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SEMICONDUCTOR PHOTORESIST COMPOSITIONS AND METHODS OF FORMING PATTERNS USING THE COMPOSITION

Abstract

A semiconductor photoresist composition and a method of forming patterns using the composition are disclosed. The semiconductor photoresist composition may include a tin (Sn)-containing organometallic compound, a compound represented by Chemical Formula 1, and a solvent.

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Background/Summary

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application claims priority to and the benefit of Korean Patent Application No. 10-2024-0022099, filed on Feb. 15, 2024, in the Korean Intellectual Property Office, the entire disclosure of which is incorporated herein by reference.

BACKGROUND

1. Field

[0002] One or more embodiments of the present disclosure relates to a semiconductor photoresist composition and a method of forming patterns using the semiconductor photoresist composition.

2. Description of the Related Art

[0003] Extreme ultraviolet (EUV) lithography is paid attention to as one technology for manufacturing a next generation semiconductor device. The EUV lithography is a pattern-forming technology using an EUV ray that has a wavelength of 13.5 nm as an exposure light source. According to the EUV lithography, an extremely fine pattern (e.g., less than or equal to 20 nm) may be formed in an exposure process during a manufacture of a semiconductor device.

[0004] The extreme ultraviolet (EUV) lithography is realized through development of compatible photoresists which may be performed at a spatial resolution of less than or equal to 16 nm. Efforts to satisfy insufficient specifications of chemically amplified (CA) photoresists, such as a resolution, a photospeed, and feature roughness (or also referred to as a line edge roughness or LER), for the next generation device have been made.

[0005] An intrinsic image blurring due to an acid-catalyzed reaction in the polymer-type or kind photoresists limits a resolution in small feature sizes in electron beam (e-beam) lithography. The CA photoresists are designed for high sensitivity. However, because their elemental makeups reduce light absorbance of the photoresists at a wavelength of 13.5 nm, it may decrease their sensitivity, and the CA photoresists may have more difficulties under an EUV exposure.

[0006] The CA photoresists may also have difficulties in the small feature sizes due to roughness issues, and line edge roughness (LER) of the CA photoresists experimentally may be increased as a photospeed is decreased partially due to an essence of acid catalyst processes. A novel high-performance photoresist is required or desired in a semiconductor industry because of these defects and problems of the CA photoresists.

[0007] In order to overcome the aforementioned drawbacks of the chemically amplified (CA) organic photosensitive composition, an inorganic photosensitive composition has been researched. The inorganic photosensitive composition has been used for negative tone patterning which has resistance against removal by a developer composition due to chemical modification through non-chemical amplification mechanism. The inorganic composition includes an inorganic element that has a higher EUV absorption rate than hydrocarbon, and thus, it may secure sensitivity through the non-chemical amplification mechanism and may be less sensitive about a stochastic effect and thus suitable to have low line edge roughness and the small number of defects.

[0008] Inorganic photoresists based on peroxopolyacids of tungsten mixed with tungsten, niobium, titanium, and/or tantalum are radiation sensitive materials for patterning.

[0009] These materials are effective for patterning large pitches for bilayer configuration as far ultraviolet (deep UV), X-ray, and electron beam sources. When cationic hafnium metal oxide sulfate (HfSO_x) materials along with a peroxo complexing agent were used to image a 15 nm half-pitch (HP) through projection EUV exposure, relatively high performance was obtained. This system exhibits a high performance of a non-CA photoresist and has a practicable photospeed near to a requirement for an EUV photoresist. However, the hafnium metal oxide sulfate material including the peroxo complexing agent has some practical drawbacks. First, these materials are

coated in a mixture of corrosive sulfuric acid/hydrogen peroxide and have insufficient shelf-life stability. Second, a structural change of the materials for performance improvement as a composite mixture is challenging. Third, development should be performed in a tetramethylammonium hydroxide (TMAH) solution at an extremely high concentration of 25 wt % and the like.

[0010] To address these issues, research has been focused on developing molecules that include tin (Sn) which have excellent or suitable absorption of extreme ultraviolet rays. As for an organotin polymer among them, alkyl ligands are dissociated by light absorption or secondary electrons produced. The dissociated alkyl ligands are then crosslinked with adjacent chains through oxo bonds, and thus, enable the negative tone patterning which may not be removed by an organic developer. Although this organotin polymer exhibits greatly improved sensitivity and maintains a desired resolution and line edge roughness, it is still desirable to further improve the patterning characteristics for commercial availability.

SUMMARY

[0011] One or more aspects of embodiments of the present disclosure are directed toward a semiconductor photoresist composition that has excellent sensitivity (or suitable sensitivity) and storage stability (or suitable storage stability).

[0012] One or more aspects of embodiments of the present disclosure are directed toward a method of forming patterns using the semiconductor photoresist composition.

[0013] A semiconductor photoresist composition according to one or more embodiments of the present disclosure include a tin (Sn)-containing organometallic compound; a compound represented by Chemical Formula 1; and a solvent.

##STR00001##

[0014] In Chemical Formula 1, [0015] X^{sup.1} may be P(=O)R^{sup.4} or S(=O)₂, [0016] R^{sup.1} to R^{sup.4} may be each independently a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, a substituted or unsubstituted C1 to C20 alkoxy group, or a substituted or unsubstituted C6 to C30 aryloxy group, [0017] R^{sup.1} and R^{sup.2} may be each independently present or may be linked to form a ring, and [0018] at least one selected from R^{sup.3} and R^{sup.4} may be a fluorine-containing group.

[0019] A method of forming patterns according to one or more embodiments of the present disclosure may include providing an etching-objective layer on a substrate, coating the semiconductor photoresist composition on the etching-objective layer to form a photoresist layer, patterning the photoresist layer to form a photoresist pattern, and etching the etching-objective layer using the photoresist pattern as an etching mask.

[0020] The semiconductor photoresist composition according to one or more embodiments of the present disclosure may implement excellent sensitivity (or suitable sensitivity) and storage stability (or suitable storage stability).

Description

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] The accompanying drawings, together with the specification, illustrate embodiments of the subject matter of the present disclosure, and, together with the description, serve to explain principles of embodiments of the subject matter of the present disclosure.

[0022] FIGS. 1A-1E are cross-sectional views for illustrating a method of forming patterns using a semiconductor photoresist composition according to one or more embodiments of the present disclosure.

DETAILED DESCRIPTION

[0023] Hereinafter, referring to the drawings, one or more embodiments of the present disclosure are described in more detail. In the following description of the present disclosure, the functions or constructions that are generally understood by a person of ordinary skill in the art may not be described in order to clarify the present disclosure.

[0024] In order to clearly illustrate embodiments of the present disclosure, certain description and relationships may be omitted, and throughout the present disclosure, the same (or substantially same) or similar configuration elements may be designated by the same (or substantially same) reference numerals. Also, because the size and thickness of each configuration shown in the drawings may be arbitrarily shown for better understanding and ease of description, embodiments of the present disclosure are not necessarily limited thereto.

