COMPOUNDS, COMPOSITIONS, METHODS FOR THE PREPARATION OF THE COMPOUNDS, AND USES OF THE COMPOUNDS

TECHNICAL FIELD

The invention relates to organometallic compounds, to compositions comprising said compounds, methods for the preparation of the compounds, and uses of the compounds. Further, the invention relates to lithography methods using the compounds, and hard masks and optical element, optically active device or optical or semiconductor device obtainable by said methods. In particular, the invention relates to spin-coatable compounds for metal hard masks.

BACKGROUND

Amorphous carbon (via chemical vapour deposition (CVD)) and spin-on carbon-based hard masks are popular in semiconductor industry. The patterns on semiconductor substrates are formed using photoresists, which predominately are carbon-based. Thicknesses of photoresists that are needed to form nanometer-sized patterns in fabrication processes of advanced semiconductor are too thin to be used to transfer the pattern to the carbon-based hard mask. Thus, industry has applied pattern transfer layers, often referred as middle layers, between the resist and the hard mask layers. Conventional middle layer materials are silicon-based. SiO_2, $SiON_x$, Si_3N_4, amongst others are deposited using CVD or physical vapor deposition (PVD) methods. During the deposition, the chamber is typically evacuated, and the temperature of the substrate or wafer is raised, if necessary. The PVD and CVD methods may be good for thin conformal coatings but when thicker (>20 nm) films are desired they require long processing time. Thus, the process cycle of these methods consumes precious time. On the other hand, the spin-on processes provide lower cost of ownership, potentially good gap filling performance, and less defectivity. Efforts have been made to develop spin-on metal hard masks that utilize metal alkoxide-based formulations and metal oxide nanoparticle dispersions.

One of the primary challenges with conventional hard mask materials, such as silicon-based hard masks, is achieving high etch selectivity. While these materials offer reasonable etch resistance, they may not provide the necessary selectivity for advanced patterning processes, particularly as feature sizes continue to decrease.

Further, accurate pattern transfer in lithography requires precise control of reflectivity. Silicon hard masks can manage reflectivity to some extent, but optimizing this control to achieve the best performance can be complex and challenging.

The rework and cleaning of, e.g., trilayer stacks, especially the removal of oxide residues using wet chemistry, present significant difficulties. These challenges impact the overall manufacturability, efficiency and costs of the lithography process, making it harder to maintain high production yields. For instance, materials that provide excellent etch resistance might be more challenging to remove or may interact negatively with other process chemicals.

In addition, as lithography techniques evolve, such as the transition to EUV lithography (EUVL), conventional photoresists and hard mask materials may not be fully compatible or effective. This evolution necessitates the development of new materials that can better handle the demands of these advanced processes. Such new materials may necessitate the use of alternate process chemicals and gases used in semiconductor fabrication processes, which in turn may be disadvantageous in certain aspects. For instance, dielectric damage may be a problem that appears when new etch gas chemistries are applied to transfer the pattern from resist and underlayers to the substrate.

The application of traditional hard mask materials often involves costly methods like CVD or atomic layer deposition (ALD). These methods require specialized equipment, which can limit their practicality and increase the overall cost of the lithography process. Further, ensuring the long-term stability, stability in solvents and solutions used in the methods, and shelf life of both hard mask materials and starting materials used to prepare hard masks is another significant issue. Some materials may degrade over time, which can adversely affect their performance during the lithography process, leading to inconsistencies and defects in the final product.

There is a myriad of different material approaches that have been developed to form patterns using EUVL. On a general level these can be classified in three different categories: organic, silicon based and metal-containing resists.

To address the challenges of organic resists, formulations have been prepared with radiation sensitive components included in the resist material. Elements which have high molar absorptivity of 13.5 nm EUV photons are usually metals. Thus, there has been an increasing interest in metal-containing resists where the metal is added to resist materials to improve sensitivity, or the metals have been employed as molecular resists, metal oxide nanoparticle, organometallic precursors or as metal-organic frameworks.

Such resists have shown high sensitivity, resolution and thus are being considered as key candidates for future EUVL resists. However, their main disadvantage is that metals are strongly disfavored in the fabrication of integrated circuits as they can disrupt the function of transistors via contamination.

Despite the advances in prior art, photoresists that provide the resolution, line-edge roughness, and sensitivity (RLS) characteristics without excessive metal contamination is still being looked for.

