

POSITIVE TONE PATTERNS FROM METAL ORGANIC RESISTS**BACKGROUND****[0001] Field**

[0002] The disclosed and claimed subject matter relates to the use of a metal organic resist (MOR) resist in positive tone processing for high resolution patterning using actinic radiation, in particular EUV radiation of 13.5 nm wavelength.

[0003] Related Art

[0004] Metal organic resists (MORs) have been found to be useful in EUV lithography since they exhibit high absorption cross sections for EUV radiation. To date, MORs have only been described for practical use in negative tone processing. Positive tone applications have been described a few times, but the unexposed material lacked the appropriate resistance to the developer at the appropriate process conditions leading to unacceptable film loss.

[0005] U.S. Patent No. 9,310,684 describes positive tone development using dry deposition of monobutyltin oxo hydrate that reacts to an oxo hydroxo cluster. The process utilizes a water-based developer (which can be basic or acidic) with sharper patterns for basic solutions. TMAH solutions (2.5% as standard developer solution in semiconductor technologies) were indicated to be preferred as there will be no metal contamination from the developer.

[0006] WO22016123 describes the use of a metal containing complex and a reactive co-reactant. Depending on the choice of the co-reactant, the films can be developed as a positive tone (like oxalyl derived moieties) or negative tone. Notably, water based alkaline solutions were preferred for wet development, while acid vapors were preferred for dry development. In addition, the disclosed systems required additives in order for the clusters to make a crosslinking for the resists.

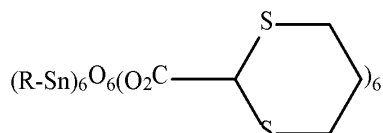
[0007] A consistent problem with the above positive tone development processes is the very short development times (*ca.* a few seconds). If the polarity of the materials is reduced, the development time can be increased. However, the only materials utilized include tin-oxo-hydroxo cluster; thus, they contain hydroxy groups that lead to undesirably short development times.

[0008] Use of the Sn6 cluster described herein provides the advantage of there being no hydroxy groups. This permits the polarity to be tuned by the choice of the carboxylic acid used for synthesis. This allows tuning of the development time significantly and makes the development process less sensitive to variations. As described herein, adjustments from less polar to more polar acids allow longer development times to be realized. In addition, TMAH showed best results in for development times. By using a water-based developer, positive tone resists based on MORs have been demonstrated. It could also be shown that tuning the MOR to less polar structures improve

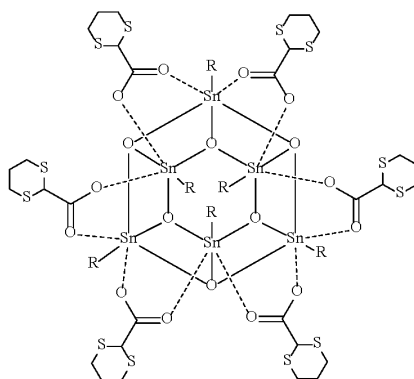
development process. Also, that using an underlayer gives better pattern retention by accounting for the change in polarity of the MOR.

SUMMARY

[0009] In one embodiment, the disclosed and claimed subject matter relates to the use of a metal organic resist (MOR) of the following formula:



where R is a C₁-C₆ alkyl group (hereinafter “(R-Sn)₆O₆(O₂C-dithiane)₆”) for positive tone processing in high resolution patterning using actinic radiation. As those skilled in the art will understand, the above MOR is Sn₆-oxo drum cluster have the following general structure:



In one aspect of this embodiment the actinic radiation is EUV radiation of 13.5 nm wavelength.

[0010] This summary section does not specify every embodiment and/or incrementally novel aspect of the disclosed and claimed subject matter. Instead, this summary only provides a preliminary discussion of different embodiments and corresponding points of novelty over conventional techniques and the known art. For additional details and/or possible perspectives of the disclosed and claimed subject matter and embodiments, the reader is directed to the Detailed Description section and corresponding figures of the disclosure as further discussed below.

[0011] The order of discussion of the different steps described herein has been presented for the sake of clarity. In general, the steps disclosed herein can be performed in any suitable order. Additionally, although each of the different features, techniques, configurations, etc. disclosed herein may be discussed in different places of this disclosure, it is intended that each of the concepts can be executed independently of each other or in combination with each other as appropriate. Accordingly, the disclosed and claimed subject matter can be embodied and viewed in many different ways.

[0012] BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The accompanying drawings, which are included to provide a further understanding of the disclosed subject matter and are incorporated in and constitute a part of this specification, illustrate embodiments of the disclosed subject matter and together with the description serve to explain the principles of the disclosed subject matter. In the drawings:

[0014] FIG. 1 illustrates the developed structure of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_6$;

[0015] FIG. 2 illustrates the developed structure of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{CH})_6$;

[0016] FIG. 3 illustrates the dose curves for the samples of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_6$ (dotted line) and $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{CH})_6$ (full line) developed in the comparative examples;

[0017] FIG. 4 illustrates the developed structure of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C dithiane})_6$;

[0018] FIG. 5 illustrates the developed structure of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C dithiane})_6$;

[0019] FIG. 6 illustrates the dose curve for developed $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C dithiane})_6$ clusters;

[0020] FIG. 7 illustrates EUV exposure of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C dithiane})_6$ (no underlayer) with a 44 nm pitch target;

[0021] FIG. 8 illustrates EUV exposure of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C dithiane})_6$ (with underlayer) with a 60 nm pitch target;

[0022] FIG. 9 illustrates EUV exposure of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C dithiane})_6$ (with underlayer) with a 44 nm pitch target;

[0023] FIG. 10 illustrates EUV exposure of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C dithiane})_6$ (with underlayer) with a 50 nm pitch target and five-minute TMAH development; and

[0024] FIG. 11 illustrates EUV exposure of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C dithiane})_6$ (with underlayer) with a 44 nm pitch target and two-minute TMAH development followed by an additional 15 second TMAH rinse.