[0025] In the drawings, the thickness of layers, films, panels, regions, etc., may be enlarged for clarity. In the drawings, the thickness of a part of layers or regions, etc., may be exaggerated for clarity. It will be understood that if (e.g., when) an element, such as a layer, film, region, or substrate, is referred to as being “on” another element, it may be directly on the other element or intervening elements may also be present.

[0026] As used herein, “substituted” refers to replacement of a hydrogen atom by deuterium, a halogen, a hydroxy group, a thiol group, a cyano group, a nitro group, —NRR’ (wherein, R and R’ may be each independently hydrogen, a substituted or unsubstituted C1 to C30 saturated or unsaturated aliphatic hydrocarbon group, a substituted or unsubstituted C3 to C30 saturated or unsaturated alicyclic hydrocarbon group, or a substituted or unsubstituted C6 to C30 aromatic hydrocarbon group), —SiRR’R’’ (wherein, R, R’, and R’’ may be each independently hydrogen, a substituted or unsubstituted C1 to C30 saturated or unsaturated aliphatic hydrocarbon group, a substituted or unsubstituted C3 to C30 saturated or unsaturated alicyclic hydrocarbon group, or a substituted or unsubstituted C6 to C30 aromatic hydrocarbon group), a C1 to C30 alkyl group, a C1 to C10 haloalkyl group, a C1 to C10 alkylsilyl group, a C3 to C30 cycloalkyl group, a C6 to C30 aryl group, a C1 to C20 alkoxy group, a C1 to C20 sulfide group, or a combination thereof. “Unsubstituted” refers to non-replacement of a hydrogen atom by another substituent and remaining of the hydrogen atom.

[0027] As used herein, if (e.g., when) a definition is not otherwise provided, “alkyl group” may refer to a linear or branched aliphatic hydrocarbon group. The alkyl group may be “saturated alkyl group” without any double bond or triple bond.

[0028] The alkyl group may be a C1 to C8 alkyl group. For example, the alkyl group may be a C1 to C7 alkyl group, a C1 to C6 alkyl group, or a C1 to C5 alkyl group. For example, the C1 to C5 alkyl group may be a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, or a 2,2-dimethylpropyl group.

[0029] As used herein, if (e.g., when) a definition is not otherwise provided, “cycloalkyl group” may refer to a monovalent cyclic aliphatic hydrocarbon group.

[0030] The cycloalkyl group may be a C3 to C8 cycloalkyl group, a C3 to C7 cycloalkyl group, or a C3 to C6 cycloalkyl group. For example, the cycloalkyl group may be a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, or a cyclohexyl group, but is not limited thereto.

[0031] As used herein, “aliphatic unsaturated organic group” refers to a hydrocarbon group including a bond in which the bond between the carbon and carbon atom in the molecule may be a double bond, a triple bond, or a combination thereof.

[0032] The aliphatic unsaturated organic group may be a C2 to C8 aliphatic unsaturated organic group. For example, the aliphatic unsaturated organic group may be a C2 to C7 aliphatic unsaturated organic group, a C2 to C6 aliphatic unsaturated organic group, a C2 to C5 aliphatic unsaturated organic group, or a C2 to C4 aliphatic unsaturated organic group. For example, the C2 to C4 aliphatic unsaturated organic group may be a vinyl group, an ethynyl group, an allyl group, a 1-propenyl group, a 1-methyl-1-propenyl group, a 2-propenyl group, a 2-methyl-2-propenyl group, a 1-propynyl group, a 1-methyl-1-propynyl group, a 2-propynyl group, a 2-methyl-2-propynyl

group, a 1-butenyl group, a 2-butenyl group, a 3-butenyl group, a 1-butylnyl group, a 2-butylnyl group, or a 3-butylnyl group.

[0033] As used herein, “aryl group” refers to a substituent in which all atoms in the cyclic substituent have a p-orbital and these p-orbitals are conjugated and may include a monocyclic, polycyclic or fused ring (e.g., rings sharing adjacent pairs of carbon atoms) functional group.

[0034] As used herein, “heteroaryl group” may refer to an aryl group including at least one heteroatom selected from among nitrogen (N), oxygen (O), sulfur(S), phosphorus (P), and silicon (Si). Two or more heteroaryl groups are linked by a sigma bond directly, or if (e.g., when) the heteroaryl group includes two or more rings, the two or more rings may be fused. If (e.g., when) the heteroaryl group is a fused ring, each ring may include one to three heteroatoms.

[0035] As used herein, unless otherwise defined, “alkenyl group” refers to an aliphatic unsaturated alkenyl group including at least one double bond as a linear or branched aliphatic hydrocarbon group.

[0036] As used herein, unless otherwise defined, “alkynyl group” refers to an aliphatic unsaturated alkynyl group including at least one triple bond as a linear or branched aliphatic hydrocarbon group.

[0037] Hereinafter, a semiconductor photoresist composition according to one or more embodiments of the present disclosure is described.

[0038] The semiconductor photoresist composition according to one or more embodiments of the present disclosure may include a tin (Sn)-containing organometallic compound, a compound represented by Chemical Formula 1, and a solvent.

##STR00002##

[0039] In Chemical Formula 1, [0040] X^{sup.1} may be P(=O)R^{sup.4} or S(=O)₂, [0041] R^{sup.1} to R^{sup.4} may be each independently a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, a substituted or unsubstituted C1 to C20 alkoxy group, or a substituted or unsubstituted C6 to C30 aryloxy group, [0042] R^{sup.1} and R^{sup.2} may be each independently present or may be linked to form a ring, and [0043] at least one selected from R^{sup.3} and R^{sup.4} may be a fluorine-containing group.

[0044] The semiconductor photoresist composition may include a compound having a structure in which a phosphate including fluorine and an imide are linked through oxygen, thereby providing a photoresist composition to have increased sensitivity (or suitable sensitivity) to extreme ultraviolet rays and improved storage stability (or suitable storage stability).

[0045] In some embodiments, the compound having a structure in which the phosphate or sulfate including fluorine and an imide are linked through oxygen may be not ionic, and therefore have relatively higher stability than ionic compounds. In some embodiments, if (e.g., when) exposed to light, the phosphate or sulfate and imide moieties may fall apart (e.g., dissociate or decompose) to generate acid, which may help improve sensitivity by causing a change in the solubility of the photosensitive material in the developer with a small amount of energy. By including fluorine, it may have relatively high efficiency in absorbing light energy, and because phosphate or sulfate is stable in the ionic state, dissociation may easily occur even with a small amount of energy.

[0046] In some embodiments, R^{sup.1} and R^{sup.2} may be linked to form a ring may be represented by Chemical Formula 1-1.

