Sn(i-Bu)(NMe_2)_3$, $Sn(t-Bu)(NMe_2)_3$, $Sn(t-Bu)_2(NMe_2)_2$, $Sn(t-Bu)(NEt_2)_3$, $Sb(NMe_2)_3$, $Sn(tbba)$, $Sn[N(SiMe_3)_2]_2$, or $Bi[N(SiMe_3)_2]_3$.

[0098] In some embodiments, each L or at least one L can include a silicon atom. In particular embodiments, one or more L can be optionally substituted trialkylsilyl or

optionally substituted bis(trialkylsilyl)amino (e.g., in formula (I) or (Ia)). Non-limiting L substituents can include, e.g., -SiMe₃, -SiEt₃, -N(SiMe₃)₂, and -N(SiEt₃)₂. Non-limiting initial precursors can include, e.g., Sn[N(SiMe₃)₂]₂, bis(trimethylsilyl)tellurium (Te(SiMe₃)₂), bis(triethylsilyl)tellurium (Te(SiEt₃)₂), or Bi[N(SiMe₃)₂]₃.

5 [0099] In some embodiments, each L or at least one L can include an oxygen atom. In particular embodiments, one or more L can be optionally substituted alkoxy (e.g., in formula (I) or (Ia)). Non-limiting L substituents include, e.g., methoxy, ethoxy, isopropoxy (*i*-PrO), *t*-butoxy (*t*-BuO), and -O=C(CH₃)-CH=C(CH₃)-O- (acac). Non-limiting initial precursors include, e.g., Sn(*t*-BuO)₄, Sn(*n*-Bu)(*t*-BuO)₃, or Sn(acac)₂.

10 [0100] Yet other initial precursors and non-limiting substituents are described herein. For instance, initial precursors can be any having a structure of formulas (I) and (Ia), as described above; or formulas (III), (IV), (V), (VI), (VII), or (VIII), as described below. Any of the substituents M, R, X, or L, as described herein, can be employed in any of formulas (I), (Ia), (III), (IV), (V), (VI), (VII), or (VIII).

15 [0101] To provide a modified precursor, an organic co-reactant is employed to react with or to replace a ligand of the initial precursor. Any useful organic co-reactant can be employed. Such an organic co-reactant can be provided in any form, e.g., as a vapor phase.

[0102] In one non-limiting instance, the organic co-reactant is a compound having formula (II):

20
$$X^1-Z-X^2 \text{ (II)}$$

wherein:

each of X¹ and X² is, independently, a leaving group (e.g., halo, H, hydroxyl, optionally substituted alkyl, optionally substituted alkoxy, etc.); and

25 Z is carbonyl, dicarbonyl, optionally substituted alkylene, optionally substituted haloalkylene, optionally substituted alkenylene, or optionally substituted alkynylene.

[0103] In some embodiments, Z is substituted with one or more oxo (=O) groups. In some embodiment, Z is C₁₋₃ alkylene optionally substituted with one or more oxo groups. In particular embodiments, Z is carbonyl, oxalyl, mesoxalyl, malonyl, or oxalacetyl. In other embodiments, Z includes one or more saturated bonds. In particular embodiments, Z is
30 ethynylene. Examples of organic co-reactants include aldehyde, ketone, carboxylic acid,

carbonyl halide, oxalyl halide (e.g., oxalyl chloride), acetylene, and others, as well as derivatives thereof. In other embodiments, Z is substituted with one or more halo groups.

[0104] In some embodiments, the organic co-reactant is an acetylene derivative having formula (IIa):



wherein:

each of X^1 and X^2 is, independently, a leaving group, such as halo, H, or optionally substituted alkyl. Such an organic co-reactant can be employed to provide an ethynyl-derived moiety, such as $-C\equiv C-X^1$, that can be directly bonded to the metal center M in the initial precursor.

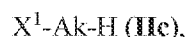
[0105] In other embodiments, the organic co-reactant is an oxalyl derivative having formula (IIb):



wherein:

each of X^1 and X^2 is, independently, a leaving group, such as halo, H, hydroxyl, optionally substituted alkyl, or optionally substituted alkoxy. Such an organic co-reactant can be employed to provide an oxalyl-derived moiety, such as $-C(O)-C(O)-$ or $-OC(O)-C(O)O-$, that can be directly bonded to the metal center M in the initial precursor.

[0106] In yet other embodiments, the organic co-reactant is an alkyl derivative having formula (IIc):

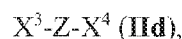


wherein:

X^1 is a leaving group, such as halo, hydroxyl, optionally substituted alkyl, or optionally substituted alkoxy; and

Ak is an optionally substituted alkylene or optionally substituted haloalkylene. Such an organic co-reactant can be employed to provide a labile alkyl-derived moiety, such as an EUV-responsive organic moiety (e.g., methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, *tert*-butyl, etc.) that can be directly bonded to the metal center M in the initial precursor.

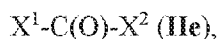
- [0107] When at least one halo is present, then the organic co-reactant can be a haloalkyl moiety or a haloalkyl derivative. In particular embodiments, the organic co-reactant is a haloalkyl derivative (e.g., in which halo is iodo), and the initial precursor is a Sn(II)-based compound. Without wishing to be limited by mechanism, the modified precursor obtained by using such compounds can involve oxidative addition of a low valent Sn(II) species or other electron rich metallic precursor across a reactive carbon-halogen bond of the added organic co-reactant (e.g., provided in vapor phase). In some instance, the reactive carbon-halogen bond is a reactive carbon-iodine bond. Non-limiting alkyl derivatives include ethyl iodide, iso-propyl iodide, *t*-butyl iodide, diiodomethane, etc.
- [0108] In some instances, the electron rich metallic precursor is a trivalent Sb or Bi precursor. Non-limiting precursors can include SbR₃ or BiR₃ (e.g., R is any described herein, such as a for formula (I), (IV), or (VI)), to which an alkyl halide could add to form a pentavalent complex. Of note, Sb and Bi are of interest due to their high EUV absorption cross section.
- [0109] Methods can also employ a chalcogenide precursor, as a counter-reactant or an organic co-reactant. In particular embodiments, the chalcogenide precursor includes a structure having formula (II_d):



wherein:

- Z is sulfur, selenium, or tellurium; and
- each of X³ and X⁴ is, independently, H, optionally substituted alkyl (e.g., methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *t*-butyl, etc.), optionally substituted alkenyl, optionally substituted aryl, optionally substituted amino, optionally substituted alkoxy, or optionally substituted trialkylsilyl.
- Such a chalcogenide precursor can be employed to provide a chalcogenide atom Z that can be directly bonded to the metal center M in the initial precursor.

[0110] In yet other embodiments, the organic co-reactant is a carbonyl derivative having formula (II_e):



- wherein:

each of X^1 and X^2 is, independently, a leaving group, such as halo, H, hydroxyl, optionally substituted alkyl, optionally substituted haloalkyl, optionally substituted heteroalkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted alkoxy, or optionally substituted aryl. Such an organic co-reactant can be employed to provide a carbonyl-derived moiety, such as $-C(O)-X^1$, that can be directly bonded to the metal center M in the initial precursor. Non-limiting carbonyl derivatives include an aldehyde, a ketone, a carbonyl halide, a carboxylic acid, and the like, as described herein. In some embodiments, at least one of X^1 and X^2 is H, halo, or hydroxyl. In other embodiments, both of X^1 and X^2 is selected from the group of optionally substituted alkyl, optionally substituted haloalkyl, optionally substituted heteroalkyl, optionally substituted alkenyl, optionally substituted alkynyl, or optionally substituted aryl (e.g., as in a ketone).

[0111] The organic co-reactant can be employed to replace at least one ligand of the initial precursor, in which the organic co-reactant provides a bound ligand for the modified precursor. In one instance, the organic co-reactant can include a structure having formula (II), and the bound ligand can include or be any useful substituent resulting from a reaction between the initial precursor and the organic co-reactant (optionally with a counter-reactant). In particular embodiments, the bound ligand in the modified precursor has a structure of $-X^a-Z-X^b-$, in which Z can be optionally substituted alkylene, optionally substituted alkenylene, or optionally substituted alkynylene (e.g., ethynylene, oxalyl, mesoxalyl, malonyl, or oxalacetyl); and each of X^a and X^b is, independently, a bond (e.g., a covalent bond), oxy, imino, carbonyl, alkylene, alkyleneoxy, heteroalkylene, and the like. In other embodiments, the bound ligand in the modified precursor has a structure of $-X^a-Z-X^c$, in which Z can be optionally substituted alkylene, optionally substituted alkenylene, or optionally substituted alkynylene (e.g., ethynylene, oxalyl, mesoxalyl, malonyl, or oxalacetyl); X^a is, independently, a bond (e.g., a covalent bond), oxy, imino, or carbonyl; and X^c is H, halo, hydroxyl, optionally substituted alkyl, or optionally substituted alkoxy.

[0112] Within the film, the bound ligand can have a structure of $-X^a-Z-X^b-$, in which this structure can be bound to directly or indirect to metal atoms. Also, within the film, the bound ligand can have a structure of $-X^a-Z-X^c$, in which X^a is bound directly or indirectly to a metal atom.

[0113] In some embodiments, the organic co-reactant includes one or more bulky substituents, thereby providing a modified precursor having a bound ligand that includes a bulky substituent. In one instance, a bulky organic co-reactant might lead to increased dry

development contrast in the film, due to an increased porosity difference between radiation exposed and unexposed areas. In another instance, a bulky organic co-reactant might lead to increased dry development rate due to increased porosity difference between radiation exposed and unexposed areas. In general, bulkier substituents may provide films having
5 increased porosity, and increased porosity would provide increased access to etchant or development chemistries. Porosity can be characterized in any useful manner, e.g., such as a volumetric gas adsorption.

[0114] FIG. 1A-1H shows non-limiting films having various organic moieties directly bonded to a metal center M that is provided by an initial precursor. The organic moiety can
10 be provided by an organic co-reactant during deposition. In particular, the presence of the organic moiety can provide a film having enhanced EUV reactivity.

[0115] An initial precursor can include one or more reactive ligands, which can be used to react with an organic co-reactant in order to provide a modified precursor. Within the modified precursor, an organic moiety is directly attached to the metal atom M provided by
15 the initial precursor. Non-limiting organic moieties include any provided by an organic co-reactant, such as an ethynyl-derived moiety, an oxalyl-derived moiety, a labile alkyl-derived moiety, and others described herein.

[0116] FIG. 1A shows a non-limiting film including a modified precursor having formula (II-1a). As can be seen, this modified precursor includes two different types of organic
20 moieties (e.g., a labile isopropyl ligand and an ethynyl-derived ligand, in which X can be H, alkyl, a metal atom, an Sn atom, a leaving group, or a labile ligand) directly attached to the Sn metal atom. Such a modified precursor can be deposited by using an initial precursor (e.g., any herein) in the presence of an organic co-reactant (e.g., any herein). In one non-limiting instance, the initial precursor has a reactive ligand (e.g., -NMe₂) that can be replaced
25 with the organic co-reactant and has a labile ligand (e.g., alkyl) that is retained until exposure to a patterning radiation. Within formula (II-1a), the modified precursor has an ethynyl-derived ligand that can be provided by an organic co-reactant and has an isopropyl ligand that is retained during film deposition.

[0117] To ensure that one or more organic moieties are provided within the deposited film,
30 reaction conditions can be optimized to promote reactions that directly attach both the counter-reactant and the organic co-reactant with the metal atom of the initial precursor. In this way, both oxygen atoms (from the counter-reactant) and organic moieties (from the

organic co-reactant) can be present within the film. For instance, by using an oxygen-containing counter-reactant within the initial precursor, the reactive ligand of the initial precursor can result in a terminal -OH moiety or a Sn-O bond; and the reactive ligand can react with the organic co-reactant to provide a bound organic ligand (herein, in formula (II-
5 1a), the bound ligand is $-C\equiv CX$). However, if the reaction is predominated by the reaction between the initial precursor and the counter-reactant (rather than with the organic co-reactant), then the deposited film may include minimal organic moieties. Thus, in some instances, deposition is performed in the presence of counter-reactants and organic co-reactants having comparable reactivity, thereby ensuring that the organic co-reactant will
10 react sufficiently with the initial precursor to incorporate the organic ligand into the deposited film.

[0118] In another example, deposition can be performed by avoiding counter-reactants that are significantly more reactive than the organic co-reactant. For instance, water, peroxide, or plasma can be significantly more reactive with the initial precursor, as compared to an
15 organic co-reactant reacting with the same initial precursor. Thus, in some instances, deposition is performed in a water-free environment, a water-deficient environment, a peroxide-free environment, a peroxide-deficient environment, a plasma-free environment, or a plasma-deficient environment. In some embodiments, the counter-reactant is not water, not a peroxide, or not a plasma. Of course, such conditions do not necessarily exclude the
20 situation in which a remaining reactive ligand (e.g., dimethylamino) within the deposited film further reacts with moisture in air, thereby forming -OH groups. But during the vapor deposition process, in some non-limiting instances, no water, peroxide, or plasma is introduced. In yet other embodiments, the organic co-reactant is provided with the initial precursor in an initial operation, and then the counter-reactant is provided in a subsequent
25 operation.

[0119] In particular instances, minimal amounts of water may be present during or after deposition. Such water may be present in an ambient environment, such as in ambient air. In this way, any remaining reactive ligands (after replacement with an organic moiety provided by the organic co-reactant) can react with water vapor to provide terminal -OH moieties.

30 [0120] Accordingly, a modified precursor can include any useful chemical bonds within the film. Non-limiting bonds include terminal -OH moieties (e.g., as a result of reacting with one or more counter-reactants or ambient moisture present in air either during or after deposition); one or more metal-oxygen-metal (M-O-M) bonds, which can be formed between

metal centers of precursors; one or more bonds resulting in a metal-carbon (M-C) bond between the metal center and an atom within the bound ligand (or organic moiety) provided by the organic co-reactant; and/or one or more bonds resulting in a metal-oxygen (M-O) bond between the metal center and an atom within the bound organic ligand provided by the organic co-reactant.

[0121] The approaches herein can provide improved modified precursors and/or improved films. For instance, state-of-the-art metal oxide EUV photoresists are generally produced from organometallic precursors having a high EUV-sensitivity element (e.g. Sn) and an EUV-responsive organic moiety directly bonded to the metal center (e.g., methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, *tert*-butyl, etc.). This precursor is optionally reacted *in situ* with a counter-reactant, such as water. As such, the resultant density of EUV-sensitive elements and EUV-sensitive organic moieties are directly coupled together by the intrinsic nature of the organometallic precursor. In contrast, the present disclosure allows for the density of EUV-sensitive elements and the density of EUV-responsive organic moieties to be modulated without requiring change of the initial precursor. In this way, different chemistries can be readily accessed by modulating the extent of reaction between the initial precursor and the organic co-reactant (e.g., by modulating the amount of the initial precursor and/or the co-reactant, the reaction time between these two compounds, and the like) and by decoupling of the density of EUV-sensitive elements and the density of EUV-responsive organic moieties within the film.

[0122] For instance, this approach can yield EUV-sensitive films with a tunable metal to carbon ratio. In one embodiment, such tuning can provide films having higher EUV responsivity than currently available photoresist (PR), thus increasing wafer patterning throughput. In other embodiments, this process could provide a tuning knob to change the dose-to-size, optimize patterning quality (e.g., enhanced line-width-roughness (LWR) and/or line-edge-roughness (LER)), and/or improve mechanical strength. Such tuning can occur between deposition of two films (e.g., thereby producing two films with differing metal to carbon ratio) or within the same film (e.g., thereby providing a single film with a gradient in metal to carbon ratio). For instance, the approaches herein could allow for a gradient density of EUV-responsive organic moieties within the film. Without wishing to be limited by mechanism, since more photons are available for absorption nearer the surface of the PR and fewer photons reach the bottom, a gradient density of EUV-sensitive organic moieties might

allow for greater homogenization of EUV absorption events, making development processes more reliable and more readily optimized.

[0123] Additionally, the physical size of the organic co-reactant might yield films with increased porosity in areas that are not exposed, which would allow for the improved
5 diffusion of gases involved in dry development into unexposed areas while reduced diffusion of dry development gases may occur in exposed areas. As a result of this difference in porosity, dry development of such films in a negative tone scheme might yield higher contrast between exposed and unexposed areas.

[0124] Furthermore, this approach can provide films that can be processed with negative
10 tone dry development strategies or positive tone wet development strategies, in which the initial precursor can be maintained and changing the organic co-reactant changes the type of film produced. Depending on the chemical structure of the ligand provided by reacting the organic co-reactant with the initial precursor, radiation exposure can result in stabilizing or destabilizing the film. As seen in FIG. 1A, after depositing the modified precursor, the
15 resultant film can be exposed to EUV radiation. In one instance, EUV exposure can result in photopolymerized cross-linking between the bound ethynyl-derived ligands, thereby providing a stabilized, cross-linked film (II-1a*). For example, the presence of the ethynyl-derived organic moiety within the film might yield high performance, negative tone patterning as a result of EUV-induced polymerization followed by dry and/or wet
20 development.

[0125] In another instance, radiation exposure can degrade areas within the film, and such a modified precursor can provide a positive tone photoresist. FIG. 1B shows use of an oxalyl-derived organic moiety within the film (e.g., by use of oxalyl chloride as an organic co-reactant), which might yield high performance positive tone patterning using EUV via wet
25 development strategies. Inclusion of oxalyl bridging groups may yield unexposed films that are resilient to positive tone wet developers (e.g., tetramethylammonium hydroxide), resulting in high contrast positive tone PR.

[0126] As seen in FIG. 1B, the deposited film includes a modified precursor having formula (II-1b). For this modified precursor, the bound organic ligand includes an oxalyl
30 substituent (-C(O)C(O)-) provided by an organic co-reactant and an oxy substituent (-O-), which can be provided by an oxygen-containing counter-reactant. Upon exposure to EUV radiation, the bound organic ligand within the modified precursor can be degraded, thereby

producing a metal hydroxide (**II-1b***) and carbon dioxide. Further treatment of EUV exposed areas with oxygen can provide a further metal oxide film.

5 [0127] In some instances, inclusion of radiation-responsive organic moieties by using an organic co-reactant may result in films that do not require post-exposure treatment to cross-link the metal species. For instance, when employing an oxalyl derivative, the bound ligand may provide a film having an oxalyl substituent that does not require post-exposure treatment. Such a film may possess improved patterning quality (e.g., improved LWR and/or LER) by reducing bake-related blurring effects and/or increased wafer patterning throughput.

10 [0128] In other instances, radiation exposed films can be further developed using development processes described herein. In some embodiments, the film can be dry developed in one or more steps involving halide chemistry (e.g., HBr, HCl, and/or BCl₃). In other embodiments, the film can be developed with wet chemistry. For instance and without limitation, use of oxalyl chloride as an organic co-reactant can yield superior positive tone wet development performance arising from oxalate linkages between metal centers, which are
15 expected to be resilient to positive tone developers (e.g., an aqueous alkaline developer, such as tetramethylammonium hydroxide (TMAH), or other wet developers described herein).

[0129] Methods herein also include the use of an initial precursor having only ligands that are reactive with the organic co-reactant or a counter-reactant. In this way, organic moieties are solely introduced into a deposited film by the organic co-reactant. For instance, **FIG. 1C**
20 shows a modified precursor (**II-2a**) including bound organic ligands (e.g., -C≡CX), hydroxyl moieties (provided by reaction between the reactive ligands of the initial precursor and a counter-reactant), and other metal-oxy bonds. In this instance, carbon content within this film is provided entirely by the organic co-reactant, rather than by the initial precursor.

[0130] Upon exposure to patterning radiation, the bound ligand within the modified
25 precursor can be cross-linked, thereby providing a film having structure (**II-2a***). In another instance, **FIG. 1D** shows a modified precursor (**II-2b**) including bound organic ligands (e.g., -OC(O)C(O)O-), hydroxyl moieties, and other metal-oxy bonds. EUV exposure can provide a film (**II-2b***) that releases a gaseous byproduct (e.g., carbon dioxide and/or carbon monoxide).

30 [0131] By decoupling the source of metal centers and organic moieties, various initial precursors can be employed. For instance, **FIG. 1E-1H** shows Sn(II)-based modified precursors that can be obtained by using an initial precursor having a tin(II) metal center. As

seen in **FIG. 1E**, a modified precursor (**II-3a**) can have an Sn(II) metal center attached to a photopolymerizable bound ligand, in which EUV exposure can provide a cross-linked film (**II-3a***).

5 **[0132]** The initial precursor and organic co-reactant can be reacted by oxidative addition with a chalcogenide precursor (e.g., TeR_2). As seen in **FIG. 1F**, a modified precursor (**II-3b**) can have an Sn(II) metal center attached to a Te atom (to provide Sn-Te bonds) and a photopolymerizable bound ligand, in which EUV exposure can provide a cross-linked film (**II-3b***). Non-limiting Te-containing precursors include any described herein, such as TeR_2 in which R can be H, optionally substituted alkyl, or optionally substituted trialkylsilyl.

10 **[0133]** **FIG. 1G** can provide a modified precursor (**II-4a**) having an Sn(II) metal center attached to an oxalyl-derived ligand. The resulting film can then be exposed to EUV to provide an exposed film (**II-4a***).

15 **[0134]** Furthermore, Sn(II)-based precursors can be reacted with an organic co-reactant to provide an Sn(IV)-based modified precursor for deposition. As can be seen, in this way, the organic co-reactant can be used with an electron-rich Sn(II) precursor to incorporate an EUV labile alkyl group (e.g., isopropyl, *t*-butyl, etc.) and an EUV absorption-enhancing ligand (e.g., iodide) into the modified precursor. As seen in **FIG. 1H**, the resulting film can then be treated with an oxygen-containing counter-reactant to provide an organometal oxide film (**II-5b**), which in turn can be exposed to EUV to provide an exposed film (**II-5b***) and release
20 the cleaved alkyl group (e.g., propylene, when the labile alkyl group is isopropyl). Then, the exposed film can be baked to provide a metal oxide film (**II-5b****).

25 **[0135]** Such EUV-absorbing and EUV-sensitive materials can be deposited in any useful manner, as described herein. Exemplary deposition techniques include atomic layer deposition (ALD) (e.g., thermal ALD and plasma-enhanced ALD (PE-ALD)), spin-coat deposition, physical vapor deposition (PVD) including PVD co-sputtering, chemical vapor deposition (CVD), plasma enhanced CVD (PE-CVD), low pressure CVD (LP-CVD), sputter deposition, electron-beam (e-beam) deposition including e-beam co-evaporation, etc., or a combination thereof. Other deposition processes and conditions are described herein.