[0025] DEFINITIONS

[0026] Unless otherwise stated, the following terms used in the specification and claims shall have the following meanings for this application.

[0027] In this application, the use of the singular includes the plural, and the words “a,” “an” and “the” mean “at least one” unless specifically stated otherwise. Furthermore, the use of the term “including,” as well as other forms such as “includes” and “included,” is not limiting. Also, terms such as “element” or “component” encompass both elements or components including one unit and elements or components that include more than one unit, unless specifically stated otherwise. As used herein, the conjunction “and” is intended to be inclusive and the conjunction “or” is not intended to be exclusive, unless otherwise indicated. For example, the phrase “or, alternatively” is intended to be exclusive. As used herein, the term “and/or” refers to any combination of the foregoing elements

including using a single element.

[0028] The term “about” or “approximately,” when used in connection with a measurable numerical variable, refers to the indicated value of the variable and to all values of the variable that are within the experimental error of the indicated value (*e.g.*, within the 95% confidence limit for the mean) or within percentage of the indicated value (*e.g.*, $\pm 10\%$, $\pm 5\%$), whichever is greater.

[0029] “Actinic radiation” shall be understood to include all radiative forms of energy which are capable of causing a chemical change in the photoresist composition, not including changes caused by purely thermal effects. Examples of actinic radiation include but are not limited to photons of wavelength 13.5 nm, 193 nm, 248 nm, or 365 nm, or electron beams or other particle beams, including but not limited to helium ion beams.

[0030] As used herein, “C_{x-y}” (where x and y are each integers) designates the number of carbon atoms in a chain. For example, C₁₋₆ alkyl refers to an alkyl chain having a chain of between 1 and 6 carbons (*e.g.*, methyl, ethyl, propyl, butyl, pentyl and hexyl). Unless specifically stated otherwise, the chain can be linear or branched.

[0031] Unless otherwise indicated, “alkyl” refers to hydrocarbon groups which can be linear, branched (*e.g.*, methyl, ethyl, propyl, isopropyl, tert-butyl and the like), cyclic (*e.g.*, cyclohexyl, cyclopropyl, cyclopentyl and the like) or multicyclic (*e.g.*, norbornyl, adamantyl and the like). Suitable acyclic groups can be methyl, ethyl, n- or iso-propyl, n-, iso, or tert-butyl, linear or branched pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl. Unless otherwise stated, alkyl refers to 1-10 carbon atom moieties. The cyclic alkyl groups may be mono cyclic or polycyclic. Suitable examples of mono-cyclic alkyl groups include substituted cyclopentyl, cyclohexyl, and cycloheptyl groups. The substituents may be any of the acyclic alkyl groups described herein. Suitable bicyclic alkyl groups include substituted bicyclo[2.2.1]heptane, bicyclo[2.2.2]octane, bicyclo[3.2.1]octane, bicyclo[3.2.2]nonane, and bicyclo[3.3.2]decane, and the like. Examples of tricyclic alkyl groups include tricyclo[5.4.0.0.^{2,9}]undecane, tricyclo[4.2.1.2.^{7,9}]undecane, tricyclo[5.3.2.0.^{4,9}]dodecane, and tricyclo[5.2.1.0.^{2,6}]decane. As mentioned herein the cyclic alkyl groups may have any of the acyclic alkyl groups as substituent. These alkyl moieties may be substituted or unsubstituted.

[0032] “Halogenated alkyl” refers to a linear, cyclic or branched saturated alkyl group as defined above in which one or more of the hydrogens has been replaced by a halogen (*e.g.*, F, Cl, Br and I). Thus, for example, a fluorinated alkyl (a.k.a. “fluoroalkyl”) refers to a linear, cyclic or branched saturated alkyl group as defined above in which one or more of the hydrogens has been replaced by fluorine (*e.g.*, trifluoromethyl, perfluoroethyl, 2,2,2-trifluoroethyl, perfluoro isopropyl, perfluorocyclohexyl and the like). Such haloalkyl moieties (*e.g.*, fluoroalkyl moieties), if not

perhalogenated/multihalogenated, may be unsubstituted or further substituted.

[0033] “Alkoxy” (a.k.a. “alkyloxy”) refers to an alkyl group as defined above which is attached through an oxy (-O-) moiety (*e.g.*, methoxy, ethoxy, propoxy, butoxy, 1,2-isopropoxy, cyclopentyloxy, cyclohexyloxy and the like). These alkoxy moieties may be substituted or unsubstituted.

[0034] “Alkyl carbonyl” refers to an alkyl group as defined above which is attached through a carbonyl group (-C(=O-)) moiety (*e.g.*, methylcarbonyl, ethylcarbonyl, propylcarbonyl, butylcarbonyl, cyclopentylcarbonyl and the like). These alkyl carbonyl moieties may be substituted or unsubstituted.

[0035] “Halo” or “halide” refers to a halogen (*e.g.*, F, Cl, Br and I).

[0036] “Hydroxy” (a.k.a. “hydroxyl”) refers to an -OH group.

[0037] Unless otherwise indicated, the term “substituted” when referring to an alkyl, alkoxy, fluorinated alkyl and the like refers to one of these moieties which also contains one or more substituents including, but not limited, to the following substituents: alkyl, substituted alkyl, unsubstituted aryl, substituted aryl, alkyloxy, alkylaryl, haloalkyl, halide, hydroxy, amino and amino alkyl. Similarly, the term “unsubstituted” refers to these same moieties where no substituents apart from hydrogen are present.