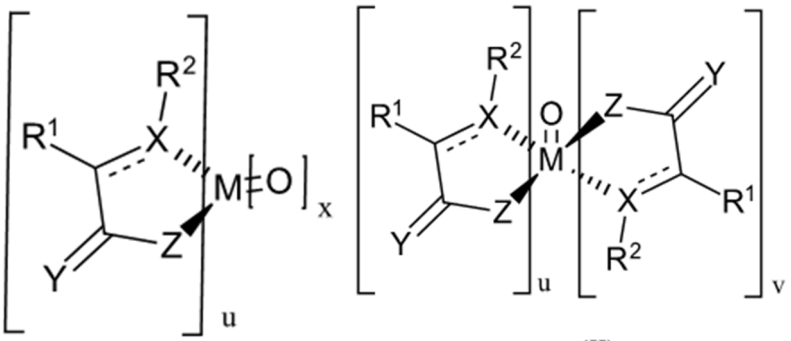
SUMMARY

This Summary is provided to introduce a selection of concepts in a simplified form that are further described below in the Detailed Description. This Summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter.

The invention is defined by the features of the independent claims. Some specific embodiments are defined in the dependent claims.

An object of the present invention is to provide an organometallic compound or a metal oxo-cluster thereof, and hard mask eliminating at least a part of the problems relating to the art.

It is an object of the present invention to provide an organometallic compound of formula (I) or formula (II):



(I) , (II) , wherein

the dotted lines represent optional bonds;

M is a metal selected from the group consisting of Ti, Zr, Hf, Sb, and W, wherein the metal has an oxidation state selected from +3, +4, +5, or +6;

X is a heteroatom selected from the group consisting of O, N, and S;

Y is a heteroatom selected from the group consisting of O, and S;

Z is a heteroatom selected from the group consisting of O, and S;

each R^1 is independently selected from the group consisting of H, and a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms;

each R^2 is independently selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms, and a C_{1-20} -alkoxy;

u and v are each independently selected from integers having a value in the range from 1 to 20; and

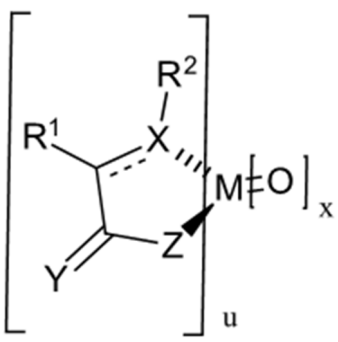
x is an integer selected from 1 and 2,

or a metal oxo-cluster thereof.

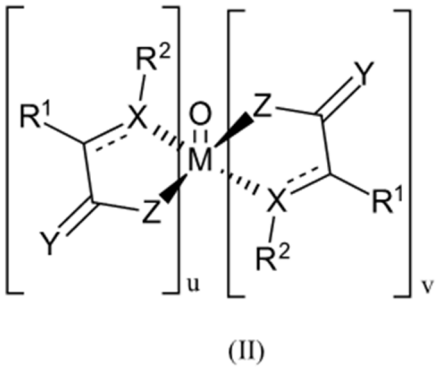
It is second object of the present invention to provide a composition comprising an organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure.

It is a third object of the present invention to provide a lithography method comprising:

i) applying an organometallic compound of formula (I) or formula (II)



(I)



(II)

, wherein

the dotted lines represent optional bonds;

M is a metal selected from the group consisting of Al, Sn, Zn, Ti, Zr, Hf, Sb, Ta, and W, wherein the metal has an oxidation state selected from +3, +4, +5, or +6;

X, Y, Z, R^1, R^2, u, v, and x are as defined in the present disclosure, or a metal oxo-cluster thereof; or

a composition comprising the organometallic compound, or the metal oxo-cluster thereof, on a substrate, thereby forming a precursor hard mask on the substrate; and

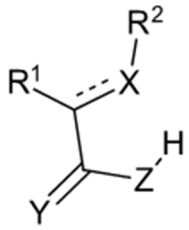
ii) heating the formed precursor hard mask at a temperature below 400 °C, preferably below 250 °C, most preferably below 200 °C, such as at a temperature selected from 60 – 400 °C, 150 – 400 °C, 150 – 250 °C, and 180 – 200 °C, preferably for 1 – 10 min, thereby forming a metal oxide layer on the substrate.

It is a fourth object of the present invention to provide a metal oxide layer obtainable by a method as defined in the present disclosure.

It is a fifth object of the present invention to provide a use of a compound, oxo-metal cluster thereof, or composition as defined in the present disclosure for the preparation of a hard mask, in the preparation of an optical element, optically active device, or optical or semiconductor device.

It is a sixth object of the present invention to provide a method for the preparation of a compound of formula (I) or formula (II), or an oxo-metal cluster thereof, as defined in the present disclosure, wherein the method comprises:

i) providing a reaction composition comprising a compound of formula (V):



(V)

, wherein

the dotted line, X, Y, Z, R^1, and R^2 are as defined in the present disclosure; and

ii) providing a salt of X, or a hydrate thereof, wherein X is as defined in the present disclosure;

iii) reacting the compound of formula (V) with the salt of X, or a hydrate thereof,

to obtain the compound of formula (I) or formula (II), or the oxo-metal cluster thereof.