##STR00003##

[0047] In Chemical Formula 1-1, [0048] X^{sup.1} may be P(=O)R^{sup.4} or S(=O)₂, [0049] R^{sup.3} and R^{sup.4} may be each independently a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, a substituted or unsubstituted C1 to C20 alkoxy group, or a

substituted or unsubstituted C6 to C30 aryloxy group, [0050] at least one selected from R.sup.3 and R.sup.4 may be a fluorine-containing group, and [0051] R.sup.5 to R.sup.8 may be each independently hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, a substituted or unsubstituted C1 to C20 alkoxy group, or a substituted or unsubstituted C6 to C30 aryloxy group.

[0052] For example, the fluorine-containing group may be a C1 to C20 alkyl group substituted with at least one fluorine, a C3 to C20 cycloalkyl group substituted with at least one fluorine, a C2 to C20 alkenyl group substituted with at least one fluorine, a C2 to C20 alkynyl group substituted with at least one fluorine, a C6 to C30 aryl group substituted with at least one fluorine, a C1 to C20 alkoxy group substituted with at least one fluorine, or a C6 to C30 aryloxy group substituted with at least one fluorine. As used herein, "at least one fluorine" may mean "at least one fluorine atom."

[0053] In some embodiments, the fluorine-containing group may include a C1 to C10 alkyl group substituted with at least one fluorine, a C3 to C10 cycloalkyl group substituted with at least one fluorine, a C2 to C10 alkenyl group substituted with at least one fluorine, a C2 to C10 alkynyl group substituted with at least one fluorine, a C6 to C12 aryl group substituted with at least one fluorine, a C1 to C10 alkoxy group substituted with at least one fluorine, or a C6 to C12 aryloxy group substituted with at least one fluorine.

[0054] For example, the fluorine-containing group may be substituted with at least two fluorines or at least three fluorines (e.g., at least two fluorine atoms or at least three fluorine atoms). In some embodiments, the fluorine-containing group may be a trifluoromethyl group, but is not limited thereto.

[0055] In some embodiments, the compound represented by Chemical Formula 1 may be one of (e.g., selected from among) the compounds listed in Group 1.

##STR00004##

[0056] The compound represented by Chemical Formula 1 may be included in an amount of about 0.01 wt % to about 10 wt % based on 100 wt % of the semiconductor photoresist composition. In some embodiments, an amount of the compound represented by Chemical Formula 1 may be about 0.01 wt % to about 10 wt % based on 100 wt % of the semiconductor photoresist composition.

[0057] For example, the compound represented by Chemical Formula 1 may be included in an amount of about 0.01 wt % to about 5 wt % or about 0.05 wt % to about 5 wt % based on 100 wt % of the semiconductor photoresist composition. In some embodiments, an amount of the compound represented by Chemical Formula 1 may be about 0.01 wt % to about 5 wt % or about 0.05 wt % to about 5 wt % based on 100 wt % of the semiconductor photoresist composition.

[0058] The Sn-containing organometallic compound may be included in an amount of about 0.5 wt % to about 30 wt % based on 100 wt % of the semiconductor photoresist composition. In some embodiments, an amount of the Sn-containing organometallic compound may be about 0.5 wt % to about 30 wt % based on 100 wt % of the semiconductor photoresist composition.

[0059] The semiconductor photoresist composition according to one or more embodiments of the present disclosure may improve the sensitivity of the photoresist by including the Sn-containing organometallic compound and the compound represented by Chemical Formula 1 within the content range as described in one or more embodiments of the present disclosure.

[0060] The semiconductor photoresist composition according to one or more embodiments of the present disclosure may include the Sn-containing organometallic compound and the compound represented by Chemical Formula 1 in a weight ratio of about 99.9:0.1 to about 80:20. In some embodiments, a weight ratio of the Sn-containing organometallic compound to the compound represented by Chemical Formula 1 may be about 99.9:0.1 to about 80:20. For example, the semiconductor photoresist composition may include the Sn-containing organometallic compound and the compound represented by Chemical Formula 1 in a weight ratio of about 95:5 to about

85:15. In some embodiments, a weight ratio of the Sn-containing organometallic compound to the compound represented by Chemical Formula 1 may be about 95:5 to about 85:15.

[0061] If (e.g., when) the weight ratio of the Sn-containing organometallic compound and the compound represented by Chemical Formula 1 satisfies the range as described in one or more embodiments of the present disclosure, a semiconductor photoresist composition having excellent or suitable sensitivity may be provided.

[0062] The Sn-containing organometallic compound may include an organic oxy group and/or an organic carbonyloxy group.

[0063] The Sn-containing organometallic compound may be represented by Chemical Formula 2.
##STR00005##

[0064] In Chemical Formula 2,

[0065] R^{sup.9} may be selected from among a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, and a substituted or unsubstituted C7 to C30 arylalkyl group,

[0066] R^{sup.10} to R^{sup.12} may be each independently a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, a substituted or unsubstituted C7 to C30 arylalkyl group, an alkoxy or aryloxy group (—OR^{sup.a}, wherein R^{sup.a} may be a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), a carboxyl group (—O(C=O)R^{sup.b}, wherein R^{sup.b} may be hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), an alkylamido or dialkylamido group (—NR^{sup.c}R^{sup.d}, wherein R^{sup.c} and R^{sup.d} may be each independently hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), an amidato group (—NR^{sup.e}(C=OR^{sup.t}), wherein R^{sup.e} and R^{sup.t} may be each independently hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), an amidinato group (—NR^{sup.g}C(NR^{sup.h})R^{sup.i}, wherein R^{sup.g}, R^{sup.h}, and R^{sup.i} may be each independently hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), an alkylthio or arylthiol group (—SR^{sup.k}, wherein R^{sup.k} may be a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), or a thiocarboxyl group (—S(C=O)R^{sup.l}, wherein R^{sup.l} may be hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), and

[0067] at least one selected from R^{sup.10} to R^{sup.12} may be selected from among an alkoxy or

aryloxy group ($\text{---OR}^{\text{sup.a}}$, wherein $\text{R}^{\text{sup.a}}$ may be a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), a carboxyl group ($\text{---O(C=O)R}^{\text{sup.b}}$, wherein $\text{R}^{\text{sup.b}}$ may be hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), an alkylamido or dialkylamido group ($\text{---NR}^{\text{sup.c}}\text{R}^{\text{sup.d}}$, wherein $\text{R}^{\text{sup.c}}$ and $\text{R}^{\text{sup.d}}$ may be each independently hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), an amidato group ($\text{---NR}^{\text{sup.e}}\text{(C=OR}^{\text{sup.f}})$, wherein $\text{R}^{\text{sup.e}}$ and $\text{R}^{\text{sup.f}}$ may be each independently hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), an amidinato group ($\text{---NR}^{\text{sup.g}}\text{C(NR}^{\text{sup.h}})\text{R}^{\text{sup.i}}$, wherein $\text{R}^{\text{sup.g}}$, $\text{R}^{\text{sup.h}}$, and $\text{R}^{\text{sup.i}}$ may be each independently hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), an alkylthio or arylthiol group ($\text{---SR}^{\text{sup.k}}$, wherein $\text{R}^{\text{sup.k}}$ may be a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), and a thiocarboxyl group ($\text{---S(C=O)R}^{\text{sup.l}}$, wherein $\text{R}^{\text{sup.l}}$ may be hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof).