[0038] Aryl groups contain 6 to 24 carbon atoms including phenyl, tolyl, xylyl, naphthyl, anthracyl, biphenyls, bis-phenyls, tris-phenyls and the like. These aryl groups may further be substituted with any of the appropriate substituents *e.g.*, alkyl, alkoxy, acyl or aryl groups mentioned hereinabove. Similarly, appropriate polyvalent aryl groups as desired may be used in this invention. Representative examples of divalent aryl groups, arylene, include phenylenes, xylylenes, naphthylenes, biphenylenes, and the like. As used herein, and unless otherwise specified, the term “aromatic” refers to unsaturated cyclic hydrocarbons having a delocalized conjugated π system and having from 4 to 20 carbon atoms (aromatic C₄-C₂₀ hydrocarbon). Exemplary aromatics include, but are not limited to benzene, toluene, xylenes, mesitylene, ethylbenzenes, cumene, naphthalene, methylnaphthalene, dimethylnaphthalenes, ethylnaphthalenes, acenaphthalene, anthracene, phenanthrene, tetraphene, naphthacene, benzanthracenes, fluoranthrene, pyrene, chrysene, triphenylene, and the like, and combinations thereof. The aromatic may optionally be substituted, *e.g.*, with one or more alkyl group, alkoxy group, halogen, *etc.* For example, the aromatic may include anisole. Additionally, the aromatic may include one or more heteroatoms. Examples of heteroatoms include, but are not limited to, nitrogen, oxygen, phosphorus, boron, and/or sulfur. Aromatics with one or more heteroatom include, but are not limited to, furan, benzofuran, thiophene, benzothiophene, oxazole, thiazole and the like, and combinations thereof. The aromatic may include monocyclic, bicyclic, tricyclic, and/or polycyclic rings (in some embodiments, at least monocyclic rings, only

monocyclic and bicyclic rings, or only monocyclic rings) and may be fused rings.

[0039] The term “non-aromatic” means four or more carbon atoms joined in at least one ring structure wherein at least one of the four or more carbon atoms in the ring structure is not an aromatic carbon atom.

[0040] The section headings used herein are for organizational purposes and are not to be construed as limiting the subject matter described. All documents, or portions of documents, cited in this application, including, but not limited to, patents, patent applications, articles, books, and treatises, are hereby expressly incorporated herein by reference in their entirety for any purpose. In the event that any of the incorporated literature and similar materials defines a term in a manner that contradicts the definition of that term in this application, this application controls.

[0041] All documents, literature sources, articles, patents, patent applications, etc. set forth herein are incorporated by reference herein in their entirety.

[0042] When referring to compositions of the chemically amplified MORs described herein in terms of weight % (aka wt %), it is understood that in no event shall the weight % of all components, including non-essential components, such as impurities, add to more than 100 weight %. In compositions “consisting essentially of” recited components, such components may add up to 100 weight % of the composition or may add up to less than 100 weight %. Where the components add up to less than 100 weight %, such composition may include some small amounts of a non-essential contaminants or impurities. For example, in one such embodiment, the formulation can contain 2% by weight or less of impurities. In another embodiment, the formulation can contain 1% by weight or less than of impurities. In a further embodiment, the formulation can contain 0.05% by weight or less than of impurities. In other such embodiments, the constituents can form at least 90 wt%, more preferably at least 95 wt%, more preferably at least 99 wt%, more preferably at least 99.5 wt%, most preferably at least 99.9 wt%, and can include other ingredients that do not material affect the performance of the wet etchant. Otherwise, if no significant non-essential impurity component is present, it is understood that the composition of all essential constituent components will essentially add up to 100 weight %.

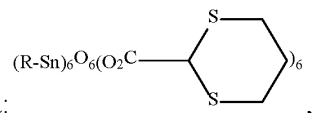
DETAILED DESCRIPTION

[0043] It is to be understood that both the foregoing general description and the following detailed description are illustrative and explanatory, and are not restrictive of the subject matter, as claimed. The objects, features, advantages and ideas of the disclosed subject matter will be apparent to those skilled in the art from the description provided in the specification, and the disclosed subject matter will be readily practicable by those skilled in the art on the basis of the description appearing herein. The description of any “preferred embodiments” and/or the examples which show preferred

modes for practicing the disclosed subject matter are included for the purpose of explanation and are not intended to limit the scope of the claims.

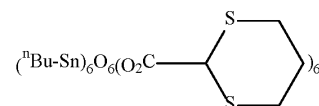
[0044] It will also be apparent to those skilled in the art that various modifications may be made in how the disclosed subject matter is practiced based on described aspects in the specification without departing from the spirit and scope of the disclosed subject matter disclosed herein.

[0045] In one embodiment, the disclosed and claimed subject matter relates to the use of a



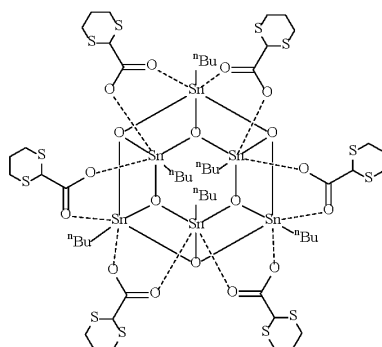
metal organic resist (MOR) of the following formula:

where R is a C₁-C₆ alkyl group (hereinafter “(R-Sn)₆O₆(O₂C-dithiane)₆”) for positive tone processing in high resolution patterning using actinic radiation. In one aspect of this embodiment, R is a methyl group. In one aspect of this embodiment, R is an ethyl group. In one aspect of this embodiment, R is a propyl group. In one aspect of this embodiment, R is a butyl group. In one aspect of this embodiment, R is a pentyl group. In one aspect of this embodiment, R is a hexyl group. In a preferred



embodiment, R is an n-butyl group, and the cluster has the formula

(hereinafter “(ⁿBu-Sn)₆O₆(O₂C-dithiane)₆”) with the following structure:



[0046] As shown above, the Sn-6 cluster includes six (6) tin atoms, that have 3 oxo bridges to other tin atoms, an organic group directly bound to tin which are in most cases alkyl chains, and two carboxylic acids bound via one of the oxygen atoms of the acids. The acids can vary broadly and can include a hydrogen (for formic acid) but also alkyl chains, a phenyl group or an organic group with hetero atoms. These clusters are also known as drum clusters.