30 **[0136]** Such precursor(s) and organic co-reactant(s) can be further used in combination with one or more counter-reactants. Counter-reactants preferably have the ability to replace the reactive moieties, ligands, or ions (e.g., L in formulas herein) so as to link at least two metal atoms via chemical bonding. Exemplary counter-reactants include oxygen-containing

counter-reactants, such as O₂, O₃, water, peroxides (e.g., hydrogen peroxide), oxygen plasma, water plasma, alcohols, di- or polyhydroxy alcohols, fluorinated di- or polyhydroxy alcohols, fluorinated glycols, formic acid, and other sources of hydroxyl moieties, as well as combinations thereof. In various embodiments, a counter-reactant reacts with the initial precursor or the modified precursor by forming oxygen bridges between neighboring metal atoms. Other potential counter-reactants include hydrogen sulfide and hydrogen disulfide, which can crosslink metal atoms via sulfur bridges and bis(trimethylsilyl)tellurium, which can crosslink metal atoms via tellurium bridges. In addition, hydrogen iodide may be utilized to incorporate iodine into the film.

5 [0137] Various atoms present in the organic co-reactant and/or counter-reactant can be provided within a gradient film. In some embodiments of the techniques discussed herein, a non-limiting strategy that can further improve the EUV sensitivity in a photoresist (PR) film is to create a film in which the film composition is vertically graded, resulting in depth-dependent EUV sensitivity. In a homogenous PR with a high absorption coefficient, the decreasing light intensity throughout the film depth necessitates a higher EUV dose to ensure the bottom is sufficiently exposed. By increasing the density of atoms with high EUV absorptivity at the bottom of the film relative to the top of the film (i.e., by creating a gradient with increasing EUV absorption), it becomes possible to more efficiently use available EUV photons while more uniformly distributing absorption (and the effects of secondary electrons) towards the bottom of more highly absorbing films. In one non-limiting instance, the gradient film includes Te, I, or other atoms towards the bottom of the film (e.g., closer to the substrate).

[0138] The strategy of engineering a vertical composition gradient in a PR film is particularly applicable to dry deposition methods, such as CVD and ALD, and can be realized by tuning the flow ratios between different reactants during deposition. The type of composition gradients that can be engineered include: the ratios between different high-absorbing metals, the percentage of metal atoms that have EUV-cleavable organic groups, the percentages of organic co-reactants and/or counter-reactants that contain high-absorbing elements, and combinations of the above.

30 [0139] The composition gradient in the EUV PR film can also bring additional benefits. For instance, high density of high-EUV-absorbing elements in the bottom part of the film can effectively generate more secondary electrons that can better expose upper portions of the film. In addition, such compositional gradients can also be directly correlated with a higher

fraction of EUV absorbing species that are not bonded to bulky, terminal substituents. For example, in the case of Sn-based resists, the incorporation of tin precursors with four leaving groups is possible, thereby promoting the formation of Sn-O-substrate bonding at the interface for improved adhesion.

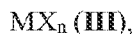
- 5 **[0140]** Such gradient films can be formed by using any initial precursors (e.g., tin or non-tin precursors), organic co-reactants, counter-reactants, and/or modified precursors described herein. Yet other films, methods, precursors, and other compounds are described in U.S. Provisional Pat. Appl. No. 62/909,430, filed October 2, 2019, and International Appl. No. PCT/US20/53856, filed October 1, 2020, published as International Pub. No.
- 10 WO 2021/067632, in which each is titled SUBSTRATE SURFACE MODIFICATION WITH HIGH EUV ABSORBERS FOR HIGH PERFORMANCE EUV PHOTORESISTS; and International Appl. No. PCT/US20/70172, filed June 24, 2020, published as International Pub. No. WO 2020/264557, and titled PHOTORESIST WITH MULTIPLE PATTERNING RADIATION-ABSORBING ELEMENTS AND/OR VERTICAL COMPOSITION
- 15 GRADIENT, the disclosures of which at least relating to the composition, deposition, and patterning of directly photopatternable metal oxide films to form EUV resist masks are incorporated by reference herein.

- [0141]** Furthermore, two or more different precursors can be employed within each layer (e.g., a film or a capping layer). For instance, two or more of any metal-containing
- 20 precursors herein can be employed to form an alloy. In one non-limiting instance, tin telluride can be formed by employing tin precursor including an -NR₂ ligand with RTeH, RTeD, or TeR₂ precursors, in which R is an alkyl, particularly *t*-butyl or *i*-propyl. In another instance, a metal telluride can be formed by using a first metal precursor including an alkoxy or a halo ligand (e.g., SbCl₃) with a tellurium-containing precursor including a trialkylsilyl
- 25 ligand (e.g., bis(trimethylsilyl)tellurium).

[0142] Yet other exemplary EUV-sensitive materials, as well as processing methods and apparatuses, are described in U.S. Pat. No. 9,996,004 and Int. Pat. Pub. No. WO 2019/217749, each of which is incorporated herein by reference in its entirety.

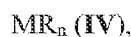
Further precursors

- 30 **[0143]** As described herein, the films, layers, and methods herein can be employed with any useful precursor. In some instances, the initial precursor includes a metal halide having the following formula (III):



in which M is a metal, X is halo, and n is 2 to 4, depending on the selection of M. Exemplary metals for M include Sn, Te, Bi, or Sb. Exemplary metal halides include SnBr_4 , SnCl_4 , SnI_4 , and SbCl_3 .

- 5 [0144] Another non-limiting metal-containing precursor includes a structure having formula (IV):



in which M is a metal; each R is independently H, an optionally substituted alkyl, amino (e.g., $-\text{NR}_2$, in which each R is independently alkyl), optionally substituted bis(trialkylsilyl) amino (e.g., $-\text{N}(\text{SiR}_3)_2$, in which each R is independently alkyl), or an optionally substituted trialkylsilyl (e.g., $-\text{SiR}_3$, in which each R is independently alkyl); and n is 2 to 4, depending on the selection of M. Exemplary metals for M include Sn, Te, Bi, or Sb. The alkyl group may be $\text{C}_n\text{H}_{2n+1}$, where n is 1, 2, 3, or greater. Exemplary organometallic agents include SnMe_4 , SnEt_4 , TeR_n , RTeR , *t*-butyl tellurium hydride ($\text{Te}(t\text{-Bu})(\text{H})$), dimethyl tellurium (TeMe_2), di(*t*-butyl)tellurium ($\text{Te}(t\text{-Bu})_2$), di(isopropyl)tellurium ($\text{Te}(i\text{-Pr})_2$), bis(trimethylsilyl)tellurium ($\text{Te}(\text{SiMe}_3)_2$), bis(triethylsilyl)tellurium ($\text{Te}(\text{SiEt}_3)_2$), tris(bis(trimethylsilyl)amido)bismuth ($\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$), $\text{Sb}(\text{NMe}_2)_3$, and the like.

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[0145] Another non-limiting metal-containing precursor can include a capping agent having the following formula (V):

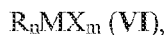


in which M is a metal; each L is independently an optionally substituted alkyl, amino (e.g., $-\text{NR}^1\text{R}^2$, in which each of R^1 and R^2 can be H or alkyl, such as any described herein), alkoxy (e.g., $-\text{OR}$, in which R is alkyl, such as any described herein), halo, or other organic substituent; and n is 2 to 4, depending on the selection of M. Exemplary metals for M include Sn, Te, Bi, or Sb. Exemplary ligands include dialkylamino (e.g., dimethylamino, methylethylamino, and diethylamino), alkoxy (e.g., *t*-butoxy, and isopropoxy), halo (e.g., F, Cl, Br, and I), or other organic substituents (e.g., acetylacetone or N^2,N^3 -di-*tert*-butyl-butane-2,3-diamino). Non-limiting capping agents include SnCl_4 , SnI_4 , $\text{Sn}(\text{NR}_2)_4$, wherein each of R is independently methyl or ethyl; or $\text{Sn}(t\text{-BuO})_4$. In some embodiments, multiple types of

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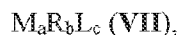
30 ligands are present.

[0146] A metal-containing precursor can include a hydrocarbyl-substituted capping agent having the following formula (VI):



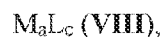
wherein M is a metal, R is a C₂₋₁₀ alkyl or substituted alkyl having a beta-hydrogen, and X is a suitable leaving group upon reaction with a hydroxyl group of the exposed hydroxyl groups. In various embodiments, n = 1 to 3, and m = 4 - n, 3 - n, or 2 - n, so long as m > 0 (or m ≥ 1). For example, R may be *t*-butyl, *t*-pentyl, *t*-hexyl, cyclohexyl, isopropyl, isobutyl, *sec*-butyl, *n*-butyl, *n*-pentyl, *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 dialkylamino (e.g., dimethylamino, methylethylamino, or diethylamino), alkoxy (e.g., *t*-butoxy, isopropoxy), halo (e.g., F, Cl, Br, or I), or another organic ligand. Examples of hydrocarbyl-substituted capping agents include *t*-butyltris(dimethylamino)tin (Sn(*t*-Bu)(NMe₂)₃), *n*-butyltris(dimethylamino)tin (Sn(*n*-Bu)(NMe₂)₃), *t*-butyltris(diethylamino)tin (Sn(*t*-Bu)(NEt₂)₃), di(*t*-butyl)di(dimethylamino)tin (Sn(*t*-Bu)₂(NMe₂)₂), *sec*-butyltris(dimethylamino)tin (Sn(*s*-Bu)(NMe₂)₃), *n*-pentyltris(dimethylamino)tin (Sn(*n*-pentyl)(NMe₂)₃), *i*-butyltris(dimethylamino)tin (Sn(*i*-Bu)(NMe₂)₃), *i*-propyltris(dimethylamino)tin (Sn(*i*-Pr)(NMe₂)₃), *t*-butyltris(*t*-butoxy)tin (Sn(*t*-Bu)(*t*-BuO)₃), *n*-butyl(tris(*t*-butoxy)tin (Sn(*n*-Bu)(*t*-BuO)₃), or isopropyltris(*t*-butoxy)tin (Sn(*i*-Pr)(*t*-BuO)₃).

[0147] In various embodiments, a metal-containing precursor includes at least one alkyl group on each metal atom that can survive the vapor-phase reaction, while other ligands or ions coordinated to the metal atom can be replaced by the counter-reactants. Accordingly, another non-limiting metal-containing precursor includes an organometallic agent having the formula (VII):



in which M is a metal; R is an optionally substituted alkyl; L is a ligand, ion, or other moiety which is reactive with the counter-reactant; a ≥ 1; b ≥ 1; and c ≥ 1. In particular embodiments, a = 1, and b + c = 4. In some embodiments, M is Sn, Te, Bi, or Sb. In particular embodiments, each L is independently amino (e.g., -NR¹R², in which each of R¹ and R² can be H or alkyl, such as any described herein), alkoxy (e.g., -OR, in which R is alkyl, such as any described herein), or halo (e.g., F, Cl, Br, or I). Exemplary agents include SnMe₃Cl, SnMe₂Cl₂, SnMeCl₃, SnMe(NMe₂)₃, SnMe₃(NMe₂), and the like.

[0148] In other embodiments, the non-limiting metal-containing precursor includes an organometallic agent having the formula (VIII):



in which M is a metal; L is a ligand, ion, or other moiety which is reactive with the counter-reactant; $a \geq 1$; and $c \geq 1$. In particular embodiments, $c = n - 1$, and n is 2, 3, or 4. In some embodiments, M is Sn, Te, Bi, or Sb. Counter-reactants preferably have the ability to replace the reactive moieties ligands or ions (e.g., L in formulas herein) so as to link at least two metal atoms via chemical bonding.

[0149] In any embodiment herein, R can be an optionally substituted alkyl (e.g., C_{1-10} alkyl). In one embodiment, alkyl is substituted with one or more halo (e.g., halo-substituted C_{1-10} alkyl, including one, two, three, four, or more halo, such as F, Cl, Br, or I). Exemplary R substituents include C_nH_{2n+1} , preferably wherein $n \geq 3$; and $C_nF_xH_{(2n+1-x)}$, wherein $2n+1 \leq x \leq 1$. In various embodiments, R has at least one beta-hydrogen or beta-fluorine. For example, R may be selected from the group consisting of *i*-propyl, *n*-propyl, *t*-butyl, *i*-butyl, *n*-butyl, *sec*-butyl, *n*-pentyl, *i*-pentyl, *t*-pentyl, *sec*-pentyl, and mixtures thereof.

[0150] In any embodiment herein, L may be any moiety readily displaced by a counter-reactant to generate an M-OH moiety, such as a moiety selected from the group consisting of an amino (e.g., $-NR^1R^2$, in which each of R^1 and R^2 can be H or alkyl, such as any described herein), alkoxy (e.g., $-OR$, in which R is alkyl, such as any described herein), carboxylates, halo (e.g., F, Cl, Br, or I), and mixtures thereof.

[0151] In particular embodiments, the metal precursor includes tin. In some embodiments, the tin precursor includes SnR or SnR_2 or SnR_4 or R_3SnSnR_3 , wherein each R is, independently, H, halo, optionally substituted C_{1-12} alkyl, optionally substituted C_{1-12} alkoxy, optionally substituted amino (e.g., $-NR^1R^2$), optionally substituted C_{2-12} alkenyl, optionally substituted C_{2-12} alkynyl, optionally substituted C_{3-8} cycloalkyl, optionally substituted aryl, cyclopentadienyl, optionally substituted bis(trialkylsilyl)amino (e.g., $-N(SiR^1R^2R^3)_2$), optionally substituted alkanoyloxy (e.g., acetate), a diketone (e.g., $-OC(R^1)-Ak-(R^2)CO-$), or a bidentate chelating dinitrogen (e.g., $-N(R^1)-Ak-N(R^1)-$). In particular embodiments, each R^1 , R^2 , and R^3 is, independently, H or C_{1-12} alkyl (e.g., methyl, ethyl, isopropyl, *t*-butyl, or neopentyl); and Ak is optionally substituted C_{1-6} alkylene. Non-limiting tin precursors include SnF_2 , SnH_4 , $SnBr_4$, $SnCl_4$, SnI_4 , tetramethyl tin ($SnMe_4$), tetraethyl tin ($SnEt_4$), trimethyl tin chloride ($SnMe_3Cl$), dimethyl tin dichloride ($SnMe_2Cl_2$), methyl tin trichloride

(SnMeCl₃), tetraallyltin, tetravinyl tin, hexaphenyl ditin (IV) (Ph₃Sn-SnPh₃, in which Ph is phenyl), dibutyldiphenyltin (SnBu₂Ph₂), trimethyl(phenyl) tin (SnMe₃Ph), trimethyl (phenylethynyl) tin, tricyclohexyl tin hydride, tributyl tin hydride (SnBu₃H), dibutyltin diacetate (SnBu₂(CH₃COO)₂), tin(II) acetylacetonate (Sn(acac)₂), SnBu₃(OEt),
 5 SnBu₂(OMe)₂, SnBu₃(OMe), Sn(*t*-BuO)₄, Sn(*n*-Bu)(*t*-BuO)₃, tetrakis(dimethylamino)tin (Sn(NMe₂)₄), tetrakis(ethylmethylamino)tin (Sn(NMeEt)₄), tetrakis(diethylamino)tin(IV) (Sn(NEt₂)₄), (dimethylamino)trimethyl tin(IV) (Sn(Me)₃(NMe₂), Sn(*i*-Pr)(NMe₂)₃, Sn(*n*-Bu)(NMe₂)₃, Sn(*s*-Bu)(NMe₂)₃, Sn(*i*-Bu)(NMe₂)₃, Sn(*t*-Bu)(NMe₂)₃, Sn(*t*-Bu)₂(NMe₂)₂, Sn(*t*-Bu)(NEt₂)₃, Sn(tbba), Sn(II) (1,3-bis(1,1-dimethylethyl)-4,5-dimethyl-(4*R*,5*R*)-1,3,2-
 10 diazastannolidin-2-ylidene), or bis[bis(trimethylsilyl)amino]tin (Sn[N(SiMe₃)₂]₂).

[0152] Exemplary organometallic agents include SnMeCl₃, (*N*²,*N*³-di-*t*-butyl-butane-2,3-diamido) tin(II) (Sn(tbba)), bis(bis(trimethylsilyl)amido) tin(II), tetrakis(dimethylamino) tin(IV) (Sn(NMe₂)₄), *t*-butyl tris(dimethylamino) tin (Sn(*t*-butyl)(NMe₂)₃), *i*-butyl tris(dimethylamino) tin (Sn(*i*-Bu)(NMe₂)₃), *n*-butyl tris(dimethylamino) tin (Sn(*n*-Bu)
 15 (NMe₂)₃), *sec*-butyl tris(dimethylamino) tin (Sn(*s*-Bu)(NMe₂)₃), *i*-propyl(tris)dimethylamino tin (Sn(*i*-Pr)(NMe₂)₃), *n*-propyl tris(diethylamino) tin (Sn(*n*-Pr)(NEt₂)₃), and analogous alkyl(tris)(*t*-butoxy) tin compounds, such as *t*-butyl tris(*t*-butoxy) tin (Sn(*t*-Bu)(*t*-BuO)₃). In some embodiments, the organometallic agents are partially fluorinated.

Film composition

20 [0153] The patterning radiation-sensitive film can be formed by using one or more modified precursors, optionally in the presence of one or more counter-reactants. Furthermore, the modified precursor can be deposited (e.g., using any deposition process described herein) and optionally processed (e.g., baked, treated, annealed, exposed to plasma, etc.) to provide a metal oxide layer (e.g., a layer including a network of metal oxide bonds,
 25 which may include other non-metal and non-oxygen groups).

[0154] FIG. 2A provides an exemplary stack including a substrate 201 (e.g., a semiconductor substrate) having a top surface and a film 202 disposed on the top surface of the substrate 201. The film can include any useful patterning radiation-sensitive material (e.g., an EUV-sensitive material, such as any described herein, which can be useful as a PR).
 30 In some embodiments, the patterning radiation-sensitive film includes a modified precursor or a deposited from thereof. The deposited form can be an organometallic material, such as an organometal oxide (e.g., RM(MO)_n, in which M is a metal and R is an organic moiety

having one or more carbon atoms, such as in alkyl, alkylamino, or alkoxy). The substrate can include any useful wafer, feature(s), layer(s), or device(s). In some embodiments, substrates are silicon wafers having any useful feature (e.g., irregular surface topography), layer (e.g., photoresist layer), or device.

- 5 **[0155]** The EUV-sensitive film can include a radiation-absorbing unit and a radiation-sensitive carbon-containing unit. In some embodiments, the radiation-absorbing unit includes or is an EUV-absorbing unit. Non-limiting examples of these include, e.g., a metal with a high EUV absorption cross-section, such as equal to or greater than $1 \times 10^7 \text{ cm}^2/\text{mol}$. In other embodiments, the radiation-absorbing unit includes or is M (e.g., in which M can be Sn, Te, Bi, Sb, Hf, or Zr, or a combination thereof). In some embodiments, the radiation-sensitive carbon-containing unit is an EUV-sensitive carbon-containing unit. In particular
- 10 embodiments, the EUV-sensitive carbon-containing unit includes an organic co-reactant or a reaction product thereof. Non-limiting examples of EUV-sensitive carbon-containing unit include, e.g., an organic moiety, such as any described herein (e.g., alkenylene moieties, alkynylene moieties, dicarbonyl moieties, carbonyl moieties, or combinations thereof).
- 15

- [0156]** In some embodiments, the EUV-sensitive film can be characterized by an increased or a decreased carbon content, such as an increase in metal-carbon or oxygen-carbon bonds or an increase in various organic moieties, such as alkenylene, alkylene, carbonyl, or dicarbonyl moieties (e.g., a substituted alkylene group having two carbonyl moieties). The
- 20 presence or use of an organic co-reactant within a film can be detected in any useful manner. Non-limiting methods include, e.g., use of Fourier-transform infrared (FTIR) spectroscopy, solid state nuclear magnetic resonance (NMR) spectroscopy, and/or ultraviolet-visible (UV-Vis) spectroscopy to detect a functional group present within the organic co-reactant. This increase or decrease in organic carbon content can optionally enhance porosity of the film, as
- 25 compared to a film formed without an organic co-reactant. Non-limiting methods to measure porosity include, e.g., volumetric gas adsorption.

- [0157]** The film can have a vertical gradient that is characterized by a vertical change in EUV absorbance (e.g., in which non-limiting methods and characteristics of gradient films are described herein). In some instances, an increase in EUV absorbance along a depth (e.g.,
- 30 going from a top surface of the film towards the substrate) can correspond with a decrease in carbon content along that same depth through the film layer. In other instances, an increase in EUV absorbance along a depth can correspond with an increase in tellurium, antimony, or iodine content along that same depth through the film layer.

- [0158] FIG. 2B provides an exemplary stack including a substrate 211 (e.g., a semiconductor substrate) having a top surface and a film 212 disposed on the top surface of the substrate 211, in which the film 212 possesses a vertical gradient characterized by a change in EUV absorbance and/or carbon content. For instance, the gradient film 212 can include a first concentration of carbon content in a top portion 212a of the film and a second concentration of carbon content in a bottom portion 212b of the film, in which the first and second concentration values are different. In one instance, the first concentration is greater than the second concentration. In another instance, the first concentration is less than the second concentration. Non-limiting gradients include a linear gradient, an exponential gradient, a sigmoidal gradient, and the like. In particular embodiments, gradient density films of EUV-responsive organic moieties can yield more homogeneous film properties of EUV exposed areas at all depths in the film, which might improve development processes, improve EUV sensitivity, and/or improve patterning quality (e.g., having improved LWR and/or LER).
- [0159] The patterning radiation-sensitive film (e.g., EUV-sensitive film) can be employed as a capping layer, which in turn is disposed on any useful layer or structure. As seen in FIG. 2C, the stack can include a substrate 221 (e.g., a semiconductor substrate) having a top surface, in which the substrate 221 further includes a photoresist layer 222. The EUV-sensitive film 223 is a capping layer disposed on a top surface of the photoresist layer 222. Such a capping layer can serve to reduce off gassing that can occur during EUV exposure of the underlying photoresist layer. This capping layer may also provide a barrier to chemical species evolved during the EUV patterning process. In particular, if the photoresist layer is formed from a metal-containing precursor (e.g., an organometallic agent, a metal halide, as well as any described herein), then the capping layer can trap evolving metal or chemical species produced during EUV exposure and, thus, minimize contamination of the lithography equipment. The capping layer can be any useful thickness (e.g., any thickness described herein, including from about 0.1 nm to about 5 nm, such as from about 0.1 nm to 0.5 nm, 0.1 nm to 1 nm, 0.1 nm to 3 nm, 0.3 nm to 0.5 nm, 0.3 nm to 1 nm, 0.3 nm to 3 nm, 0.3 nm to 5 nm, 0.5 nm to 1 nm, 0.5 nm to 3 nm, 0.5 nm to 5 nm, 0.8 nm to 1 nm, 0.8 nm to 3 nm, 0.8 nm to 5 nm, 1 nm to 3 nm, 1 nm to 5 nm, or 3 nm to 5 nm).