[0068] In some embodiments, at least one selected from $\text{R}^{\text{sup.10}}$ to $\text{R}^{\text{sup.12}}$ may be selected from among an alkoxy or aryloxy group ($\text{---OR}^{\text{sup.a}}$, wherein $\text{R}^{\text{sup.a}}$ may be a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), and a carboxyl group ($\text{---O(C=O)R}^{\text{sup.b}}$, wherein $\text{R}^{\text{sup.b}}$ may be hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof).

[0069] In some embodiments, the compound represented by Chemical Formula 2 may include $\text{---OR}^{\text{sup.a}}$ or $\text{---OC(=O)R}^{\text{sup.b}}$ as a ligand so that a pattern formed using a semiconductor photoresist composition including the compound may exhibit excellent or suitable limiting resolution.

[0070] In some embodiments, the $\text{---OR}^{\text{sup.a}}$ or $\text{---OC(=O)R}^{\text{sup.b}}$ ligand may determine the solubility of the compound represented by Chemical Formula 2 in a solvent.

[0071] $\text{R}^{\text{sup.9}}$ may be a substituted or unsubstituted C1 to C8 alkyl group, a substituted or unsubstituted C3 to C8 cycloalkyl group, a substituted or unsubstituted C2 to C8 aliphatic unsaturated organic group including one or more double bonds or triple bonds, a substituted or unsubstituted C6 to C20 aryl group, a substituted or unsubstituted C4 to C20 heteroaryl group, a carbonyl group, an ethoxy group, a propoxy group, or a combination thereof,

[0072] R.sup.a may be a substituted or unsubstituted C1 to C8 alkyl group, a substituted or unsubstituted C3 to C8 cycloalkyl group, a substituted or unsubstituted C2 to C8 alkenyl group, a substituted or unsubstituted C2 to C8 alkynyl group, a substituted or unsubstituted C6 to C20 aryl group, or a combination thereof, and

[0073] R.sup.b may be hydrogen, a substituted or unsubstituted C1 to C8 alkyl group, a substituted or unsubstituted C3 to C8 cycloalkyl group, a substituted or unsubstituted C2 to C8 alkenyl group, a substituted or unsubstituted C2 to C8 alkynyl group, a substituted or unsubstituted C6 to C20 aryl group, or a combination thereof.

[0074] R.sup.9 may be a methyl group, an ethyl group, a propyl group, a butyl group, an isopropyl group, a tert-butyl group, a 2,2-dimethylpropyl group, a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, an ethenyl group, a propenyl group, a butenyl group, an ethynyl group, a propynyl group, a butynyl group, a phenyl group, a tolyl group, a xylene group, a benzyl group, a formyl group, an acetyl group, a propanoyl group, a butanoyl group, a pentanoyl group, an ethoxy group, a propoxy group, or a combination thereof,

[0075] R.sup.a may be an ethyl group, a propyl group, a butyl group, an isopropyl group, a tert-butyl group, a 2,2-dimethylpropyl group, a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, an ethenyl group, a propenyl group, a butenyl group, an ethynyl group, a propynyl group, a butynyl group, a phenyl group, a tolyl group, a xylene group, a benzyl group, or a combination thereof, and

[0076] R.sup.b may be hydrogen, an ethyl group, a propyl group, a butyl group, an isopropyl group, a tert-butyl group, a 2,2-dimethylpropyl group, a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, an ethenyl group, a propenyl group, a butenyl group, ethynyl group, propynyl group, butynyl group, phenyl group, tolyl group, xylene group, benzyl group, or a combination thereof.

[0077] In some embodiments, the Sn-containing organometallic compound may be represented by Chemical Formula 3 or Chemical Formula 4.

R.sup.13.sub.zSnO.sub.(2-(z/2)-(x/2)(OH).sub.x Chemical Formula 3

[0078] In Chemical Formula 3, [0079] R.sup.13 may be a C1 to C31 hydrocarbonyl group, $0 < z \leq 2$, and $0 < (z+x) \leq 4$;

R.sup.14.sub.nSn.sub.mX.sub.lY.sub.k Chemical Formula 4 [0080] wherein, in Chemical Formula 4, [0081] R.sup.14 may be a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 aliphatic unsaturated organic group including one or more double bonds or triple bonds, a substituted or unsubstituted C6 to C30 aryl group, a substituted or unsubstituted C4 to C30 heteroaryl group, a carbonyl group, an ethylene oxide group, a propylene oxide group, or a combination thereof, [0082] X may be sulfur(S), selenium (Se), or tellurium (Te), [0083] Y may be —OR.sup.m or —OC(=O)R.sup.n, [0084] wherein R.sup.m may be a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof, [0085] R.sup.n may be hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof, and [0086] n, m, l, and k may be each independently an integer of 1 to 20. [0087] The solvent of the semiconductor photoresist composition according to one or more embodiments of the present disclosure may be an organic solvent, and may be, for example, aromatic compounds (e.g., xylene, toluene, etc.), alcohols (e.g., 4-methyl-2-pentenol, 4-methyl-2-propanol, 1-butanol, methanol, isopropyl alcohol, 1-propanol), ethers (e.g., anisole,

tetrahydrofuran), esters (n-butyl acetate, propylene glycol monomethyl ether acetate (PGMEA), ethyl acetate, ethyl lactate), ketones (e.g., methyl ethyl ketone, 2-heptanone), or a mixture thereof, but is not limited thereto.

[0088] The semiconductor photoresist composition according to one or more embodiments of the present disclosure may further include a resin in addition to the Sn-containing organometallic compound, compound represented by Chemical Formula 1, and solvent as described in one or more embodiments of the present disclosure.

[0089] The resin may be a phenol-based resin including at least one aromatic moiety of Group 2.

##STR00006## ##STR00007##

[0090] The resin may have a weight average molecular weight of about 500 g/mol to about 20,000 g/mol.

[0091] The resin may be included in an amount of about 0.1 wt % to about 50 wt % based on a total amount of the semiconductor photoresist composition. An amount of the resin may be about 0.1 wt % to about 50 wt % based on a total amount of the semiconductor photoresist composition.

[0092] If (e.g., when) the resin is included in the content range as described in one or more embodiments of the present disclosure, it may have excellent or suitable etch resistance and heat resistance.

[0093] In some embodiments, the semiconductor photoresist composition according to one or more embodiments of the present disclosure may consist of the Sn-containing organometallic compound, compound represented by Chemical Formula 1, solvent, and resin as described in one or more embodiments of the present disclosure.

[0094] However, the semiconductor photoresist composition according to the one or more embodiments of the present disclosure may further include additives as needed 1 or desired. Examples of the additives may be a surfactant, a crosslinking agent, a leveling agent, an organic acid, a quencher, or a combination thereof.