[0047] In another embodiment, the disclosed and claimed subject matter relates to the use of the above MORs for positive tone processing in high resolution patterning using actinic radiation, where the method of using the MORs includes, consists essentially of or consists of the steps of (i) spin coating a

composition that includes the above-described MORs (*e.g.*, the compositions disclosed above) and at least one spin-coatable solvent on a substrate and (ii) exposing the spin-coated composition to actinic radiation. Suitable substrates include silicon, aluminum, polymeric resins, silicon dioxide, doped silicon dioxide, silicon nitride, tantalum, copper, polysilicon, ceramics, aluminum/copper mixtures; gallium arsenide and other such Group III/V compounds. The photoresist may also be coated over antireflective coatings or other underlayers, including but not limited to underlayers specifically designed for EUV photoresists, or on hard masks such as used for pattern transfer in trilayer processes. In one aspect of this embodiment the actinic radiation is EUV radiation of 13.5 nm wavelength. In one aspect of this embodiment the actinic radiation is one of electron radiation and soft x-ray radiation.

[0048] In one aspect of this embodiment, the at least one spin-coatable solvent of step (i) includes, consists essentially of or consists of one or more solvents suitable for spin coating. Examples of such solvents include, but are not limited to, a glycol ether derivative such as ethyl cellosolve, methyl cellosolve, propylene glycol monomethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, dipropylene glycol dimethyl ether, propylene glycol n-propyl ether, or diethylene glycol dimethyl ether; a glycol ether ester derivative such as ethyl cellosolve acetate, methyl cellosolve acetate, or propylene glycol monomethyl ether acetate; carboxylates such as ethyl acetate, n-butyl acetate and amyl acetate; carboxylates of di-basic acids such as diethyloxylate and diethylmalonate; dicarboxylates of glycols such as ethylene glycol diacetate and propylene glycol diacetate; and hydroxy carboxylates such as methyl lactate, ethyl lactate, ethyl glycolate, and ethyl-3-hydroxy propionate; a ketone ester such as methyl pyruvate or ethyl pyruvate; an alkoxycarboxylic acid ester such as methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, ethyl 2-hydroxy-2-methylpropionate, or methylethoxypropionate; a ketone derivative such as methyl ethyl ketone, acetyl acetone, cyclopentanone, cyclohexanone or 2-heptanone; a ketone ether derivative such as diacetone alcohol methyl ether; a ketone alcohol derivative such as acetol or diacetone alcohol; lactones such as butyrolactone; an amide derivative such as dimethylacetamide or dimethylformamide, anisole, and mixtures thereof. In one embodiment, preferred solvents include propylene glycol mono-alkyl ether, propylene glycol alkyl (*e.g.*, methyl) ether acetate, ethyl-3-ethoxypropionate, toluene, xylene, diglyme, amyl acetate, ethyl lactate, butyl acetate, 2-heptanone, ethylene glycol monoethyl ether acetate, and mixtures thereof. In another embodiment, preferred solvents include, but are not limited to, anisole, 4-methyl-2-pentanol, cyclohexanone, toluene, propylene glycol monomethyl ether and 2-heptanone. In another aspect, the compositions include more than one solvent.

[0049] In a further aspect, the composition that includes the above-described MORs and the at least one spin-coatable solvent has a solvent content of about 49% to about 99% of the total weight of

the composition.

[0050] In another aspect of this embodiment, the method further optionally includes, consist essentially of or consists of the step of (i-2) conducting a post application bake (“PAB”) thermal treatment of the substrate carrying the spin-coated composition prior to exposure (*i.e.*, before step (ii)). The purpose of this step is to dry the spin coated photoresist layer (*i.e.*, removal of any remaining solvent(s)) prior to exposure. This PAB step is alternatively called a prebake or softbake. The PAB is usually carried out on a hotplate or an oven. For hotplate PABs, preferred temperatures are from about 80 °C to about 150 °C, more preferred from about 90 °C to about 130 °C, most preferred from about 90 °C to about 120 °C. For hotplate PABs, preferred times are from about 45 seconds to about 180 seconds, more preferred times from about 45 seconds to about 120 seconds, most preferred times from about 60 seconds to about 120 seconds. Oven PABs may employ different times and temperatures based on the type of oven and method of contact.

[0051] In another aspect of this embodiment, the method further optionally includes, consist essentially of or consists of the step of (iii) conducting a post exposure bake (“PEB”). In a further aspect, the PEB occurs at a temperature above the ambient temperature. In a further aspect, the PEB occurs at a temperature between about 80 °C and about 200 °C. In a further aspect, the PEB occurs at a temperature between about 90 °C and about 170 °C. In a further aspect, the PEB occurs at a temperature between about 120 °C and about 150 °C. In a further aspect, the PEB occurs at a temperature between about 150 °C and about 180 °C. In a further aspect, the PEB occurs at a temperature of about 80 °C. In a further aspect, the PEB occurs at a temperature of about 85 °C. In a further aspect, the PEB occurs at a temperature of about 90 °C. In a further aspect, the PEB occurs at a temperature of about 100 °C. In a further aspect, the PEB occurs at a temperature of about 110 °C. In a further aspect, the PEB occurs at a temperature of about 120 °C. In a further aspect, the PEB occurs at a temperature of about 130 °C. In a further aspect, the PEB occurs at a temperature of about 140 °C. In a further aspect, the PEB occurs at a temperature of about 150 °C. In a further aspect, the PEB occurs at a temperature of about 160 °C. In a further aspect, the PEB occurs at a temperature of about 170 °C. In a further aspect, the PEB occurs at a temperature of about 180 °C. In a further aspect, the PEB occurs at a temperature of about 190 °C. In a further aspect, the PEB occurs at a temperature of about 200 °C. In a further aspect, the PEB occurs for about 30 seconds to about 300 seconds. In a further aspect, the PEB occurs for about 50 seconds to about 180 seconds. In a further aspect, the PEB occurs for about 60 seconds to about 120 seconds.

