CLAIMS

1. A method of depositing a photoresist material on a substrate, the method comprising:

providing the substrate in a reaction chamber;

providing a first reactant and a second reactant to the reaction chamber and initiating a reaction between the first reactant and the second reactant to thereby deposit the photoresist material on the substrate, wherein the first reactant and the second reactant are each provided to the reaction chamber in vapor phase,

wherein the first reactant is an organo-metallic precursor having a formula of $M1_aR1_bL1_c$, where:

M1 is a~~n element~~metal having a high patterning radiation-absorption cross-section,

R1 is an organic group that survives the reaction between the first reactant and the second reactant and is cleavable from M1 under exposure to patterning radiation,

L1 is a ligand, ion, or other moiety that reacts with the second reactant,

$a \geq 1$,

$b \geq 1$, and

$c \geq 1$, and

wherein ~~at least one of the following conditions is satisfied:~~

~~(a) the photoresist material comprises two or more elements having a high patterning radiation-absorption cross-section, and/or~~

~~(b)~~ the photoresist material comprises a composition gradient along a thickness of the photoresist material.

2. The method of claim 1, wherein the photoresist material is an extreme ultraviolet (EUV) photoresist material, and wherein M1 has a high EUV-absorption cross-section.

3. The method of claim 2, wherein the second reactant comprises a hydroxyl moiety or a material that can form oxygen bridges between metal atoms.

4. The method of claim 2, wherein the second reactant comprises a material selected from the group consisting of: water, a peroxide, a di- or polyhydroxy alcohol, a fluorinated di- or polyhydroxy alcohol, a fluorinated glycol, and combinations thereof.

5. The method of any of claims 2-4, wherein the second reactant comprises a material that can crosslink metal atoms via sulfur bridges and/or tellurium bridges.

6. The method of any of claims 2-5, wherein the second reactant comprises a material selected from the group consisting of: hydrogen sulfide, hydrogen disulfide, bis(trimethylsilyl)tellurium, and combinations thereof.

7. The method of any of claims 2-6, wherein the second reactant comprises hydrogen iodide or an alkyl iodide.

8. The method of any of claims 2-7, wherein the second reactant replaces one or more L1 to thereby crosslink two or more atoms of M1 via chemical bonding.

9. The method of any of claims 2-8, wherein the EUV-absorption cross-section of M1 is equal to or greater than $1x10^7$ cm^2/mol.

10. The method of any of claims 2-9, wherein M1 comprises a~~n element~~metal selected from the group consisting of: Sn, Sb, In, Bi, Te, and combinations thereof.

11. The method of any of claims 2-10, wherein R1 comprises an alkyl group or a halogen-substituted alkyl group.

12. The method of claim 11, wherein the alkyl group comprises three or more carbon atoms.

13. The method of any of claims 2-12, wherein R1 comprises at least one beta-hydrogen or beta-fluorine.

14. The method of claim 13, wherein R1 is selected from the group consisting of: i-propyl, n-propyl, t-butyl, i-butyl, n-butyl, sec- butyl, n-pentyl, i-pentyl, t-pentyl, sec-pentyl, and combinations thereof.

15. The method of any of claims 2-14, wherein L1 comprises a moiety selected from the group consisting of: an amine, an alkoxy, a carboxylate, a halogen, and combinations thereof.

16. The method of any of claims 2-15, wherein the first reactant comprises a material selected from the group consisting of: t-butyl tris(dimethylamino) tin, i-butyl tris(dimethylamino) tin, n-butyl tris(dimethylamino) tin, sec-butyl tris(dimethylamino) tin, i-propyl(tris)dimethylamino tin, n-propyl tris(diethylamino) tin, t-butyl tris(t-butoxy) tin, i-butyl tris(t-butoxy) tin, n-butyl tris(t-butoxy) tin, sec-butyl tris(t-butoxy) tin, i-propyl(tris)t-butoxy tin, n-propyl tris(t-butoxy) tin, t-butyltrichlorotin, i-butyltrichlorotin, n-butyltrichlorotin, sec-butyltrichlorotin, i-propyltrichlorotin, n-propyltrichlorotin, t-butyltribromotin, i-butyltribromotin, n-butyltribromotin, sec-butyltribromotin, i-propyltribromotin, n-propyltribromotin, and combinations thereof.

17. The method of any of claims 2-16, further comprising exposing the substrate to plasma to replace some M1-L1 bonds with M1-H bonds.

18. The method of any of claims 2-17, wherein the reaction between the first reactant and the second reactant is a chemical vapor deposition reaction, an atomic layer deposition reaction, or a combination thereof.

19. The method of any of claims 2-18, wherein the first reactant and the second reactant are provided to the reaction chamber concurrently.