[0095] The surfactant may include, for example, an alkyl benzene sulfonate salt, an alkyl pyridinium salt, polyethylene glycol, a quaternary ammonium salt, or a combination thereof, but is not limited thereto.

[0096] The crosslinking agent may be, for example, a melamine-based crosslinking agent, a substituted urea-based crosslinking agent, an acryl-based crosslinking agent, an epoxy-based crosslinking agent, or a polymer-based crosslinking agent, but is not limited thereto. It may be a crosslinking agent having at least two crosslinking forming substituents, for example, a compound, such as methoxymethylated glycoluril, butoxymethylated glycoluril, methoxymethylated melamine, butoxymethylated melamine, methoxymethylated benzoguanamine, butoxymethylated benzoguanamine, 4-hydroxybutyl acrylate, acrylic acid, urethane acrylate, acryl methacrylate, 1,4-butanediol diglycidyl ether, glycidol, diglycidyl 1,2-cyclohexane dicarboxylate, trimethylpropane triglycidyl ether, 1,3-bis(glycidoxypropyl)tetramethyldisiloxane, methoxymethylated urea, butoxymethylated urea, methoxymethylated thiourea, and/or the like.

[0097] The leveling agent may be used for improving coating flatness during printing and may be a leveling agent which is generally used or generally available.

[0098] The organic acid may include p-toluenesulfonic acid, benzenesulfonic acid, p-dodecylbenzenesulfonic acid, 1,4-naphthalenedisulfonic acid, methanesulfonic acid, a fluorinated sulfonium salt, malonic acid, citric acid, propionic acid, methacrylic acid, oxalic acid, lactic acid, glycolic acid, succinic acid, or a combination thereof, but is not limited thereto.

[0099] The quencher may be diphenyl (p-tolyl) amine, methyl diphenyl amine, triphenyl amine, phenylenediamine, naphthylamine, diaminonaphthalene, or a combination thereof.

[0100] In some embodiments, an acid compound may be mixed in the semiconductor photoresist composition according to one or more embodiments of the present disclosure.

[0101] A use amount of the additives may be controlled depending on suitable or desired properties.

[0102] In some embodiments, the semiconductor photoresist composition may further include a silane coupling agent as an adherence enhancer in order to improve a close-contacting force with the substrate (e.g., in order to improve adherence of the semiconductor photoresist composition to the substrate). The silane coupling agent may be, for example, a silane compound including a carbon-carbon unsaturated bond, such as vinyltrimethoxysilane, vinyl triethoxysilane, vinyl trichlorosilane, vinyl tris(β -methoxyethoxy) silane, and/or 3-methacryloxypropyltrimethoxysilane, 3-acryloxypropyltrimethoxysilane, p-styryl trimethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-methacryloxypropylmethyl diethoxysilane, trimethoxy[3-(phenylamino)propyl]silane, and/or the like, but is not limited thereto.

[0103] The semiconductor photoresist composition may be formed into a pattern having a high aspect ratio without a collapse. In some embodiments, in order to form a fine pattern having a width of, for example, about 5 nm to about 100 nm, for example, about 5 nm to about 80 nm, for example, about 5 nm to about 70 nm, for example, about 5 nm to about 50 nm, for example, about 5 nm to about 40 nm, for example, about 5 nm to about 30 nm, or, for example, about 5 nm to about 20 nm, the semiconductor photoresist composition may be used for a photoresist process using light in a wavelength range from about 5 nm to about 150 nm, for example, about 5 nm to about 100 nm, about 5 nm to about 80 nm, about 5 nm to about 50 nm, about 5 nm to about 30 nm, or about 5 nm to about 20 nm. In some embodiments, the semiconductor photoresist composition according to one or more embodiments of the present disclosure may be used to realize extreme ultraviolet lithography using an EUV light source of a wavelength of about 13.5 nm.

[0104] According to one or more embodiments of the present disclosure, a method of forming patterns using the semiconductor photoresist composition as described in one or more embodiments of the present disclosure is provided. For example, the manufactured pattern may be a photoresist pattern.

[0105] The method of forming patterns according to one or more embodiments of the present disclosure may include providing (e.g., forming) an etching-objective layer on a substrate, coating the semiconductor photoresist composition on the etching-objective layer to form a photoresist layer, patterning the photoresist layer to form a photoresist pattern, and etching the etching-objective layer using the photoresist pattern as an etching mask.

[0106] Hereinafter, a method of forming patterns using the semiconductor photoresist composition is described referring to FIGS. 1A-1E. FIGS. 1A-1E are cross-sectional views for illustrating a method of forming patterns using a semiconductor photoresist composition according to one or more embodiments of the present disclosure.

[0107] Referring to FIG. 1A, an object for etching may be prepared. The object for etching may be a thin film **102** formed on a semiconductor substrate **100**. Hereinafter, the object for etching may be limited to the thin film **102**. A surface of the thin film **102** may be washed to remove impurities and the like remaining thereon. The thin film **102** may be, for example, a silicon nitride layer, a polysilicon layer, and/or a silicon oxide layer.

[0108] Subsequently, the resist underlayer composition for forming a resist underlayer **104** may be spin-coated on the surface of the washed thin film **102**. However, the present disclosure is not limited thereto, and generally used or generally available other suitable coating methods, for example, a spray coating, a dip coating, a knife edge coating, a printing method, for example, an inkjet printing and/or a screen printing, and/or the like may be used.

[0109] Description of the coating process of the resist underlayer may not be repeated hereinafter, and hereinafter, a process including a coating of the resist underlayer may be described.

[0110] Then, the coated composition may be dried and baked to form a resist underlayer **104** on the thin film **102**. The baking may be performed at about 100° C. to about 500° C., for example, about 100° C. to about 300° C.

[0111] The resist underlayer **104** may be formed between the substrate **100** and a photoresist layer **106**, and thus, may prevent non-uniformity (e.g., substantial non-uniformity) and pattern

formability (or reduce a degree or occurrence of non-uniformity (e.g., substantial non-uniformity) and/or reduce pattern formability) of a photoresist line width that may otherwise occur if (e.g., when) a ray reflected from on the interface between the substrate **100** and the photoresist layer **106** and/or a hardmask between layers is scattered into an unintended photoresist region.

[0112] Referring to FIG. **1B**, the photoresist layer **106** may be formed by coating the semiconductor photoresist composition on the resist underlayer **104**. The photoresist layer **106** may be obtained by coating the semiconductor photoresist composition according to one or more embodiments of the present disclosure on the thin film **102** formed on the substrate **100** and then, curing it through a heat treatment.

[0113] For example, the formation of a pattern by using the semiconductor photoresist composition may include coating the semiconductor resist composition on the substrate **100** having the thin film **102** through spin coating, slit coating, inkjet printing, and/or the like and then, drying it to form the photoresist layer **106**.

[0114] The semiconductor photoresist composition has already been illustrated in more detail in one or more embodiments of the present disclosure and may not be illustrated again hereinafter.