Methods employing modified precursors

[0160] The present disclosure generally includes any useful method that employs an initial precursor in combination with an organic co-reactant. Such methods can include any useful lithography processes, deposition processes, radiation exposure processes, development
5 processes, and post-application processes, as described herein. In some embodiments, the choice of the organic co-reactant can provide either a positive tone resist or a negative tone resist. Accordingly, the method herein also includes those that employ a positive tone resist or a negative tone resist.

[0161] While the following may describe techniques as relating to EUV processes, such
10 techniques may also be applicable to other next generation lithographic techniques. Various radiation sources may be employed, including EUV (generally about 13.5 nm), DUV (deep-UV, generally in the 248 nm or 193 nm range with excimer laser sources), X-ray (including EUV at the lower energy range of the X-ray range), and e-beam (including a wide energy range).

15 [0162] FIG. 3A provides an exemplary method 300, which includes providing an initial precursor 30 in the presence of an organic co-reactant 32 (e.g., any described herein). In particular, the organic co-reactant replaces at least one ligand in the initial precursor to provide a modified precursor. The method 300 further includes depositing 301 a modified precursor as a film 312 on a top surface of a substrate 311, wherein the film 312 includes an
20 EUV-sensitive material.

[0163] The method can further include steps to treat the deposited EUV-sensitive film. Such steps, while not required for creating the film, can be useful for using the film as a PR. Accordingly, the method 300 further includes patterning the film by an EUV exposure 302 to provide an exposed film having EUV exposed areas 312b and EUV unexposed areas 312c.
25 Patterning can include use of a mask 314 having EUV transparent regions and EUV opaque regions, in which EUV beams 315 are transmitted through the EUV transparent region and into the film 312. EUV exposure can include, e.g., an exposure having a wavelength in the range of about 10 nm to about 20 nm in a vacuum ambient (e.g., about 13.5 nm in a vacuum ambient).

30 [0164] Once a pattern is provided, the method 300 can include developing 303 the film, thereby either (i) removing the EUV exposed areas to provide a pattern within a positive tone resist film or (ii) removing the EUV unexposed areas to provide a pattern within a negative

tone resist. Path (i) in **FIG. 3A** results in selectively removing the EUV exposed areas **312b**, which can be facilitated by using organic co-reactant(s) that provide bound ligands that are less stable after EUV exposure (e.g., that release a gaseous by-product upon being exposed to EUV radiation). Alternatively, path (ii) in **FIG. 3A** results in maintaining the EUV exposed areas **312b**, which can be facilitated by using organic co-reactant(s) that provide bound ligands that are more stable after EUV exposure (e.g., that are more resistant to development after EUV exposure).

[0165] Developing steps can include use of halide chemistry (e.g., HBr chemistry) in a gas phase or use of aqueous or organic solvents in a liquid phase. Developing steps can include any useful experimental conditions, such as a low pressure condition (e.g., of from about 1 mTorr to about 100 mTorr), a plasma exposure (e.g., in the presence of vacuum), and/or a thermal condition (e.g., of from about -10°C to about 100°C) that may be combined with any useful chemistry (e.g., halide chemistry or aqueous chemistry). Development can include, e.g., a halide-based etchant, such as HCl, HBr, H₂, Cl₂, Br₂, BCl₃, or combinations thereof, as well as any halide-based development process described herein; an aqueous alkali development solution; or an organic development solution. Additional development process conditions are described herein.

[0166] The substrate may include other layers or structures. As seen in **FIG. 3B**, the method **320** includes providing a substrate **331** including a photoresist layer **332**, as well as providing an initial precursor **30** in the presence of an organic co-reactant **32** (e.g., any described herein), thereby resulting in in situ formation of a modified precursor. The method **320** further includes depositing **321** the modified precursor as a film **333** on a top surface of the photoresist layer **332**, wherein the film **333** includes an EUV-sensitive material. Furthermore, the film **333** can serve as a capping layer for the photoresist layer **332**, and the photoresist layer **332** can further include an EUV-sensitive material. The EUV-sensitive material in the capping and photoresist layers can possess different metal to carbon ratios, in which the capping layer **333** can have an increased carbon content, as compared to the photoresist layer **332**.

[0167] In particular embodiments, a different metal to carbon ratio can be achieved by using the same initial precursor and the same organic co-reactant in both the capping and photoresist layer, but the ratio of the initial precursor to the organic co-reactant can be modulated during deposition to provide a different metal to carbon ratio. In other embodiments, a different metal to carbon ratio can be achieved by using the same initial

precursor but different organic co-reactant in the two layers. For instance, the capping layer can include use of a co-reactant having a bulkier organic substituent (e.g., ethyl, propyl, or butyl) than the organic substituent for the co-reactant of the photoresist layer (e.g., methyl).

[0168] The photoresist layer **332** can be provided in any useful manner. In one instance, the photoresist layer is provided by depositing an initial precursor (e.g., an organometallic agent, a metal halide, or any herein) optionally in the presence of a counter-reactant. In another instance, the photoresist layer is provided by depositing an initial precursor in the presence of an organic co-reactant, such as by employing operation **301** in method **300** of **FIG. 3A**. After producing the photoresist layer, a capping layer can be provided by employing operation **321** in method **320** in **FIG. 3B**.

[0169] The capping layer may be present during patterning and, in some instances, reduce emission of volatile chemical and metal species from the photoresist layer during EUV exposure. Thus, in particular instances, the method **320** can include patterning the photoresist layer by an EUV exposure **322** to provide an exposed film having EUV exposed areas **332b** and EUV unexposed areas **332c**, in which patterning can include use of a mask **334** having EUV transparent regions and EUV opaque regions and in which EUV beams **335** are transmitted through the EUV transparent region, into the capping layer **333**, and further into the photoresist layer **332**. Developing **323** the photoresist layer and the capping layer can result in selectively removing the EUV exposed areas **332b** (as in path (i)) and maintaining the EUV unexposed areas **332c**; or selectively removing the EUV unexposed areas **332c** (as in path (ii)) and maintaining the EUV exposed areas **332b**.

[0170] Optional steps may be conducted to further modulate, modify, or treat the EUV-sensitive film(s), substrate, photoresist layer(s), capping layer(s), and/or in any method herein. **FIG. 3C** provides a flow chart of an exemplary method **350** having various operations, including optional operations. As can be seen, in operation **352**, an initial precursor is provided in the presence of an organic co-reactant, which provides a modified precursor (e.g., within a chamber). In operation **354**, a film is deposited employing the modified precursor. Next, operation **356** is an optional process to change the amount of the initial precursor and the organic co-reactant, thereby providing a further modified precursor. Such a change can include increasing or decreasing the amount of the initial precursor and/or the organic co-reactant. Optional operation **358** includes depositing the further modified precursor. Operations **356,358** can be repeated, as desired, to form a film having the modified precursor.

[0171] In operation 360, the film is exposed to EUV radiation to develop a pattern. Generally, the EUV exposure causes a change in the chemical composition of the film, creating a contrast in etch selectivity that can be used to remove a portion of the film. Such a contrast can provide a positive tone resist or a negative tone resist, as described herein.

5 [0172] Operation 362 is an optional post exposure bake (PEB) to further increase contrast in etch selectivity of the exposed film. Non-limiting examples of temperature for PEB include, for example from about 90°C to 600°C, 100°C to 400°C, 125°C to 300°C, 170°C to 250°C or more, 190°C to 240°, as well as others described herein. In other instances, the PEB step is conducted at a temperature less than about 180°C, less than about 200°C, or less
10 than about 250°C.

[0173] In one instance, the exposed film can be thermally treated (e.g., optionally in the presence of various chemical species) to promote reactivity within the EUV exposed portions of the resist upon exposure to a stripping agent (e.g., a halide-based etchant, such as HCl, HBr, H₂, Cl₂, Br₂, BCl₃, or combinations thereof, as well as any halide-based development
15 process described herein; an aqueous alkali development solution; or an organic development solution) or a positive tone developer. In another instance, the exposed film can be thermally treated to further cross-link ligands within the EUV exposed portions of the resist, thereby providing EUV unexposed portions that can be selectively removed upon exposure to a stripping agent (e.g., a negative tone developer).

20 [0174] Then, in operation 364, the PR pattern is developed. In various embodiments of development, the exposed regions are removed (positive tone) or the unexposed regions are removed (negative tone). In various embodiments, these steps may be dry processes or wet processes.

[0175] Other optional steps may be performed. Optionally, the method can include (e.g.,
25 after deposition) cleaning the backside surface or bevel of the substrate or removing an edge bead of the deposited film that was deposited in the prior step. Such cleaning or removing steps can be useful for removing particles that may be present after depositing a film layer. The removing step can include processing the wafer with a wet metal oxide (MeOx) edge bead removal (EBR) step.

30 [0176] In another instance, the method can include an optional step of performing a post application bake (PAB) of the deposited film or capping layer, thereby removing residual moisture; or pretreating the deposited film or capping layer in any useful manner. The

optional PAB can occur after film deposition and prior to EUV exposure; and the PAB can involve a combination of thermal treatment, chemical exposure, and moisture to increase the EUV sensitivity of the film, thereby reducing the EUV dose to develop a pattern in the film.

In particular embodiments, the PAB step is conducted at a temperature greater than about 100°C or at a temperature of from about 100°C to about 200°C or from about 100°C to about 250°C. In some instances, a PAB is not performed within the method. In other instances, the PAB step is conducted at a temperature less than about 180°C, less than about 200°C, or less than about 250°C.

[0177] In yet another instance, the method can include an optional step of performing a post exposure bake (PEB) of the exposed film, thereby further removing residual moisture or promoting chemical condensation within the film; or post-treating the film in any useful manner. In another instance, the method can include (e.g., after development) hardening the patterned film, thereby providing a resist mask disposed on a top surface of the substrate. Hardening steps can include any useful process to further crosslink or react the EUV unexposed or exposed areas, such as steps of exposing to plasma (e.g., O₂, Ar, He, or CO₂ plasma), exposing to ultraviolet radiation, annealing (e.g., at a temperature of about 180°C to about 240°C), thermal baking, or combinations thereof that can be useful for a post development baking (PDB) step. In other instances, the PDB step is conducted at a temperature less than about 180°C, less than about 200°C, or less than about 250°C. Additional post-application processes are described herein and may be conducted as an optional step for any method described herein.

[0178] Any useful type of chemistry can be employed during the depositing, patterning, and/or developing steps. Such steps may be based on dry processes employing chemistry in a gaseous phase or wet processes employing chemistry in a wet phase. Various embodiments include combining all dry operations of film formation by vapor deposition, (EUV) lithographic photopatterning, dry stripping, and dry development. Various other embodiments include dry processing operations described herein advantageously combined with wet processing operations, for example, spin-on EUV photoresists (wet process), such as available from Inpria Corp., may be combined with dry development or other wet or dry processes as described herein. In various embodiments, the wafer clean may be a wet process as described herein, while other processes are dry processes. In yet other embodiments, a wet development process may be used.

[0179] Without limiting the mechanism, function, or utility of the present technology, dry processes of the present technology may provide various benefits relative to wet development processes. For example, dry vapor deposition techniques described herein can be used to deposit thinner and more defect free films than can be applied using spin-coating techniques, in which the exact thickness of the deposited film can be modulated and controlled simply by increasing or decreasing the length of the deposition step or sequence.

[0180] In other embodiments, dry and wet operations can be combined to provide a dry/wet process. For any of the process herein (e.g., for lithographic processes, deposition processes, EUV exposure processes, development processes, pre-treatment processes, post-application processes, etc.), various specific operation can include wet, dry, or wet and dry embodiments. For instance, a wet deposition can be combined with a dry development; or wet deposition can be combined with wet development; or dry deposition can be combined with wet development; or dry deposition can be combined with dry development. Any of these, in turn, can be combined with wet or dry pre- and post-application processes, as described herein.

[0181] Accordingly, in some non-limiting embodiments, a dry process may provide more tunability and give further critical dimension (CD) control and scum removal. Dry development can improve performance (e.g., prevent line collapse due to surface tension in wet development) and/or enhance throughput (e.g., by avoiding wet development track). Other advantages may include eliminating the use of organic solvent developers, reducing sensitivity to adhesion issues, avoiding the need to apply and remove wet resist formulations (e.g., avoiding scumming and pattern distortion), improving line edge roughness, patterning directly over device topography, offering the ability to tune hardmask chemistry to the specific substrate and semiconductor device design, and avoiding other solubility-based limitations. Yet, in some instances, wet development may be useful or preferred. Additional details, materials, processes, steps, and apparatuses are described herein.

Lithographic processes

[0182] EUV lithography makes use of EUV resists, which may be polymer-based chemically amplified resists produced by liquid-based spin-on techniques or metal oxide-based resists produced by dry vapor-deposited techniques. Such EUV resists can include any EUV-sensitive film or material described herein. Lithographic methods can include patterning the resist, e.g., by exposure of the EUV resist with EUV radiation to form a photo

pattern, followed by developing the pattern by removing a portion of the resist according to the photo pattern to form a mask.

[0183] It should also be understood that while the present disclosure relates to lithographic patterning techniques and materials exemplified by EUV lithography, it is also applicable to 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 248 nm or 193 nm 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 (e.g., optionally having exposed hydroxyl groups) is contacted with a metal-containing precursor (e.g., any described herein) to form a metal oxide (e.g., a layer including a network of metal oxide bonds, which may include other non-metal and non-oxygen groups) film as the imaging/photoresist (PR) layer on the surface of the substrate. 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.

[0184] Directly photopatternable EUV resists may be composed of or contain metals and/or metal oxides mixed within organic components. The metals/metal oxides are highly promising in that they can enhance the EUV photon adsorption and generate secondary electrons and/or show increased etch selectivity to an underlying film stack and device layers. To date, these resists have been developed using a wet (solvent) approach, which requires the wafer to move to the track, where it is exposed to developing solvent, dried and baked. Wet development does not only limit productivity but can also lead to line collapse due to surface tension effects during the evaporation of solvent between fine features.

[0185] Dry development techniques have been proposed to overcome these issues by eliminating substrate delamination and interface failures. Dry development has its own challenges, including etch selectivity between unexposed and EUV exposed resist material which can lead to a higher dose to size requirement for effective resist exposure when compared to wet development. Suboptimal selectivity can also cause PR corner rounding due to longer exposures under etching gas, which may increase line CD variation in the following transfer etch step. Yet, in some instances, wet development may be useful or preferred. Additional processes employed during lithography are described in detail below.

Deposition processes, including dry deposition

[0186] 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. Methods include those where polymerized organometallic materials are produced in a vapor and deposited on a substrate. In some embodiments, dry deposition can employ any useful metal-containing precursor (e.g., metal halides, capping agents, or organometallic agents described herein). In other embodiments, a spin-on formulation may be used. Deposition processes can include applying a EUV-sensitive material as a resist film and/or as a capping layer upon the resist film. Exemplary EUV-sensitive materials are described herein.

[0187] The present technology includes methods by which EUV-sensitive films are deposited on a substrate, such films being operable as resists for subsequent EUV lithography and processing. Furthermore, a secondary EUV-sensitive film can be deposited upon an underlying primary EUV-sensitive film. In one instance, the secondary film constitutes a capping layer, and the primary film constitutes the imaging layer.

[0188] Such EUV-sensitive films comprise materials which, upon exposure to EUV, undergo changes, such as the loss of bulky pendant ligands bonded to metal atoms in low density M-OH rich materials, allowing their crosslinking to denser M-O-M bonded metal oxide materials. In other embodiments, EUV exposure results in further cross-linking between ligands bonded to metal atoms, thereby providing denser M-L-M bonded organometallic materials, in which L is a ligand. In yet other embodiments, EUV exposure results in loss of ligands to provide M-OH materials that can be removed by positive tone developers.

[0189] Through EUV patterning, areas of the film are created that have altered physical or chemical properties relative to unexposed areas. These properties may be exploited in subsequent processing, such as to dissolve either unexposed or exposed areas or to selectively deposit materials on either the exposed or unexposed areas. In some embodiments, the unexposed film has a hydrophobic surface, and the exposed film has a hydrophilic surface (it being recognized that the hydrophilic properties of exposed and unexposed areas are relative to one another) under the conditions at which such subsequent processing is performed. For example, the removal of material may be performed by leveraging differences in chemical

composition, density, and cross-linking of the film. Removal may be by wet processing or dry processing, as further described herein.

[0190] The thickness of the EUV-patternable film formed on the surface of the substrate may vary according to the surface characteristics, materials used, and processing conditions.

- 5 In various embodiments, the film thickness may range from about 0.5 nm to about 100 nm. Preferably, the film has a sufficient thickness to absorb most of the EUV light under the conditions of EUV patterning. For example, the overall absorption of the resist film may be 30% or less (e.g., 10% or less, or 5% or less), so that the resist material at the bottom of the resist film is sufficiently exposed. In some embodiments, the film thickness is from 10 nm to
10 20 nm. Without limiting the mechanism, function, or utility of the present disclosure, it is believed that, unlike wet, spin-coating processes, the processes of the present disclosure have fewer restrictions on the surface adhesion properties of the substrate, and therefore can be applied to a wide variety of substrates. Moreover, as discussed above, the deposited films may closely conform to surface features, providing advantages in forming masks over
15 substrates, such as substrates having underlying features, without “filling in” or otherwise planarizing such features.

- [0191]** The film (e.g., imaging layer) or capping layer may be composed of a metal oxide layer deposited in any useful manner. Such a metal oxide layer can be deposited or applied by using any EUV-sensitive material described herein, such as a metal-containing precursor
20 (e.g., a metal halide, a capping agent, or an organometallic agent) in combination with an organic co-reactant. In exemplary processes, a polymerized organometallic material is formed in vapor phase or in situ on the surface of the substrate in order to provide the metal oxide layer. The metal oxide layer may be employed as a film, an adhesion layer, or a capping layer.

- 25 **[0192]** Optionally, the metal oxide layer can include a hydroxyl-terminated metal oxide layer, which can be deposited by employing a capping agent (e.g., any described herein) with an oxygen-containing counter-reactant. Such a hydroxyl-terminated metal oxide layer can be employed, e.g., as an adhesion layer between two other layers, such as between the substrate and the film and/or between the photoresist layer and the capping layer.

- 30 **[0193]** Exemplary deposition techniques (e.g., for a film or a capping layer) include any described herein, such as ALD (e.g., thermal ALD and plasma-enhanced ALD), spin-coat deposition, PVD including PVD co-sputtering, CVD (e.g., PE-CVD or LP-CVD), sputter

deposition, e-beam deposition including e-beam co-evaporation, etc., or a combination thereof, such as ALD with a CVD component, such as a discontinuous, ALD-like process in which metal-containing precursors, organic co-reactants, and counter-reactants are separated in either time or space.

5 **[0194]** Further description of precursors and methods for their deposition as EUV photoresist films applicable to this disclosure may be found in International Appl. No. PCT/US19/31618, published as International Pub. No. WO 2019/217749, filed May 9, 2019, and titled METHODS FOR MAKING EUV PATTERNABLE HARD MASKS. The thin films may include optional materials in addition to an initial precursor, an organic co-
10 reactant, and a counter-reactant to modify the chemical or physical properties of the film, such as to modify the sensitivity of the film to EUV or enhancing etch resistance. Such optional materials may be introduced, such as by doping during vapor phase formation prior to deposition on the substrate, after deposition of the film, or both. In some embodiments, a gentle remote H₂ plasma may be introduced so as to replace some Sn-L bonds with Sn-H, for
15 example, which can increase reactivity of the resist under EUV.

[0195] In general, methods can include mixing a vapor stream of an initial precursor (e.g., a metal-containing precursor, such as an organometallic agent) with a vapor stream of an organic co-reactant and an optional vapor stream of a counter-reactant so as to form a polymerized organometallic material, and depositing the organometallic material onto the
20 surface of the semiconductor substrate. In some embodiments, mixing the metal-containing precursor with the organic co-reactant and optional counter-reactant can form a polymerized organometallic material. As will be understood by one of ordinary skill, the mixing and depositing aspects of the process may be concurrent, in a substantially continuous process.

[0196] In an exemplary continuous CVD process, two or more gas streams, in separate inlet
25 paths, of sources of initial precursor, organic co-reactant, and optional counter-reactant are introduced to the deposition chamber of a CVD apparatus, where they mix and react in the gas phase, to form agglomerated polymeric materials (e.g., via metal-oxygen-metal bond formation) or a film on the substrate. Gas streams may be introduced, for example, using separate injection inlets or a dual-plenum showerhead. The apparatus is configured so that
30 the streams of initial precursor, organic co-reactant, and optional counter-reactant are mixed in the chamber, allowing the initial precursor, organic co-reactant, and optional counter-reactant to react to form a polymerized organometallic material or a film (e.g., a metal oxide

coating or agglomerated polymeric materials, such as via metal-oxygen-metal bond formation).

5 [0197] For depositing metal oxide, 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 pressures from 1 Torr to 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.

10 [0198] For depositing agglomerated polymeric materials, the CVD process is generally conducted at reduced pressures, such as from 10 mTorr to 10 Torr. In some embodiments, the process is conducted at from 0.5 to 2 Torr. The temperature of the substrate is preferably at or 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. In various processes, deposition of the polymerized organometallic material on the substrate occurs at rates inversely proportional to surface temperature. Without limiting the mechanism,
15 function or utility of present technology, it is believed that the product from such vapor-phase reaction becomes heavier in molecular weight as metal atoms are crosslinked by organic co-reactants and/or counter-reactants, and is then condensed or otherwise deposited onto the substrate. In various embodiments, the steric hindrance of the bulky alkyl groups (e.g., provided by the organic co-reactant) further prevents the formation of densely packed
20 network and produces low density films having increased porosity.

[0199] A potential advantage of using dry deposition methods is ease of tuning the composition of the film as it grows. In a CVD process, this may be accomplished by changing the relative flows of the initial precursor and the organic co-reactant during deposition. Deposition may occur between 30°C and 200°C and at pressures between 0.01
25 Torr to 100 Torr, but more generally between about 0.1 Torr and 10 Torr.

[0200] A film (e.g., a metal oxide coating or agglomerated polymeric materials, such as via metal-oxygen-metal bond formation) may also be deposited by an ALD process. For example, the initial precursor, organic co-reactant, and optional counter-reactant are introduced at separate times, representing an ALD cycle. The precursors and organic co-
30 reactants react on the surface, forming up to a monolayer of material at a time for each cycle. This may allow for 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 Torr to 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.

