

Solution processable metallo-organic complexes and uses thereof**Field of Invention**

5 The present invention relates to radiation sensitive resist compositions comprising solution processable metal-organic complexes and methods of preparation thereof. In particular, the invention concerns novel functional solution processable organo/poly-metallic electron or photo resist complexes and metal-organic and organopoly-metal-complex compositions useful for coating of semiconductors and optical substrates and for forming metal oxide
10 films.

Background

Advanced lithography methods which use electron beam or extreme ultraviolet light (EUV)
15 as the radiation source have been of great interest due to their capabilities of patterning at sub-10 nm resolution. However, existing EUV resist materials still face many challenges and there is generally a trade-off between sensitivity (S), line edge roughness (L), and resolution (R).

20 Presently, chemically amplified resists (CAR) are utilized to increase sensitivity. The CAR's mainly consist of a main polymeric or molecular component as a matrix, photoacid generator molecules, and base quencher molecules. Upon irradiation, the photo-acid generator molecules (PAGs) interact with the light to generate acids; then a change in dissolution rate of the matrix begins during a subsequent post-exposure bake (PEB) step.
25 During this step reactions of specific groups of the matrix are catalyzed by the photogenerated acid molecules changing hydrophilicity, or inducing crosslinking or backbone scission, and hence alter solubility in developers, such as aqueous base developers.

A considerable disadvantage of present CAR's is acid diffusion that can cause a large
30 stochastic effect which leads to undesired bridging between patterns, hydrodynamic radii of polymers in CAR, making it inherently difficult to accomplish a sub-10 nm feature size. The root-mean-square end-to-end distance for polymer chains in conventional CAR photoresists ranges from 6 to 10 nm and the presence of additives could, in fact, lead to an increase in defects.

35 Non-CAR compositions, which utilize metal clusters or metal complexes, avoid some of the disadvantages of CAR's but still have inadequate shelf-life stability due to the presence of

environmentally susceptible or moisture sensitive functionalities/functional groups that limit the use of the materials for industrial scale production.

It is an aim of the present invention to address at least some of these problems by providing
5 new resist materials.

Summary of the Invention

The present invention relates to novel metal-organic complexes which have a first metal
10 chelating moiety and a second polymerizable, organic moiety. The present invention also provides the use of the novel complexes as well as oligo- and polymers thereof for forming layers and films, such as metal oxide layers and films, in particular in lithographic applications.

15 Thus, it is an object of the present invention to provide novel resist compositions, in particular compositions based on functional metal-organic complexes and polymers thereof.

It is another object of the present invention to provide methods of producing novel functional metal-organic complex resist compositions.

20 It is a third object of the present invention to provide coatings comprising functional metal-organic resist composition.

It is a fourth object of the present invention to provide photon or electron beam resist
25 coatings comprising functional metal-organic resist compositions.

It is a fifth object of the present invention to provide underlayer coatings comprising metal-organic compositions.

30 It is a sixth object of the present invention to provide patternable/non-patternable hard mask coatings comprising metal-organic compositions.

The present metal-organic complexes comprise metal complexing ligands derived from compounds having the basic structure $R_2-C(=A)-N(OH)-R_1$, in which A stands for a
35 heteroatom, R_1 stands for hydrogen or an optionally substituted hydrocarbyl residue and R_2 stands for a functionally substituted, polymerizable hydrocarbyl residue. The ligands are capable of chelating metal ions.

The novel metal-organic complexes can be condensed as such into oligomers and polymers, which are useful in coating applications and lithographic applications on substrate. The novel metal-organic complexes can also be incorporated into oligomers or polymers by subjecting their polymerizable moiety, R₂, to polymerization or
5 copolymerization with other reactive moieties.

The complexes as well as oligomers, polymers and copolymers thereof are useful precursors for forming coatings and film on semiconductor substrates, and they can be used as precursors for metal oxide coatings and films.

10

More specifically, the present invention is mainly characterized by what it stated in the characterizing parts of the independent claims.

Considerable advantages are obtained by the present invention.

15

It has been found that resins that comprise a functional metal-organic complex of the present kind, such as a metal-hydroxamate, containing a metal-oxygen bond adjacent to the nitrogen at one part of the molecule and a polymerizable/cross-linkable moiety in another part have many attributes which are useful in photo-resist coatings.

20

Generally, complexes and polymers and oligomers based thereupon provided by embodiments of the present invention exhibit high absorption at extreme ultraviolet wavelength and stable polymerizable/cross-linkable group while retaining outstanding mechanical properties which makes useful in photo or electron-lithography applications.

25

Thus, in one aspect, the existence of hydrocarbon part of the metal or poly-metal-complexes make them suitable candidates for the solution processing in organic solvents that enables the coating of these type of materials on semiconductor substrates.

30 Further, the solution processable organometallic complexes and poly-metal complexes and clusters of the present invention have excellent shelf life and high sensitivity in lithography. They are suitable for advanced patterning lithography, carried out for example using 248 nm (KrF), 193 nm (ArF), electron-beam, and in particular extreme ultraviolet lithography (EUV) due to the presence of atomic absorption of elements at 13.5 nm wavelength. They
35 exhibit high etch resistance and good mechanical properties of metal containing resists.

Materials according to embodiments of the invention yield coatings with desirable optical, mechanical and compositional properties which make them useful in optical lithography applications.

5 Solutions according to embodiments of the invention can further be used to cast films on semiconductor or other substrates to be used as such to direct light favorable or used in semiconductor fabrication processes to adjust the optical properties of the coating to achieve improved reflectivity control.

10 In some embodiment, solutions of such embodiments also contribute to the cure process or the pattern shape of the resist coated, exposed and developed on top of the said coating.

Thus, the present solutions can be used for casting coatings on semiconductor substrates to form a coating that has predetermined optical properties in terms of refractive index and
15 absorption coefficient.

In some embodiments, the present metal-organic complexes can be employed as additives in underlayer coatings in lithography for, e.g., adjusting the refractive index, the absorption coefficient at lithographic wavelengths, etch resistance, as well as to facilitate the cure
20 process, and improve the surface energy of the coating.

In some embodiments, the present metal-organic complexes can be polymerized by means of thermal or photochemical irradiation by addition of thermo or photoradical initiators into the formulation of their respective coatings.
25

In some embodiments, the present metal-organic complexes can be polymerized by means of condensation in presence of organic or inorganic base or acid in organic solvent by removing few of ligands to obtained -M-O-M-O- type of linkage and corresponding by products
30

An underlayer poly-metal-organic complex composition comprising novel functional metal-organic complex having a metal-oxygen bond adjacent to the nitrogen in one moiety and a polymerizable and/or cross-linkable group in another moiety yields coatings that have high refractive index in the visible wavelengths and can be used in coating compositions to adjust
35 optical constants in lithographic wavelengths. In addition, the present novel functional metal-organic complex, when used as a precursor for a polymer, yields coatings which have surprising beneficial effects in the interfaces of subsequent layers and high etch resistant.

Due to process simplicity, good optical performance, room temperature applicability, and time saving the present organic-inorganic hybrid resist materials are attractive for EUV applications e.g. as a photoresists as well as underlayer where atomic absorption is prerequisite to reduce the dose, improve sensitivity, and ultimately enhance throughput a

5 key requirement for the realization of EUV photoresist.

Additionally, the presence of metal in the organic-inorganic hybrid materials makes them resistant to etching in oxygen plasma, resulting in efficient pattern transfer onto the underlying organic layer.

10

The chemical stability of the materials allows for lithographic methods using dry development of the non-exposed or exposed part of the film with low or high density plasma and gases can including typical etch and plasma treatment gases such oxygen, nitrogen, argon, forming gas, CF₄ and CF₃H to mention a few. Further, partial or full oxidation of

15 patterned or non-patterned layers is also possible.

The present metal-organic complexes and polymers and copolymers thereof can be used as solution processable precursors of metal oxide films.

20 Further features and advantages of the present technology will appear from the following detailed description of embodiments.

Brief Description of the Drawings

25 Figure 1 show in sideview schematically the principal steps of forming a trilayered lithography stack and

Figure 2 shows the NMR of a novel functional metal-hydroxamate consist of metal-oxygen bond adjacent to the nitrogen in one moiety with a polymerizable/cross-linkable group (methacrylate) in another moiety of the complex of Example 1.

30 Figure 3 shows the applicability of present invention in a 4-layered structure comprising a photoresist layer 120 on top a Silicon hard mask Si-BARC or Silicon oxynitride or metal oxides 130 and SOC or CVD or ALD carbon or high temperature SOC 140 layers, which are deposited upon a substrate 150.

Figure 4 shows the exposer of newly developed material/photoresist layer under 250 nm

35 lamp, and

Figure 5 shows the SEM upon irradiation of electron-beam exposer on a novel functional metal-hydroxamate to yield lines with 50 nm HP using a 2 % solution prepared in Example 1 at a dose of 150 $\mu\text{C}/\text{cm}^2$.

5

Embodiments

Unless otherwise stated herein or clear from the context, any percentages referred to herein are expressed as percent by weight based on a total weight of the respective composition.

10 Molecular weight is expressed as weight average molecular weight.

Unless otherwise stated, properties that have been experimentally measured or determined herein have been measured or determined at room temperature. Unless otherwise indicated, room temperature is 25 °C.

15

It must also be noted that, as used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless otherwise specified.

As used herein, the term “about” refers to a value which is $\pm 5\%$ of the stated value. As used herein, the term “about” refers to the actual given value, and also to an approximation to such given value that would reasonably be inferred to one of ordinary skill in the art, including approximations due to the experimental and/or measurement conditions for such given value.

25 As used herein, the structure of complex obtained by using nuclear magnetic resonance using dimethyl sulfoxide as a reference.

The resist films were exposed to electron beam lithography using Raith EBPG 5200 system. SEM images are taken by Zeiss Supra 35.

30

In the present context, the term “precursor or complex” is used synonymously with the term “monomer” to designate a molecule (also referred to as “compound” or “complex”) that can, on its own, or as a co-monomer with other functional monomers possessing cross-linkable groups, form a part of a linear or branched or cross-linked polymer backbone.

35

In the following, the term “polymer” is used for covering both oligomers and polymers, i.e. the term covers polymeric molecules having at least 2 monomeric units, in particular at least 4, such as at least 6 or at least 8 monomeric units.

- 5 The present materials can be characterized as “metal-organic complexes” in which a metal ion is chelated by at least one, usually several metal complexing ligands derived from compounds having the structure $R_2-C(=A)-N(OH)-R_1$, in which A stands for a heteroatom, R_1 stands for hydrogen or an optionally substituted hydrocarbyl residue and R_2 stands for a functionally substituted, polymerizable hydrocarbyl residue. Through deprotonation of the
- 10 compounds a dianion is provided which gives rise to A,O bidentate ligands, thus forming metal organic complexes when contacted with a metal ion. To that end, the complexes typically undergo interconversion into their *cis* form. Depending on the valency of the complexed metal ion, the number of ligands in the novel metal organic complexes is typically 1 to 4.