[0115] Subsequently, a substrate **100** having the photoresist layer **106** may be subjected to a first baking process. The first baking process may be performed at about 80° C. to about 120° C.

[0116] Referring to FIG. **1C**, the photoresist layer **106** may be selectively exposed using a patterned mask **110**.

[0117] For example, the exposure may use an activation radiation including light having a high energy wavelength, such as EUV (extreme ultraviolet; a wavelength of about 13.5 nm), an E-Beam (an electron beam), and/or the like, as well as a short wavelength, such as an i-line (a wavelength of about 365 nm), a KrF excimer laser (a wavelength of about 248 nm), an ArF excimer laser (a wavelength of about 193 nm), and/or the like.

[0118] For example, light for the exposure according to one or more embodiments of the present disclosure may have a short wavelength in a range from about 5 nm to about 150 nm and a high energy wavelength, for example, EUV (extreme ultraviolet; a wavelength of 13.5 nm), an E-Beam (an electron beam), and/or the like.

[0119] The exposed region **106b** of the photoresist layer **106** may have a different solubility from the unexposed region **106a** of the photoresist layer **106** by forming a polymer by a crosslinking reaction, such as condensation between organometallic compounds.

[0120] Subsequently, the substrate **100** may be subjected to a second baking process. The second baking process may be performed at a temperature of about 90° C. to about 200° C. The exposed region **106b** of the photoresist layer **106** may become easily indissoluble regarding a developer due to the second baking process.

[0121] In FIG. **1D**, the unexposed region **106a** of the photoresist layer may be dissolved and removed using the developer to form a photoresist pattern **108**. For example, the unexposed region **106a** of the photoresist layer may be dissolved and removed by using an organic solvent, such as 2-heptanone and/or the like, to complete the photoresist pattern **108** corresponding to the negative tone image.

[0122] According to one or more embodiments of the present disclosure, a developer used in a method of forming patterns according to one or more embodiments of the present disclosure may be an organic solvent. The organic solvent used in the method of forming patterns according to one or more embodiments of the present disclosure may be, for example, ketones, such as methylethylketone, acetone, cyclohexanone, 2-heptanone, and/or the like, alcohols, such as 4-methyl-2-propanol, 1-butanol, isopropanol, 1-propanol, methanol, and/or the like, esters, such as propylene glycol monomethyl ether acetate (PGMEA), ethyl acetate, ethyl lactate, n-butyl acetate, butyrolactone, and/or the like, aromatic compounds, such as benzene, xylene, toluene, and/or the like, or a combination thereof.

[0123] However, the photoresist pattern according to one or more embodiments of the present

disclosure may not necessarily be limited to the negative tone image but may be formed to have a positive tone image. Herein, a developer used for forming the positive tone image may be a quaternary ammonium hydroxide composition, such as tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, or a combination thereof.

[0124] According to one or more embodiments of the present disclosure, exposure to light having a high energy, such as EUV (extreme ultraviolet; a wavelength of 13.5 nm), an E-Beam (an electron beam), and/or the like, as well as light having a wavelength, such as i-line (wavelength of about 365 nm), KrF excimer laser (wavelength of about 248 nm), ArF excimer laser (wavelength of about 193 nm), and/or the like, may provide a photoresist pattern **108** having a width of a thickness of about 5 nm to about 100 nm. For example, the photoresist pattern **108** may have a width of a thickness of about 5 nm to about 90 nm, about 5 nm to about 80 nm, about 5 nm to about 70 nm, about 5 nm to about 60 nm, about 5 nm to about 50 nm, about 5 nm to about 40 nm, about 5 nm to about 30 nm, or about 5 nm to about 20 nm.

[0125] In some embodiments, the photoresist pattern **108** may have a pitch of having a half-pitch of less than or equal to about 50 nm, for example, less than or equal to about 40 nm, for example, less than or equal to about 30 nm, for example, less than or equal to about 20 nm, or, for example, less than or equal to about 15 nm, and a line width roughness of less than or equal to about 10 nm, or less than or equal to about 5 nm, less than or equal to about 3 nm, or less than or equal to about 2 nm.

[0126] Subsequently, the photoresist pattern **108** may be used as an etching mask to etch the resist underlayer **104**. Through this etching process, an organic layer pattern **112** may be formed. The organic layer pattern **112** also may have a width corresponding to that of the photoresist pattern **108**.

[0127] Referring to FIG. 1E, the exposed thin film **102** may be etched by applying the photoresist pattern **108** as an etching mask. As a result, the thin film may be formed as a thin film pattern **114**.

[0128] The etching of the thin film **102** may be, for example, dry etching using an etching gas and the etching gas may be, for example, CHF₃, CF₄, Cl₂, BCl₃ and/or a mixed gas thereof.

[0129] In the exposure process, the thin film pattern **114** formed by using the photoresist pattern **108** formed through the exposure process performed by using an EUV light source may have a width corresponding to that of the photoresist pattern **108**. For example, the thin film pattern **114** may have a width of about 5 nm to about 100 nm which may be equal to that of the photoresist pattern **108**. For example, the thin film pattern **114** formed by using the photoresist pattern **108** formed through the exposure process performed by using an EUV light source may have a width of about 5 nm to about 90 nm, about 5 nm to about 80 nm, about 5 nm to about 70 nm, about 5 nm to about 60 nm, about 5 nm to about 50 nm, about 5 nm to about 40 nm, about 5 nm to about 30 nm, or about 5 nm to about 20 nm, and in some embodiments, a width of less than or equal to about 20 nm, like that of the photoresist pattern **108**.

[0130] Hereinafter, the subject matter of the present disclosure will be described in more detail through examples of the preparation of the semiconductor photoresist composition according to one or more embodiments of the present disclosure. However, the present disclosure is technically not restricted by the following examples.

Synthesis Example 1

[0131] 40.7 g of t-butylSnPh₃ and 300 g of propionic acid were added to a 250 mL two-neck round bottom flask and were heated and refluxed for 24 hours.

[0132] By removing unreacted propionic acid under reduced pressure, a compound represented by Chemical Formula 5 was obtained.

##STR00008##

Synthesis Example 2

[0133] 30 mL of anhydrous pentane was added to 10 g of t-AmylSnCl₃, the temperature was

maintained at 0° C., then 7.4 g of diethyl amine and 6.1 g of ethanol were added thereto and stirred at room temperature for 1 hour. When the reaction was completed, filtration, concentration, and drying under vacuum were performed to obtain a compound represented by Chemical Formula 6.

##STR00009##

Synthesis Example 3

[0134] 10 g of dibutyltin dichloride was dissolved 30 mL of ether, 70 mL of a 1 M sodium hydroxide (NaOH) aqueous solution was added thereto and then, stirred for 1 hour. After the stirring, a solid produced therein was filtered, three times washed with 25 mL of deionized water, and dried at 100° C. under a reduced pressure to obtain an organometallic compound represented by Chemical Formula 7 and having a weight average molecular weight of 1,500 g/mol.