5 **[0201]** Any of the deposition methods herein can be modified to allow for use of two or more different initial precursors. In one embodiment, the precursors can include the same metal but different ligands. In another embodiment, the precursors can include different metal groups. In one non-limiting instance, alternating flows of various volatile metal-containing precursors can provide a mixed metal layer, such as use of a metal alkoxide precursor having a first metal (e.g., Sn) with a silyl-based precursor having a different second
10 metal (e.g., Te).

15 **[0202]** Also, any of the deposition methods herein can be modified to allow for use of two or more different organic co-reactants. In one embodiment, the organic co-reactants can provide different bound ligands to the metal centers. In one non-limiting instance, alternating flows of various organic co-reactants can provide a layer with varying carbon content, such as in a gradient film.

20 **[0203]** Furthermore, any of the deposition methods herein can be modified to provide one or more layers within a film or a capping layer. In one instance, different initial precursors and/or organic co-reactants can be employed in each layer. In another instance, the same precursor may be employed for each layer, but the top-most layer can possess a different chemical composition (e.g., a different density of metal-ligand bonds, a different metal to carbon ratio, or a different bound ligand, as provided by modulating or changing the organic co-reactant).

25 **[0204]** Processes herein can be used to achieve a surface modification. In some iterations, a vapor of the initial precursor may be passed over the wafer. The wafer may be heated to provide thermal energy for the reaction to proceed. In some iterations, the heating can be between about 50°C to about 250°C. In some cases, pulses of the organic co-reactant may be used, separated by pump and/or purging steps. For instance, an organic co-reactant may be pulsed between the precursor pulses resulting in ALD or ALD-like growth. In other cases, both the precursor and the organic co-reactant may be flowed at the same time. Examples of
30 elements useful for surface modification include I, F, Sn, Bi, Sb, Te, and oxides or alloys of these compounds.

- [0205] The processes herein can be used to deposit a thin metal oxide or metal by ALD or CVD. Examples include SnOx, BiOx, and Te. Following deposition, the film may be capped with an alkyl substituted precursor of the form $M_aR_bL_c$, as described elsewhere herein. A counter-reactant may be used to better remove the ligands, and multiple cycles may be repeated to ensure complete saturation of the substrate surface. The surface can then ready for the EUV-sensitive film to be deposited. One possible method is to produce a thin film of SnOx. Possible chemistries include growth of SnO₂ by cycling tetrakis(dimethylamino)tin and a counter-reactant such as water or O₂ plasma. After the growth, a capping agent could be used. For example, isopropyltris(dimethylamino)tin vapor may be flown over the surface.
- [0206] Deposition processes can be employed on any useful surface. 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 a surface can be present on a substrate (e.g., upon which a film is to be deposited), on a film (e.g., upon which a capping layer is to be deposited), or on a capping layer.
- [0207] Any useful substrate can be employed, including 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.
- [0208] 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.
- Without limiting the mechanism, function, or utility of the present technology, it is believed that, in some embodiments, methods of the present technology offer advantages relative to methods among those in which photolithographic films are deposited on the surface of substrates using spin casting methods. Such advantages may derive from the conformance of the films of the present technology to underlying features without “filling in” or otherwise planarizing such features, and the ability to deposit films on a wide variety of material surfaces.

[0209] In some embodiments, an incoming wafer can be prepared with a substrate surface of a desired material, with the uppermost material being the layer into which the resist pattern is transferred. While the material selection may vary depending on integration, it is generally desired to select a material that can be etched with high selectivity to (i.e., much faster than) the EUV resist or imaging layer. Suitable substrate materials can include various carbon-based films (e.g., ashable hard mask (AHM)), silicon-based films (e.g., silicon, silicon oxide, silicon nitride, silicon oxynitride, or silicon oxycarbonitride, as well as doped forms thereof, including SiO_x , SiO_xN_y , $\text{SiO}_x\text{C}_y\text{N}_z$, a-Si:H, poly-Si, or SiN), or any other (generally sacrificial) film applied to facilitate the patterning process.

[0210] 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.

[0211] In some non-limiting embodiments, a substrate comprises an underlayer. An underlayer may be deposited on a hard mask or other layer and is generally underneath an imaging layer (or film), as described herein. An underlayer may be used to improve the sensitivity of a PR, increase EUV absorptivity, and/or increase the patterning performance of the PR. In cases where there are device features present on the substrate to be patterned which create significant topography, another important function of the underlayer can be to overcoat and planarize the existing topography so that the subsequent patterning step may be performed on a flat surface with all areas of the pattern in focus. For such applications, the underlayer (or at least one of multiple underlayers) may be applied using spin-coating techniques. When the PR material being employed possesses a significant inorganic component, for example it exhibits a predominately metal oxide framework, the underlayer may advantageously be a carbon-based film, applied either by spin-coating or by dry vacuum-based deposition processes. The layer may include various ashable hard mask (AHM) films with carbon- and hydrogen-based compositions and may be doped with additional elements, such as tungsten, boron, nitrogen, or fluorine.

[0212] In some embodiments, a surface activation operation may be used to activate the surface (e.g., of the substrate and/or a film) for future operations. For example, for a SiO_x surface, a water or oxygen/hydrogen plasma may be used to create hydroxyl groups on the

surface. For a carbon- or hydrocarbon-based surface, various treatment (e.g., a water, hydrogen/oxygen, CO₂ plasma, or ozone treatment) may be used to create carboxylic acids/or hydroxyl groups. Such approaches can prove critical for improving the adhesion of resist features to the substrate, which might otherwise delaminate or lift off during handling or within the solvent during development.

[0213] Adhesion may also be enhanced by inducing roughness in the surface to increase the surface area available for interaction, as well as directly improve mechanical adhesion. For example, first a sputtering process using Ar or other non-reactive ion bombardment can be used to produce rough surfaces. Then, the surface can be terminated with a desired surface functionality as described above (e.g., hydroxyl and/or carboxylic acid groups). On carbon, a combination approach can be employed, in which a chemically reactive oxygen-containing plasma such as CO₂, O₂, or H₂O (or mixtures of H₂ and O₂) can be used to etch away a thin layer of film with local non-uniformity and simultaneously terminate with -OH, -OOH, or -COOH groups. This may be done with or without bias. In conjunction with the surface modification strategies mentioned above, this approach could serve the dual purpose of surface roughening and chemical activation of the substrate surface, either for direct adhesion to an inorganic metal-oxide based resist or as an intermediate surface modification for further functionalization.

[0214] In various embodiments, the surface (e.g., of the substrate and/or the film) 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. Such hydroxyl groups may be formed on the surface by surface treatment of a substrate using oxygen plasma, water plasma, or ozone. In other embodiments, the surface of the film can be treated to provide exposed hydroxyl groups, upon which a capping layer can be applied. In various embodiments, the hydroxyl-terminated metal oxide 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.

EUV exposure processes

[0215] EUV exposure of the film can provide EUV exposed areas having activated reactive centers including a metal atom (M), which are produced by EUV-mediated cleavage events. Such reactive centers can include dangling metal bonds, M-H groups, cleaved M-ligand groups, dimerized M-M bonds, or M-O-M bridges. In other embodiments, EUV exposure

provides cross-linked organic moieties by photopolymerizing ligands within the film; or EUV exposures releases gaseous by-products resulting from photolysis of bonds within a ligand.

5 [0216] EUV exposure can have a wavelength in the range of about 10 nm to about 20 nm in a vacuum ambient, such as a wavelength of from 10 nm to 15 nm, e.g., 13.5 nm. In particular, patterning can provide EUV exposed areas and EUV unexposed areas to form a pattern.

10 [0217] The present technology can include patterning using EUV, as well as 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 known methods and equipment.

20 [0218] In some EUV lithography techniques, an organic hardmask (e.g., an ashable hardmask of PECVD amorphous hydrogenated carbon) is patterned. During photoresist exposure, EUV radiation is absorbed in the resist and in the substrate below, producing highly energetic photoelectrons (e.g., about 100 eV) and in turn a cascade of low-energy secondary electrons (e.g., about 10 eV) that diffuse laterally by several nanometers. These electrons increase the extent of chemical reactions in the resist which increases its EUV dose sensitivity. However, a secondary electron pattern that is random in nature is superimposed on the optical image. This unwanted secondary electron exposure results in loss of resolution, observable line edge roughness (LER) and linewidth variation in the patterned resist. These defects are replicated in the material to be patterned during subsequent pattern transfer etching.

30 [0219] A vacuum-integrated metal hardmask process and related vacuum-integrated hardware that combines film formation (deposition/condensation) and optical lithography with the result of greatly improved EUV lithography (EUVL) performance – e.g. reduced line edge roughness – is disclosed herein.

[0220] In various embodiments described herein, a deposition (e.g., condensation) process (e.g., ALD or MOCVD carried out in a PECVD tool, such as the Lam Vector®) can be used

to form a thin film of a metal-containing film, such a photosensitive metal salt or metal-containing organic compound (organometallic compound), with a strong absorption in the EUV (e.g., at wavelengths on the order of 10 nm to 20 nm), for example at the wavelength of the EUVL light source (e.g., 13.5 nm = 91.8 eV). This film photo-decomposes upon EUV exposure and forms a metal mask that is the pattern transfer layer during subsequent etching (e.g., in a conductor etch tool, such as the Lam 2300® Kryo®).

[0221] Following deposition, the EUV-patternable thin film is patterned by exposure to a beam of EUV light, typically under relatively high vacuum. For EUV exposure, the metal-containing film can then be deposited in a chamber integrated with a lithography platform (e.g., a wafer stepper such as the TWINSCAN NXE: 3300B® platform supplied by ASML of Veldhoven, NL) and transferred under vacuum so as not to react before exposure. Integration with the lithography tool is facilitated by the fact that EUVL also requires a greatly reduced pressure given the strong optical absorption of the incident photons by ambient gases such as H₂O, O₂, etc. In other embodiments, the photosensitive metal film deposition and EUV exposure may be conducted in the same chamber.

Development processes, including dry development

[0222] EUV exposed or unexposed areas, as well as capping layers, can be removed by any useful development process. In one embodiment, the EUV exposed area can have activated reactive centers, such as dangling metal bonds, M-H groups, or dimerized M-M bonds. In particular embodiments, M-H groups can be selectively removed by employing one or more dry development processes (e.g., halide chemistry) or wet development processes. In other embodiments, M-M bonds can be selectively removed by employing a wet development process, e.g., use of hot ethanol and water to provide soluble M(OH)_n groups. In yet other embodiments, EUV exposed areas are removed by use of wet development (e.g., by using a positive tone developer). In some embodiments, EUV unexposed areas are removed by use of dry development.

[0223] Dry development processes can include use of halides, such as HCl- or HBr-based processes. While this disclosure is not limited to any particular theory or mechanism of operation, the approach is understood to leverage the chemical reactivity of the dry-deposited EUV photoresist films with the clean chemistry (e.g., HCl, HBr, and BCl₃) to form volatile products using vapors or plasma. The dry-deposited EUV photoresist films can be removed with etch rates of up to 1 nm/s. The quick removal of dry-deposited EUV photoresist films

by these chemistries is applicable to chamber cleaning, backside clean, bevel clean, and PR developing. Although the films can be removed using vapors at various temperatures (e.g., HCl or HBr at a temperature greater than -10°C , or BCl_3 at a temperature greater than 80°C , for example), a plasma can also be used to further accelerate or enhance the reactivity.

- 5 **[0224]** Plasma processes include transformer coupled plasma (TCP), inductively coupled plasma (ICP) or capacitively coupled plasma (CCP), employing known equipment and techniques. For example, a process may be conducted at a pressure of > 0.5 mTorr (e.g., such as from 1 mTorr to 100 mTorr), at a power level of < 1000 W (e.g., < 500 W). Temperatures may be from 30°C to 300°C (e.g., 30°C to 120°C), at flow rate of 100 to 1000 standard cubic centimeters per minute (sccm), e.g., about 500 sccm, for from 1 to 3000 seconds (e.g., 10
10 seconds to 600 seconds).

- [0225]** Where the halide reactant flows are of hydrogen gas and halide gas, a remote plasma/UV radiation is used to generate radicals from the H_2 and Cl_2 and/or Br_2 , and the hydrogen and halide radicals are flowed to the reaction chamber to contact the patterned EUV
15 photoresist on the substrate layer of the wafer. Suitable plasma power may range from 100 W to 500 W, with no bias. It should be understood that while these conditions are suitable for some processing reactors, e.g., a Kryo etch tool available from Lam Research Corporation, Fremont, CA, a wider range of process conditions may be used according to the capabilities of the processing reactor.

- 20 **[0226]** In thermal development processes, the substrate is exposed to dry development chemistry (e.g., a Lewis Acid) in a vacuum chamber (e.g., oven). Suitable chambers can include a vacuum line, a dry development hydrogen halide chemistry gas (e.g., HBr, HCl) line, and heaters for temperature control. In some embodiments, the chamber interior can be coated with corrosion resistant films, such as organic polymers or inorganic coatings. One
25 such coating is polytetrafluoroethylene ((PTFE), e.g., TeflonTM). Such materials can be used in thermal processes of this disclosure without risk of removal by plasma exposure.

- [0227]** The process conditions for the dry development may be reactant flow of 100 sccm to 500 sccm (e.g., 500 sccm HBr or HCl), temperature of -10°C to 120°C (e.g., -10°C), pressure of 1 mTorr to 500 mTorr (e.g., 300 mTorr) with no plasma and for a time of about
30 10 sec to 1 min, dependent on the photoresist film and capping layer and their composition and properties.

5 [0228] In various embodiments, methods of the present disclosure combine all dry steps of film deposition, formation by vapor deposition, (EUV) lithographic photopatterning, and dry development. In such processes, a substrate may directly go to a dry development/etch chamber following photopatterning in an EUV scanner. Such processes may avoid material and productivity costs associated with a wet development. A dry process can also provide more tunability and give further CD control and/or scum removal.

10 [0229] In various embodiments, the EUV photoresist, containing some amount of metal, metal oxide and organic components, can be dry developed by a thermal, plasma (e.g., including possibly photoactivated plasma, such as lamp-heated or UV lamp heated), or a mixture of thermal and plasma methods while flowing a dry development gas including a compound of formula R_xZ_y , where $R = B, Al, Si, C, S, SO$ with $x > 0$ and $Z = Cl, H, Br, F, CH_4$ and $y > 0$. The dry development can result in a positive tone, in which the R_xZ_y species selectively removes the exposed material, leaving behind the unexposed counterpart as a mask. In some embodiments, the exposed portions of organotin oxide-based photoresist films are removed by dry development in accordance with this disclosure. Positive tone dry development may be achieved by the selective dry development (removal) of EUV exposed regions exposed to flows comprising hydrogen halides or hydrogen and halides, including HCl and/or HBr without striking a plasma, or flows of H_2 and Cl_2 and/or Br_2 with a remote plasma or UV radiation generated from plasma to generate radicals.

20 [0230] In some embodiments, dry and wet operations can be combined to provide a dry/wet process. For any of the process herein (e.g., for lithographic processes, deposition processes, EUV exposure processes, development processes, pre-treatment processes, post-application processes, etc.), various specific operation can include wet, dry, or wet and dry embodiments. For instance, a wet deposition can be combined with a dry development; or wet deposition can be combined with wet development; or dry deposition can be combined with wet development; or dry deposition can be combined with dry development. Any of these, in turn, can be combined with wet or dry pre- and post-application processes, as described herein.

30 [0231] Thus, wet development methods can also be employed. In particular embodiments, such wet developments methods are used to remove EUV exposed regions to provide a positive tone photoresist or a negative tone resist. Exemplary, non-limiting wet development can include use of an alkaline developer (e.g., an aqueous alkaline developer), such as those including ammonium, e.g., ammonium hydroxide (NH_4OH); ammonium-based ionic liquids,

e.g., tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide (TEAH), tetrapropylammonium hydroxide (TPAH), tetrabutylammonium hydroxide (TBAH), or other quaternary alkylammonium hydroxides; an organoamine, such as mono-, di-, and tri-organamines (e.g., diethylamine, diethylamine, ethylenediamine, triethylenetetramine); or
 5 an alkanolamine, such as monoethanolamine, diethanolamine, triethanolamine, or diethyleneglycolamine. In other embodiments, the alkaline developer can include nitrogen-containing bases, e.g., compounds having the formula $R^{N1}NH_2$, $R^{N1}R^{N2}NH$, $R^{N1}R^{N2}R^{N3}N$, or $R^{N1}R^{N2}R^{N3}R^{N4}N^+X^{N1-}$, where each of R^{N1} , R^{N2} , R^{N3} , and R^{N4} is, independently, an organo substituent (e.g., optionally substituted alkyl or any described herein), or two or more organo
 10 substituents that can be joined together, and X^{N1-} may comprise OH^- , F^- , Cl^- , Br^- , I^- , or other art-known quaternary ammonium cationic species. These bases may also comprise heterocyclyl nitrogen compounds, some of which are described herein.

[0232] Other development methodologies can include use of an acidic developer (e.g., an aqueous acidic developer or an acid developer in an organic solvent) that includes a halide
 15 (e.g., HCl or HBr), an organic acid (e.g., formic acid, acetic acid, or citric acid), or an organofluorine compound (e.g., trifluoroacetic acid); or use of an organic developer, such as a ketone (e.g., 2-heptanone, cyclohexanone, or acetone), an ester (e.g., γ -butyrolactone or ethyl 3-ethoxypropionate (EEP)), an alcohol (e.g., isopropyl alcohol (IPA)), or an ether, such as a glycol ether (e.g., propylene glycol methyl ether (PGME) or propylene glycol methyl
 20 ether acetate (PGMEA)), as well as combinations thereof. Yet other development methodologies can include use of an aqueous developer (e.g., water).

[0233] In particular embodiments, the positive tone developer is an aqueous alkaline developer (e.g., including NH_4OH , TMAH, TEAH, TPAH, or TBAH). In other
 embodiments, the negative tone developer is an aqueous developer (e.g., water), an aqueous
 25 acidic developer, an acidic developer in an organic solvent, or an organic developer (e.g., HCl, HBr, formic acid, trifluoroacetic acid, 2-heptanone, IPA, PGME, PGMEA, or combinations thereof).

[0234] The composition of the film may affect its development. For instance, **FIG. 8** shows solid state ^{13}C -NMR spectra of a first film **801** (formed without an organic co-reactant)
 30 and a second film **802** (formed with an organic co-reactant). These data show that the second film **802** has a different ratio of 5-coordinated and 6-coordinated Sn atoms, as compared to the first film **801**, suggesting difference(s) in molecular structure.

[0235] FIG. 9 provides results for development of non-limiting films. The film included an organotin-based photoresist, which was exposed to varying radiation doses, incubated at various temperatures, developed with the indicated developer for 10 seconds, and then rinsed for 10 seconds (with the same solvent as the developer). After development, the thickness of the film was measured for each exposed dose.

[0236] In particular, FIG. 9 shows the use of water 901 or 2-heptanone 902 as the developer. Films were incubated at 175°C (for development with water) or at 100°C (for development with 2-heptanone). As can be seen, the same film can be developed with an aqueous solvent (e.g., water) or an organic solvent (e.g., 2-heptanone).

[0237] FIG. 10 shows line and space patterns obtained with a very low dose. In particular, films were patterned with interference EUV lithography, incubated at 210°C for 4 minutes, and then dry developed using halide chemistry. As can be seen, line and space patterns down to a pitch of 24 nm (P24, having alternating 12 nm lines and 12 nm spacing) was observed with the dose in the 20-30 mJ/cm² range.

15 *Post-application processes*

[0238] The methods herein can include any useful post-application processes, as described below.

[0239] For the backside and bevel clean process, the vapor and/or the plasma can be limited to a specific region of the wafer to ensure that only the backside and the bevel are removed, without any film degradation on the frontside of the wafer. The dry-deposited EUV photoresist films being removed are generally composed of Sn, O and C, but the same clean approaches can be extended to films of other metal oxide resists and materials. In addition, this approach can also be used for film strip and PR rework.

[0240] Suitable process conditions for a dry bevel edge and backside clean may be a reactant flow of 100 sccm to 500 sccm (e.g., 500 sccm HCl, HBr, or H₂ and Cl₂ or Br₂, BCl₃ or H₂), temperature of -10°C to 120°C (e.g., 20°C), pressure of 20 mTorr to 500 mTorr (e.g., 300 mTorr), plasma power of 0 to 500W at high frequency (e.g., 13.56 MHz), and for a time of about 10 sec to 20 sec, dependent on the photoresist film and composition and properties. It should be understood that while these conditions are suitable for some processing reactors, e.g., a Kiyo etch tool available from Lam Research Corporation, Fremont, CA, a wider range of process conditions may be used according to the capabilities of the processing reactor.

[0241] Photolithography processes typically involve one or more bake steps, to facilitate the chemical reactions required to produce chemical contrast between exposed and unexposed areas of the photoresist. For high volume manufacturing (HVM), such bake steps are typically performed on tracks where the wafers are baked on a hot-plate at a pre-set
5 temperature under ambient air or in some cases N₂ flow. More careful control of the bake ambient as well as introduction of additional reactive gas component in the ambient during these bake steps can help further reduce the dose requirement and/or improve pattern fidelity.

[0242] According to various aspects of this disclosure, one or more post treatments to metal and/or metal oxide-based photoresists after deposition (e.g., post-application bake (PAB))
10 and/or exposure (e.g., post-exposure bake (PEB)) and/or development (e.g., post-development bake (PDB)) are capable of increasing material property differences between exposed and unexposed photoresist and therefore decreasing dose to size (DtS), improving PR profile, and improving line edge and width roughness (LER/LWR) after subsequent dry development. Such processing can involve a thermal process with the control of temperature,
15 gas ambient, and moisture, resulting in improved dry development performance in processing to follow. In some instances, a remote plasma might be used.

[0243] In the case of post-application processing (e.g., PAB), a thermal process with control of temperature, gas ambient (e.g., air, H₂O, CO₂, CO, O₂, O₃, CH₄, CH₃OH, N₂, H₂, NH₃, N₂O, NO, Ar, He, or their mixtures) or under vacuum, and moisture can be used after
20 deposition and before exposure to change the composition of unexposed metal and/or metal oxide photoresist. The change can increase the EUV sensitivity of the material and thus lower dose to size and edge roughness can be achieved after exposure and dry development.

[0244] In the case of post-exposure processing (e.g., PEB), a thermal process with the control of temperature, gas atmosphere (e.g., air, H₂O, CO₂, CO, O₂, O₃, CH₄, CH₃OH, N₂,
25 H₂, NH₃, N₂O, NO, Ar, He, or their mixtures) or under vacuum, and moisture can be used to change the composition of both unexposed and exposed photoresist. The change can increase the composition/material properties difference between the unexposed and exposed photoresist and the etch rate difference of dry development etch gas between the unexposed and exposed photoresist. A higher etch selectivity can thereby be achieved. Due to the
30 improved selectivity, a squarer PR profile can be obtained with improved surface roughness, and/or less photoresist residual/scum. In particular embodiments, PEB can be performed in air and in the optional presence of moisture and CO₂.