[0052] In another aspect of this embodiment, the method further optionally includes, consist essentially of or consists of the step of (iv) developing the substrate in a solvent. In a further aspect

developing of the substrate occurs for about 30 seconds to about 300 seconds. In a further aspect, the solvent developer is a polar solvent such as ketone-based solvent, ester-based solvent, alcohol-based solvent, amide-based solvent and ether-based solvent, and a hydrocarbon-based solvent can be used. Examples of the ketone-based solvent include 1-octanone, 2-octanone, 1-nonanone, 2-nonanone, acetone, 2-heptanone, 4-heptanone, 1-hexanone, 2-hexanone, diisobutyl ketone, cyclohexanone, methylcyclohexanone, phenylacetone, methyl ethyl ketone, methyl isobutyl ketone, acetylacetone, actonylacetone, ion one, diacetyl alcohol, acetyl carbinol, acetophenone, methyl naphthyl ketone, isophorone and propylene carbonate. Examples of the ester-based solvent include methyl acetate, butyl acetate, ethyl acetate, isopropyl acetate, amyl acetate, propylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, ethyl-3-ethoxypropionate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, methyl formate, ethyl formate, butyl formate, propyl formate, ethyl lactate, butyl lactate and propyl lactate. Examples of the alcohol-based solvent include an alcohol Such as methyl alcohol, ethyl alcohol, n-propyl alcohol, iso propyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, isobutyl alcohol, n-hexyl alcohol, n-heptyl alcohol, n-octyl alcohol and n-decanol; a glycol-based solvent such as ethylene glycol, diethylene glycol and triethylene glycol; and a glycol ether-based solvent such as ethylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monoethyl ether, diethylene glycol monomethyl ether, triethylene glycol monoethyl ether and methoxy methylbutanol. Examples of the ether-based solvent include the glycol ether-based solvent cited above, dioxane and tetrahydrofuran. Examples of the amide-based solvent include N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, hexamethylphosphoric triamide and 1,3-dimethyl-2-imidazolidinone. Examples of the hydrocarbon-based solvent include an aromatic hydrocarbon-based solvent such as toluene and xylene, and an aliphatic hydrocarbon-based solvent such as pentane, hexane, heptane, octane, nonane and decane, or the type of petroleum distillate generally known as white spirit. A plurality of these solvents may be mixed, or the solvent may be used by mixing it with a solvent other than described above or water.

[0053] In another aspect of this embodiment, the method further optionally includes, consist essentially of or consists of the step of (v) conducting a solvent rinse. Suitable solvents for rinsing include, but are not limited to, one or more hydrocarbon-based solvent, ketone-based solvent, ester-based solvent, alcohol-based solvent, amide-based solvent and ether-based solvent. More preferably, a step of washing the resist film by using a rinsing solution containing at least one kind of an organic solvent selected from a ketone-based solvent, an ester-based solvent, an alcohol-based solvent and an amide-based solvent is preformed after negative tone development; still more preferably, a step of

washing the resist film by using a rinsing solution containing an alcohol based solvent or an ester-based solvent is performed after development; yet still more preferably, a step of washing the resist film by using a rinsing solution containing a monohydric alcohol is performed after development. The monohydric alcohol used in the rinsing step after negative tone development includes a linear, branched or cyclic monohydric alcohol, and specific examples of the monohydric alcohol which can be used include 1-butanol, 2-butanol, 3-methyl-1-butanol, tert-butyl alcohol, 1-pentanol, 2-pentanol, 1-Hexanol, 1-heptanol, 1-octanol, 2-hexanol, 2-heptanol, 2-octanol, 3-hexanol, 3-heptanol, 3-octanol, and 4-octanol, are preferred. In another aspect, the solvent rinse includes more than one solvent.

[0054] In another aspect of this embodiment, the method further optionally includes, consist essentially of or consists of the step of (vi) developing the substrate in an aqueous base developer. In a further aspect developing of the substrate occurs for about 30 seconds to about 300 seconds. In one embodiment, the developers are buffered or unbuffered solutions of NaOH or KOH. In one embodiment, the aqueous developers are metal ion free (MIF) developers. Examples of such MIF developers include but are not limited to tetramethyl ammonium hydroxide (TMAH), tetra-n-butyl ammonium hydroxide (TBAH), tetraethylammonium hydroxide (TEAH) or choline hydroxide in concentrations from 0.05 to 3 N, preferably from 0.1 to 3 N, most preferred 2.3 to 2.7 N. A preferred developer is TMAH.

[0055] In one aspect of this embodiment, the development step is followed by a rinse with an aqueous rinse solution. This rinse solution may include surface active agents that reduce its surface tension below that of pure water. Such solutions are used in order to minimize pattern collapse due to capillary forces, which theory predicts are directly proportional to the surface tension. They may further include other additives that reduce pattern collapse and help maintain the pattern shape of resist structures during the rinse. Such solutions are described in, *e.g.*, M. Padmanaban *et al.*, *Proc. SPIE Vol. 8682*, 868215 (2013), doi: 10.1117/12.2013363; K. Yamamoto *et al.*, *Proc. SPIE, Vol. 10143*, 101431X (2017), DOI: 10.1117/12.2257393; and U.S. Patent No. 10,451,974.