##STR00010##

Synthesis Example 4

[0135] 10 g of N-hydroxysuccinimide was dissolved in 100 mL of dichloromethane, add bis(trifluoromethyl) phosphinic chloride and 15 mL of triethylamine, and stirred for 2 hours, the resulting solid was filtered and washed three times with 25 mL of deionized water, and dried under reduced pressure. Thus, a compound represented by Chemical Formula 8 was obtained.

##STR00011##

Synthesis Example 5

[0136] A compound represented by Chemical Formula 9 was obtained in substantially the same manner as in Synthesis Example 4, except that methyl-(trifluoromethyl)phosphonochloridate was used instead of bis(trifluoromethyl)phosphinic chloride.

##STR00012##

Preparation of Semiconductor Photoresist Compositions Examples 1 to 9, and Comparative Examples 1 to 4

[0137] The compounds represented by Chemical Formulas 5 to 7 obtained according to Synthesis Examples 1 to 3, the compounds represented by Chemical Formulas 8 and 9 obtained according to Synthesis Examples 4 and 5, and compounds represented by Chemical Formulas 10 and 11 were respectively dissolved in 4-methyl-2-pentanol at a concentration of 2 wt % in a weight ratio shown in Table 1 and then, filtered with a 0.1 μm PTFE (polytetrafluoroethylene) syringe filter to prepare semiconductor photoresist compositions.

##STR00013##

[0138] N-(Trifluoromethanesulfonyloxy)-5-norbornene-2,3-dicarboximide; TCI

##STR00014##

[0139] Bis (4-tert-butylphenyl) iodonium perfluoro-1-butanesulfonate; Sigma-Aldrich Corp.
TABLE-US-00001
TABLE 1
Compound represented by Organometallic compound Chemical Formula 1 (wt %) (wt %) Example 1 Chemical Formula 5 Chemical Formula 8 (2.95) (0.05)
Example 2 Chemical Formula 5 Chemical Formula 8 (2.90) (0.10) Example 3 Chemical Formula 5 Chemical Formula 9 (2.90) (0.10) Example 4 Chemical Formula 5 Chemical Formula 9 (2.85) (0.15) Example 5 Chemical Formula 6 Chemical Formula 8 (2.90) (0.10) Example 6 Chemical Formula 6 Chemical Formula 9 (2.85) (0.15) Example 7 Chemical Formula 7 Chemical Formula 8 (2.90) (0.10) Example 8 Chemical Formula 7 Chemical Formula 9 (2.90) (0.10) Example 9 Chemical Formula 5 Chemical Formula 10 (2.90) (0.10) Comparative Chemical Formula 5 — Example 1 (3.00) Comparative Chemical Formula 6 — Example 2 (3.00) Comparative Chemical Formula 7 — Example 3 (3.00) Comparative Chemical Formula 5 Chemical Formula 11 Example 4 (2.90) (0.10)

Evaluation 1: Evaluation of Sensitivity

[0140] Each of the photoresist compositions according to the examples and the comparative examples was spin-coated at 1500 rpm for 30 seconds on a 200 mm circular silicon wafer of which the surface was deposited with HMDS, baked at 110° C. for 60 seconds (post-apply baked (PAB)), and then, allowed to stand at room temperature (23±2° C.) for 30 seconds.

[0141] Subsequently, a linear array of 50 circular pads with a diameter of 500 μm was projected onto the wafer coated with each of the photoresist compositions by using EUV light (Lawrence Berkeley National Laboratory Micro Exposure Tool, MET). Herein, pad exposure time was adjusted to ensure that increased EUV dose was applied to each pad.

[0142] Then, the resist and the substrate were baked at 160° C. for 120 seconds on a hot plate after the exposure. The baked film was developed in a propylene glycol monomethyl ether acetate (PGMEA) solvent to form a negative tone image. Finally, the obtained film was baked again at 150° C. for 2 minutes on the hot plate, completing the process.

[0143] The residual resist thickness of the exposed pad was measured using an ellipsometer. The remaining thickness for each exposure dose was measured and graphed as a function of the exposure dose to measure sensitivity. Sensitivity was evaluated according to the following criteria, and the results are shown in Table 2.

Evaluation Criteria

[0144] A: less than 16 mJ/cm.² [0145] B: greater than or equal to 16 mJ/cm.² and less than 20 mJ/cm.² [0146] C: greater than or equal to 20 mJ/cm.²

Evaluation 2: Evaluation of Storage Stability

[0147] The photoresist compositions according to the Examples and Comparative Examples were sealed in a container and stored in an oven at 40° C. Two weeks later, whether the solution remained transparent was visually evaluated and the results thereof are shown in Table 2.

Evaluation Criteria

[0148] o: Clear solution remains after 2 weeks [0149] X: Solution changes to cloudy after 2 weeks

TABLE-US-00002 TABLE 2 Sensitivity Storage stability Example 1 B ○ Example 2 A ○ Example 3 A ○ Example 4 A ○ Example 5 A ○ Example 6 A ○ Example 7 A ○ Example 8 A ○ Example 9 A ○ Comparative Example 1 C ○ Comparative Example 2 C ○ Comparative Example 3 C ○ Comparative Example 4 A X

[0150] Referring to the results of Table 2, the patterns formed by respectively using the semiconductor photoresist compositions according to Examples 1 to 9 exhibited excellent sensitivity and/or excellent storage stability, compared with those formed by respectively using the semiconductor photoresist compositions according to Comparative Examples 1 to 4.

[0151] Hereinbefore, certain embodiments have been described and illustrated, however, it may be apparent to a person having ordinary skill in the art that the present disclosure is not limited to one or more embodiments of the present disclosure, and may be suitably modified and transformed without departing from the spirit and scope of the present disclosure. In some embodiments, the modified or transformed embodiments as such may not be understood separately from the technical ideas and aspects of one or more embodiments of the present disclosure, and the modified embodiments may be within the scope of the appended claims of the present disclosure, and equivalents thereof.

TABLE-US-00003 Description of symbols 100: substrate 102: thin film 104: resist underlayer 106: photoresist layer 106a: unexposed region 106b: exposed region 108: photoresist pattern 112: organic layer pattern 110: patterned mask 114: thin film pattern

Claims

1. A semiconductor photoresist composition, comprising: a tin (Sn)-containing organometallic compound; a compound represented by Chemical Formula 1; and a solvent: ##STR00015## wherein, in Chemical Formula 1, X.^{sup.1} is P(=O)R.^{sup.4} or S(=O).₂, R.^{sup.1} to R.^{sup.4} are each independently a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30

aryl group, a substituted or unsubstituted C1 to C20 alkoxy group, or a substituted or unsubstituted C6 to C30 aryloxy group, R.sup.1 and R.sup.2 are each independently present or are linked to form a ring, and at least one selected from R.sup.3 and R.sup.4 is a fluorine-containing group.