[0245] In the case of post-development processing (e.g., post development bake or PDB), a thermal process with the control of temperature, gas atmosphere (e.g., air, H₂O, CO₂, CO, O₂, O₃, CH₄, CH₃OH, N₂, H₂, NH₃, N₂O, NO, Ar, He, or their mixtures) or under vacuum (e.g., with UV), and moisture can be used to change the composition of the unexposed photoresist.

5 In particular embodiments, the condition also includes use of plasma (e.g., including O₂, O₃, Ar, He, or their mixtures). The change can increase the hardness of material, which can be beneficial if the film will be used as a resist mask when etching the underlying substrate.

[0246] In these cases, in alternative implementations, the thermal process could be replaced by a remote plasma process to increase reactive species to lower the energy barrier for the
10 reaction and increase productivity. Remote plasma can generate more reactive radicals and therefore lower the reaction temperature/time for the treatment, leading to increased productivity.

[0247] Accordingly, one or multiple processes may be applied to modify the photoresist itself to increase dry development selectivity. This thermal or radical modification can
15 increase the contrast between unexposed and exposed material and thus increase the selectivity of the subsequent dry development step. The resulting difference between the material properties of unexposed and exposed material can be tuned by adjusting process conditions including temperature, gas flow, moisture, pressure, and/or RF power. The large process latitude enabled by dry development, which is not limited by material solubility in a
20 wet developer solvent, allows more aggressive conditions to be applied further enhancing the material contrast that can be achieved. The resulting high material contrast feeds back a wider process window for dry development and thus enables increased productivity, lower cost, and better defectivity performance.

[0248] A substantial limitation of wet-developed resist films is limited temperature bakes.
25 Since wet development relies on material solubility, heating to or beyond 220°C, for example, can greatly increase the degree of cross-linking in both exposed and unexposed regions of a metal-containing PR film such that both become insoluble in the wet development solvents, so that the film can no longer be reliably wet developed. For instance, for wet spin-on or wet-developed metal-containing PR films, baking such as PAB, PEB may
30 be performed, for example at temperatures below 180°C or below 200°C. For dry-developed resist films, in which the etch rate difference (i.e., selectivity) between the exposed and unexposed regions of the PR is relied upon for removal of just the exposed or unexposed portion of the resist, the treatment temperature in a PAB, PEB, or PDB can be varied across a

much broader window to tune and optimize the treatment process, for example from about 90°C to 250°C, such as 90°C to 190°C, 90°C to 600° C, 100°C to 400°C, 125°C to 300° C, and about 170°C to 250°C or more, such as 190°C to 240°C (e.g., for PAB, PEB, and/or PDB). Decreasing etch rate and greater etch selectivity has been found to occur with higher
5 treatment temperatures in the noted ranges.

[0249] In particular embodiments, the PAB, PEB, and/or PDB treatments may be conducted with gas ambient flow in the range of 100 sccm to 10000 sccm, moisture content in the amount of a few percent up to 100% (e.g., 20%-50%), at a pressure between atmospheric and vacuum, and for a duration of about 1 to 15 minutes, for example about 2
10 minutes.

[0250] These findings can be used to tune the treatment conditions to tailor or optimize processing for particular materials and circumstances. For example, the selectivity achieved for a given EUV dose with a 220°C to 250°C PEB thermal treatment in air at about 20% humidity for about 2 minutes can be made similar to that for about a 30% higher EUV dose
15 with no such thermal treatment. So, depending on the selectivity requirements/constraints of the semiconductor processing operation, a thermal treatment such as described herein can be used to lower the EUV dose needed. Or, if higher selectivity is required and higher dose can be tolerated, much higher selectivity, up to 100 times exposed vs. unexposed, can be obtained than would be possible in a wet development context.

[0251] Yet other steps can include in situ metrology, in which physical and structural characteristics (e.g., critical dimension, film thickness, etc.) can be assessed during the photolithography process. Modules to implement in situ metrology include, e.g., scatterometry, ellipsometry, downstream mass spectroscopy, and/or plasma enhanced
20 downstream optical emission spectroscopy modules.

25 *Apparatuses*

[0252] The present disclosure also includes any apparatus configured to perform any methods described herein. In one embodiment, the apparatus for depositing a film includes a deposition module comprising a chamber for depositing an EUV-sensitive material as a film by providing an initial precursor in the presence of an organic co-reactant; a patterning
30 module comprising an EUV photolithography tool with a source of sub-30 nm wavelength radiation; and a development module comprising a chamber for developing the film.

[0253] The apparatus can further include a controller having instructions for such modules. In one embodiment, the controller includes one or more memory devices, one or more processors, and system control software coded with instructions for conducting deposition of the film or the capping layer. Such includes can include for, in the deposition module, depositing a modified precursor as a film on a top surface of a substrate or a photoresist layer; in the patterning module, patterning the film with sub-30 nm resolution directly by EUV exposure, thereby forming a pattern within the film; and in the development module, developing the film. In particular embodiments, the development module provides for removal of the EUV exposed or EUV unexposed areas, thereby providing a pattern within the film.

[0254] FIG. 4 depicts a schematic illustration of an embodiment of process station 400 having a process chamber body 402 for maintaining a low pressure environment that is suitable for implementation of described dry stripping and development embodiments. A plurality of process stations 400 may be included in a common low pressure process tool environment. For example, FIG. 5 depicts an embodiment of a multi-station processing tool 500, such as a VECTOR® processing tool available from Lam Research Corporation, Fremont, CA. In some embodiments, one or more hardware parameters of the process station 400 including those discussed in detail below may be adjusted programmatically by one or more computer controllers 450.

[0255] A process station may be configured as a module in a cluster tool. FIG. 7 depicts a semiconductor process cluster tool architecture with vacuum-integrated deposition and patterning modules suitable for implementation of the embodiments described herein. Such a cluster process tool architecture can include resist deposition, resist exposure (EUV scanner), resist dry development and etch modules, as described herein with reference to FIG. 6 and FIG. 7.

[0256] In some embodiments, certain of the processing functions can be performed consecutively in the same module, for example dry development and etch. And embodiments of this disclosure are directed to methods and apparatus for receiving a wafer, including a photopatterned EUV resist thin film layer disposed on a layer or layer stack to be etched, to a dry development/etch chamber following photopatterning in an EUV scanner; dry developing photopatterned EUV resist thin film layer; and then etching the underlying layer using the patterned EUV resist as a mask, as described herein.

[0257] Returning to FIG. 4, process station 400 fluidly communicates with reactant delivery system 401a for delivering process gases to a distribution showerhead 406 by a connection 405. Reactant delivery system 401a optionally includes a mixing vessel 404 for blending and/or conditioning process gases, for delivery to showerhead 406. One or more mixing vessel inlet valves 420 may control introduction of process gases to mixing vessel 404. Where plasma exposure is used, plasma may also be delivered to the showerhead 406 or may be generated in the process station 400. Process gases can include, e.g., any described herein, such as an organic co-reactant, an initial precursor, or a counter-reactant.

[0258] FIG. 4 includes an optional vaporization point 403 for vaporizing liquid reactant to be supplied to the mixing vessel 404. The liquid reactant can include an organic co-reactant, an initial precursor, or a counter-reactant. In some embodiments, a liquid flow controller (LFC) upstream of vaporization point 403 may be provided for controlling a mass flow of liquid for vaporization and delivery to process station 400. For example, the LFC may include a thermal mass flow meter (MFM) located downstream of the LFC. A plunger valve of the LFC may then be adjusted responsive to feedback control signals provided by a proportional-integral-derivative (PID) controller in electrical communication with the MFM.

[0259] Showerhead 406 distributes process gases toward substrate 412. In the embodiment shown in FIG. 4, the substrate 412 is located beneath showerhead 406 and is shown resting on a pedestal 408. Showerhead 406 may have any suitable shape and may have any suitable number and arrangement of ports for distributing process gases to substrate 412.

[0260] In some embodiments, pedestal 408 may be raised or lowered to expose substrate 412 to a volume between the substrate 412 and the showerhead 406. It will be appreciated that, in some embodiments, pedestal height may be adjusted programmatically by a suitable computer controller 450.

[0261] In some embodiments, pedestal 408 may be temperature controlled via heater 410. In some embodiments, the pedestal 408 may be heated to a temperature of greater than 0°C and up to 300°C or more, for example 50°C to 120°C, such as about 65°C to 80°C, during non-plasma thermal exposure of a photopatterned resist to dry development chemistry, such as HBr, HCl, or BCl₃, as described in disclosed embodiments.

[0262] Further, in some embodiments, pressure control for process station 400 may be provided by a butterfly valve 418. As shown in the embodiment of FIG. 4, butterfly valve 418 throttles a vacuum provided by a downstream vacuum pump (not shown). However, in

some embodiments, pressure control of process station 400 may also be adjusted by varying a flow rate of one or more gases introduced to the process station 400.

5 [0263] In some embodiments, a position of showerhead 406 may be adjusted relative to pedestal 408 to vary a volume between the substrate 412 and the showerhead 406. Further, it will be appreciated that a vertical position of pedestal 408 and/or showerhead 406 may be varied by any suitable mechanism within the scope of the present disclosure. In some embodiments, pedestal 408 may include a rotational axis for rotating an orientation of substrate 412. It will be appreciated that, in some embodiments, one or more of these example adjustments may be performed programmatically by one or more suitable computer
10 controllers 450.

[0264] Where plasma may be used, for example in gentle plasma-based dry development embodiments and /or etch operations conducted in the same chamber, showerhead 406 and pedestal 408 electrically communicate with a radio frequency (RF) power supply 414 and matching network 416 for powering a plasma 407. In some embodiments, the plasma energy
15 may be controlled by controlling one or more of a process station pressure, a gas concentration, an RF source power, an RF source frequency, and a plasma power pulse timing. For example, RF power supply 414 and matching network 416 may be operated at any suitable power to form a plasma having a desired composition of radical species. Examples of suitable powers are up to about 500 W.

20 [0265] In some embodiments, instructions for a controller 450 may be provided via input/output control (IOC) sequencing instructions. In one example, the instructions for setting conditions for a process phase may be included in a corresponding recipe phase of a process recipe. In some cases, process recipe phases may be sequentially arranged, so that all instructions for a process phase are executed concurrently with that process phase. In some
25 embodiments, instructions for setting one or more reactor parameters may be included in a recipe phase. For example, a recipe phase may include instructions for setting a flow rate of a dry development chemistry reactant gas, such as HBr or HCl, and time delay instructions for the recipe phase. In some embodiments, the controller 450 may include any of the features described below with respect to system controller 550 of FIG. 5.

30 [0266] As described above, one or more process stations may be included in a multi station processing tool. FIG. 5 shows a schematic view of an embodiment of a multi station processing tool 500 with an inbound load lock 502 and an outbound load lock 504, either or

both of which may include a remote plasma source. A robot 506 at atmospheric pressure is configured to move wafers from a cassette loaded through a pod 508 into inbound load lock 502 via an atmospheric port 510. A wafer is placed by the robot 506 on a pedestal 512 in the inbound load lock 502, the atmospheric port 510 is closed, and the load lock is pumped

5 down. Where the inbound load lock 502 includes a remote plasma source, the wafer may be exposed to a remote plasma treatment to treat the silicon nitride surface in the load lock prior to being introduced into a processing chamber 514. Further, the wafer also may be heated in the inbound load lock 502 as well, for example, to remove moisture and adsorbed gases. Next, a chamber transport port 516 to processing chamber 514 is opened, and another robot
10 (not shown) places the wafer into the reactor on a pedestal of a first station shown in the reactor for processing. While the embodiment depicted in FIG. 5 includes load locks, it will be appreciated that, in some embodiments, direct entry of a wafer into a process station may be provided.

[0267] The depicted processing chamber 514 includes four process stations, numbered
15 from 1 to 4 in the embodiment shown in FIG. 5. Each station has a heated pedestal (shown at 518 for station 1), and gas line inlets. It will be appreciated that in some embodiments, each process station may have different or multiple purposes. For example, in some embodiments, a process station may be switchable between dry development and etch process modes. Additionally or alternatively, in some embodiments, processing chamber 514
20 may include one or more matched pairs of dry development and etch process stations. While the depicted processing chamber 514 includes four stations, it will be understood that a processing chamber according to the present disclosure may have any suitable number of stations. For example, in some embodiments, a processing chamber may have five or more stations, while in other embodiments a processing chamber may have three or fewer stations.

25 [0268] FIG. 5 depicts an embodiment of a wafer handling system 590 for transferring wafers within processing chamber 514. In some embodiments, wafer handling system 590 may transfer wafers between various process stations and/or between a process station and a load lock. It will be appreciated that any suitable wafer handling system may be employed. Non limiting examples include wafer carousels and wafer handling robots. FIG. 5 also
30 depicts an embodiment of a system controller 550 employed to control process conditions and hardware states of process tool 500. System controller 550 may include one or more memory devices 556, one or more mass storage devices 554, and one or more processors 552.

Processor 552 may include a CPU or computer, analog, and/or digital input/output connections, stepper motor controller boards, etc.

[0269] In some embodiments, system controller 550 controls all of the activities of process tool 500. System controller 550 executes system control software 558 stored in mass storage device 554, loaded into memory device 556, and executed on processor 552. Alternatively, the control logic may be hard coded in the controller 550. Applications Specific Integrated Circuits, Programmable Logic Devices (e.g., field-programmable gate arrays, or FPGAs) and the like may be used for these purposes. In the following discussion, wherever “software” or “code” is used, functionally comparable hard coded logic may be used in its place. System control software 558 may include instructions for controlling the timing, mixture of gases, gas flow rates, chamber and/or station pressure, chamber and/or station temperature, wafer temperature, target power levels, RF power levels, substrate pedestal, chuck and/or susceptor position, and other parameters of a particular process performed by process tool 500. System control software 558 may be configured in any suitable way. For example, various process tool component subroutines or control objects may be written to control operation of the process tool components used to carry out various process tool processes. System control software 558 may be coded in any suitable computer readable programming language.

[0270] In some embodiments, system control software 558 may include input/output control (IOC) sequencing instructions for controlling the various parameters described above. Other computer software and/or programs stored on mass storage device 554 and/or memory device 556 associated with system controller 550 may be employed in some embodiments. Examples of programs or sections of programs for this purpose include a substrate positioning program, a process gas control program, a pressure control program, a heater control program, and a plasma control program.

[0271] A substrate positioning program may include program code for process tool components that are used to load the substrate onto pedestal 518 and to control the spacing between the substrate and other parts of process tool 500.

[0272] A process gas control program may include code for controlling various gas compositions (e.g., HBr or HCl gas as described herein) and flow rates and optionally for flowing gas into one or more process stations prior to deposition in order to stabilize the pressure in the process station. A pressure control program may include code for controlling

the pressure in the process station by regulating, for example, a throttle valve in the exhaust system of the process station, a gas flow into the process station, etc.

5 [0273] A heater control program may include code for controlling the current to a heating unit that is used to heat the substrate. Alternatively, the heater control program may control delivery of a heat transfer gas (such as helium) to the substrate.

[0274] A plasma control program may include code for setting RF power levels applied to the process electrodes in one or more process stations in accordance with the embodiments herein.

10 [0275] A pressure control program may include code for maintaining the pressure in the reaction chamber in accordance with the embodiments herein.

[0276] In some embodiments, there may be a user interface associated with system controller 550. The user interface may include a display screen, graphical software displays of the apparatus and/or process conditions, and user input devices such as pointing devices, keyboards, touch screens, microphones, etc.

15 [0277] In some embodiments, parameters adjusted by system controller 550 may relate to process conditions. Non-limiting examples include process gas composition and flow rates, temperature, pressure, plasma conditions (such as RF bias power levels), etc. These parameters may be provided to the user in the form of a recipe, which may be entered utilizing the user interface.

20 [0278] Signals for monitoring the process may be provided by analog and/or digital input connections of system controller 550 from various process tool sensors. The signals for controlling the process may be output on the analog and digital output connections of process tool 500. Non-limiting examples of process tool sensors that may be monitored include mass flow controllers, pressure sensors (such as manometers), thermocouples, etc. Appropriately
25 programmed feedback and control algorithms may be used with data from these sensors to maintain process conditions.

[0279] System controller 550 may provide program instructions for implementing the above-described deposition processes. The program instructions may control a variety of process parameters, such as DC power level, RF bias power level, pressure, temperature, etc.
30 The instructions may control the parameters to operate dry development and/or etch processes according to various embodiments described herein.

5 **[0280]** The system controller **550** will typically include one or more memory devices and one or more processors configured to execute the instructions so that the apparatus will perform a method in accordance with disclosed embodiments. Machine-readable media containing instructions for controlling process operations in accordance with disclosed
embodiments may be coupled to the system controller **550**.

10 **[0281]** In some implementations, the system controller **550** is part of a system, which may be part of the above-described examples. Such systems can include semiconductor processing equipment, including a processing tool or tools, chamber or chambers, a platform or platforms for processing, and/or specific processing components (a wafer pedestal, a gas
flow system, etc.). These systems may be integrated with electronics for controlling their operation before, during, and after processing of a semiconductor wafer or substrate. The electronics may be referred to as the “controller,” which may control various components or subparts of the system or systems. The system controller **550**, depending on the processing
15 conditions and/or the type of system, may be programmed to control any of the processes disclosed herein, including the delivery of processing gases, temperature settings (e.g., heating and/or cooling), pressure settings, vacuum settings, power settings, radio frequency (RF) generator settings, RF matching circuit settings, frequency settings, flow rate settings, fluid delivery settings, positional and operation settings, wafer transfers into and out of a tool and other transfer tools and/or load locks connected to or interfaced with a specific system.

20 **[0282]** Broadly speaking, the system controller **550** may be defined as electronics having various integrated circuits, logic, memory, and/or software that receive instructions, issue instructions, control operation, enable cleaning operations, enable endpoint measurements, and the like. The integrated circuits may include chips in the form of firmware that store program instructions, digital signal processors (DSPs), chips defined as application specific
25 integrated circuits (ASICs), and/or one or more microprocessors, or microcontrollers that execute program instructions (e.g., software). Program instructions may be instructions communicated to the system controller **550** in the form of various individual settings (or program files), defining operational parameters for carrying out a particular process on or for a semiconductor wafer or to a system. The operational parameters may, in some
30 embodiments, be part of a recipe defined by process engineers to accomplish one or more processing steps during the fabrication of one or more layers, materials, metals, oxides, silicon, silicon dioxide, surfaces, circuits, and/or dies of a wafer.

[0283] The system controller 550, in some implementations, may be a part of or coupled to a computer that is integrated with, coupled to the system, otherwise networked to the system, or a combination thereof. For example, the system controller 550 may be in the “cloud” or all or a part of a fab host computer system, which can allow for remote access of the wafer processing. The computer may enable remote access to the system to monitor current progress of fabrication operations, examine a history of past fabrication operations, examine trends or performance metrics from a plurality of fabrication operations, to change parameters of current processing, to set processing steps to follow a current processing, or to start a new process. In some examples, a remote computer (e.g. a server) can provide process recipes to a system over a network, which may include a local network or the Internet. The remote computer may include a user interface that enables entry or programming of parameters and/or settings, which are then communicated to the system from the remote computer. In some examples, the system controller 550 receives instructions in the form of data, which specify parameters for each of the processing steps to be performed during one or more operations. It should be understood that the parameters may be specific to the type of process to be performed and the type of tool that the system controller 550 is configured to interface with or control. Thus, as described above, the system controller 550 may be distributed, such as by including one or more discrete controllers that are networked together and working towards a common purpose, such as the processes and controls described herein. An example of a distributed controller for such purposes would be one or more integrated circuits on a chamber in communication with one or more integrated circuits located remotely (such as at the platform level or as part of a remote computer) that combine to control a process on the chamber.

[0284] Without limitation, example systems may include a plasma etch chamber or module, a deposition chamber or module, a spin-rinse chamber or module, a metal plating chamber or module, a clean chamber or module, a bevel edge etch chamber or module, a physical vapor deposition (PVD) chamber or module, a chemical vapor deposition (CVD) chamber or module, an ALD chamber or module, an atomic layer etch (ALE) chamber or module, an ion implantation chamber or module, a track chamber or module, an EUV lithography chamber (scanner) or module, a dry development chamber or module, and any other semiconductor processing systems that may be associated or used in the fabrication and/or manufacturing of semiconductor wafers.

[0285] As noted above, depending on the process step or steps to be performed by the tool, the system controller 550 might communicate with one or more of other tool circuits or modules, other tool components, cluster tools, other tool interfaces, adjacent tools, neighboring tools, tools located throughout a factory, a main computer, another controller, or tools used in material transport that bring containers of wafers to and from tool locations and/or load ports in a semiconductor manufacturing factory.

[0286] Inductively coupled plasma (ICP) reactors which, in certain embodiments, may be suitable for etch operations suitable for implementation of some embodiments, are now described. Although ICP reactors are described herein, in some embodiments, it should be understood that capacitively coupled plasma reactors may also be used.

[0287] FIG. 6 schematically shows a cross-sectional view of an inductively coupled plasma apparatus 600 appropriate for implementing certain embodiments or aspects of embodiments such as dry development and/or etch, an example of which is a Kiyo® reactor, produced by Lam Research Corp. of Fremont, CA. In other embodiments, other tools or tool types having the functionality to conduct the dry development and/or etch processes described herein may be used for implementation.

[0288] The inductively coupled plasma apparatus 600 includes an overall process chamber structurally defined by chamber walls 601 and a window 611. The chamber walls 601 may be fabricated from stainless steel or aluminum. The window 611 may be fabricated from quartz or other dielectric material. An optional internal plasma grid 650 divides the overall process chamber into an upper sub-chamber 602 and a lower sub-chamber 603. In most embodiments, plasma grid 650 may be removed, thereby utilizing a chamber space made of sub-chambers 602 and 603. A chuck 617 is positioned within the lower sub-chamber 603 near the bottom inner surface. The chuck 617 is configured to receive and hold a semiconductor wafer 619 upon which the etching and deposition processes are performed. The chuck 617 can be an electrostatic chuck for supporting the wafer 619 when present. In some embodiments, an edge ring (not shown) surrounds the chuck 617 and has an upper surface that is approximately planar with a top surface of the wafer 619, when present over the chuck 617. The chuck 617 also includes electrostatic electrodes for chucking and dechucking the wafer 619. A filter and DC clamp power supply (not shown) may be provided for this purpose.

[0289] Other control systems for lifting the wafer 619 off the chuck 617 can also be provided. The chuck 617 can be electrically charged using an RF power supply 623. The RF power supply 623 is connected to matching circuitry 621 through a connection 627. The matching circuitry 621 is connected to the chuck 617 through a connection 625. In this manner, the RF power supply 623 is connected to the chuck 617. In various embodiments, a bias power of the electrostatic chuck may be set at about 50 V or may be set at a different bias power depending on the process performed in accordance with disclosed embodiments. For example, the bias power may be between about 20 V and about 100 V, or between about 30 V and about 150 V.