15

- When A stands for oxygen, the ligands can be characterized as being derived from hydroxamic acid having the formula $R_2-C(=O)-N(OH)-R_1$, wherein R_1 and R_2 have the same meaning as above. In the present context, the term “metal-hydroxamate” stands for a compound having metal oxygen bond in which the oxygen atom directly connected to the
- 20 substituted nitrogen next to electron withdrawing carbonyl. A first deprotonation of the hydroxyl on the $-NR_1-$ group gives rise to a hydroxamate anion, followed by a second deprotonation at the oxo group, which gives rise to a hydroximate anion. As a result, the hydroxamic acid will yield O,O' bidentate ligands upon deprotonation. Such ligands will form *bis*-hydroxamate complexes with bivalent metal ions, such as zinc, *tris*-hydroxamate
- 25 complexes with trivalent metals, such as aluminium, *tetrakis*-hydroxamate complexes with tetravalent metals, such as tin, and *pentakis*-hydroxamate with pentavalent metalloids, such as antimony.

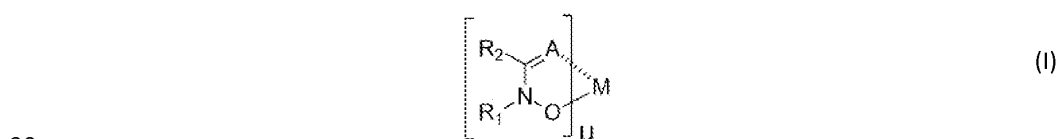
- In a first embodiment, the present metal-organic complexes contain a plurality of, generally
- 30 more than 1 and up to 10, typically 2 to 5 or 2 to 4, identical ligands. In such an embodiment, the ligands have substituents R_1 that are the same as substituents R_1 of other ligands, and substituents R_2 that are the same as substituents R_2 of other ligands.

- In a second embodiment, the present metal-organic complexes contain a plurality of,
- 35 generally more than 1 and up to 10, typically 2 to 5 or 2 to 4, ligands, of which at least one differs structurally from the other ligands. In one variant of the second embodiment, at least one ligand exhibits a substituent R_1 or substituent R_2 , or both, that differ from corresponding substituent R_1 or substituent R_2 or both of one or several ligands.

In one embodiment, substituents R_1 are selected from hydrogen or hydrocarbyl residues, such as alkyl residues having one to ten carbon atoms, whereas the substituents R_2 substituents stand for reactive groups, such as acrylate, methacrylate, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, silyl, carboxy, carboxylate, acrylate, alkacrylate (wherein alkyl
 5 has 1 to 10 carbon atoms, typically 1 to 6 carbon atoms), and halogen, or for hydrocarbyl groups, with 1 to 10 carbon atoms, substituted with such reactive groups. In the second embodiment, where there are one or more ligands that differ structurally from the other ligands, substituent R_2 can also be selected from non-reactive groups or hydrocarbyl
 10 residues, such as alkyl groups having 1 to 10 carbon atoms, typically 1 to 6 carbon atoms.

In a second variant of the second embodiment, there is at least one ligand that has a structure that does not meet the definition of metal-organic complexes given above. Rather, such a different ligand can be a inorganic or organic ligand, typically a monodentate or
 15 bidentate ligand.

One embodiment comprises an organometallic compound represented by Formula (I) or Formula (II) or both:



wherein

M stands for a metal, transition metals, non-metals, and metalloids found in groups 1 to 15;
 25 R_1 stands for hydrogen or an optionally substituted hydrocarbyl residue;
 R_2 stands for a hydrogen, a hydrocarbyl residue comprising a saturated or unsaturated hydrocarbon that is linear or branched or cyclic and optionally substituted with one or more groups that contain hetero atom(s), or R_2 is selected from amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, an alkenyl group with 2 to 10 carbon
 30 atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; silyl, carboxy, carboxylate, acrylate, alkacrylate, wherein the alkyl residue has 1 to 10 carbon atoms, and halogen;

R₃ can be same as compound above of Formula (I) (excluding the M) in which R₂ can be optionally independently selected units can be for example acrylates, thiols, cyano, mercapto, silyl and glycidyl groups or alkyl, aryl, cyclic or branched independently substituted hydrocarbyl groups or

- 5 R₃ is an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; an acrylate, methacrylate, carbamate, thiocarbamate, acetate, or derived from a compound of an alkali metal salt of corresponding acrylates, methacrylates, carbamates, thiocarbamates, and acetates; A stands for a heteroatom; and
- 10 u and v independently stand for integers having a value in the range from 1 to 10.

In particular, R₃ represents a residue corresponding to the structure placed within the left-hand side brackets of Formula (II), whereby R₁ stands for hydrogen or an optionally substituted hydrocarbyl residue and R₂ stands for hydrogen, a hydrocarbyl residue of a saturated or unsaturated, linear, branched or cyclic hydrocarbon, optionally substituted with one or more, reactive or non-reactive groups optionally containing heteroatoms, at least one of said substituents R₁ and R₂ in the meaning of R₃ being different from the corresponding substituents of the structure placed within the left-hand side brackets of Formula (II).

20

Additionally, or alternatively, the organometallic compound has Formula (II), wherein R₃ represents a residue corresponding to the structure placed within the left-hand side brackets of Formula (II), whereby R₁ stands for hydrogen or an optionally substituted hydrocarbyl residue and R₂ stands for hydrogen, a hydrocarbyl residue of a saturated or unsaturated, linear, branched or cyclic hydrocarbon, optionally substituted with one or more reactive or non-reactive groups optionally containing heteroatoms, at least one of said substituents R₁ and R₂ in the meaning of R₃ being different from the corresponding substituents of the structure placed within the left-hand side brackets of Formula (II). Additionally, or alternatively, R₁ is selected from the group consisting of an optionally substituted, linear or cyclic alkyl groups with 1 to 10 carbon atoms; and a bridging hydrocarbyl radical that can be independently selected from optionally functionalized linear, branched, or cyclic, bivalent, saturated or unsaturated hydrocarbyl radicals, such as an optionally functionalized linear, branched or cyclic alkylene, alkenylene or alkynylene group; or an optionally functionalized aromatic or polyaromatic group having 5 to 30 carbon atoms; and R₂ is selected from amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; silyl, carboxy, carboxylate,

acrylate, alkacrylate (wherein the alkyl residue has 1 to 10 carbon atoms), and halogen. Additionally, or alternatively, R₂ is ethenyl or prop-1-en-2-yl.

In the meaning of an optionally substituted hydrocarbyl residue, R₁ represents, for example:

- 5 – an optionally substituted, linear or cyclic alkyl groups with 1 to 10 carbon atoms;
- a bridging hydrocarbyl radical that can be independently selected from optionally functionalized linear, branched, or cyclic, bivalent, saturated or unsaturated hydrocarbyl radicals, such as an optionally functionalized linear, branched or cyclic alkylene, alkenylene or alkynylene group; or an optionally functionalized aromatic
- 10 or polyaromatic group having 5 to 30 carbon atoms.

The hydrocarbyl is preferably functionalized with one or more functional (reactive) groups selected from hydroxy, oxo, amino, amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acyl, acetyl, silyl, carboxy, carboxylate, acrylate, alkacrylate (wherein

15 the alkyl residue has 1 to 10 carbon atoms), and halogen.

Additionally, or alternatively, R₂ stands for a hydrocarbyl residue of a saturated or unsaturated, linear, branched or cyclic hydrocarbon having 1 to 10 carbon atoms.

- 20 In embodiments, R₂ represents, for example:
- amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; silyl, carboxy, carboxylate, acrylate, alkacrylate (wherein the alkyl residue has 1 to 10 carbon atoms), and halogen.

25 In the meaning of a hydrocarbyl residue R₂ represents, for example, an alkyl group with 1 to 10 carbon atoms, an aryl group with 5 to 18 carbon atoms, an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; or an aralkyl group with 6 to 21 carbon atoms, whereby the

30 alkyl, aryl or aralkyl exhibits one or more substituent groups selected from hydroxy, amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, silyl, carboxy, carboxylate, acrylate, alkacrylate (wherein the alkyl residue has 1 to 10 carbon atoms) and halogen and combinations thereof.

- 35 Additionally, or alternatively, R₂ stands for an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms. Additionally, or alternatively, R₂ stands for ethenyl or prop-1-en-2-yl.

R₁ is selected from hydrogen and a linear or branched alkyl group with 1 to 10 carbon atoms, and R₂ is an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms, preferably R₂ is ethenyl or prop-1-en-2-yl.

5

In embodiments, specific examples of monomeric units R₃ in Formula (III) include but are not limited to cross-linkable units possessing acrylates, thiols, cyano, mercapto, and glycidyl groups but also silyl derived from silanes, such as

- γ-mercaptopropyltrimethoxysilane, γ-mercaptopropyltriethoxysilane,
10 β-cyanoethyltriethoxysilane, γ-mercaptopropylmethyldimethoxysilane,
γ-mercaptopropyldiethoxysilane, glycidoxymethyltrimethoxysilane,
glycidoxymethyltriethoxysilane, α-glycidoxyethyltrimethoxysilane,
α-glycidoxyethyltriethoxysilane, β-glycidoxyethyltrimethoxysilane,
β-glycidoxyethyltriethoxysilane, α-glycidoxypropyltrimethoxysilane,
15 α-glycidoxypropyltriethoxysilane, β-glycidoxypropyltrimethoxysilane,
β-glycidoxypropyltriethoxysilane, γ-glycidoxypropyltrimethoxysilane,
γ-glycidoxypropyltriethoxysilane, γ-glycidoxypropyltripropoxysilane,
γ-glycidoxypropyltributoxysilane, γ-glycidoxypropyltriphenoxysilane,
α-glycidoxybutyltrimethoxysilane, α-glycidoxybutyltriethoxysilane,
20 β-glycidoxybutyltriethoxysilane, γ-glycidoxybutyltrimethoxysilane,
γ-glycidoxybutyltriethoxysilane, δ-glycidoxybutyltrimethoxysilane,
δ-glycidoxybutyltriethoxysilane, (3,4-epoxycyclohexyl)methyltrimethoxysilane,
(3,4-epoxycyclohexyl)methyltriethoxysilane, β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
β-(3,4-epoxycyclohexyl)ethyltriethoxysilane, β-(3,4-epoxycyclohexyl)ethyltripropoxysilane,
25 β-(3,4-epoxycyclohexyl)ethyltributoxysilane, β-(3,4-epoxycyclohexyl)ethyltriphenoxysilane,
γ-(3,4-epoxycyclohexyl)propyltrimethoxysilane,
γ-(3,4-epoxycyclohexyl)propyltriethoxysilane,
δ-(3,4-epoxycyclohexyl)butyltrimethoxysilane, δ-(3,4-epoxycyclohexyl)butyltriethoxysilane,
glycidoxymethylmethyldimethoxysilane, glycidoxymethylmethyldiethoxysilane,
30 α-glycidoxyethylmethyldimethoxysilane, α-glycidoxyethylmethyldiethoxysilane,
β-glycidoxyethylmethyldimethoxysilane, β-glycidoxyethylethyldimethoxysilane,
α-glycidoxypropylmethyldimethoxysilane, α-glycidoxypropylmethyldiethoxysilane,
β-glycidoxypropylmethyldimethoxysilane, β-glycidoxypropylethyldimethoxysilane,
γ-glycidoxypropylmethyldimethoxysilane, γ-glycidoxypropylmethyldiethoxysilane,
35 γ-glycidoxypropylmethyldipropoxysilane, γ-glycidoxypropylmethyldibutoxysilane,
γ-glycidoxypropylmethyldiphenoxysilane, γ-glycidoxypropylethyldimethoxysilane,
γ-glycidoxypropylethyldiethoxysilane, γ-glycidoxypropylvinylmethoxysilane,

- γ -glycidoxypolyvinylidiethoxysilane, and phenylsulfonylaminopropyltriethoxysilane, vinyltrimethoxysilane, vinyltrichlorosilane, vinyltriacetoxysilane, vinyltriethoxysilane, methylvinylmethoxysilane, methylvinyltriethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane,
- 5 γ -methacryloxypropylmethyldiethoxysilane, (methacryloxymethyl)methyldiethoxysilane, (methacryloxymethyl)methyldimethoxysilane, methacryloxymethyltriethoxysilane, methacryloxymethyltrimethoxysilane, methacryloxypropyltrichlorosilane, methacryloxypropyltriethoxysilane, methacryloxypropyltriisopropoxysilane.