2. The semiconductor photoresist composition as claimed in claim 1, wherein: Chemical Formula 1 is represented by Chemical Formula 1-1: ##STR00016## wherein, in Chemical Formula 1-1, X.sup.1 is P(=O)R.sup.4 or S(=O).sub.2, R.sup.3 and R.sup.4 are each independently a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, a substituted or unsubstituted C1 to C20 alkoxy group, or a substituted or unsubstituted C6 to C30 aryloxy group, at least one selected from R.sup.3 and R.sup.4 is a fluorine-containing group, and R.sup.5 to R.sup.8 are each independently hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, a substituted or unsubstituted C1 to C20 alkoxy group, or a substituted or unsubstituted C6 to C30 aryloxy group.

3. The semiconductor photoresist composition as claimed in claim 1, wherein: the fluorine-containing group is a C1 to C20 alkyl group substituted with at least one fluorine, a C3 to C20 cycloalkyl group substituted with at least one fluorine, a C2 to C20 alkenyl group substituted with at least one fluorine, a C2 to C20 alkynyl group substituted with at least one fluorine, a C6 to C30 aryl group substituted with at least one fluorine, a C1 to C20 alkoxy group substituted with at least one fluorine, or a C6 to C30 aryloxy group substituted with at least one fluorine.

4. The semiconductor photoresist composition as claimed in claim 1, wherein: the compound represented by Chemical Formula 1 is one selected from among the compounds listed in Group 1: ##STR00017##

5. The semiconductor photoresist composition as claimed in claim 1, wherein: an amount of the compound represented by Chemical Formula 1 is about 0.01 wt % to about 10 wt % based on 100 wt % of the semiconductor photoresist composition.

6. The semiconductor photoresist composition as claimed in claim 1, wherein: an amount of the compound represented by Chemical Formula 1 is about 0.05 wt % to about 5 wt % based on 100 wt % of the semiconductor photoresist composition.

7. The semiconductor photoresist composition as claimed in claim 1, wherein: an amount of the Sn-containing organometallic compound is about 0.5 wt % to about 30 wt % based on 100 wt % of the semiconductor photoresist composition.

8. The semiconductor photoresist composition as claimed in claim 1, wherein: a weight ratio of the Sn-containing organometallic compound to the compound represented by Chemical Formula 1 is about 99.9:0.1 to about 80:20.

9. The semiconductor photoresist composition as claimed in claim 1, wherein: the semiconductor photoresist composition further comprises an additive of a surfactant, a crosslinking agent, a leveling agent, an organic acid, a quencher, or a combination thereof.

10. The semiconductor photoresist composition as claimed in claim 1, wherein: the Sn-containing organometallic compound comprises at least one selected from an organic oxy group and an organic carbonyloxy group.

11. The semiconductor photoresist composition as claimed in claim 1, wherein: the Sn-containing organometallic compound is represented by Chemical Formula 2: ##STR00018## wherein, in Chemical Formula 2, R.sup.9 is selected from among a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, and a substituted or unsubstituted C7 to C30 arylalkyl group, R.sup.10 to R.sup.12 are each independently a substituted or unsubstituted C1 to C20 alkyl group,

[illegible]

independently hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), an alkylthio or arylthiol group ($\text{—SR}^{\text{sup.k}}$, wherein $\text{R}^{\text{sup.k}}$ is a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof), and a thiocarboxyl group ($\text{—S(C=O)R}^{\text{sup.l}}$, wherein $\text{R}^{\text{sup.l}}$ is hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof).

12. The semiconductor photoresist composition as claimed in claim 11, wherein: $\text{R}^{\text{sup.9}}$ is a substituted or unsubstituted C1 to C8 alkyl group, a substituted or unsubstituted C3 to C8 cycloalkyl group, a substituted or unsubstituted C2 to C8 aliphatic unsaturated organic group comprising one or more double bonds or triple bonds, a substituted or unsubstituted C6 to C20 aryl group, a substituted or unsubstituted C4 to C20 heteroaryl group, a carbonyl group, an ethoxy group, a propoxy group, or a combination thereof, $\text{R}^{\text{sup.a}}$ is a substituted or unsubstituted C1 to C8 alkyl group, a substituted or unsubstituted C3 to C8 cycloalkyl group, a substituted or unsubstituted C2 to C8 alkenyl group, a substituted or unsubstituted C2 to C8 alkynyl group, a substituted or unsubstituted C6 to C20 aryl group, or a combination thereof, and $\text{R}^{\text{sup.b}}$ is hydrogen, a substituted or unsubstituted C1 to C8 alkyl group, a substituted or unsubstituted C3 to C8 cycloalkyl group, a substituted or unsubstituted C2 to C8 alkenyl group, a substituted or unsubstituted C2 to C8 alkynyl group, a substituted or unsubstituted C6 to C20 aryl group, or a combination thereof.

13. The semiconductor photoresist composition as claimed in claim 1, wherein: the Sn-containing organometallic compound is represented by Chemical Formula 3 or Chemical Formula 4:

$\text{R}^{\text{sup.13.sub.z}}\text{SnO}^{\text{sub.(2-(z/2)-(x/2)(OH).sub.x}}$ Chemical Formula 3 wherein, in Chemical Formula 3, $\text{R}^{\text{sup.13}}$ is a C1 to C31 hydrocarbonyl group, $0 < z \leq 2$, and $0 < (z+x) \leq 4$;

$\text{R}^{\text{sup.14.sub.n}}\text{Sn}^{\text{sub.m}}\text{X}^{\text{sub.l}}\text{Y}^{\text{sub.k}}$ Chemical Formula 4 wherein, in Chemical Formula 4, $\text{R}^{\text{sup.14}}$ is a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 aliphatic unsaturated organic group comprising one or more double bonds or triple bonds, a substituted or unsubstituted C6 to C30 aryl group, a substituted or unsubstituted C4 to C30 heteroaryl group, a carbonyl group, an ethylene oxide group, a propylene oxide group, or a combination thereof, X is sulfur(S), selenium (Se), or tellurium (Te), Y is $\text{—OR}^{\text{sup.m}}$ or $\text{—OC(=O)R}^{\text{sup.n}}$, wherein $\text{R}^{\text{sup.m}}$ is a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof, $\text{R}^{\text{sup.n}}$ is hydrogen, a substituted or unsubstituted C1 to C20 alkyl group, a substituted or unsubstituted C3 to C20 cycloalkyl group, a substituted or unsubstituted C2 to C20 alkenyl group, a substituted or unsubstituted C2 to C20 alkynyl group, a substituted or unsubstituted C6 to C30 aryl group, or a combination thereof, and n, m, l, and k are each independently an integer of 1 to 20.

14. A method of forming patterns, comprising: providing an etching-objective layer on a substrate; coating the semiconductor photoresist composition as claimed in claim 1 on the etching-objective layer to form a photoresist layer; patterning the photoresist layer to form a photoresist pattern; and etching the etching-objective layer using the photoresist pattern as an etching mask.