[0290] Elements for plasma generation include a coil 633 positioned above window 611. In some embodiments, a coil is not used in disclosed embodiments. The coil 633 is fabricated from an electrically conductive material and includes at least one complete turn. The example of a coil 633 shown in FIG. 6 includes three turns. The cross sections of coil 633 are shown with symbols, and coils having an "X" extend rotationally into the page, while coils having a "•" extend rotationally out of the page. Elements for plasma generation also include an RF power supply 641 configured to supply RF power to the coil 633. In general, the RF power supply 641 is connected to matching circuitry 639 through a connection 645. The matching circuitry 639 is connected to the coil 633 through a connection 643. In this manner, the RF power supply 641 is connected to the coil 633. An optional Faraday shield 649 is positioned between the coil 633 and the window 611. The Faraday shield 649 may be maintained in a spaced apart relationship relative to the coil 633. In some embodiments, the Faraday shield 649 is disposed immediately above the window 611. In some embodiments, a Faraday shield is between the window 611 and the chuck 617. In some embodiments, the Faraday shield is not maintained in a spaced apart relationship relative to the coil 633. For example, a Faraday shield may be directly below the window without a gap. The coil 633, the Faraday shield 649, and the window 611 are each configured to be substantially parallel to one another. The Faraday shield 649 may prevent metal or other species from depositing on the window 611 of the process chamber.

[0291] Process gases may be flowed into the process chamber through one or more main gas flow inlets 660 positioned in the upper sub-chamber 602 and/or through one or more side gas flow inlets 670. Likewise, though not explicitly shown, similar gas flow inlets may be used to supply process gases to a capacitively coupled plasma processing chamber. A vacuum pump, e.g., a one or two stage mechanical dry pump and/or turbomolecular pump

640, may be used to draw process gases out of the process chamber and to maintain a pressure within the process chamber. For example, the vacuum pump may be used to evacuate the lower sub-chamber 603 during a purge operation of ALD. A valve-controlled conduit may be used to fluidically connect the vacuum pump to the process chamber so as to
5 selectively control application of the vacuum environment provided by the vacuum pump. This may be done employing a closed loop-controlled flow restriction device, such as a throttle valve (not shown) or a pendulum valve (not shown), during operational plasma processing. Likewise, a vacuum pump and valve controlled fluidic connection to the capacitively coupled plasma processing chamber may also be employed.

10 [0292] During operation of the apparatus 600, one or more process gases may be supplied through the gas flow inlets 660 and/or 670. In certain embodiments, process gas may be supplied only through the main gas flow inlet 660, or only through the side gas flow inlet 670. In some cases, the gas flow inlets shown in the figure may be replaced by more complex gas flow inlets, one or more showerheads, for example. The Faraday shield 649
15 and/or optional grid 650 may include internal channels and holes that allow delivery of process gases to the process chamber. Either or both of Faraday shield 649 and optional grid 650 may serve as a showerhead for delivery of process gases. In some embodiments, a liquid vaporization and delivery system may be situated upstream of the process chamber, such that once a liquid reactant or precursor is vaporized, the vaporized reactant or precursor is
20 introduced into the process chamber via a gas flow inlet 660 and/or 670.

[0293] Radio frequency power is supplied from the RF power supply 641 to the coil 633 to cause an RF current to flow through the coil 633. The RF current flowing through the coil 633 generates an electromagnetic field about the coil 633. The electromagnetic field generates an inductive current within the upper sub-chamber 602. The physical and chemical
25 interactions of various generated ions and radicals with the wafer 619 etch features of and selectively deposit layers on the wafer 619.

[0294] If the plasma grid 650 is used such that there is both an upper sub-chamber 602 and a lower sub-chamber 603, the inductive current acts on the gas present in the upper sub-chamber 602 to generate an electron-ion plasma in the upper sub-chamber 602. The optional
30 internal plasma grid 650 limits the amount of hot electrons in the lower sub-chamber 603. In some embodiments, the apparatus 600 is designed and operated such that the plasma present in the lower sub-chamber 603 is an ion-ion plasma.

[0295] Both the upper electron-ion plasma and the lower ion-ion plasma may contain positive and negative ions, though the ion-ion plasma will have a greater ratio of negative ions to positive ions. Volatile etching and/or deposition byproducts may be removed from the lower sub-chamber 603 through port 622. The chuck 617 disclosed herein may operate at
5 elevated temperatures ranging between about 10°C and about 250°C. The temperature will depend on the process operation and specific recipe.

[0296] Apparatus 600 may be coupled to facilities (not shown) when installed in a clean room or a fabrication facility. Facilities include plumbing that provide processing gases, vacuum, temperature control, and environmental particle control. These facilities are coupled
10 to apparatus 600, when installed in the target fabrication facility. Additionally, apparatus 600 may be coupled to a transfer chamber that allows robotics to transfer semiconductor wafers into and out of apparatus 600 using typical automation.

[0297] In some embodiments, a system controller 630 (which may include one or more physical or logical controllers) controls some or all of the operations of a process chamber.
15 The system controller 630 may include one or more memory devices and one or more processors. In some embodiments, the apparatus 600 includes a switching system for controlling flow rates and durations when disclosed embodiments are performed. In some embodiments, the apparatus 600 may have a switching time of up to about 600 ms, or up to about 750 ms. Switching time may depend on the flow chemistry, recipe chosen, reactor
20 architecture, and other factors.

[0298] In some implementations, the system controller 630 is part of a system, which may be part of the above-described examples. Such systems can include semiconductor processing equipment, including a processing tool or tools, chamber or chambers, a platform or platforms for processing, and/or specific processing components (a wafer pedestal, a gas
25 flow system, etc.). These systems may be integrated with electronics for controlling their operation before, during, and after processing of a semiconductor wafer or substrate. The electronics may be integrated into the system controller 630, which may control various components or subparts of the system or systems. The system controller, depending on the processing parameters and/or the type of system, may be programmed to control any of the
30 processes disclosed herein, including the delivery of processing gases, temperature settings (e.g., heating and/or cooling), pressure settings, vacuum settings, power settings, radio frequency (RF) generator settings, RF matching circuit settings, frequency settings, flow rate settings, fluid delivery settings, positional and operation settings, wafer transfers into and out

of a tool and other transfer tools and/or load locks connected to or interfaced with a specific system.

[0299] Broadly speaking, the system controller 630 may be defined as electronics having various integrated circuits, logic, memory, and/or software that receive instructions, issue instructions, control operation, enable cleaning operations, enable endpoint measurements, and the like. The integrated circuits may include chips in the form of firmware that store program instructions, digital signal processors (DSPs), chips defined as application specific integrated circuits (ASICs), and/or one or more microprocessors, or microcontrollers that execute program instructions (e.g., software). Program instructions may be instructions communicated to the controller in the form of various individual settings (or program files), defining operational parameters for carrying out a particular process on or for a semiconductor wafer or to a system. The operational parameters may, in some embodiments, be part of a recipe defined by process engineers to accomplish one or more processing steps during the fabrication or removal of one or more layers, materials, metals, oxides, silicon, silicon dioxide, surfaces, circuits, and/or dies of a wafer.

[0300] The system controller 630, in some implementations, may be a part of or coupled to a computer that is integrated with, coupled to the system, otherwise networked to the system, or a combination thereof. For example, the controller may be in the “cloud” or all or a part of a fab host computer system, which can allow for remote access of the wafer processing. The computer may enable remote access to the system to monitor current progress of fabrication operations, examine a history of past fabrication operations, examine trends or performance metrics from a plurality of fabrication operations, to change parameters of current processing, to set processing steps to follow a current processing, or to start a new process. In some examples, a remote computer (e.g. a server) can provide process recipes to a system over a network, which may include a local network or the Internet. The remote computer may include a user interface that enables entry or programming of parameters and/or settings, which are then communicated to the system from the remote computer. In some examples, the system controller 630 receives instructions in the form of data, which specify parameters for each of the processing steps to be performed during one or more operations. It should be understood that the parameters may be specific to the type of process to be performed and the type of tool that the controller is configured to interface with or control. Thus, as described above, the system controller 630 may be distributed, such as by including one or more discrete controllers that are networked together and working towards a common purpose,

such as the processes and controls described herein. An example of a distributed controller for such purposes would be one or more integrated circuits on a chamber in communication with one or more integrated circuits located remotely (such as at the platform level or as part of a remote computer) that combine to control a process on the chamber.

5 **[0301]** Without limitation, example systems may include a plasma etch chamber or module, a deposition chamber or module, a spin-rinse chamber or module, a metal plating chamber or module, a clean chamber or module, a bevel edge etch chamber or module, a physical vapor deposition (PVD) chamber or module, a chemical vapor deposition (CVD) chamber or module, an ALD chamber or module, an ALE chamber or module, an ion implantation
10 chamber or module, a track chamber or module, an EUV lithography chamber (scanner) or module, a dry development chamber or module, and any other semiconductor processing systems that may be associated or used in the fabrication and/or manufacturing of semiconductor wafers.

[0302] As noted above, depending on the process step or steps to be performed by the tool,
15 the controller might communicate with one or more of other tool circuits or modules, other tool components, cluster tools, other tool interfaces, adjacent tools, neighboring tools, tools located throughout a factory, a main computer, another controller, or tools used in material transport that bring containers of wafers to and from tool locations and/or load ports in a semiconductor manufacturing factory.

20 **[0303]** EUVL patterning may be conducted using any suitable tool, often referred to as a scanner, for example the TWINSCAN NXE: 3300B® platform supplied by ASML of Veldhoven, NL. The EUVL patterning tool may be a standalone device from which the substrate is moved into and out of for deposition and etching as described herein. Or, as described below, the EUVL patterning tool may be a module on a larger multi-component
25 tool. **FIG. 7** depicts a semiconductor process cluster tool architecture with vacuum-integrated deposition, EUV patterning and dry development/etch modules that interface with a vacuum transfer module, suitable for implementation of the processes described herein. While the processes may be conducted without such vacuum integrated apparatus, such apparatus may be advantageous in some implementations.

30 **[0304]** **FIG. 7** depicts a semiconductor process cluster tool architecture with vacuum-integrated deposition and patterning modules that interface with a vacuum transfer module, suitable for implementation of processes described herein. The arrangement of transfer

modules to “transfer” wafers among multiple storage facilities and processing modules may be referred to as a “cluster tool architecture” system. Deposition and patterning modules are vacuum-integrated, in accordance with the requirements of a particular process. Other modules, such as for etch, may also be included on the cluster.

5 **[0305]** A vacuum transport module (VTM) **738** interfaces with four processing modules **720a-720d**, which may be individually optimized to perform various fabrication processes. By way of example, processing modules **720a-720d** may be implemented to perform deposition, evaporation, ELD, dry development, etch, strip, and/or other semiconductor processes. For example, module **720a** may be an ALD reactor that may be operated to
10 perform in a non-plasma, thermal atomic layer depositions as described herein, such as a Vector tool, available from Lam Research Corporation, Fremont, CA. And module **720b** may be a PECVD tool, such as the Lam Vector®. It should be understood that the figure is not necessarily drawn to scale.

[0306] Airlocks **742** and **746**, also known as a loadlocks or transfer modules, interface with
15 the VTM **738** and a patterning module **740**. For example, as noted above, a suitable patterning module may be the TWINSCAN NXE: 3300B® platform supplied by ASML of Veldhoven, NL. This tool architecture allows for work pieces, such as semiconductor substrates or wafers, to be transferred under vacuum so as not to react before exposure. Integration of the deposition modules with the lithography tool is facilitated by the fact that
20 EUVL also requires a greatly reduced pressure given the strong optical absorption of the incident photons by ambient gases such as H₂O, O₂, etc.

[0307] As noted above, this integrated architecture is just one possible embodiment of a tool for implementation of the described processes. The processes may also be implemented with a stand-alone EUVL scanner and a deposition reactor, such as a Lam Vector tool, either
25 stand alone or integrated in a cluster architecture with other tools, such as etch, strip etc. (e.g., Lam Kiyo or Gamma tools), as modules, for example as described with reference to **FIG. 7** but without the integrated patterning module.

[0308] Airlock **742** may be an “outgoing” loadlock, referring to the transfer of a substrate out from the VTM **738** serving a deposition module **720a** to the patterning module **740**, and
30 airlock **746** may be an “ingoing” loadlock, referring to the transfer of a substrate from the patterning module **740** back in to the VTM **738**. The ingoing loadlock **746** may also provide an interface to the exterior of the tool for access and egress of substrates. Each process

module has a facet that interfaces the module to VTM 738. For example, deposition process module 720a has facet 736. Inside each facet, sensors, for example, sensors 1-18 as shown, are used to detect the passing of wafer 726 when moved between respective stations.

Patterning module 740 and airlocks 742 and 746 may be similarly equipped with additional facets and sensors, not shown.

[0309] Main VTM robot 722 transfers wafer 726 between modules, including airlocks 742 and 746. In one embodiment, robot 722 has one arm, and in another embodiment, robot 722 has two arms, where each arm has an end effector 724 to pick wafers such as wafer 726 for transport. Front-end robot 744, in is used to transfer wafers 726 from outgoing airlock 742 into the patterning module 740, from the patterning module 740 into ingoing airlock 746. Front-end robot 744 may also transport wafers 726 between the ingoing loadlock and the exterior of the tool for access and egress of substrates. Because ingoing airlock module 746 has the ability to match the environment between atmospheric and vacuum, the wafer 726 is able to move between the two pressure environments without being damaged.

[0310] It should be noted that a EUVL tool typically operates at a higher vacuum than a deposition tool. If this is the case, it is desirable to increase the vacuum environment of the substrate during the transfer between the deposition to the EUVL tool to allow the substrate to degas prior to entry into the patterning tool. Outgoing airlock 742 may provide this function by holding the transferred wafers at a lower pressure, no higher than the pressure in the patterning module 740, for a period of time and exhausting any off-gassing, so that the optics of the patterning tool 740 are not contaminated by off-gassing from the substrate. A suitable pressure for the outgoing, off-gassing airlock is no more than 1E-8 Torr.

[0311] In some embodiments, a system controller 750 (which may include one or more physical or logical controllers) controls some or all of the operations of the cluster tool and/or its separate modules. It should be noted that the controller can be local to the cluster architecture, or can be located external to the cluster architecture in the manufacturing floor, or in a remote location and connected to the cluster architecture via a network. The system controller 750 may include one or more memory devices and one or more processors. The processor may include a central processing unit (CPU) or computer, analog and/or digital input/output connections, stepper motor controller boards, and other like components. Instructions for implementing appropriate control operations are executed on the processor. These instructions may be stored on the memory devices associated with the controller or

they may be provided over a network. In certain embodiments, the system controller executes system control software.

[0312] The system control software may include instructions for controlling the timing of application and/or magnitude of any aspect of tool or module operation. System control software may be configured in any suitable way. For example, various process tool component subroutines or control objects may be written to control operations of the process tool components necessary to carry out various process tool processes. System control software may be coded in any suitable compute readable programming language. In some embodiments, system control software includes input/output control (IOC) sequencing instructions for controlling the various parameters described above. For example, each phase of a semiconductor fabrication process may include one or more instructions for execution by the system controller. The instructions for setting process conditions for condensation, deposition, evaporation, patterning and/or etching phase may be included in a corresponding recipe phase, for example.

[0313] In various embodiments, an apparatus for forming a negative pattern mask is provided. The apparatus may include a processing chamber for patterning, deposition and etch, and a controller including instructions for forming a negative pattern mask. The instructions may include code for, in the processing chamber, patterning a feature in a chemically amplified (CAR) resist on a semiconductor substrate by EUV exposure to expose a surface of the substrate, dry developing the photopatterned resist, and etching the underlying layer or layer stack using the patterned resist as a mask.

[0314] It should be noted that the computer controlling the wafer movement can be local to the cluster architecture or can be located external to the cluster architecture in the manufacturing floor, or in a remote location and connected to the cluster architecture via a network.

Conclusion

[0315] Although the foregoing embodiments have been described in some detail for purposes of clarity of understanding, it will be apparent that certain changes and modifications may be practiced within the scope of the appended claims. Embodiments disclosed herein may be practiced without some or all of these specific details. In other instances, well-known process operations have not been described in detail to not unnecessarily obscure the disclosed embodiments. Further, while the disclosed embodiments

will be described in conjunction with specific embodiments, it will be understood that the specific embodiments are not intended to limit the disclosed embodiments. It should be noted that there are many alternative ways of implementing the processes, systems, and apparatus of the present embodiments. Accordingly, the present embodiments are to be
5 considered as illustrative and not restrictive, and the embodiments are not to be limited to the details given herein.

CLAIMS

1. A stack comprising:
a semiconductor substrate having a top surface; and
a patterning radiation-sensitive film disposed on the top surface of the semiconductor substrate, wherein the film comprises a radiation-absorbing unit and a radiation-sensitive carbon-containing unit from an organic co-reactant.
2. The stack of claim 1, wherein the radiation-absorbing unit comprises an element selected from the group consisting of tin (Sn), tellurium (Te), hafnium (Hf), and zirconium (Zr), or a combination thereof.
3. The stack of claim 1, wherein the radiation-sensitive carbon-containing unit is selected from the group consisting of alkenylene moieties, alkynylene moieties, carbonyl moieties, and dicarbonyl moieties, or a combination thereof.
4. The stack of claim 1, wherein the patterning radiation-sensitive film comprises an extreme ultraviolet (EUV)-sensitive film.
5. The stack of claim 4, wherein EUV-sensitive film comprises a plurality of polymerizable moieties, alkenylene moieties, alkynylene moieties, carbonyl moieties, or dicarbonyl moieties.
6. The stack of claim 4, wherein the EUV-sensitive film comprises a vertical gradient characterized by a change in EUV absorbance.
7. The stack of claims 4-6, wherein the EUV-sensitive film comprises an organometallic material.

8. A method of forming a film, the method comprising:
 providing an initial precursor in the presence of an organic co-reactant, wherein the initial precursor comprises an organometallic compound having at least one ligand, and wherein the organic co-reactant replaces the at least one ligand to provide a modified precursor; and
 depositing the modified precursor on a surface of a substrate to provide a patterning radiation-sensitive film.
9. The method of claim 8, wherein the patterning radiation-sensitive film comprises an Extreme Ultraviolet (EUV)-sensitive film.
10. The method of claim 9, wherein the modified precursor comprises an increased or a decreased carbon content, as compared to the initial precursor.
11. The method of claim 9, wherein said providing further comprises providing a molar ratio of the initial precursor to the organic co-reactant of from about 1000:1 to about 1:4.
12. The method of claim 8, wherein the initial precursor comprises a structure having formula (I):



wherein:

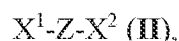
- M is a metal;
- each R is, independently, halo, optionally substituted alkyl, optionally substituted aryl, optionally substituted amino, optionally substituted alkoxy, or L;
- each L is, independently, is a ligand, ion, or other moiety that is reactive with the organic co-reactant or a counter-reactant, in which R and L with M, taken together, can optionally form a heterocyclyl group or in which R and L, taken together, can optionally form a heterocyclyl group;
- $a \geq 1$; $b \geq 1$; and $c \geq 1$.

13. The method of claim 12, wherein each R is L and/or M is tin (Sn).

14. The method of claim 12, wherein each L is, independently, H, halo, optionally substituted alkyl, optionally substituted aryl, optionally substituted amino, optionally substituted bis(trialkylsilyl)amino, optionally substituted trialkylsilyl, or optionally substituted alkoxy.

15. The method of claim 8, wherein the organic co-reactant comprises one or more polymerizable moieties, alkynyl moieties, carbonyl moieties, dicarbonyl moieties, or haloalkyl moieties.

16. The method of claim 15, wherein the organic co-reactant comprises a structure having formula (II):



wherein:

each of X^1 and X^2 is, independently, a leaving group; and

Z is carbonyl, dicarbonyl, optionally substituted alkylene, optionally substituted haloalkylene, optionally substituted alkenylene, or optionally substituted alkynylene.

17. The method of claim 8, wherein said providing comprises providing the initial precursor and the organic co-reactant in vapor form.

18. The method of claims 8-17, wherein said providing further comprises providing a counter-reactant.

19. The method of claim 18, wherein the counter-reactant comprises oxygen or a chalcogenide precursor.

20. The method of claim 18, wherein the counter-reactant is not water.

21. The method of claim 8, wherein said depositing comprises depositing the modified precursor in vapor form.

22. The method of claim 8, wherein said depositing comprises chemical vapor deposition, atomic layer deposition, or molecular layer deposition.
23. A method of employing a resist, the method comprising:
providing an initial precursor in the presence of an organic co-reactant, wherein the initial precursor comprises an organometallic compound having at least one ligand, and wherein the organic co-reactant replaces at least some significant, detectable percentage of one ligand to provide a modified precursor;
depositing the modified precursor on a surface of a substrate to provide a patterning radiation-sensitive film as a resist film;
patterning the resist film by exposure to patterning radiation, thereby providing an exposed film having radiation exposed areas and radiation unexposed areas; and
developing the exposed film, thereby removing the radiation exposed areas to provide a pattern within a positive tone resist film or removing the radiation unexposed areas to provide a pattern within a negative tone resist.
24. The method of claim 23, wherein the patterning radiation-sensitive film comprises an Extreme Ultraviolet (EUV)-sensitive film.
25. The method of claim 24, wherein the patterning radiation comprises an EUV exposure having a wavelength in the range of about 10 nm to about 20 nm in a vacuum ambient.
26. The method of claim 23, wherein said patterning further comprises a release of carbon dioxide and/or carbon monoxide from the exposed film.
27. The method of claim 23, wherein post-exposure baking of the exposed film and/or said developing comprises an oxygen-containing agent, water in vapor form, and/or carbon dioxide.
28. The method of claim 23, wherein said patterning further comprises photopolymerization occurring within the exposed film.

29. An apparatus for forming a resist film, the apparatus comprising:
- a deposition module comprising a chamber for depositing a patterning radiation-sensitive film;
 - a patterning module comprising a photolithography tool with a source of sub-300 nm wavelength radiation;
 - a development module comprising a chamber for developing the resist film; and
 - a controller including one or more memory devices, one or more processors, and system control software coded with instructions comprising machine-readable instructions for:
 - in the deposition module, causing deposition of a modified precursor on a top surface of a semiconductor substrate to form the patterning radiation-sensitive film as a resist film, wherein an initial precursor is provided the presence of an organic co-reactant to provide the modified precursor;
 - in the patterning module, causing patterning of the resist film with sub-300 nm resolution directly by patterning radiation exposure, thereby forming an exposed film having radiation exposed areas and radiation unexposed areas; and
 - in the development module, causing development of the exposed film to remove the radiation exposed areas or the radiation unexposed areas to provide a pattern within the resist film.
30. The apparatus of claim 29, wherein the patterning radiation-sensitive film comprises an Extreme Ultraviolet (EUV)-sensitive film.
31. The apparatus of claim 30, wherein the source for the photolithography tool is a source of sub-30 nm wavelength radiation.