- 10 In embodiments, A is oxygen, nitrogen, and sulphur, in particular oxygen or sulphur.

- The ion M is, for example, selected from the group of transition metals, or from the group of metals and metalloids of groups 1 to 15, or 3 to 15, comprising zinc, tin, antimony, indium, bismuth, hafnium, zirconium, gallium, aluminium, germanium, silicon and
- 15 selenium. In particular M stands for a high EUV photon absorbing element, most preferably M stands for zinc, gallium, indium, tin or antimony.

In one particular embodiment of metal-organic complexes according to Formula (I) or Formula (II)

- 20 – R₁ is selected from the group of hydrogen, methyl, ethyl, allyl, halo-alkyl, and phenyl,
- R₂ stands for acrylate or methacrylate, or for ethenyl or prop-1-en-2-yl, or for an alkyl group with 1 to 10 carbon atoms, an aryl group with 5 to 18 carbon atoms, or an aralkyl group with 6 to 21 carbon atoms, said alkyl, aryl or aralkyl being
- 25 substituted with one or more acrylate or methacrylate groups,
- R₃ can be same as compound above of Formula (I) in which R₂ can be optionally independently selected units can be for example acrylates, ethenyl or prop-1-en-2-yl, thiols, cyano, mercapto, and glycidyl groups or alkyl, aryl, cyclic or branched independently substituted hydrocarbyl groups.
- 30 – R₃ can be an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; an acrylate, methacrylate, carbamate, thiocarbamate, acetate, or a compound of alkali metal salt of corresponding acrylates, methacrylate, carbamates, thiocarbamates, and acetates.
- 35 – A stands for oxygen or sulphur, and
- u, v is an independent integer having a value in the range from 1 to 10.

In one embodiment, the reactive moiety comprises one or more ethenyl, prop-1-en-2-yl, or (meth)acrylic groups, i.e. groups exhibiting carbon-carbon double bond adjacent to the electron withdrawing carbonyl group. The present materials can also contain other functional groups exhibiting connectivity to metals center typically along its main chain,
5 along its main metal-oxygen chain.

In one embodiment, there are about 1–20 mole-% of the novel metal-organic compound/complex per repeating unit of the poly-metal organic complex resin main chain. In one further embodiment, there is less than 5 mole-% of the novel metal-organic complex
10 for each unit of the poly-metal-organic complex resin main chain.

Embodiments of the present technology relate to methods of manufacturing cross-link metal-organic complex resin, in particular metal-hydroxamate resin, solutions containing a novel functional metal-organic complex that exhibits a metal-oxygen bond adjacent to a
15 nitrogen at one part and a polymerizable/cross-linkable group to another part of the molecule. The cross-linkable group, such as an acrylate group or a methacrylate group, can, in some embodiments, be subjected to photo or thermo-cross-linking reactions alone or with suitable other precursors that contain the same, or different, functionality. In particular, in one embodiment an acrylate or methacrylate substituted metal-organic
20 complex or resin, is reacted with another acrylate or methacrylate precursors.

Embodiments also relate to the use of the functional cross-linkable metal-organic complexes or polymers thereof in solutions to cast coatings on semiconductor substrates in the lithography process to form patterns through subsequent bake, irradiation and
25 development steps. In particular, the invention relates to the ability to control the microstructure of the resin in such way it is industrially feasible and solves the drawbacks of prior art.

Embodiments of the present technology relates to application of novel metal containing
30 photoresist-coating in lithography stack layers (cf. Figure 4). In such a scheme, the stack consists of a novel functional metal-organic complex (e.g. metal-hydroxamate), having metal-oxygen bond adjacent to the nitrogen at one part while polymerizable/cross-linkable group to another part of molecule, as a photoresist layer 120 of 40–50 nm, a Si-BARC or Silicon oxynitride or metal oxide layer 130 of 20–50 nm, a spin on carbon (SOC), or high
35 temperature SOC layer, or amorphous carbon layer 140 obtained by chemical vapor deposition of 200–400 nm, and a substrate 150, respectively.

In a stack of the above-identified kind, a photoresist layer obtained from a metal-organic complex surprisingly can be patterned at very low-dose under irradiation of electron-beam lithography. This low-dose fine patterning with high resolution makes them potential candidates for the development of advanced lithographic resist solution.

5

A decreased dose means a shorter time for the exposure step which, again, stands for means improved efficiency and high lithographic throughput for commercial application. Additionally, a decreased dose may positively affect necessary maintenance procedures increasing the economic benefit obtained by the use of such high absorbing, low dose photo-resist materials.

10

According to an embodiment, the present technology relates to a composition suitable for formation of a layer of a cross-linkable complex on a substrate, said composition comprising a poly-metal-organic complex with metal-oxygen moieties, and the composition preferably further comprising photo-cross-linkable units, acid, and/or base and a solvent.

15

In one embodiment, a compound of Formula (I) or Formula (II) is used in an amount of 1–10 mole%. The cross-linkable metal-hydroxamate composition can be obtained by irradiation of electron beam or photo-lithography wavelength.

20

As mentioned above, the present complexes or metal-hydroxamates, respectively, can be converting into polymers, also referred to as poly-metal-organic complexes or “poly-metal-hydroxamates”.

In one embodiment, such polymers are obtained by reacting the reactive groups of R_2 , in particular by subjecting the compound to conditions of polymerization, for example to conditions of radical polymerization.

25

In some embodiments, the present metal-organic complexes can be polymerized by means of condensation in presence of organic or inorganic base or acid in organic solvent by removing few of ligands to obtained -M-O-M-O- type of linkage and corresponding byproducts.

30

In one embodiment, polymers of the present complexes can be obtained by subjecting the present metal-organic complexes of Formula (I) or Formula (II) to conditions of polymerization in the presence of cross-linkable monomers to obtain copolymers. It is also possible to subject the present metal-organic complexes of Formula (I) or Formula (II) to condensation to form polymers. The polymers can be cross-linked. Additionally, or

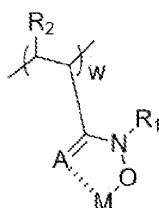
35

alternatively, the conditions of polymerization are free of other reactive monomers than the metal-organic complexes of Formula (I) or Formula (II).

5 Additionally, or alternatively, the polymer obtained by subjecting one or more organometallic compound represented by of Formula (I) and/or (II) as defined in the present disclosure to conditions of polymerization, for example to conditions of radical polymerization, in the presence of cross-linkable monomers to obtain copolymers, or in the absence of cross-linkable monomers.

10 In one embodiment, poly-metal-hydroxamates are obtained by addition of photo or thermo-radical initiators into the metal-hydroxamate formulation comprising one or more organic/inorganic solvents cured under thermal or photochemical reactions.

15 The present invention is particularly well suited for the production of compositions comprising a poly-metal-hydroxamate obtained by the photo or thermo radical initiator reacted with the novel functional metal-hydroxamate consist of metal-oxygen bond adjacent to the nitrogen at one part while polymerizable/cross-linkable group to another part of the molecule of Formula (III) below:



(III)

20

wherein R_1 , R_2 , A and M have the same meaning as above in Formulas (I) and (II); and w is an integer having a value in the range from 100 to 100,000.

25 The poly-metal-organic compound (in particular hydroxamate) of Formula (III) where R_1 and R_2 are independently selected from hydrogen, a hydrocarbyl residue of a saturated or an unsaturated, linear or branched hydrocarbon with 1 to 10 carbon atoms, acrylic, methacrylic, alkyl groups, aryl groups, aralkyl groups, halogenated alkyl groups, halogenated aryl groups, halogenated aralkyl groups, alkenyl groups, organic groups having one or more
30 epoxy groups, mercapto groups, alkoxyaryl groups, acyloxyaryl groups, isocyanurate groups, hydroxy groups, cyclic amino groups, or cyano groups and combinations thereof.

The poly-metal-organic compound (poly-metal-hydroxamate) composition of Formula (III) where A is any heteroatom including oxygen, sulphur, and nitrogen, preferably sulphur or nitrogen or oxygen, and most preferably oxygen and sulphur, where, M represents any metal, non-metal, and metalloids selected from groups 1 to 15 or 3 to 15, the preferable
5 metals include Zn, Ga, Sn, Hf, Sb, Zr, Bi, Al, In, and other transition metals, and w represents possible number of monomeric units of the Formula (I). Additionally, or alternatively, R₁ and R₂ are independently selected from hydrogen, a hydrocarbyl residue of a saturated or an unsaturated, linear or branched hydrocarbon with 1 to 10 carbon atoms, preferably R₁ is selected from hydrogen and a linear or branched alkyl group with 1 to 10
10 carbon atoms and R₂ is a saturated, linear or branched hydrocarbon with 1 to 10 carbon atoms.

In one of embodiments the poly-metal-organic compound (poly-metal-hydroxamate) of Formula (III) obtained by addition of photo or thermo-radical initiator into the metal-
15 hydroxamate formulation comprising one or more organic/inorganic solvents cured under thermal or photochemical reactions.

In one of embodiments, the novel functional metal-organic compounds or metal-hydroxamate consist of metal-oxygen bond adjacent to the nitrogen at one part while
20 polymerizable/cross-linkable group to another part of the molecule present in the formulation comprising photo-radical initiator exposed to various wavelengths near IR to deep UV to obtained patterns.

In one of embodiments the novel functional metal-organic compound or metal-hydroxamate consist of metal-oxygen bond adjacent to the nitrogen at one part while
25 polymerizable/cross-linkable group to another part of the molecule present in the formulation comprising thermo-radical initiator cured by applying various temperature range 50 to 250 °C.

30 According to one embodiment, the cross-linking of the novel functional metal-organic complex either alone or in a variety of molar percentages with monomers containing other or same functionalities, such as acrylate or methacrylate, is carried out completely without solvents in the presence of photo or thermo additives in the formulation. In one embodiment, the cross-linking reaction of a novel functional metal-organic complexes is carried out in
35 presence of a photo-radical initiator or thermo-radical initiator or a combination thereof.

In one embodiment, the co-poly-metal-organic compound or co-poly-metal-hydroxamate of Formula (III) obtained by addition of photo or thermo-radical initiator into the metal-organic

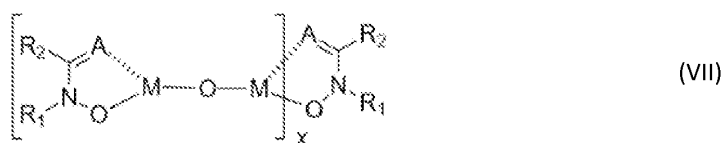
complex of Formula (I) or Formula (II) are incorporated into a formulation comprising one or more organic/inorganic solvents and cured under thermal or photochemical reactions.