[0056] In another aspect of this embodiment, the method further optionally includes, consist essentially of or consists of the step of (vii) a thermal treatment step following development and rinse (*i.e.*, a hardbake). This hardbake step can be carried out on a hotplate or in an oven, or optionally using microwave or infrared irradiation, including a rapid thermal annealing (RTA) system or a laser irradiation system. If the hardbake is carried out on a hotplate, preferred temperatures are from about 110 °C to about 300 °C, more preferred from about 130 °C to about 220 °C. Preferred hardbake times on hotplates are from about 30 seconds to about 300 seconds, more preferred from about 50 seconds to about 120 seconds. Hardbake times in ovens are typically longer than on hotplates to compensate for less efficient heat transfer. The hardbake may be carried out in normal atmospheric conditions,

under humidity exclusion, under increased humidity, in an oxygen-enriched atmosphere or in pure oxygen, or under oxygen exclusion in an inert gas, including but not limited to nitrogen or argon.

[0057] EXAMPLES

[0058] Reference will now be made to more specific embodiments of the present disclosure and experimental results that provide support for such embodiments. The examples are given below to more fully illustrate the disclosed subject matter and should not be construed as limiting the disclosed subject matter in any way.

[0059] It will be apparent to those skilled in the art that various modifications and variations can be made in the disclosed subject matter and specific examples provided herein without departing from the spirit or scope of the disclosed subject matter. Thus, it is intended that the disclosed subject matter, including the descriptions provided by the following examples, covers the modifications and variations of the disclosed subject matter that come within the scope of any claims and their equivalents.

[0060] Materials and Methods:

[0061] The disclosed and claimed processes utilizes commercially available materials (*e.g.* THF, PGME, cyclohexanone, toluene, formic acid, acetic acid, 1,3-Dithiane-2-carboxylic acid (CAS 20461-89-6), CDCl_3 , C_6D_6 . All cluster materials were prepared according to modified literature procedures. *See Chandrasekhar et al., Inorg. Chem.*, 26, 1050 (1987).

[0062] Comparative Examples

[0063] Resists of Sn-6 formyl cluster (*i.e.*, $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{CH})_6$) and Sn-6 acetate cluster (*i.e.*, $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_6$) were formulated in cyclohexanone with 20 g/l (formyl cluster) and in toluene with 10 g/l (acetate cluster), respectfully. These formulations were spin coated on Si wafers, that were treated with oxygen plasma (400 W, 10 min). After a soft bake of 100° C for 2 minutes one set of wafers were cleaved into pieces and time to fully remove the film was determined for both coatings with TMAH based developer AZ 726 MIF. For the formyl cluster this was 25 s, for the acetate cluster this was 60 s.

[0064] Another set of coated wafers were exposed with an e-beam (30kV) with dose levels from 10 to 5000 $\mu\text{C}/\text{cm}^2$. After exposure, a post exposure bake was done at 120° C for 2 minutes. Then both wafers were developed with TMAH solution AZ 726 MIF, the formyl cluster for 13 s and the acetate cluster for 30 s. Afterward, the wafers were rinsed with water and dried under nitrogen.

[0065] FIG. 1 shows the pattern of the Sn6 acetate cluster after development with TMAH. FIG. 2 shows the pattern of the Sn6 formyl cluster after development with TMAH. FIG. 3 illustrates the dose curves for developed Sn6 formyl cluster $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{CH})_6$ and Sn6 acetate cluster $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_6$.

[0066] As can be seen from FIGs. 1-3, for both clusters well-defined pattern can be observed.

The surface of the acetate cluster is rougher than of the formyl cluster after TMAH development, but the thickness loss is less than that of the formyl cluster. The dose curves in FIG. 3 show a better contrast for the acetate cluster. This was already expected looking at the very short development time for the formyl cluster. Due to the low contrast of the formyl cluster, it shows higher photo speed but with 50% film thickness loss.

[0067] Example 1

[0068] A 10 g/l resist formulation of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ in toluene was prepared and applied with 3500 rpm spin speed and dried at 100 °C for 120 seconds. One coating was exposed to TMAH (2.36 wt%) for 300s and showed no film thickness loss. Another coating was exposed by e-beam with dose levels from 10 to 5000 $\mu\text{C}/\text{cm}^2$ at an acceleration voltage of 30 kV. After a post exposure bake at 120 °C for 120 seconds the coatings were developed in TMAH for 60 seconds followed by a rinse in water.

[0069] FIG. 4 and FIG. 5 show the developed structure of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ after treatment with TMAH for 60 s. FIG. 6 illustrates the dose curves for developed $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ clusters. The dose curves of FIG. 6 show that $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ has better sensitivity and better contrast compared to the formic acid and acetic acid clusters in comparative examples.

[0070] Following the above-results EUV exposures were conducted at Paul Scherrer Institute in Villigen, Switzerland. A 10 g/l resist of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ in toluene was spin coated to obtain a 25 nm film. A PAB of 100 °C and PEB of 120 °C were utilized. Development time of 120-300 s was utilized after PEB. First patterning conducted on bare silicon wafer at varying pitch from 100nm down to a pitch of 44 nm was targeted with 120s TMAH (2.38 wt%) development. As can be seen in FIG. 7, severe pattern collapse is observed. Use of an underlayer (Merck underlayer AZExp O6010) significantly improved the results for the same formulation and processing conditions. In FIG. 8, EUV patterning is shown of the $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ cluster for a pitch of 60 nm with underlayer AZExp O6010. At 67 mJ/cm^2 and 120 s TMAH (2.38 wt%) development a defined pattern is observed. In FIG. 9, EUV patterning is shown of the $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ cluster for a pitch of 44 nm with underlayer AZExp O6010. At 62 mJ/cm^2 and 120s TMAH (2.38 wt%) development a defined pattern is observed.