32. The apparatus of claim 31, wherein the instructions comprising machine-readable instructions further comprises instructions for:

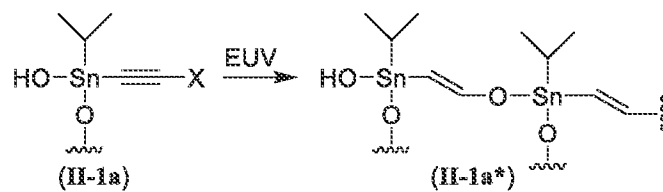
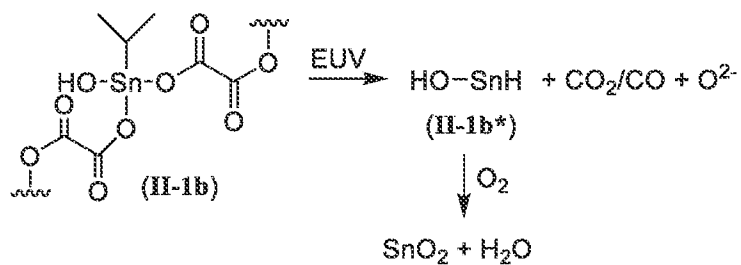
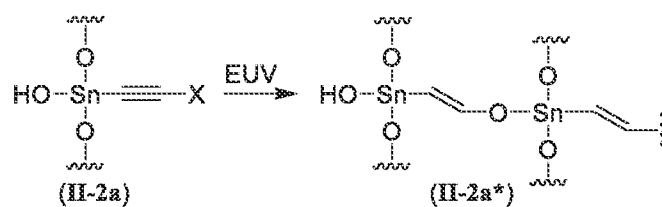
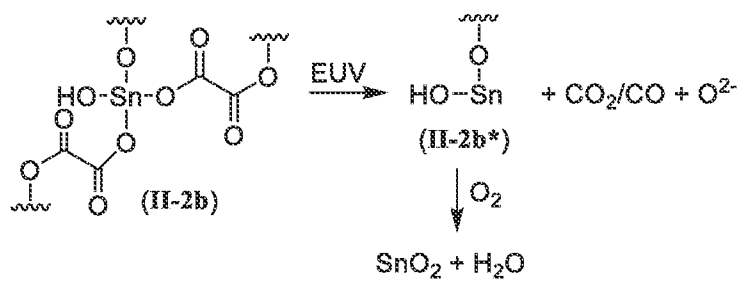
in the patterning module, causing patterning of the resist film with sub-30 nm resolution directly by EUV exposure, thereby forming the exposed film having EUV exposed areas and EUV unexposed areas.

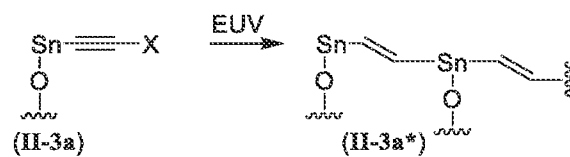
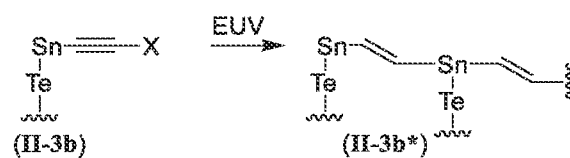
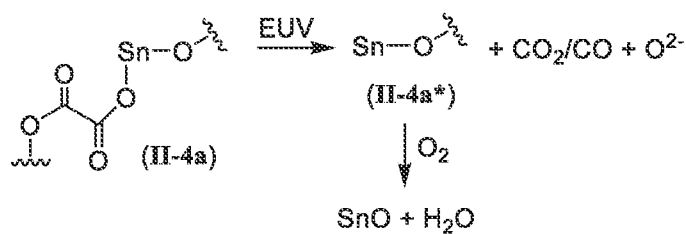
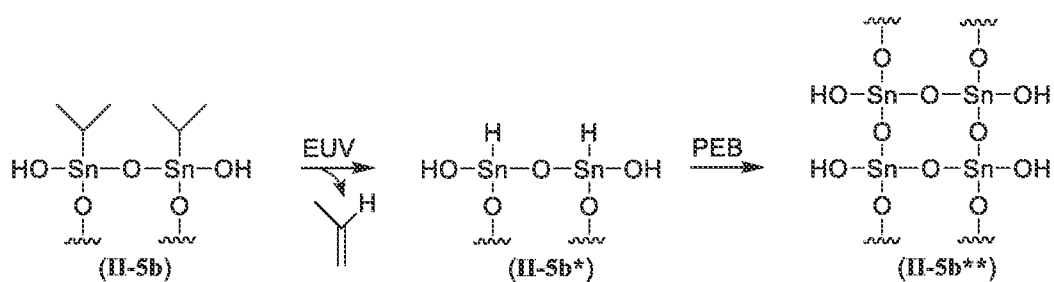
33. The apparatus of claim 32, wherein the instructions comprising machine-readable instructions further comprises instructions for:

in the development module, causing development of the exposed film to remove the EUV exposed areas or the EUV unexposed areas to provide a pattern within the resist film.

34. The apparatus of claim 29, wherein the instructions comprising machine-readable instructions further comprises instructions for:

in the deposition module, causing change of a molar ratio of the initial precursor and the organic co-reactant to provide a further modified precursor to form the patterning radiation-sensitive film.

**FIG. 1A****FIG. 1B****FIG. 1C****FIG. 1D**

**FIG. 1E****FIG. 1F****FIG. 1G****FIG. 1H**

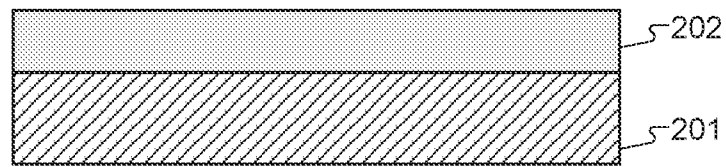


FIG. 2A

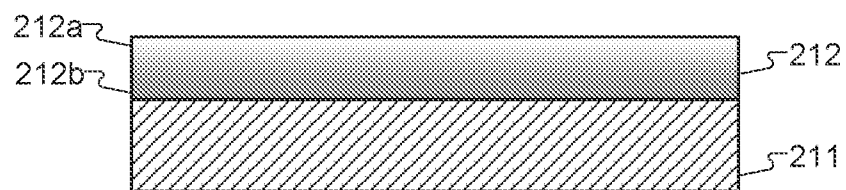


FIG. 2B

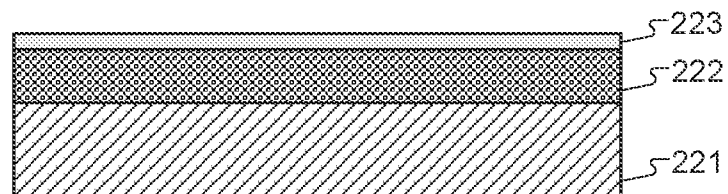
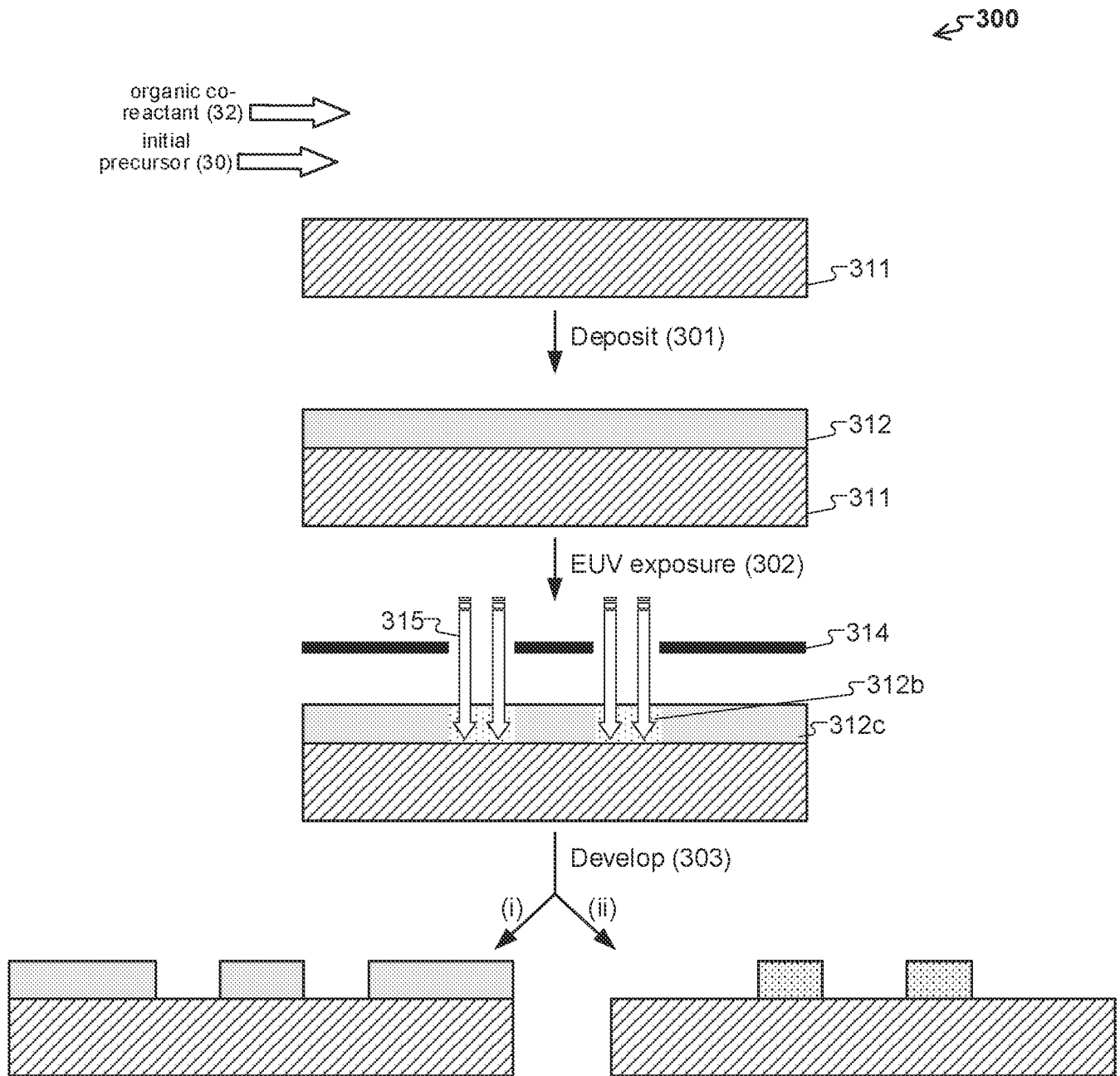


FIG. 2C

**FIG. 3A**

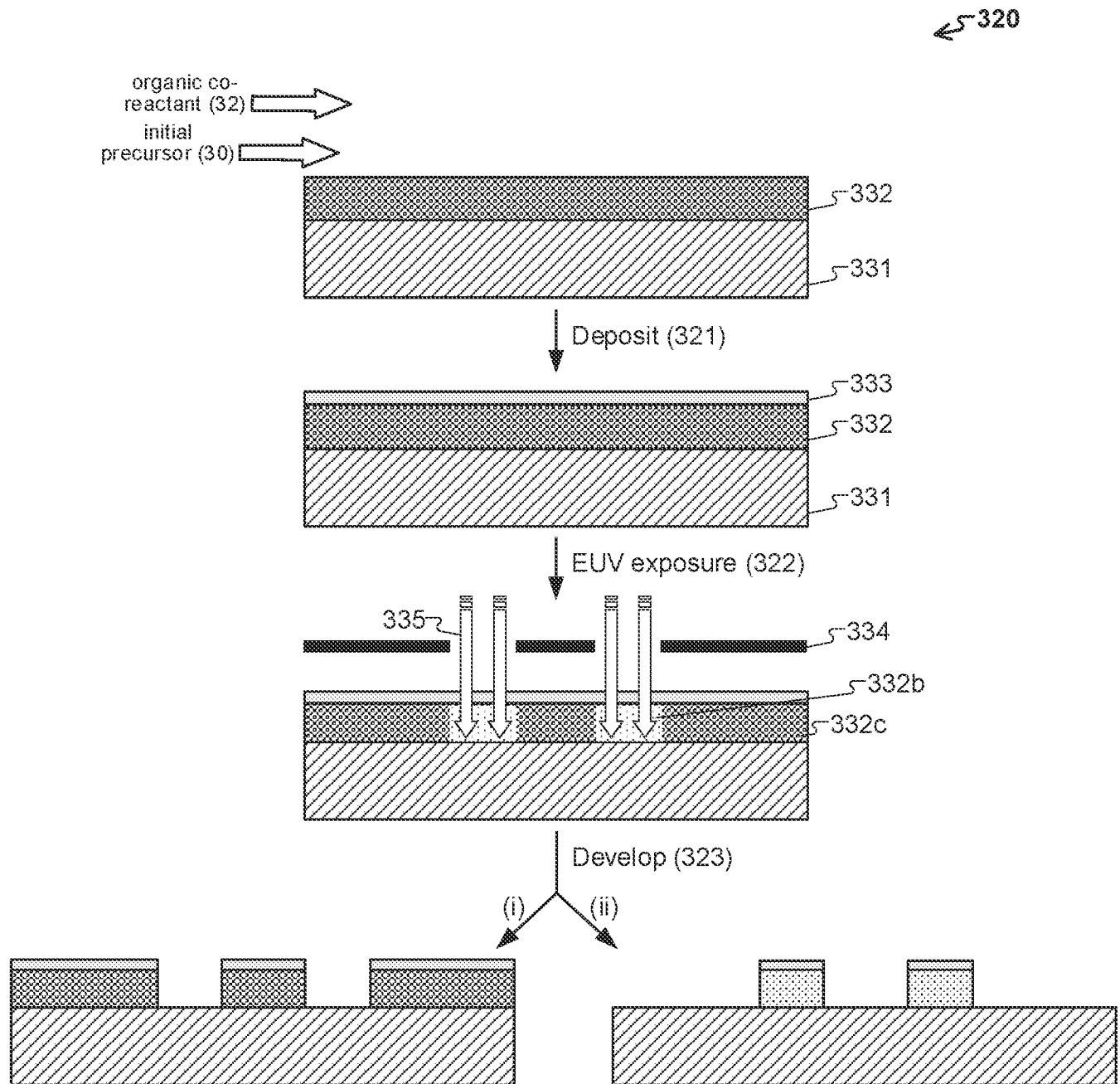
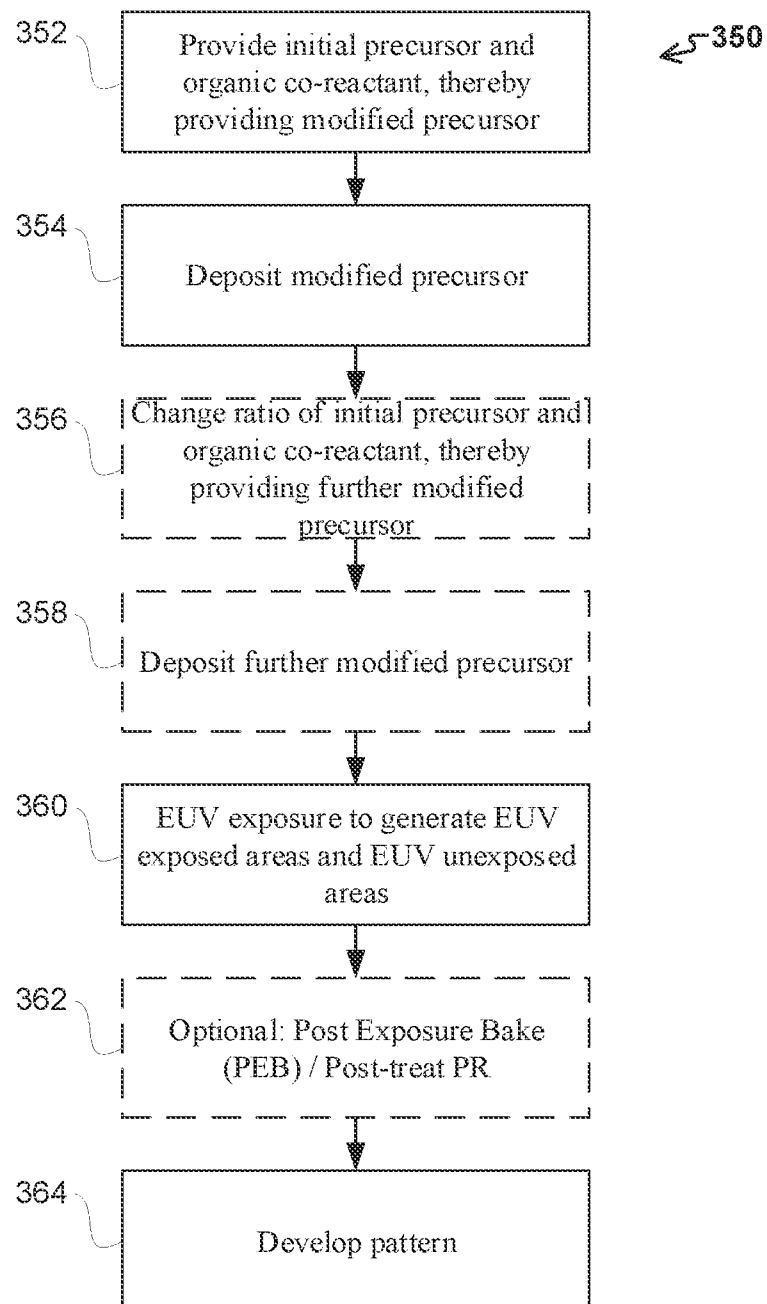


FIG. 3B

**FIG. 3C**

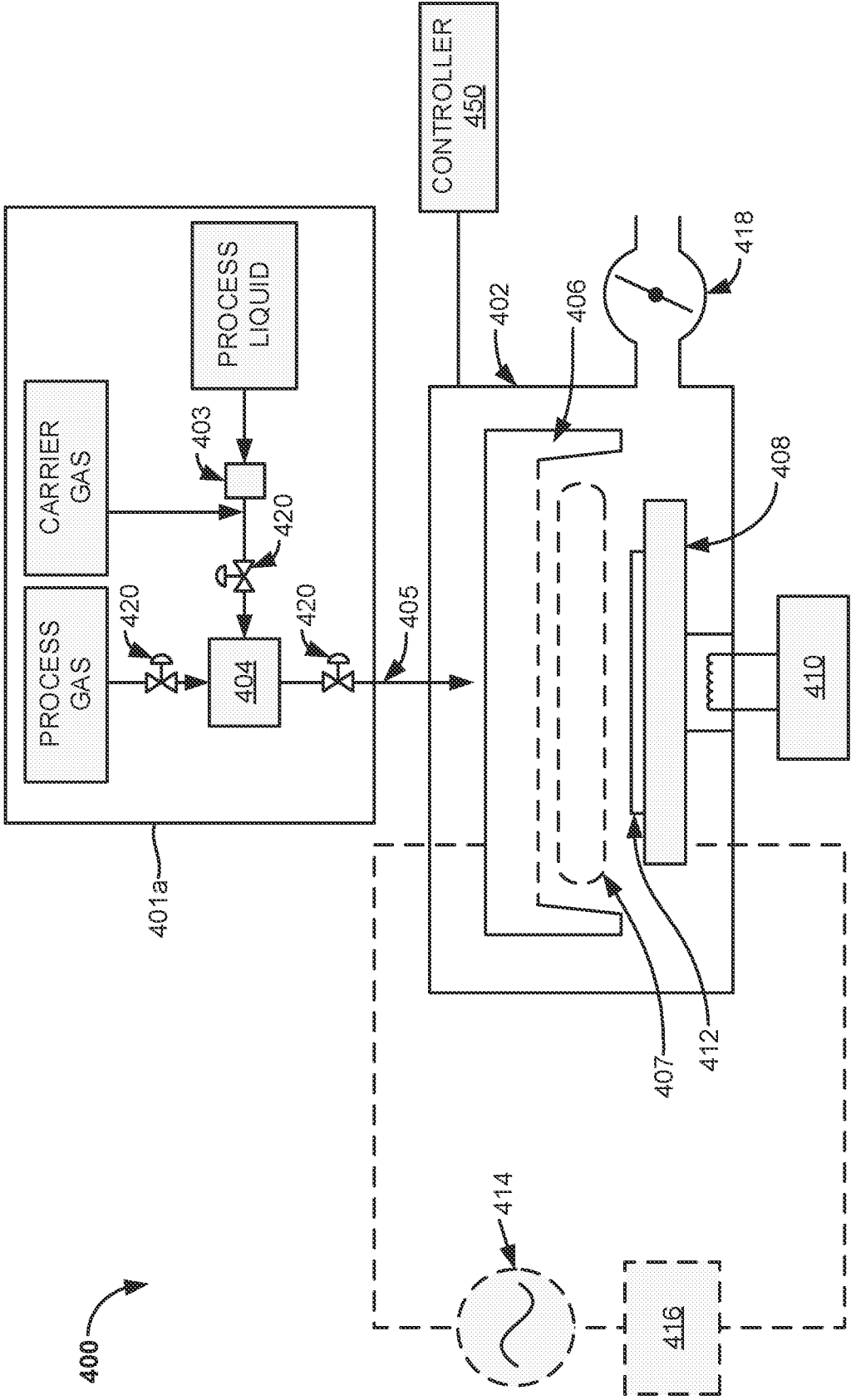
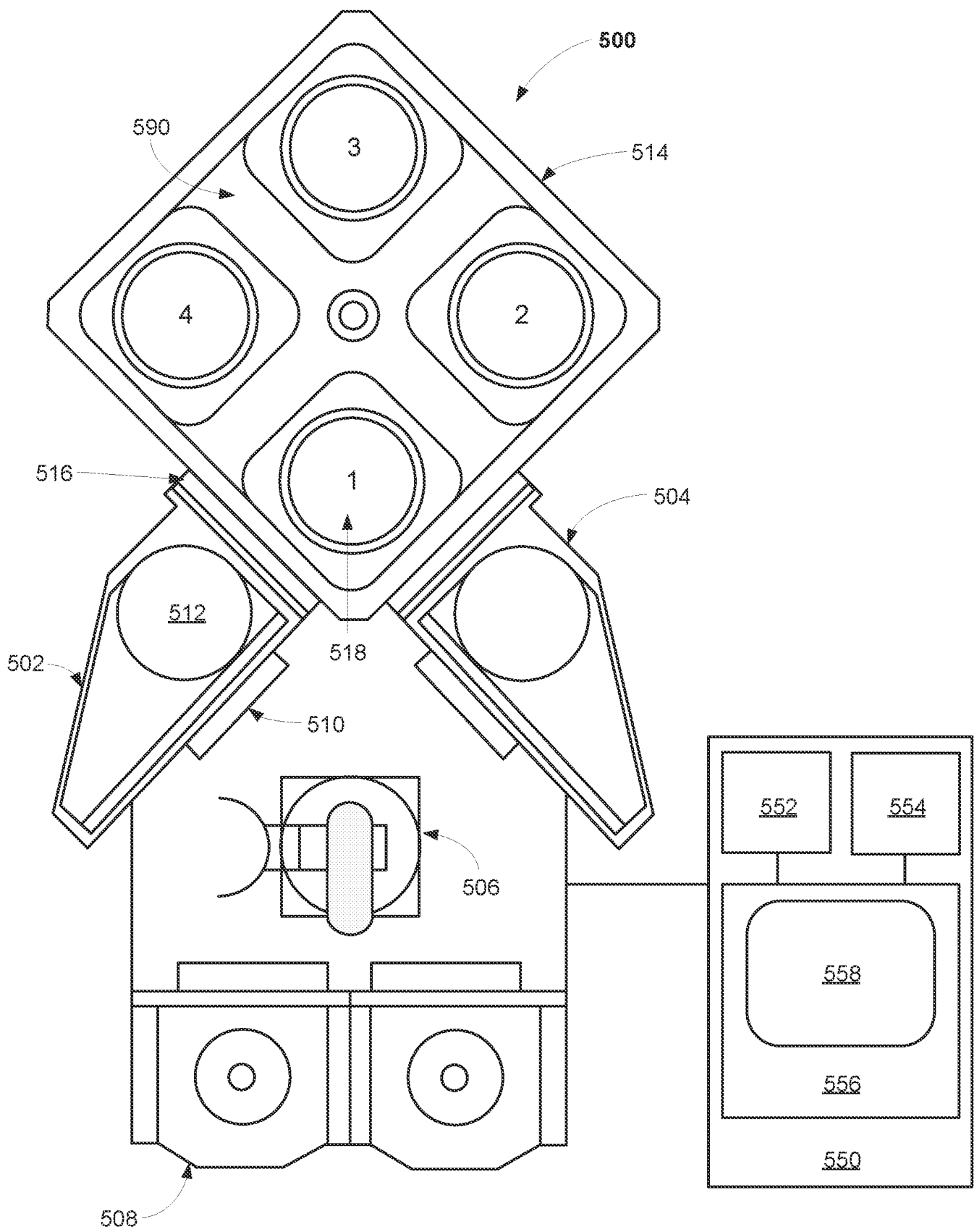