- 5 In one embodiment, the functional metal-organic complex is present in the formulation of Formula (I) or (II) and the formulation further comprises a photo-radical initiator exposed to various wavelengths in the range from near IR to deep UV to obtained patterns.

- 10 In one embodiment, the amount of thermo or photo labile compounds in the formulation amounts to 0.1 to 20 %, most preferably 0.2 to 10 %, e.g. 0.5 to 7.5 %, corresponding to the solid content of the metal-complex.

In one embodiment, curing of the functional metal-organic complex of Formula (I) or (II) formulation is carried out at a temperature in the range of 50 to 250 °C.

- 15 The present invention also relates to the compositions comprising condensation of a metal-organic compound of Formula (I), the obtained polymer represented by Formula (VII)



20

wherein

R₁, R₂, A, and M have the same meaning as above in Formula (I); and
x in the metal oxide polymer is an integer of 1 to 100.

- 25 In one embodiment, applicable to any of the fore-going embodiments, R₁ is selected from hydrogen and a linear or branched alkyl group with 1 to 10 carbon atoms, and R₂ is selected from an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; acrylate, methacrylate, allyl, vinyl, epoxy or thiols, preferably R₁ is selected from hydrogen and methyl, and R₂ from
30 ethenyl, prop-1-en-2-yl, acrylate and methacrylate.

In one embodiment, in the obtained polymer of Formula (VII), A is selected from the group of oxygen, sulphur, and nitrogen. Preferably A is selected from the group of sulphur, nitrogen and oxygen, in particular A is oxygen or sulphur.

35

In one embodiment, M represents zinc, tin, hafnium, antimony, zirconium, bismuth, aluminium or indium, in particular M represents an EUV photon absorbing element, such as zinc, gallium, indium, tin or antimony.

- 5 In another embodiment a polymer is obtained in presence of at least one organic solvent for, optionally in mixture with water in presence of organic/inorganic acid or base and corresponding byproducts.

To improve the coating performance in terms of coating uniformity, different surfactants, such as one or more silicone or fluoro surfactants or combinations thereof, can be used for example for lowering the surface tension of the metal-organic complex formulation coating. The use of such surfactants may improve coating quality. The amount of surfactant is in a range of 0.001 % to no more than 10 % by mass compared to the metal-organic complex.

- 15 The present metal-organic complex or compositions thereof can be used for spin coating of substrates, such as silicon substrates, for example silicon wafers. By such layers, the molar absorptivity can be increased.

The present novel functional metal-organic complexes can be used as additives to adjust, i.e. to “tune”, the polymer film thickness, index of refraction (n), molar absorptivity (k), and contact angle (CA) of corresponding photoresists.

In one embodiment, compounds of formula (I) spin-coated film heated with respect to the temperature 50 to 350 degrees to achieve high refractive index metal oxide film.

25

In one embodiment, compounds of Formula (I) where A represents O, i.e. metal-hydroxamate compounds, are prepared by converting an ester derivative into hydroxamic acid which is then reacted with a metal source to yield the desired metal-hydroxamate by a two-step method.

30

Thus, A method of producing a metal-hydroxamate derivative according to any of the preceding claims, comprising the steps of

- reacting a carboxylic acid or an ester or esters having Formula (IVa)

35



in which R_2 has the same meaning as in Formula (I), or an activated form thereof,

with an amine having Formula (V), R_4 is hydrogen or a linear, branched or cyclic or heterocyclic alkyl group having 1 to 10 carbon atoms, optionally having 1 to 3 aryl substituents,



or a salt thereof,

wherein R_5 stands for hydrogen or for a linear, branched or cyclic or heterocyclic alkyl group having 1 to 10 carbon atoms, optionally having 1 to 3 aryl substituents,
 10 or R_5 stands for silyl group of formula $-SiR_7R_8R_9$, in which R_7 , R_8 and R_9 are independently selected from linear or branched alkyl groups having 1 to 10 carbon atoms; and R_6 stands for hydrogen or a linear, branched or cyclic alkyl group having 1 to 10 carbon atoms or an aryl group having 6 to 18 carbon atoms,

15 to produce a hydroxyamic acid salt having Formula (VI),



wherein R_2 has the same meaning as above,

20 and X is cation of alkali or alkaline earth metals or organic tetra-alkyl ammonium or phosphonium or sulfonium hydrocarbon.

- reacting the hydroxyamic acid salt of Formula (VI) with a compound of a metal or a metalloid or a non-metal, of groups 1 to 15 or 3 to 15, to form a metal-hydroxamate derivative according to Formula (I).

25

“Carboxylic acid having Formula (IVa) or an activated form thereof” refers to an activated form of the carboxylic acid of Formula R_2COOH , i.e., a derivative of R_2COOH , in which the carboxylic acid has been activated with a group, therefore, in terms of reactivity the (activated) carboxylic acid derivative is more reactive than the carboxylic acid. This
 30 activated form thereof may be also referred to an activated carboxylic acid.

Additionally, or alternatively, the carboxylic acid or an ester or esters having Formula (IVa)



35 in which R_2 has the same meaning as in Formula (I), or an activated form thereof, is a compound of Formula (IVab)



in which R_2 has the same meaning as in Formula (I), and R_{4b} is a halogen, preferably Cl or Br; or a sulfonyl, preferably tosyl, mesyl, or trifyl.

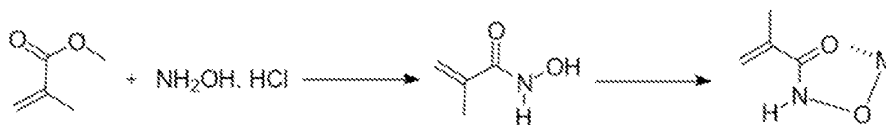
In one embodiment the activated form of the carboxylic acid of Formula (IVa) comprises
 5 an ester or acyl halide, acetyl sulfonylic, acetyl tosylic or acetyl mesylic.

In another embodiment the activated form of the carboxylic acid of Formula (IVa) comprises an amide having Formula (IVb)

10 $R_2C(=O)NH_2$ (IVb)

wherein R_2 has the same meaning as above.

One embodiment of the general method, viz. the use of methacrylic acid as an acid ester
 15 for reacting with hydroxylamine hydrochloride to prepare metal-hydroxamate having an acrylate, ethenyl, or prop-1-en-2-yl substituent at R_2 , as is shown in Scheme 1.



Scheme 1. General method for the synthesis of metal-hydroxamate precursor or additive of
 20 Formula (I).

In the first step of the method, the carboxylic acid, as an ester or other active species, is added to suitable solvent. Then, a substitution reaction is carried out in the presence of a suitable inorganic or organic base, by reacting the ester with an amine compound that
 25 contains a free hydroxyl group and a primary or secondary amine. The amine is for example selected from hydroxylamine hydrochloride, methylamine hydrochloride, allylamine hydrochloride, or ethylamine hydrochloride. Most preferably the amine is hydroxylamine hydrochloride.

30 The reaction can be carried out at variable temperatures, preferably between -30 and 150 $^{\circ}\text{C}$, or 0 to 100 $^{\circ}\text{C}$. The reaction temperature can for example be between 25 and 70 $^{\circ}\text{C}$, or between 25 and 45 $^{\circ}\text{C}$, or from 25 to 35 $^{\circ}\text{C}$. In one embodiment, the reaction is carried out at ambient pressure. The reaction time can be varied until the reaction completion has been determined by means of precipitation. Generally, the time is about 1 min to 48 hours,
 35 typically of 2 to 24 h is preferred and 2 h is most preferred.

After this, an intermediate reaction product is obtained that can be purified by column chromatography, crystallization, sublimation or distillation.

- 5 In the second step, the intermediate, in crude or purified form, is then contacted with a metal compound, optionally in a solvent, and a reaction is carried out in the presence of a base to form an oxygen-metal bond while thus yielding the corresponding metal-hydroxamate that can be precipitated in an aqueous medium. Again, the reaction can be carried out at variable temperatures, such as -30 to 150°C or 0 to 100°C . The reaction temperature can for
10 example be between 25 and 70°C , or between 25 and 45°C , or from 25 to 35°C . In one embodiment, the reaction is carried out at ambient pressure. The reaction time can be varied until the reaction completion has been determined by means of precipitation. Generally, the time is about 1 min to 48 hours, typically of 2 to 24 h. Lower reaction temperatures generally provide improved control of the reaction, whereas high
15 temperatures will increase the reaction rate.

In one embodiment, the metal compound selected from metal nitrates, metal chlorides, metal acetates, metal sulfates, metal acetyl acetonates and metal alkoxides and combinations thereof is used to obtain the novel hydroxamate complexes in presence of
20 basic conditions. Examples of such materials are nitrates or halides or alkoxides or sulphates or acetates or acetyl acetonates of Zn, Sn, Cu, Ni, Co, Sb, Bi, In, Ge, Ga, Tl, Al, and other transition metals respectively. Using appropriate conditions, the method according to the present invention yields quantitative reaction product of molecular weight (g/mol) range of 100 to 1000 . Most preferably 200 to 550 (g/mol).

25 Finally, optional solvents and excess of reagents are removed prior to final purification of the desired compound. The reaction steps can also be carried out consecutively without separation of the intermediate reaction product.

30 Although Scheme 1 shows the preparation of acrylate derivatives (an methacrylohydroxamic acid is shown), the above method can be utilized to achieve amine hydroxy compound/s with hydrocarbon substituents that contain other kind of unsaturation, such as vinyl or alkynyl double bonds adjacent to the electron withdrawing carbonyl in an initial stage. Just as in the case of (meth)acrylates or (meth)acrylate derivatives (e.g., 2-
35 methylprop-2-enehydroxamic acid, as shown in Scheme 1), the compound is then further reacted with metal precursors or compounds, such as salts or compounds selected from metal nitrates, metal halides, metal acetates, metal acetyl acetate precursors or compounds to achieve the corresponding metal-hydroxamate.

In one embodiment, the aqueous solution used during the formation of the metal-organic complex contains an organic or inorganic base or a combination thereof. Typical inorganic bases and metal hydroxides, carbonates, bicarbonates and other salts that yield an alkaline water solution. Examples of such materials are sodium hydroxide, potassium hydroxide, cesium hydroxide, calcium hydroxide, sodium carbonate, and sodium bicarbonate. Organic bases on the other hand comprise a larger group consisting of metal salts of organic acids (such as sodium acetate, potassium acetate, sodium acrylate, sodium methacrylate, sodium benzoate), linear branched or cyclic alkylamines (such as diaminoethane, putrescine, cadaverine, triethylamine, butylamine, dibutylamine, tributylamine, piperidine) amidines and guanidines (such as 8-diazabicyclo(5.4.0)undec-7-ene, 1,1,3,3-tetramethylguanidine, 1,5,7-triazabicyclo[4.4.0]-dec-5-ene), phosphazanes (such as P₁-t-Bu, P₂-t-Bu, P₄-t-Bu), and quarternary ammonium compounds (such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide).