20. The method of any of claims 2-18, wherein the first reactant and the second reactant are not delivered to the reaction chamber concurrently.

21. The method of any of claims 2-20, wherein a temperature of the substrate is at or below a temperature of the first and second reactants when they are delivered to the reaction chamber.

22. The method of any of claims 2-21, wherein initiating the reaction between the first and second reactants comprises exposing the substrate to plasma.

23. The method of any of claims 2-21, wherein initiating the reaction between the first and second reactants comprises exposing the substrate to thermal energy.

24. The method of any of claims 2-23, further comprising providing a third reactant to the reaction chamber and initiating a reaction between the second reactant and the third reactant or between the third reactant and a fourth reactant.

25. The method of claim 24, wherein each of the first and third reactants comprises a~~n element~~metal selected from the group consisting of Sn, Sb, In, Bi, and Te, and wherein the metal in the first reactant is different from the metal in the second reactant.

~~26. The method of any of claims 2-25, wherein the photoresist material deposited on the substrate comprises the composition gradient along a thickness of the photoresist material.~~

~~27~~26. The method of claim ~~26~~1, wherein the photoresist material comprises M2 in addition to M1, wherein M2 is a metal having a high EUV-absorption cross-section and is different from M1, wherein the composition gradient in the photoresist material provides different ratios of M1:M2 at different vertical positions within the photoresist material.

~~28~~27. The method of claim ~~26~~1, wherein the composition gradient in the photoresist material provides different ratios of M1:R1 at different vertical positions within the photoresist material.

~~29~~28. The method of claim ~~28~~27, wherein a percentage of metal atoms bonded to R1 varies at different vertical positions within the photoresist material.

~~30~~29. The method of claim ~~26~~1, wherein the composition gradient in the photoresist material provides different concentrations of I or Te at different vertical positions within the photoresist material.

~~31~~30. The method of any of claims ~~26-30~~26-29, wherein the composition gradient provides a higher density of high-EUV absorbing elements in a bottom part of the photoresist material compared to a top part of the photoresist material, the bottom part being deposited before the top part.

~~32~~31. The method of ~~any of~~ claim~~s~~ ~~2-31~~1, further comprising before providing the first reactant to the reaction chamber, providing a third reactant to the reaction chamber and initiating a reaction between the second reactant and the third reactant, or between the third reactant and a fourth reactant, to thereby deposit an initial portion of the photoresist material,

wherein the third reactant has a formula $M2_aL2_c$, where:

M2 is a metal with a high EUV-absorption cross-section,

L2 is a ligand, ion, or other moiety that reacts with the second reactant or with the fourth reactant,

$a \geq 1$, and

$c \geq 1$,

such that the initial portion of the photoresist material does not incorporate R1.

~~33~~32. The method of any of claims ~~2-32~~2-31, further comprising repeatedly exposing the substrate to plasma to remove some R1 from the photoresist material, wherein conditions used to generate the plasma change over time such that there is a gradient in the concentration of M1-R1 bonds within the photoresist material.

~~34~~33. The method of claim ~~33~~32, wherein a power used to generate the plasma is reduced over time such that there is a relatively lower concentration of M1-R1 bonds near a bottom of the photoresist material, and a relatively higher concentration of M1-R1 bonds near a top of the photoresist material.

~~35~~34. The method of any of claims 2-~~34~~33, wherein the photoresist material comprises a vertical density gradient.

~~36~~35. The method of any of claims 2-~~35~~34, further comprising exposing the photoresist material to EUV radiation and developing the photoresist material to form a pattern, wherein developing the photoresist material occurs through wet processing or dry processing.

~~37~~36. The method of any of claims 2-~~36~~35, wherein the photoresist material provides depth-dependent EUV sensitivity.

~~38~~37. A method of depositing a photoresist material on a substrate, the method comprising:

providing the substrate in a reaction chamber;

providing a first reactant and a second reactant to the reaction chamber and initiating a reaction between the first reactant and the second reactant to thereby deposit the photoresist material on the substrate, wherein the first reactant and the second reactant are each provided to the reaction chamber in vapor phase, wherein the photoresist material provides a plurality of patterning radiation absorber species and/or depth-dependent sensitivity to patterning radiation.

~~39. A photoresist material formed by any of the methods of claims 1-38.~~

~~40~~38. An apparatus for depositing a photoresist material on a substrate, the apparatus comprising:

a reaction chamber;

an inlet for introducing gas phase reactants;

an outlet for removing materials from the reaction chamber;

a substrate support in the reaction chamber; and

a controller having at least one processor, wherein the at least one processor is configured to cause any of the methods of claims 1-~~38~~37.

39. The method of claim 31, wherein the third reactant comprises tetrakis(dimethylamino)tin.