[0071] The unexposed $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ cluster is resistant to TMAH (2.38 wt%) for greater than 300 s. The same formulation, 10 g/l resist of $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ in toluene was employed on AZExp O6010 but with a longer development time of 300s. In FIG. 10, EUV patterning is shown of the $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ cluster for a pitch of 50 nm with underlayer AZExp O6010 shows at 49 mJ/cm^2 a defined pattern. FIG. 11 illustrates the same $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ formulation but includes a further 20s TMAH (2.38%) rinse after an initial 120s development. In FIG.

11, EUV patterning is shown of the $(^n\text{Bu-Sn})_6\text{O}_6(\text{O}_2\text{C-dithiane})_6$ cluster for a pitch of 44 nm with underlayer AZExp O6010. At 53 mJ/cm² a defined pattern is observed with reduced scumming compared to those without the rinse or elongated 300s development time.

[0072] Although the disclosed and claimed subject matter has been described and illustrated with a certain degree of particularity, it is understood that the disclosure has been made only by way of example, and that numerous changes in the conditions and order of steps can be resorted to by those skilled in the art without departing from the spirit and scope of the disclosed and claimed subject matter.

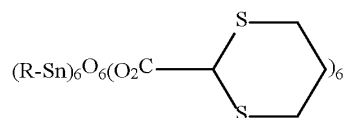
Claims

What is claimed is:

1. A method for positive tone processing comprising the steps of:

(i) spin coating a composition comprising

(a) a metal organic resist (MOR) of the following formula:



wherein R is a C₁-C₆ alkyl group; and

(b) at least one spin-coatable solvent on a substrate; and

(ii) exposing the spin-coated composition to actinic radiation.

2. The method of claim 1, wherein R is a methyl group.

3. The method of claim 1, wherein R is an ethyl group.

4. The method of claim 1, wherein R is a propyl group.

5. The method of claim 1, wherein R is a butyl group.

6. The method of claim 1, wherein R is a pentyl group.

7. The method of claim 1, wherein R is a hexyl group.

8. The method of claim 1, wherein the step (i) substrate comprises one or more of silicon, aluminum, polymeric resins, silicon dioxide, doped silicon dioxide, silicon nitride, tantalum, copper, polysilicon, ceramics, aluminum/copper mixtures; gallium arsenide and other such Group III/V compounds.

9. The method of claim 1, wherein the step (i) composition is coated over one or more of an antireflective coating, an underlayer and a hard mask.

10. The method of claim 1, wherein the step (i) at least one spin-coatable solvent comprises at least one of a glycol ether derivative, a glycol ether ester derivative, a carboxylate, carboxylates of di-basic acids, dicarboxylates of glycols hydroxy carboxylates, a ketone ester, an alkoxycarboxylic acid ester, a ketone derivative, a ketone ether derivative, a ketone alcohol derivative, a lactone, an amide derivative, anisole and mixtures thereof.

11. The method of claim 1, wherein the step (i) at least one spin-coatable solvent comprises at least one of propylene glycol mono-alkyl ether, propylene glycol alkyl (e.g., methyl) ether acetate, ethyl-3-ethoxypropionate, toluene, xylene, diglyme, amyl acetate, ethyl lactate, butyl acetate, 2-heptanone, ethylene glycol monoethyl ether acetate and mixtures thereof.

12. The method of claim 1, wherein the step (i) at least one spin-coatable solvent comprises at least one of anisole, 4-methyl-2-pentanol, cyclohexanone, toluene, propylene glycol monomethyl ether and

2-heptanone.

13. The method of claim 1, wherein the step (i) at least one spin-coatable solvent comprises more than one solvent.
14. The method of claim 1, wherein the metal organic resist and at least one solvent of step (i) comprise about 49% to about 99% by weight of the composition.
15. The method of claim 1, wherein the actinic radiation is EUV radiation of 13.5 nm wavelength.
16. The method of claim 1, wherein the actinic radiation is one of electron radiation and soft x-ray radiation.
17. The method of claim 1, further comprising a step (i-2) of conducting a post apply bake ("PAB") thermal treatment of the substrate carrying the spin-coated composition prior to step (ii).
18. The method of claim 1, further comprising a step (iii) of conducting a post exposure bake ("PEB") thermal treatment of the substrate carrying the spin-coated composition after step (ii).
19. The method of claim 18, wherein the PEB occurs at a temperature above the ambient temperature.
20. The method of claim 18, wherein the PEB occurs at a temperature between about 80 °C and about 200 °C.
21. The method of claim 18, wherein the PEB occurs at a temperature between about 90 °C and about 170 °C.
22. The method of claim 18, wherein the PEB occurs at a temperature between about 120 °C and about 150 °C.
23. The method of claim 18, wherein the PEB occurs at a temperature between about 150 °C and about 180 °C.
24. The method of claim 18, wherein the PEB occurs at a temperature of about 80 °C.
25. The method of claim 18, wherein the PEB occurs at a temperature of about 85 °C.
26. The method of claim 18, wherein the PEB occurs at a temperature of about 90 °C.
27. The method of claim 18, wherein the PEB occurs at a temperature of about 100 °C.
28. The method of claim 18, wherein the PEB occurs at a temperature of about 110 °C.
29. The method of claim 18, wherein the PEB occurs at a temperature of about 120 °C.
30. The method of claim 18, wherein the PEB occurs at a temperature of about 130 °C.
31. The method of claim 18, wherein the PEB occurs at a temperature of about 140 °C.
32. The method of claim 18, wherein the PEB occurs at a temperature of about 150 °C.
33. The method of claim 18, wherein the PEB occurs at a temperature of about 160 °C.
34. The method of claim 18, wherein the PEB occurs at a temperature of about 170 °C.