In another embodiment the solvent in which complex synthesis is carried out (the “first solvent”), is after drying the complex changed for another solvent or a mixture of solvents (the “second solvent”). Typically, the second solvent is selected such that it provides the material with better coating performance and product storage properties.

In one embodiment, this is achieved through stabilization.

An embodiment provides a composition comprising a metal-hydroxamate resin in liquid phase, comprising a metal-hydroxamate, as described herein, in the liquid phase formed by at least one organic solvent for the metal-hydroxamate resin, optionally in mixture with water. The composition can be formulated for use in a method of a coating a substrate by casting.

In one embodiment, the organic liquid preferably has a flash point of at least 10° C and a vapor pressure at 20° C of less than about 10 kPa.

Examples of stabilizing organic solvent system are represented by one or more organic ethers optionally in mixture with other co-solvent or co-solvents.

In one embodiment, the organic ether is a linear, branched or cyclic ether comprising generally 4 to 26 carbon atoms and optionally other functional groups, such as hydroxyl groups. Particularly suitable examples are five and six membered cyclic ethers, which optionally bear substituents on the ring, and ethers, such as (C₁₋₂₀) alkanediol (C₁₋₆) alkyl ethers. Examples of said alkanediol alkyl ethers are propylene glycol monomethyl ether,

propylene glycol dimethyl ether, propylene glycol n-butyl ether, dipropylene glycol monomethyl ether, dipropylene glycol dimethyl ether, dipropylene glycol n-butyl ether, tripropylene glycol monomethyl ether and mixtures thereof.

- 5 Particularly preferred examples of the present ethers are methyl tetrahydrofurfuryl ether, tetrahydrofurfuryl alcohol, propylene glycol n-propyl ether, dipropylene glycol dimethyl ether, propylene glycol n-methyl ether, propylene glycol n-ethyl ether (PGEE) and mixtures thereof. The stabilizing solvent system consists of a solvent comprising of the ether of this kind alone, or of a mixture of such ether with a typical reaction medium of the hydrolyzation
10 or other solvents such as propylene glycol monomethyl ether acetate (PGMEA). The proportion of the ether is, in such a case, about 10 to 99 wt%, in particular about 50 to 80 wt%, such as 70 to 99 wt%, of the total amount of the solvent.

- In one embodiment, the liquid phase of the present compositions comprises a solvent
15 selected from PGMEA, PGEE, THF and mixtures thereof.

- The solid content of a formulation comprising, consisting of or consisting essentially of solvents and resin material is in the range of 0.1% to no more than 50 %. Most preferably the solid content is in the range of 0.5 % to 10 %, such as 1 to 4 %, calculated from the
20 weight of the formulation.

The solid content (or metal-hydroxamate content) is used to adjust the resultant film thickness during the coating process.

- 25 In one embodiment, the present compositions exhibit a metal content higher than 20 %, more preferably higher than 25 %, most preferably more than 30 %, calculated from the dry weight of the composition.

- Figure 1 shows schematically a typical lithographic process in which the present invention
30 uses metal-organic complex containing a cross-linkable moiety as a resist as the preferred method to achieve both stack simplification and high etch performance.

- As shown in Figure 1 a substrate 10 is coated with a predominantly organic coating 15 in the form of a spin on carbon or an amorphous carbon layer in EUV. The thin patternable
35 film according to present invention 20 is based on metal hydroxamate and poly-metal-hydroxamate resin.

In the process, underlayer coatings 15 and 20 are sequentially coated and baked, prior to deposition of the following coating layer. After this, the radiation sensitive resist layer is selectively irradiated e.g. through a mask containing the desired patterns. The patterning is then developed and subsequently the obtained pattern is transferred by an etch process using fluorine chemistries either in the gas or liquid phase to underlayer. Then the pattern is transferred by a gas phase plasma enhanced etch process to the carbon-based underlayer 15. Of typical importance in this step is the etch selectivity between layers 15 and 20. Finally, the obtained pattern is transferred to the substrate. The resist and the underlayers are typically removed upon completion of the process.

10

Figure 2 shows NMR spectra of newly made monomer and corresponding integration of ligand peaks.

Figure 3 shows a lithographic process utilizing a novel resist layer in a lithographic process. On a substrate 150, a layer based on a spin on carbon (SOC) or an α -carbon by chemical vapor deposition is deposited 140 with a thickness of 200–400 nm. Thereafter, a high silicon-based middle layer Si-BARC or silicon oxynitride or metal oxide layer 130 of a thickness of 20–50 nm is deposited on the previous layer (layer 140). After this, a layer 120 of a photoresist sensitive to light (e.g. at a wavelength of 13.5 nm, 193 nm, 248 nm or 365 nm, but not limited to these) or electron beam radiation is deposited on layer 130 at a thickness of 40–50 nm. In the device, the photoresist layer 120 is irradiated with light having a preselected wavelength or with electron beam through a mask of desired patterns. The patterning is then developed and subsequently the obtained pattern is transferred by an etch process using fluorine chemistries either in the gas or liquid phase. Finally, the obtained pattern is transferred to the substrate. The resist and the underlayers are typically removed upon completion of the process.

The newly designed functional metal-hydroxamate consist of metal-oxygen bond adjacent to the nitrogen at one part while polymerizable/cross-linkable group to another part of the molecule required significantly low dose to obtained fine features shown in figure 4.

After application of resist material using spin coating, a pre-bake step is employed to remove any solvents and volatile traces which are included in coating metal-hydroxamate resist solution. This is necessary to avoid contamination in the manufacturing equipment.

35

Pre-bake can be done at various temperature and times depending on the evaporation of solvents utilized in coatings. Usually, pre-baking can be done at 50 to 120 °C for 10 to 120 seconds and up to 10 minutes. After the drying or pre-baking step, exposure of the coating

to electron beam light or EUV light or similar exposure methods through an optionally used mask is employed to obtain predetermined patterns on the substrate. The dose requirement to generate patterns is, at minimum, $70 \mu\text{C}/\text{cm}^2$ and, at maximum, $1000 \mu\text{C}/\text{cm}^2$ in electron beam lithography Figure 4.

5

As noted above, a lower dose is preferable for achieving high throughput on an industrial scale production of integrated circuits and addressing the issue of RLS trade-off. A post-exposure bake is optionally carried out after exposure of novel photoresist materials. The post-exposure could improve crosslinking of the exposed regions, which in turn improves contrast of photoresist materials. Post-exposure bake can be done in range of temperatures of 80°C and up to 120°C for a time ranging from 10 seconds and up to 10 minutes.

10

Development is carried out to remove the unexposed region of the photoresist material, thus obtaining a predetermined fine pattern. During the development step, non-exposed regions of the photoresist material dissolve in the developer.

15

For development of the resist, organic developers for the novel metal-hydroxamate resist are typically used; the organic developers include, but are not limited to, methyl tetrahydrofurfuryl ether, tetrahydrofurfuryl alcohol, propylene glycol n-propyl ether, dipropylene glycol dimethyl ether, propylene glycol n-methyl ether, propylene glycol n-ethyl ether (PGEE), propylene glycol methyl/ethyl/propyl/butyl/hydrocarbyl ether acetates, methyl ethyl ketone, methyl iso-butyl ketone, di-alkyl ketone, toluene, and various organic solvents.

20

The development is typically carried out by commonly known methods using a spray or puddle of the developer solution method to apply the developer. Alternatively, the substrate can be immersed in a bath containing the developer.

25

In one embodiment, a curing step to densify the exposed and developed patterns is carried out to obtain an enhanced cross-linking of the material or to alter the shape of the resist pattern through a process where the material exhibits some reflow, or both. Such a step leads to improved etch resistance of the material compared to that of the material prepared without a curing step.

30

In one embodiment, curing is carried out at 120°C to 400°C for 1 to 20 minutes and typically up to no more than 10 minutes. It can be done by heating the coating placed on hot plate or in an oven.

35

The present technology also provides for underlayer coatings for, e.g., semiconductors and components thereof. In particular the present materials are suitable as underlayers of photoresist materials. For example, a thin metal-hydroxamate layer can be oxidized with a UV (photon) or plasma treatment and prior coating similar or conventional photoresist on it.

5

In one embodiment, a method for producing a semiconductor device typically comprises the steps of:

- applying the poly or -metal-hydroxamate resist underlayer film forming composition onto a semiconductor substrate and baking the composition to form a resist underlayer film;
- exposing the resist film to light at, e.g., 13.5 nm, 193 nm, 248 nm or 365 nm, or to electron beam radiation;
- developing the resist film after the exposing to obtain a patterned resist film;
- etching the resist underlayer film according to a pattern of the patterned resist film; and
- processing the semiconductor substrate according to a pattern of the resist film and the resist underlayer film.

In one embodiment, a method for producing a semiconductor device comprises:

- forming an organic functional underlayer film on a semiconductor substrate;
- applying the resist underlayer film forming composition onto the organic underlayer film and baking the composition to form a resist underlayer film;
- applying a composition for a resist onto the resist underlayer film to form a resist film;
- exposing the resist film to light at, e.g., 13.5 nm, 193 nm, 248 nm or 365 nm or to electron beam radiation;
- developing the resist film after the exposing to obtain a patterned resist film;
- etching the resist underlayer film according to a pattern of the patterned resist film;
- etching the organic underlayer film according to a pattern of the patterned resist underlayer film; and
- processing the semiconductor substrate according to a pattern of the patterned organic underlayer film.

In one embodiment, a method for producing an optical or semiconductor device comprises:

- applying a spin on carbon (SOC) with various thermal stabilities, e.g. high temperature (350-400 °C) SOC, or α -carbon layer obtained by CVD or ALD on a substrate
- 5 – applying a composition of high silicon content layer or silicon oxynitride or various metal oxide layer.
- applying a functional coating layer comprising a poly-metal-hydroxamate.
- applying a composition for a resist onto the resist underlayer functional layer to obtain a resist film.
- 10 – exposing the resist film to light at, e.g., 13.5 nm, 193 nm, 248 nm, or 365 nm, or to electron beam radiation
- developing the resist film after the exposing to obtain a patterned resist film to achieve significantly lower doses;
- etching the resist underlayer film according to a pattern of the patterned resist film; and processing the substrate according to a pattern of the resist film and 15 the resist underlayer film.

One embodiment comprises the use of a metal-organic complex or a polymer thereof or a metal-hydroxamate or a poly-metal-hydroxamate as an additive, in particular to tune the polymer film thickness, index of refraction (n), molar absorptivity (k), and etch properties of 20 a desired compositions.

A method for producing an optical element or an optically active device:

- applying the resist underlayer film forming composition onto a substrate and baking the composition to form a resist underlayer film;
- 25 – applying a composition for a resist onto the resist underlayer film to form a resist film;
- exposing the resist film to light at, e.g., 13.5 nm, 193 nm, 248 nm or 365 nm or to electron beam radiation;
- developing the resist film after the exposing to obtain a patterned resist film;
- 30 – etching the resist underlayer film according to a pattern of the patterned resist film; and
- processing the substrate according to a pattern of the resist film and the resist underlayer film.