FIG. 4

**FIG. 5**

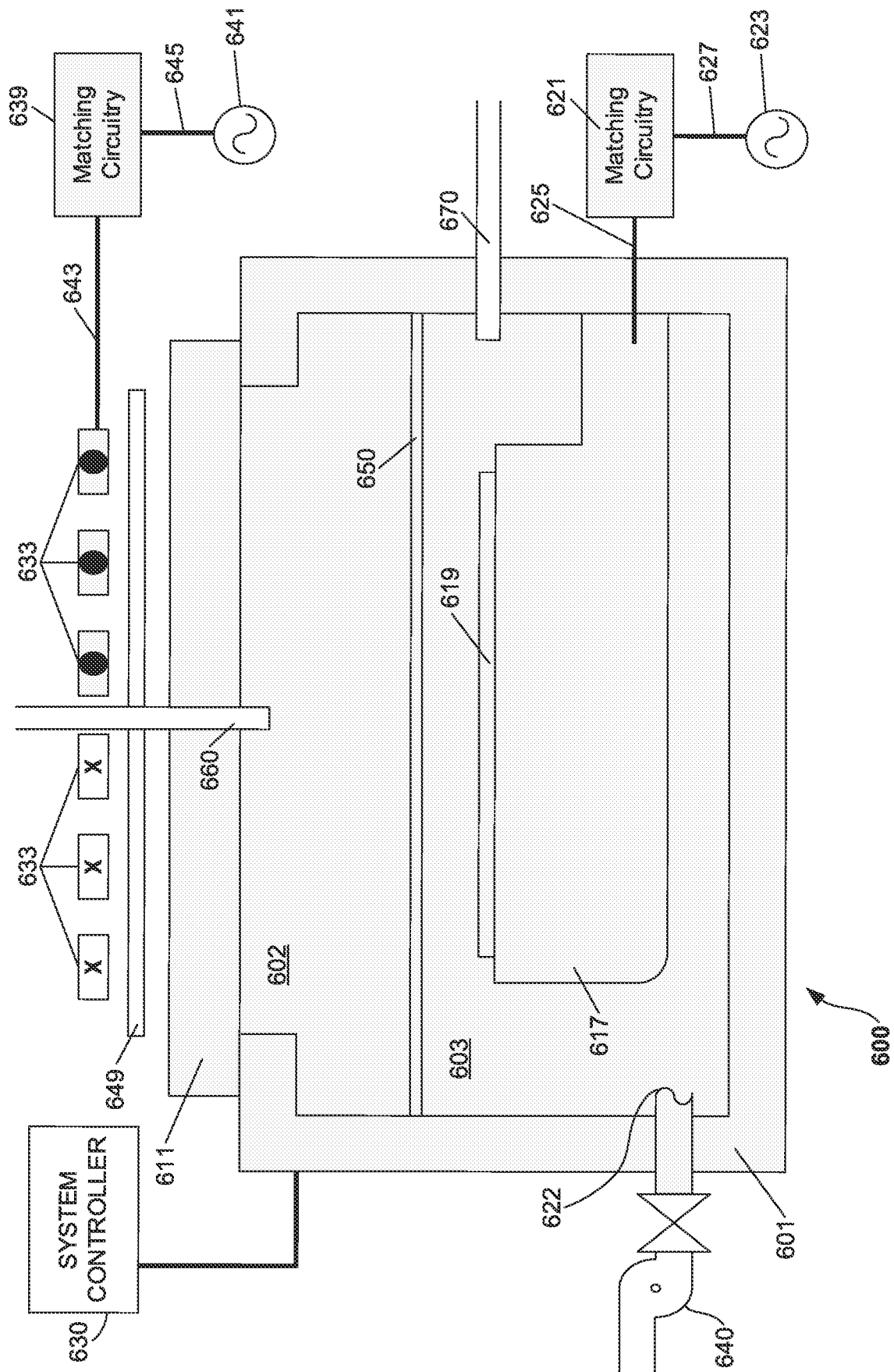


FIG. 6

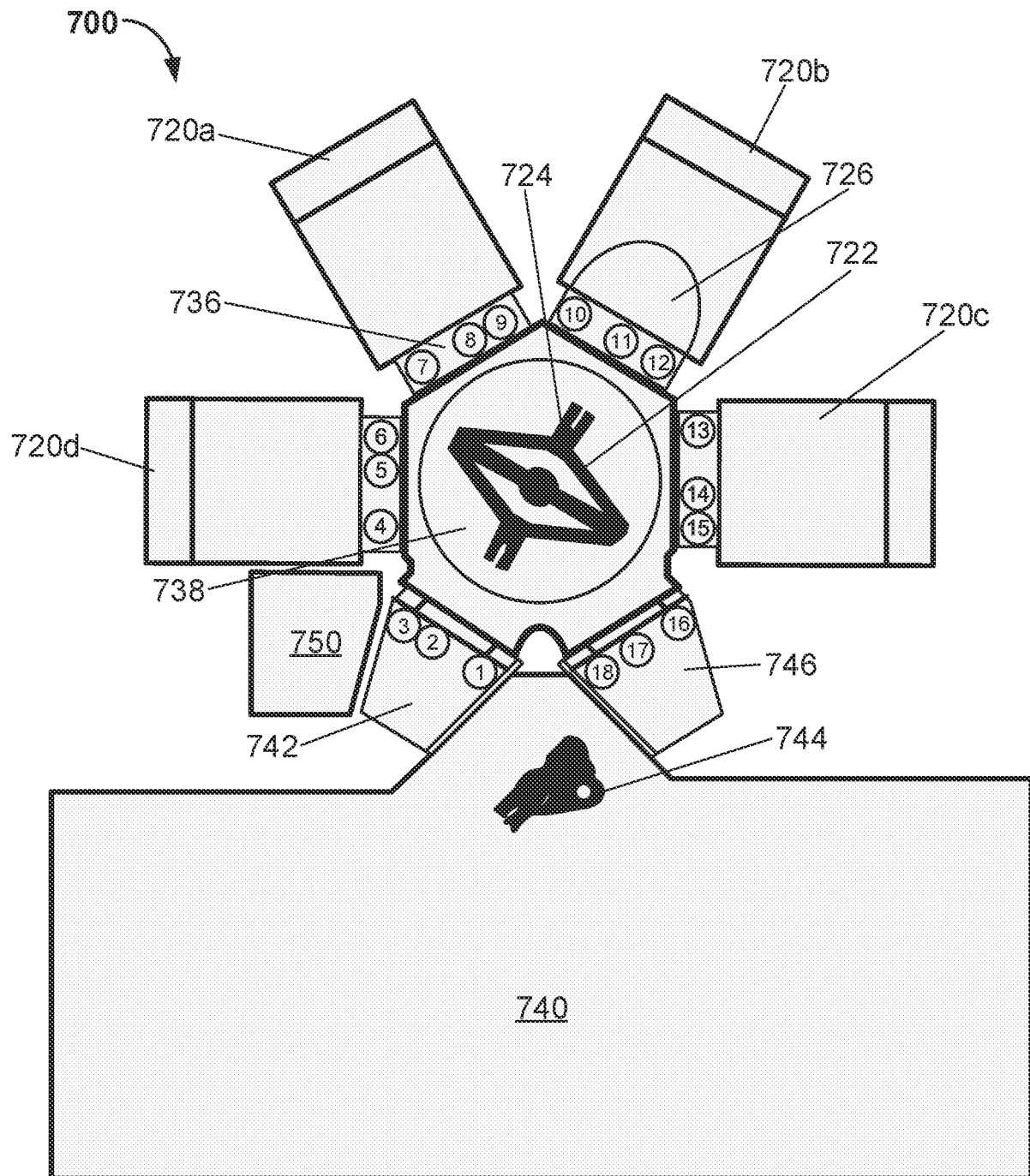


FIG. 7

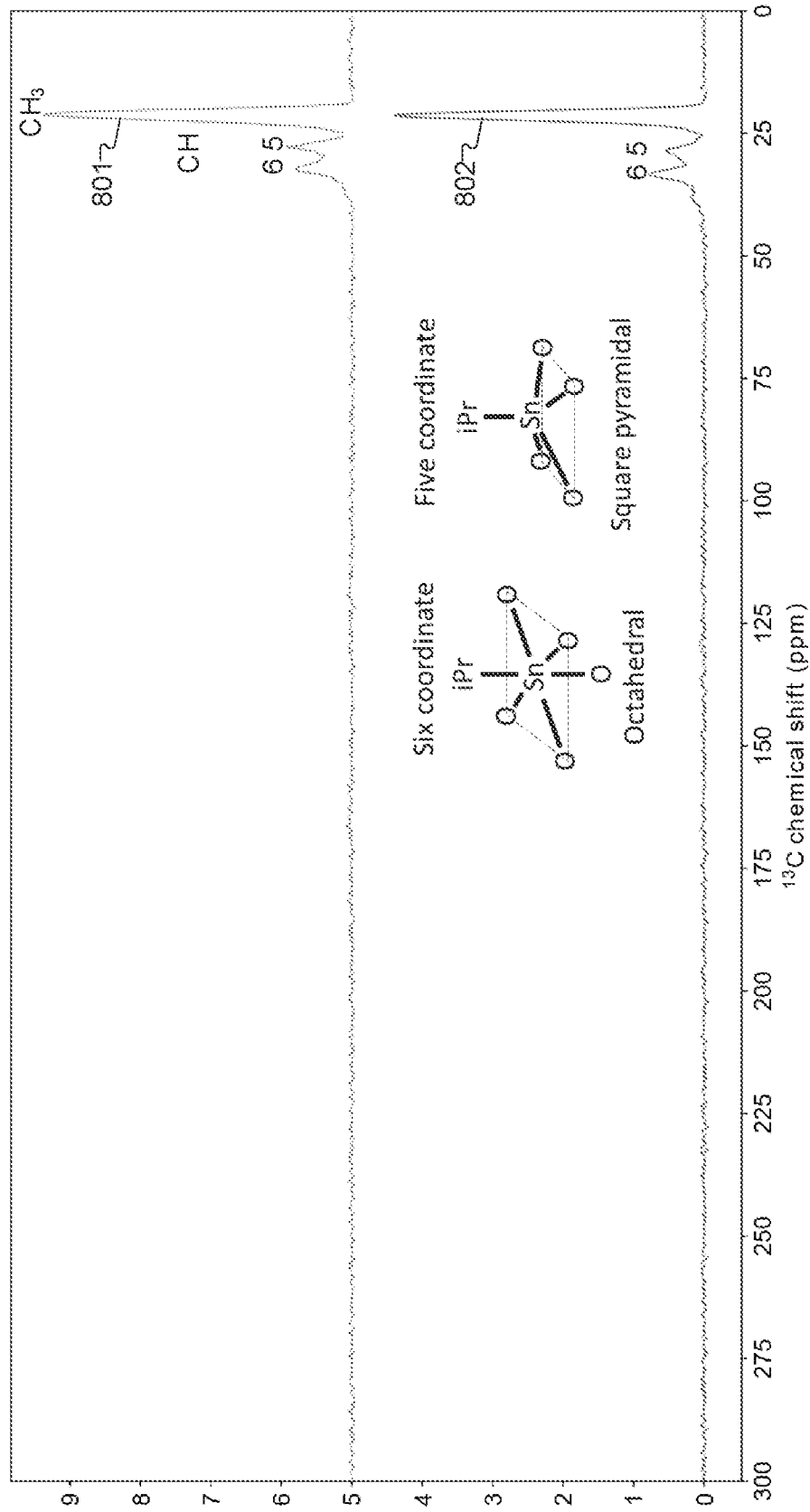


FIG. 8

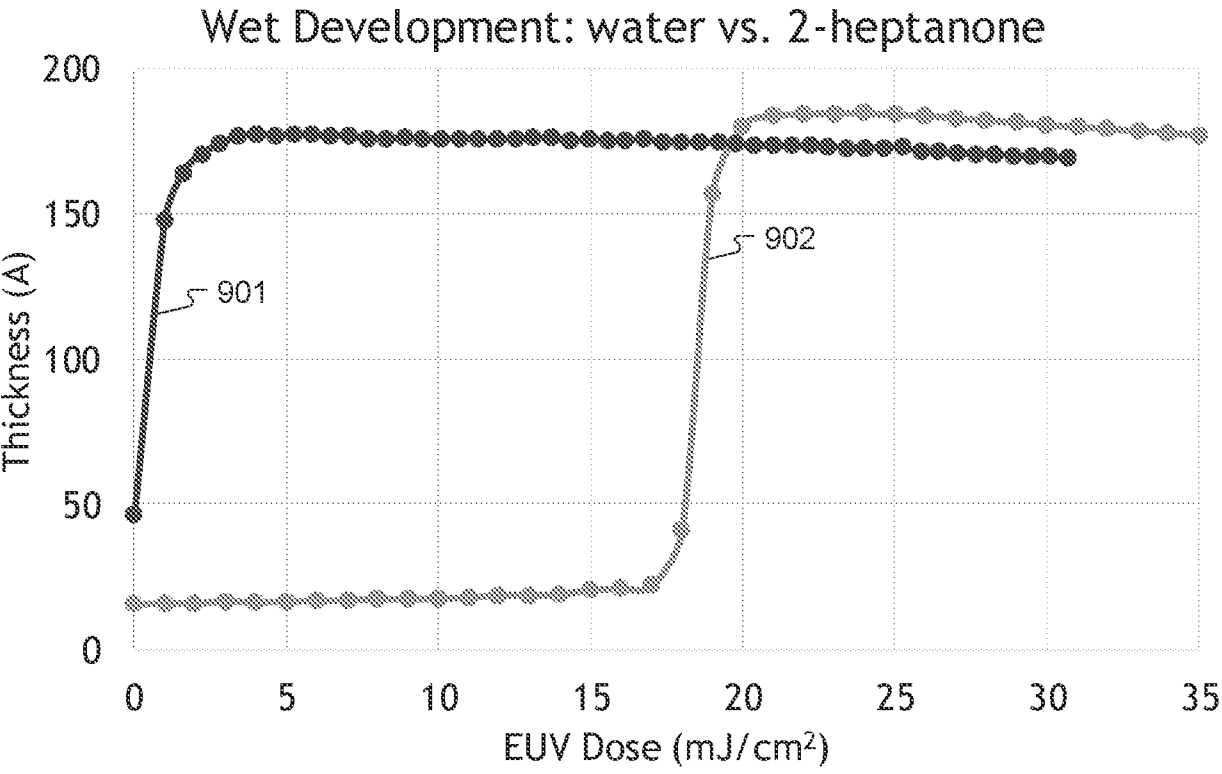


FIG. 9

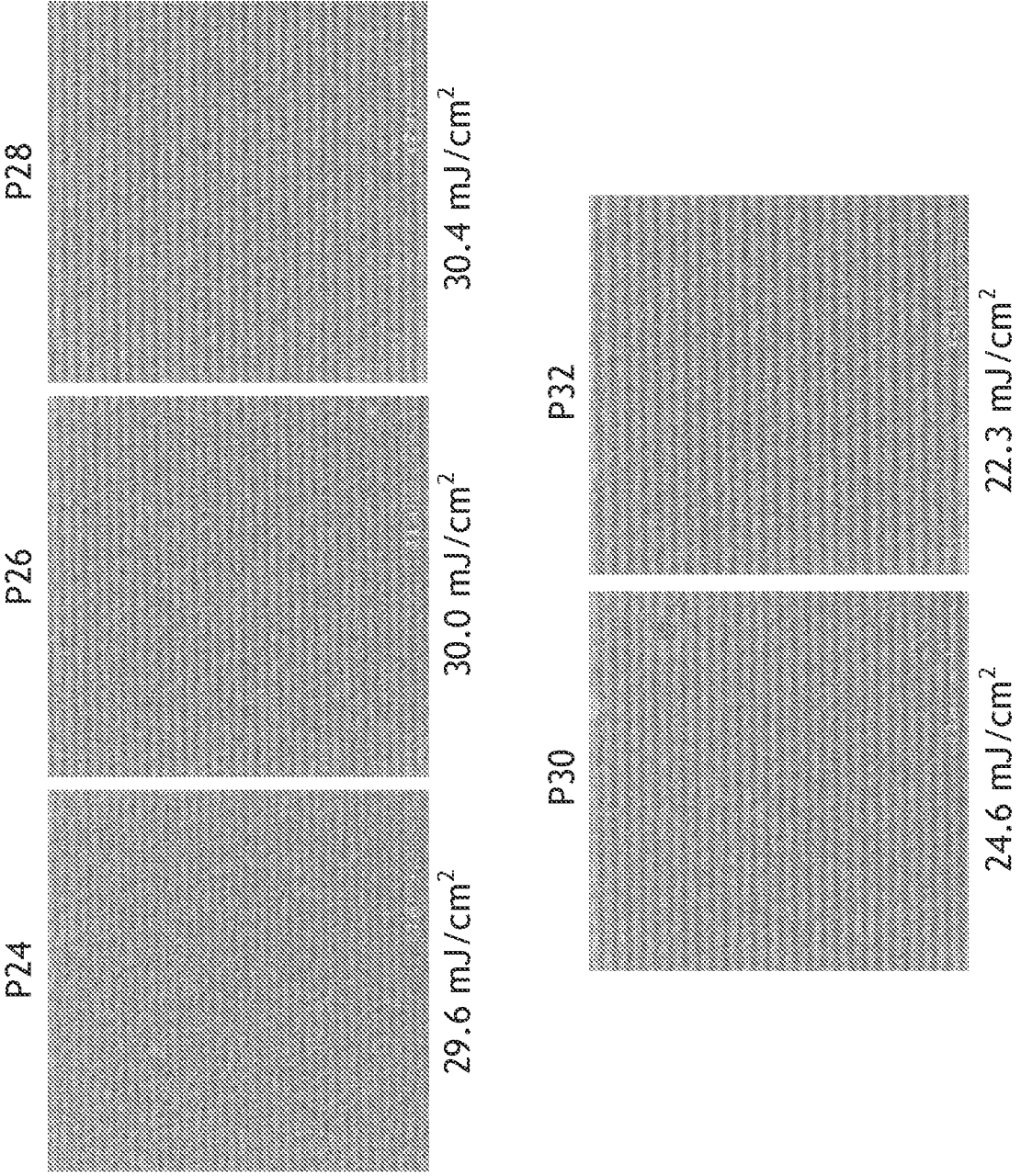


FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2021/042103

A. CLASSIFICATION OF SUBJECT MATTER

G03F 7/004(2006.01)i; **G03F 7/16**(2006.01)i; **G03F 7/20**(2006.01)i; **G03F 7/26**(2006.01)i; **H01L 21/027**(2006.01)i;
H01L 21/67(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(2006.01); G03F 1/22(2012.01); G03F 7/00(2006.01); G03F 7/20(2006.01); G03F 7/32(2006.01)

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: precursor, co-reactant, depositing, patterning, developing, baking, photoresist, semiconductor, extreme ultraviolet(EUV)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2018-0054917 A (INPRIA CORPORATION) 24 May 2018 (2018-05-24) claim 28; paragraphs [0004]-[0143]	1-17,21-27,29-34
Y		18-20,28
Y	WO 2019-217749 A1 (LAM RESEARCH CORPORATION) 14 November 2019 (2019-11-14) claims 1-9; figure 1	18-20,28
A	KR 10-2017-0066225 A (LAM RESEARCH CORPORATION) 14 June 2017 (2017-06-14) the whole document	1-34
A	US 2016-0116839 A1 (INPRIA CORPORATION) 28 April 2016 (2016-04-28) the whole document	1-34
A	MOLLOY, K. C., "Precursors for the formation of tin (IV) oxide and related materials", Journal of Chemical Research, 2008, Vol. 2008, No. 10, pages 549-554 the whole document	1-34



Further documents are listed in the continuation of Box C.



See patent family annex.

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 "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

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Date of the actual completion of the international search

04 November 2021

Date of mailing of the international search report

04 November 2021

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US2021/042103

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				TW	1730015	B	11 June 2021
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International application No.

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