35. The method of claim 18, wherein the PEB occurs for about 30 seconds to about 300 seconds.
36. The method of claim 18, wherein the PEB occurs for about 50 seconds to about 180 seconds.
37. The method of claim 18, wherein the PEB occurs for about 60 seconds to about 120 seconds.
38. The method of claim 1, further comprising a step (iv) of developing the substrate in a solvent.
39. The method of claim 38, wherein the developing of the substrate in the solvent developer occurs for about 30 seconds to about 300 seconds.
40. The method of claim 38, wherein the solvent developer comprises one or more polar solvents.
41. The method of claim 38, wherein the solvent developer comprises one or more of a ketone-based solvent, ester-based solvent, alcohol-based solvent, amide-based solvent, ether-based solvent, a hydrocarbon-based solvent and combinations thereof.
42. The method of claim 38, wherein the solvent developer comprises one or more of acetone, 2-heptanone, 4-heptanone, 1-hexanone, 2-hexanone, diisobutyl ketone, cyclohexanone, methylcyclohexanone, phenylacetone, methyl ethyl ketone, methyl isobutyl ketone, acetylacetone, actonylacetone, ion one, diacetonyl alcohol, acetyl carbinol, acetophenone, methyl naphthyl ketone, isophorone, propylene carbonate and combinations thereof.
43. The method of claim 38, wherein the solvent developer comprises one or more of methyl acetate, butyl acetate, ethyl acetate, isopropyl acetate, amyl acetate, propylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, ethyl-3-ethoxypropionate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, methyl formate, ethyl formate, butyl formate, propyl formate, ethyl lactate, butyl lactate, propyl lactate and combinations thereof.
44. The method of claim 38, wherein the solvent developer comprises one or more of methyl alcohol, ethyl alcohol, n-propyl alcohol, iso propyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, isobutyl alcohol, n-hexyl alcohol, n-heptyl alcohol, n-octyl alcohol, n-decanol, ethylene glycol, diethylene glycol, triethylene glycol, ethylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monoethyl ether, diethylene glycol monomethyl ether, triethylene glycol monoethyl ether, methoxy methylbutanol and combinations thereof.
45. The method of claim 38, wherein the solvent developer comprises one or more of dioxane, tetrahydrofuran and combinations thereof.
46. The method of claim 38, wherein the solvent developer comprises one or more of N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, hexamethylphosphoric triamide, 1,3-dimethyl-2-imidazolidinone and combinations thereof.
47. The method of claim 38, wherein the solvent developer comprises one or more of toluene,

xylene, pentane, hexane, heptane, octane, nonane, decane, white spirit and combinations thereof.

48. The method of claim 1, further comprising a step of **(v)** a solvent rinse.

49. The method of claim 48, wherein the step (v) solvent rinse comprises one or more of a hydrocarbon-based solvent, ketone-based solvent, ester-based solvent, alcohol-based solvent, amide-based solvent, ether-based solvent and combinations thereof.

50. The method of claim 48, wherein the step (v) solvent rinse comprises one or more of 1-butanol, 2-butanol, 3-methyl-1-butanol, tert-butyl alcohol, 1-pentanol, 2-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 2-hexanol, 2-heptanol, 2-octanol, 3-hexanol, 3-heptanol, 3-octanol, 4-octanol and combinations thereof.

51. The method of claim 1, further comprising a step of **(vi)** developing the substrate in an aqueous base developer.

52. The method of claim 51, wherein the step (vi) aqueous base developer comprises one or more of alkaline developer.

53. The method of claim 51, wherein the step (vi) aqueous base developer comprises one or more of NaOH or KOH.

54. The method of claim 51, wherein the step (vi) aqueous base developer comprises one or more metal ion free (MIF) developer.

55. The method of claim 51, wherein the step (vi) aqueous developer comprises one or more of tetramethyl ammonium hydroxide (TMAH), tetra-n-butyl ammonium hydroxide and choline hydroxide.

56. The method of claim 51, wherein the step (vi) aqueous base developer comprises tetramethyl ammonium hydroxide (TMAH).

57. The method of claim 1, further comprising a step **(vii)** of conducting a thermal treatment step following step (vi).

58. The method of claim 57, wherein the thermal treatment occurs at a temperature of from about 110 °C to about 300 °C.

59. The method of claim 57, wherein the thermal treatment occurs at a temperature of from about 130 °C to about 220 °C.

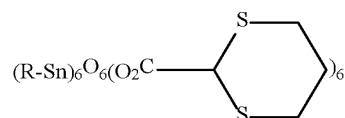
60. The method of claim 57, wherein the thermal treatment occurs for about 30 seconds to about 300 seconds.

61. The method of claim 57, wherein the thermal treatment occurs for about 50 seconds to about 120 seconds.

62. The method of claim 57, wherein the thermal treatment occurs under one or more of atmospheric conditions, under humidity exclusion, under increased humidity, in an oxygen-enriched

atmosphere, in pure oxygen, or under oxygen exclusion in an inert gas.

63. Use of a metal organic resist (MOR) of the following formula:



wherein R is a C₁-C₆ alkyl group for positive tone processing in high resolution patterning using actinic radiation.

- 64.** The use of claim 63, wherein R is a methyl group.
- 65.** The use of claim 63, wherein R is an ethyl group.
- 66.** The use of claim 63, wherein R is a propyl group.
- 67.** The use of claim 63, wherein R is a butyl group.
- 68.** The use of claim 63, wherein R is a pentyl group.
- 69.** The use of claim 63, wherein R is a hexyl group.