35 In one embodiment, the substrate is TiO_2 , Si, GaAs or other substrate used in diffractive or meta optical element.

One embodiment comprises a method for patterning a semiconductor substrate including the steps of

-
- forming an organic underlayer film on a surface of a semiconductor substrate;
 - forming an inorganic oxide containing middle layer on the organic underlayer;
 - 5 – applying the resist underlayer film forming composition according to any of claims preceding claims onto the inorganic oxide containing middle layer film and baking the composition to form a resist underlayer film;
 - applying a composition for a resist onto the resist underlayer film to form a resist film;
 - 10 – exposing the resist film to light at a wavelength selected from 13.5 nm, 193 nm, 248 nm and 365 nm, or to electron beam radiation:
 - developing the resist film after the exposing to obtain a patterned resist film;
 - etching the resist underlayer film according to a pattern of the patterned resist film;
 - 15 – etching the inorganic oxide containing middle layer film according to a pattern of the patterned resist film;
 - etching the organic underlayer film according to a pattern of the patterned resist underlayer film; and
 - 20 – processing the semiconductor substrate according to a pattern of the patterned organic underlayer film.

In one embodiment, a resist underlayer coating for lithography comprises

- a metal-complex, at least one among a cross-linkable group, a cross-link product thereof, and an exposed cross-link product thereof, wherein
- 25 – the metal-hydroxamate includes the metal compound of Formula (I) or (II) alone or as a homo-polymer of formula (III) or as polymer with M-O-M-O linkage of formula (IV).

In one embodiment, the resist underlayer film is obtained by applying a poly or co- or
30 metal-hydroxamate composition onto a semiconductor substrate, and baking the composition.

In one embodiment, present material can be employed as a functional layer coating applied to form lithographic stacks including the following:

- 35 – Photoresist (organic, inorganic, hybrid, metal oxide) layer of 40-50 nm.
- Functional layer of novel metal-hydroxamate complexes
- Si-BARC or silicon oxynitride or metal oxide layer of 20-50 nm

- SOC included both low and high temperature spin-on carbon 200-360 °C or chemical vapor deposition (CVD) or atomic layer deposition (ALD) α -carbon layer of 200-400 nm and finally substrate.
- 5 One further embodiment provides a method of producing a semiconductor device. The method comprises generally the steps of
- applying a film forming composition as disclosed above onto a semiconductor substrate and baking the composition to form a resist underlayer film;
 - applying a composition for a resist onto the resist underlayer film to form a resist film;
 - 10 – exposing the resist film to light at a wavelength selected from the group of 13.5 nm, 193 nm, 248 nm and 365 nm or to electron beam radiation;
 - developing the resist film after the exposing to obtain a patterned resist film;
 - etching the resist underlayer film according to a pattern of the patterned resist film; and
 - 15 – processing the semiconductor substrate according to a pattern of the resist film and the resist underlayer film.

20 The present technology provides for the forming of anti-reflective (ARC) film by application of a composition as described above for forming a resist underlayer film onto a semiconductor substrate and baking the composition.

In one embodiment, there is provided a method for producing a semiconductor device, comprising:

- 25 – applying a resist underlayer film or several underlayer films onto a semiconductor substrate and baking the composition to form one or more resist underlayer films;
- applying a composition according to comprising Formula (I) as an ARC onto one or more resist underlayer films to form a resist film;
- 30 – exposing the resist film to light;
- after the light exposure, developing the resist film to form a resist pattern;
- etching the resist underlayer film using the resist pattern; and
- fabricating the semiconductor substrate using the resist film thus patterned and the resist underlayer film thus patterned.

35

In one embodiment, there is provided a method for producing a semiconductor device, comprising:

- forming an organic underlayer film on a semiconductor substrate;
- applying the composition for forming a resist film onto the organic underlayer film and baking the composition to form a resist film;
- exposing the resist film to light;
- 5 – after the light exposure, developing the resist film to form a resist pattern;
- etching the resist underlayer film using the resist pattern;
- etching the organic underlayer film using the resist underlayer film thus patterned; and
- fabricating the semiconductor substrate using the organic underlayer film thus
- 10 patterned.

The technology also provides for a method of producing a semiconductor device, the method comprising:

- applying a resist underlayer film or several underlayer films onto a
- 15 semiconductor substrate and baking the composition to form one or more resist underlayer films;
- applying a composition according to Formula (I) as an ARC onto one or more resist underlayer films to form a resist film;
- exposing the resist film to light;
- 20 – after the light exposure, developing the resist film to form a resist pattern;
- etching the resist underlayer film using the resist pattern; and
- fabricating the semiconductor substrate using the resist film thus patterned and the resist underlayer film thus patterned.

25 The present solutions can be used for cast coatings on semiconductor substrates as bottom anti-reflective coating (BARC) before the coating of photoresist layer. In particularly, the newly made functional metal-hydroxamate consist of metal-oxygen bond adjacent to the nitrogen at one part while polymerizable/cross-linkable group to another part of the molecule and its composition upon application as BARC effectively address the photolithographic

30 limitations e.g., substrate reflectivity, swing effect, and reflective notching in addition to act as a photoresist.

It is also worth to note that the absence of hydrolyzable groups in the new metal-hydroxamate resin composition presented herein makes it particularly attractive and provide

35 an efficient solution to storage stability, low-dose, and solution poor processability of existing technologies. Moreover, by incorporation of the novel metal-hydroxamate complex into underlayer formulations EUV photon absorption can be significantly enhanced due to

presence of atomic element in the structure of molecule. More importantly due to its organic-inorganic hybrid nature, the poly-metal-hydroxamate composition is used in one embodiment for providing resistance to oxygen plasma and hence high etch selectivity.

- 5 Surprisingly it has been found that, in some embodiments, when the novel designed functional metal-hydroxamate comprises a metal-oxygen bond adjacent to the nitrogen in one moiety of the molecule while a polymerizable/cross-linkable group is present in another moiety of the molecule, thermally curing at 300 degrees C gives significant enhancement in refractive index of the material which means that a metal oxide layer is formed. This
10 indicates that the present complexes are a class of materials that can be used in applications where solution processable metal oxides are required.

The composition mentioned in Formula (I) or (II) comprises functional metal-hydroxamate consist of metal-oxygen bond adjacent to the nitrogen at one part while
15 polymerizable/cross-linkable group to another part of the molecule that strongly absorb light in the range of 200 to 400 nm wavelength.

The metal-hydroxamate composition of the Formula (I) or (II), spin-coated on silicon wafer, pre-bake at 80 °C for 1 minute before it exposed to 250 nm wavelength for 5 minutes,
20 resulted into formation of contrast between the exposed and unexposed parts of the wafer.

In embodiments the mentioned Formula (I) or (II) when the silicon wafer inserted for 60 seconds to organic developers there is clear contrast/distinction between exposed and unexposed part of the wafer can be seen in Figure 5.

25 In embodiments the mentioned Formula (I) or (II) gave excellent contrast upon development using organic developers shown in Figure 5, 111 is original resist coated wafer, 112 developed by using n-butyl acetate, 113 developed by using 2-heptanone, and 114 developed by using PGMEA respectively.

30 In another embodiment when the novel functional metal-hydroxamate consists of metal-oxygen bond adjacent to the nitrogen at one part while polymerizable/cross-linkable group to another part of the molecule formulated to 1-3% spin coated on silicon wafers, soft bake for 1 min at 80°C. The e-beam doses were varied from 70 to 1000 $\mu\text{C}/\text{cm}^2$ at 100 kV and
35 current of 1 nA, the development was carried out by immersing the film into respective organic developers for give time in this case 10 to 60 seconds before washed with nitrogen gas.

Synthesis of metal-hydroxamate of Formula (I)

Example 1

- 5 Synthesis of a metal-hydroxamate having a cross-linkable unit at one part of the molecule was carried out in a 500 ml round bottom flask. Methyl methacrylate (10.0 g, 0.099 mol), hydroxylamine hydrochloride (6.93 g, 0.099 mol) and de-ionized water (100 ml) were added to the round bottom flask equipped with a magnetic stirrer and a reflux condenser. To the above solution sodium hydroxide (7.98 g, 0.2 mol) was added. Upon the addition, the above
- 10 solution became transparent, which is a clear indication of the formation of a sodium salt of the corresponding hydroxamate. After stirring solution for 30 min, zinc nitrate hexahydrate (14.8 g, 0.05 mol) was added to the solution, and stirring of the solution continued at room temperature for 2 hr.
- 15 After 2 hr of stirring of the above solution, precipitation of a newly formed complex took place. The precipitate was filtered off and washed with water several times. Subsequently, 200 g of methyl tert.-butyl ether was added to the solid and the product was dried using rotary evaporator (50 °C, 500–10 mbar). After drying product (8.5 g, 68 % yield), structural confirmation was done by using nuclear magnetic resonance (NMR) spectroscopy.
- 20 The NMR chart presented in Figure 2, bears evidence that the compound corresponds to Formula (I) Example 1.

Example 2

- 25 Following the procedure described in Example 1, instead of sodium hydroxide, an organic base was used to carried out the reaction to avoid metal especially sodium contamination. An amount of 18.19 g (0.2 mol) of tetramethyl ammonium hydroxide was used to carry out the reaction to obtain the product (7.2 g, 58 % yield).

Example 3

- 30 Following the procedure described in Example 1, gallium nitrate (10 g, 0.04 mol) was used instead of zinc nitrate, methyl methacrylate (11.75 g, 0.12 mol), sodium hydroxide (9.38 g, 0.23 mol), hydroxylamine hydrochloride (8.15 g, 0.12 mol), and 150 g of distilled water was
- 35 used to carried out the reaction to obtained white solid product (8.5 g, 59 % yield).

Example 4

Following the procedure described in Example 1, indium nitrate (6.2 g, 0.02 mol) was used instead of zinc nitrate, methyl methacrylate (6.2 g, 0.06 mol), sodium hydroxide (4.94 g, 0.12 mol), hydroxylamine hydrochloride (4.29 g, 0.06 mol), and 100 g of distilled water was used to carried out the reaction to obtained white solid product (5.3 g, 60 % yield).

5

Formulation

Formulations comprising films samples were prepared by spin coating of a 2 % solution of the polymer with a spinning speed of 1500 rpm for 30 seconds. Soft bake was then carried out with temperature ranging from 80 °C to 150 °C for 30 seconds to 2 minutes.

10

Results

As discussed above the biggest challenges of existing resist materials in the market is the need for patterning at low doses while maintaining good environmental stability and good resolution as well as low line edge roughness. Surprisingly, the present invention is capable of addressing these issues and provides a solution to at least a part of them.

15

When a formulation of the newly designed functional metal-hydroxamate having a metal-oxygen bond adjacent to the nitrogen at one part and a polymerizable, cross-linkable group at another part of the molecule was exposed to electron beam lithography it showed lines at a surprisingly low dose of 150 $\mu\text{C}/\text{cm}^2$ (Figure 5).

20

One important feature of the present metal-organic complexes is the absence of any environmentally sustainable or sensitive groups or moieties or functionalities which make them unique candidates for large-scale production and commercialization. Additionally, the presence of highly photo or electron cross-linkable groups renders them capable of changing solubility at very low doses of radiation.

25

Another important feature of the present materials is the presence of a metal or non-metal or metalloid elements which provide unique advantages at the use of such type of materials in advanced patterning lithography. For example, it is beneficial to use them in extreme ultraviolet lithography where atomic absorption is a prerequisite for the development of photoresists.

30

35

A still further feature of the present materials is the relatively small size of the metal-hydroxamate complex that gives freedom to pattern the material uniformly. Therefore, monodisperse batch-to-batch reproducibility of these materials will be easily attainable.

A fourth feature of the present materials is the absence of photoacid or photo-base generators. As a result, the present complexes will achieve low line edge roughness due to the absence of any acid diffusion mechanism in CAR that otherwise can cause a stochastic effect, which in turn leads to undesirable bridging between patterns.

A fifth feature of the present materials is that their unique solution processability makes them excellent candidates for coating on semiconductor substrates. The fact that they are readily developed using non-toxic organic solvents provides further usefulness of these novel complexes in commercial applications.

A sixth feature of the present materials is that the presence of a nitrogen-oxygen bond adjacent to an electron withdrawing carbonyl group makes them unique candidates for both positive and negative tone resist material development.

The following embodiments are particularly preferred:

An organo-metal compound represented by Formula (I),



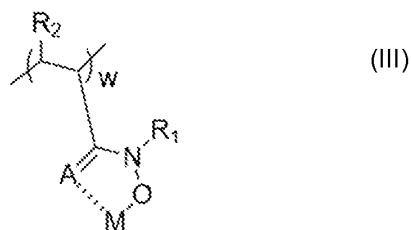
wherein

- R_1 is selected from the group of hydrogen, methyl, ethyl, allyl, halo-alkyl, linear or branched alkyl, and phenyl, in particular hydrogen or methyl;
- R_2 stands for ethenyl, prop-1-en-2-yl, acrylate or methacrylate, or for an alkyl group with 1 to 10 carbon atoms, an aryl group with 5 to 18 carbon atoms, or an aralkyl group with 6 to 21 carbon atoms, said alkyl, aryl or aralkyl being substituted with one or more acrylate or methacrylate, amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, silyl, carboxy, carboxylate, and halogen groups,
- A stands for oxygen and
- u is 2.

Zinc, tin or antimony hydroxamate exhibiting a reactive group selected from ethenyl, prop-1-en-2-yl, acrylate, methacrylate, amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, silyl, carboxy, carboxylate, and halogen groups.

- 5 A polymer obtained by subjecting a compound according to Formula (I) to polymerization, optionally in the presence of cross-linkable monomers to obtain a copolymer.

A copolymer having Formula (III)



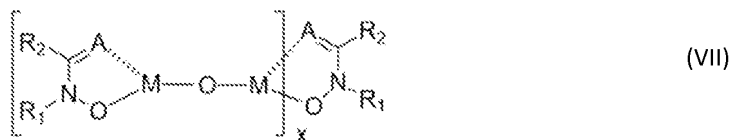
10

wherein

R_1 , R_2 , A and M have the same meaning as above in Formulas (I) and II; and w is an integer having a value in the range from 100 to 100,000.

15

A polymer comprising units of Formula (VII),



20 wherein

R_1 , R_2 , A, and M have the same meaning as above in Formula (I), and x stands for an integer having a value in the range from 1 to 100.

- 25 The use of the above-mentioned organic-metal compound or a polymer or copolymer, for example of Formulas (III) or (VII) as a precursor for metal oxide films.

The use of the above-mentioned organic-metal compounds or polymers or copolymers in compositions comprising solvents for coatings or films in semiconductors or optical components.

30

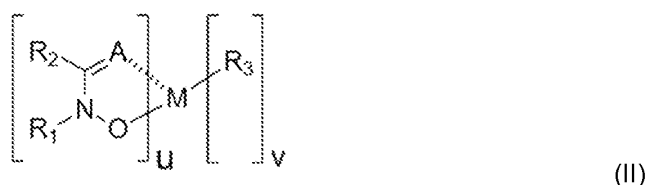
The use of the above-mentioned organic-metal compounds or polymers or copolymers as a precursor for metal oxide films.

Claims:

1. An organometallic compound represented by Formula (I) or Formula (II),



5



wherein

M stands for a metal, in particular a transition metal, a non-metal or a metalloid of groups 1 to 15;

R₁ stands for hydrogen or an optionally substituted hydrocarbonyl residue;

R₂ stands for hydrogen, a hydrocarbonyl residue of a saturated or unsaturated, linear, branched or cyclic hydrocarbon, optionally substituted with one or more, reactive or non-reactive groups optionally containing hetero atoms, or R₂ is selected from amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; silyl, carboxy, carboxylate, acrylate, alkacrylate, wherein the alkyl residue has 1 to 10 carbon atoms, and halogen;

20 R₃ stands for an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; an acrylate, methacrylate, carbamate, thiocarbamate, acetate, or an alkali metal salt of an acrylate, methacrylate, carbamate, thiocarbamate or acetate, or

R₃ represents a residue corresponding to the structure placed within the left-hand side brackets of Formula (I), whereby R₁ stands for hydrogen or an optionally substituted hydrocarbyl residue and R₂ stands for hydrogen, a hydrocarbyl residue of a saturated or unsaturated, linear, branched or cyclic hydrocarbon, optionally substituted with one or more, reactive or non-reactive groups optionally containing heteroatoms, or R₁ stands for hydrogen or an optionally substituted hydrocarbyl residue and R₂ is selected from amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl

groups having 1 to 10 carbon atoms; silyl, carboxy, carboxylate, acrylate, alkacrylate, wherein the alkyl residue has 1 to 10 carbon atoms, and halogen, at least one of said substituents R_1 and R_2 in the meaning of R_3 being different from the corresponding substituents of the structure placed within the left-hand side brackets of Formula (I);

5 A stands for a heteroatom; and

u and v are independently selected from integers having a value in the range from 1 to 10.

2. The compound according to claim 1, wherein R_1 stands for

- a hydrogen atom
 - 10 – an optionally substituted, linear or cyclic alkyl groups with 1 to 10 carbon atoms;
 - a bridging hydrocarbyl radical that can be independently selected from optionally functionalized linear, branched, or cyclic, bivalent, saturated or unsaturated hydrocarbyl radicals, such as an optionally functionalized linear, branched or cyclic alkylene, alkenylene or alkynylene group; or
 - 15 – an optionally functionalized aromatic or polyaromatic group having 5 to 30 carbon atoms;
- said hydrocarbyl optionally being functionalized with one or more functional groups selected from amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, silyl, carboxy, carboxylate, acrylate, alkacrylate, and halogen.

20

3. The compound according to claim 1 or 2, wherein R_2 stands for

- amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; silyl, carboxy, 25 carboxylate, acrylate, alkacrylate, and halogen, or
- hydrocarbyl residues substituted with one or more, typically 1 to 3 groups selected from, amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl, silyl, carboxy, carboxylate, acrylate, alkacrylate and halogen.

30 4. The compound according to any of claims 1 to 3, wherein R_2 stands for

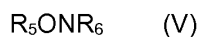
- an alkyl group with 1 to 10 carbon atoms, an aryl group with 5 to 18 carbon atoms, an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; or an aralkyl group with 6 to 21 carbon atoms,
- 35 – said alkyl, aryl or aralkyl exhibiting one or more substituent groups selected from, amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acetyl,

silyl, carboxy, carboxylate, acrylate, alkacrylate and halogen and combinations thereof.

5. The compound according to any of claims 1 to 4, wherein R_3 can be
- 5 – same as in Formula (I) where R_1 and R_2 are independently optionally substituted hydrogen or hydrocarbyl compounds of 1 to 10 carbon atoms, an aryl group with 5 to 18 carbon atoms, or an aralkyl group with 6 to 21 carbon atoms,
- R_3 can be the same as in Formula (I) where R_2 is independently selected group substituted by for example acrylate, an alkenyl group with 2 to 10 carbon atoms,
- 10 said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; thiol, cyano, mercapto, silyl and glycidyl groups or alkyl, aryl, cyclic or branched independently substituted hydrocarbyl groups.
6. The compound according to any of the preceding claims, wherein A is oxygen, nitrogen,
- 15 or sulphur.
7. The compound according to any of claims 1 to 6, wherein M is selected from the group of transition metals and metalloids of groups 3 to 15, for example zinc, tin, gallium, indium, antimony, hafnium, zirconium, aluminium, silicon, and titanium, in particular M stands for a
- 20 high EUV photon absorbing element, most preferably M stands for zinc, tin, gallium, zirconium, or antimony.
8. The compound according to any of the preceding claims, wherein
- R_1 is selected from the group of hydrogen, methyl, ethyl, allyl, halo-alkyl, linear or
- 25 branched alkyl, and phenyl,
- R_2 stands for acrylate or methacrylate, or for ethenyl or prop-1-en-2-yl, or for an alkyl group with 1 to 10 carbon atoms, an aryl group with 5 to 18 carbon atoms, or an aralkyl group with 6 to 21 carbon atoms, said alkyl, aryl or aralkyl being substituted with one or more acrylate or methacrylate groups,
- 30 – A stands for oxygen or sulphur or nitrogen and
- u is 1 to 4, preferably 2, 3 or 4, most preferably 2.
- v is 1 to 4, preferably 1 or 2.
9. A method of producing a metal-hydroxamate derivative according to any of the
- 35 preceding claims, comprising the steps of
- reacting a carboxylic acid or esters of having Formula (IVa)



in which R_2 has the same meaning as in Formula (I), or an activated form thereof,
with an amine having Formula (V), R_4 hydrogen or for a linear, branched or cyclic
or heterocyclic alkyl group having 1 to 10 carbon atoms, optionally having 1 to 3
5 aryl substituents,



or a salt thereof,
10 wherein R_5 stands for hydrogen or for a linear, branched or cyclic or heterocyclic
alkyl group having 1 to 10 carbon atoms, optionally having 1 to 3 aryl substituents,
or R_5 stands for silyl group of formula $-SiR_7R_8R_9$, in which R_7 , R_8 and R_9 are
independently selected from linear or branched alkyl groups having 1 to 10 carbon
atoms; and R_6 stands for hydrogen or a linear, branched or cyclic alkyl group
15 having 1 to 10 carbon atoms or an aryl group having 6 to 18 carbon atoms,

to produce a hydroxyamic acid salt having Formula (VI),



20 wherein R_2 has the same meaning as above,
and X is cation of alkali or alkaline earth metals or organic tetra-alkyl ammonium or
phosphonium or sulfonium hydrocarbon.
– reacting the hydroxyamic acid salt of Formula (VI) with compound of group 1 to 15
25 of a metal or a metalloid or a non-metal to form a metal-hydroxamate derivative
according to Formula (I).

10. The method according to claim 9, wherein the activated form of the carboxylic acid of
Formula (IVa) comprises an ester or acyl halide, acetyl sulfonylic, acetyl tosylic or acetyl
30 mesylic.

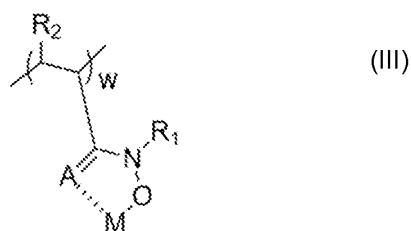
11. The method according to claim 9, wherein the activated form of the carboxylic acid of
Formula (IVa) comprises an amide having Formula (IVb)



wherein R_2 has the same meaning as above.

12. The method according to any of claims 9 to 11, wherein the reaction of the carboxylic acid of Formula (IVa) or an activated form thereof or an amide of Formula (IVb) with an amine of Formula (V) or a salt thereof is carried out in a solvent and in the presence of an inorganic or organic base.
13. The method according to any of claims 9 to 12, wherein the group 1 to 15 transition metal or metalloid or non-metal salt or compound is selected from the group of halides, nitrates, acyl acetates, acetates, sulphates and combinations thereof, in particular a metal or metalloid chloride or nitrate.
14. The method according to any of claims 9 to 13, wherein the reaction of the hydroxamic acid of Formula (VI) with a salt or compound of a salt is carried out in solution and in the presence of an inorganic or organic base, and the metal-hydroxamic acid derivative is precipitated in an aqueous phase.
15. The method according to any of claims 9 to 14, wherein the amine is selected from hydroxylamine hydrochloride, methylamine hydrochloride, allylamine hydrochloride, or ethylamine hydrochloride, most preferably the amine is hydroxylamine hydrochloride.
16. The method according to any of claims 9 to 15, the base utilized is an inorganic or organic hydroxide, such as sodium or potassium hydroxide or tetraalkyl ammonium hydroxide, preferably an aqueous solution of tetramethyl ammonium hydroxide.
17. The method according to any of claims 9 to 16, wherein the reaction solvent is a polar organic methanol or ethanol or inorganic solution, more preferably distilled water, and most preferably de-ionized water.
18. A polymer comprising units of a compound according to any of claims 1 to 8.
19. The polymer according to claim 18, obtained by subjecting one or more compounds according to any of claims 1 to 8 to conditions of polymerization, for example to conditions of radical polymerization.
20. The polymer according to claims 18 or 19 obtained by subjecting a compound according to any of claims 1 to 8 to conditions of polymerization in the presence of cross-linkable monomers to obtain copolymers.

21. The polymer according to claim 20, comprising a copolymer having Formula (III)



5 wherein

R_1 , R_2 , A and M have the same meaning as above in Formulas (I) and II; and

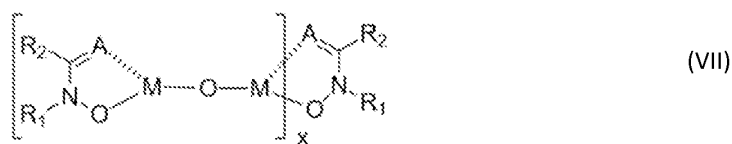
w is an integer having a value in the range from 100 to 100,000.

22. The polymer according to any of claims 18 to 21, obtained by addition of photo or
10 thermo-radical initiator into a composition of compounds according to any of claims 1 to 8 dissolved in one or more organic or inorganic solvents.

23. The polymer according to claim 22, obtained by addition of photo additives/radicals,
comprising Norish type I additives, Norish type II additives and combinations thereof,
15 simple aromatic ketones, hydroxy, dimethylamino, methoxy, chloro, and diketo ketones, as well as ionic (positive and negative) photoadditives, responsive towards deep UV to visible wavelength of light.

24. The polymer according to claim 22 or 23, obtained by addition of thermoradical
20 initiators including peroxides, azo-compounds and ionic complexes.

25. A polymer comprising units of a compound according to any of claims 1 to 8 afforded metal oxide metal polymer comprising two or more condensed units of a Formula (VII),



25 wherein

R_1 , R_2 , A, and M have the same meaning as above in Formula (I), and

x stands for an integer having a value in the range from 1 to 100.

26. The polymer according to any of claims 18 to 25, wherein R_1 is selected from the
30 group of hydrogen and linear or branched alkyl groups with 1 to 10 carbon atoms, and R_2

is selected from the group of acrylate, methacrylate, allyl, vinyl, epoxy and thiols, preferably R_1 is selected from hydrogen and methyl, and R_2 from acrylate and methacrylate.

- 5 27. The polymer according to any of claims 18 to 26, wherein A is selected from the group of oxygen, sulphur, and nitrogen, in particular A is oxygen or sulphur.
28. The polymer according to any of claims 18 to 27, wherein M represents zinc, tin, hafnium, antimony, zirconium, bismuth, aluminium or indium, in particular M represents an
10 EUV photon absorbing element, such as zinc, tin or antimony.
29. A composition comprising a compound according to any of claims 1 to 8 or a polymer according to any of claims 18 to 28, or both, in a liquid phase formed by at least one organic solvent for the polymer or the compound, optionally in mixture with water and in
15 the presence of organic/inorganic acid or base.
30. The composition according to claim 29, wherein the liquid phase comprises an organic liquid and from about 0.001 M to about 1 M of said compound or polymer or both and said formulation having a flash point of at least 10 °C and a vapor pressure at 20 °C of less
20 than about 10 kPa.
31. The composition according to any of claims 29 or 30, wherein the liquid phase comprises a solvent selected from the group of PGMEA, PGEE, PGME, toluene and mixtures thereof, which makes up 80–95 % more preferably 90 to 85 % and most
25 preferably 95–98 % of the total weight of the liquid.
32. The composition according to any of claims 29 to 31, wherein the liquid phase comprises an organic or inorganic acid as an additive, preferably an alkanoic acid, and most preferably acetic acid, and 1 to 20 % of water most preferably 5 to 10 % by weight of
30 the liquid.
33. The composition according to any of claims 29 to 32, wherein the solids content of the polymer or compound in liquid is 1 to 4 % by weight.
- 35 34. A coating or film obtained by casting or coating of the composition according to claim 28 to 33 to a surface of a substrate, which composition is formulated for use in a method of a coating a substrate by casting.

35. A coating or film according to claim 34, comprising or consisting of a polymer of formula (III or IV) or an organo-metallic complex of formula (I or II) according to any of the preceding claims.

36. The coating or film according to claim 34 or 35, forming a high refractive index coating in photolithography before or after the photoresist layer in order to reduce standing wave and thin-film interference.

37. The coating or film according to any of claims 34 to 36 obtained by spin coating of a
10 composition according to any of claims 28 to 33 on a substrate, in particular on a silicon
substrate.

38. A resist underlayer film, obtained by applying a resist underlayer film composition according to any of claims 29 to 33 onto a semiconductor substrate, and baking the composition.

39. The resist underlayer film according to claim 38, wherein the composition contains a metal-hydroxamate derivative according to Formula (I)



wherein

M stands for zinc, tin, gallium, or antimony;

R₁ stands for hydrogen or a linear or branched alkyl having 1 to 6 carbon atoms;

25 R₂ stands for acrylate, methacrylate, amine, cyano, isocyanurate, nitrile, epoxy, glycidyl, mercapto, vinyl, allyl, acyl, an alkenyl group with 2 to 10 carbon atoms, said alkenyl being optionally substituted with one or more alkyl groups having 1 to 10 carbon atoms; acetyl, silyl, carboxy, carboxylate, acrylate, alkacrylate or halogen, said alkyl group having 1 to 6 carbon atoms;

A stands for oxygen; and

30 u is 2 or 3.

40. A method for producing a semiconductor device, the method comprising:

- applying a film forming composition as claimed in any of claims 29 to 33 onto a semiconductor substrate and baking the composition to form a resist underlayer film;
- applying a composition for a resist onto the resist underlayer film to form a resist film;
- exposing the resist film to light at a wavelength selected from the group of 13.5 nm, 193 nm, 248 nm and 365 nm or to electron beam radiation;
- developing the resist film after the exposing to obtain a patterned resist film;
- etching the resist underlayer film according to a pattern of the patterned resist film; and
- processing the semiconductor substrate according to a pattern of the resist film and the resist underlayer film.

41. A method for producing a semiconductor device, the method comprising:

- forming an organic underlayer film on a surface of a semiconductor substrate;
- applying the resist underlayer film forming composition according to any of claims 29 to 33 onto the organic underlayer film and baking the composition to form a resist underlayer film;
- applying a composition for a resist onto the resist underlayer film to form a resist film;
- exposing the resist film to light at a wavelength selected from 13.5 nm, 193 nm, 248 nm and 365 nm or to electron beam radiation;
- developing the resist film after the exposing to obtain a patterned resist film;
- etching the resist underlayer film according to a pattern of the patterned resist film;
- etching the organic underlayer film according to a pattern of the patterned resist underlayer film; and
- processing the semiconductor substrate according to a pattern of the patterned organic underlayer film.

42. A method for producing an optical or semiconductor device, the method comprising:

- applying a spin on carbon (SOC) with various thermal stabilities, e.g. High temperature (350–400 °C) SOC, or α -carbon layer obtained by CVD on a surface of a substrate;
- applying a composition of high silicon content layer or silicon oxynitride or various metal oxide layer;

- applying a functional coating layer comprising a metal-organic complex according to any of claims 1 to 8 or a polymer or copolymer thereof poly-metal-hydroxamate according to any one of claims 18 to 29;
- applying a composition for a resist onto the resist underlayer functional layer to obtain a resist film;
- exposing the resist film to light at a wavelength selected from 13.5 nm, 193 nm, 248 nm and 365 nm, or to electron beam radiation;
- developing the resist film after the exposing to obtain a patterned resist film to achieve a 35–20 % decrease in dose compared to that achieved without functional layer;
- etching the resist underlayer film according to a pattern of the patterned resist film; and
- processing the substrate according to a pattern of the resist film and the resist underlayer film.

15

43. Use of a compound according to any of claims 1 to 8 or a polymer according to any of claims 18 to 28 as an additive, in particular to tune the polymer film thickness, index of refraction (n), molar absorptivity (k), etch properties, and contact angle (CA) of a desired composition.

20

44. A method for producing an optical element or an optically active device:

- applying the resist underlayer film forming composition according to any of claims 29 to 33 onto a surface of a substrate and baking the composition to form a resist underlayer film;
- exposing the resist film to light at a wavelength selected from 13.5 nm, 193 nm, 248 nm and 365 nm or to electron beam radiation;
- developing the resist film after the exposing to obtain a patterned resist film;
- etching the resist underlayer film according to a pattern of the patterned resist film; and
- processing the substrate according to a pattern of the resist film and the resist underlayer film.

25

30

45. A method according to claim 44, wherein the substrate is TiO₂, Si, GaAs or other substrate used in a diffractive or meta-optical element.

35

46. A method for patterning a semiconductor substrate, comprising:

- forming an organic underlayer film on a surface of a semiconductor substrate;

- forming an inorganic oxide containing middle layer on the organic underlayer;
- applying the resist underlayer film forming composition according to any of claims preceding claims onto the inorganic oxide containing middle layer film and baking the composition to form a resist underlayer film;
- 5 – applying a composition for a resist onto the resist underlayer film to form a resist film;
- exposing the resist film to light at a wavelength selected from 13.5 nm, 193 nm, 248 nm and 365 nm or to electron beam radiation;
- developing the resist film after the exposing to obtain a patterned resist film;
- 10 – etching the resist underlayer film according to a pattern of the patterned resist film;
- etching the inorganic oxide containing middle layer film according to a pattern of the patterned resist film;
- etching the organic underlayer film according to a pattern of the patterned resist underlayer film; and
- 15 – processing the semiconductor substrate according to a pattern of the patterned organic underlayer film.

47. The use of a compound according to any of claims 1 to 8 or a polymer according to
20 any of claims 18 to 28 as a precursor for forming metal oxide coatings and film on semiconductor substrates.