It is a seventh object of the present invention to provide an optical element, optically active device or optical or semiconductor device obtainable by a method as defined in the present disclosure.

As one more object, the invention pertains to a patterned substrate comprising a substrate with a surface and a first coating at selected regions along the surface and absent at other regions along the surface, wherein the first coating comprises a metal oxide layer, preferably a hard mask, obtainable by a method as defined in the present disclosure, and the metal oxide layer, preferably the hard mask, has an etch rate in an oxygen plasma or ashing process that is lower than 5 nm/min.

Considerable advantages are obtained by the present invention.

The metal oxide layers (hard masks) as disclosed in the present disclosure utilizes small molecule metal oxide precursors that may be based on ketoacidoximate chemistry that provides spin-coatable formulations in solvents such as propylene glycol methyl ether (PGME) and propylene glycol methyl ether acetate (PGMEA). Surprisingly, compounds, or a metal oxo-cluster thereof, disclosed in the present disclosure decompose at low temperatures, such as between 100 – 200 °C, to a metal oxide layer, which may be used as a hard mask in lithography methods. The metal oxide layers (or hard masks) have refractive indices that are close to their respective amorphous metal oxides. The metal oxide layers (hard masks) also show

high etch resistance in oxygen-containing plasmas. A further surprising effect of these compounds, or a metal oxo-cluster thereof, as disclosed in the present disclosure is the ability to obtain defect-free, or at least partially defect-free, sub-10 nm metal oxide hard mask (films) after baking them at 350 °C or less, preferably at 250 °C or less, more preferably 200 °C or less.

Specifically, the invention described herein addresses challenges in patterning of sub-20 nm features. In addition, materials described offer high oxygen plasma etch resistance making the simplification of the lithographic stack possible. Additionally, to our surprise, the organometallic compounds as disclosed in the present disclosure decompose at a low decomposition temperature, such as at 350 °C or less or between 100 – 200 °C, making them suitable to be used as precursor in the preparation of hard masks.

Thus, the present solutions can be used to cast coatings on semiconductor substrates to form patterns through subsequent bake, irradiation and development steps. In particular, the invention allows for the controlling of the microstructure of the layers used in lithography methods as disclosed in the present disclosure in such way it is industrially feasible and solves, at least partially, drawbacks of the prior art.

The invention described herein addresses key etch rate challenges, and in addition offers high oxygen plasma etch resistance making the simplification of the lithographic stack possible.

The described invention provides benefits over commonly used silicon-based hard mask materials by permitting improved compatibility with alternate etch process gases that are needed for advanced EUV resist materials. In this way they can address challenges with dielectric damage taking place with such alternate gases.

Additionally, the invention provides convenient way to determine and evaluate refractive index after bake, and after etch in comparison to known references. Thus, industrially feasible, high throughput screening methods such as ellipsometry can be used to evaluate hard mask quality in process.

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

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows in a schematic fashion some embodiments of lithography methods as disclosed in the present disclosure, as well as an optical element, optically active device or optical or semiconductor device as disclosed in the present disclosure;

Figure 2 shows in a schematic fashion, in side-view, the assembly of a four-layer lithography stack.

DETAILED DESCRIPTION

The following explanations of terms and methods are provided to better describe the present compositions, porous polysiloxane films, semiconductor devices, methods, and uses and to guide those of ordinary skill in the art in the practice of the present disclosure. It is also to be understood that the terminology used in the disclosure is for the purpose of describing particular embodiments and examples only and is not intended to be limiting.

It is to be understood that the embodiments of the invention disclosed are not limited to the particular structures, process steps, or materials disclosed herein, but are extended to equivalents thereof as would be recognized by those ordinarily skilled in the relevant arts. It should also be understood that terminology employed herein is used for the purpose of describing particular embodiments only and is not intended to be limiting.

Reference throughout this specification to “one embodiment” or “an embodiment” means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily all referring to the same embodiment.

As used herein, a plurality of items, structural elements, compositions, compositional elements, and/or materials may be presented in a common list for convenience. However, these lists should be construed as though each member of the list is individually identified as a separate and unique member. Thus, no individual member of such list should be construed as a *de facto* equivalent of any other member of the same list solely based on their presentation in a common group without indications to the contrary. In addition, various embodiments and example

of the present invention may be referred to herein along with alternatives for the various components thereof. It is understood that such embodiments, examples, and alternatives are not to be construed as *de facto* equivalents of one another, but are to be considered as separate and autonomous representations of the present invention.

Furthermore, the described features, structures, or characteristics may be combined in any suitable manner in one or more embodiments. In the following description, numerous specific details are provided, such as examples of weights, amounts, lengths, widths, shapes, etc., to provide a thorough understanding of embodiments of the invention. One skilled in the relevant art will recognize, however, that the invention can be practiced without one or more of the specific details, or with other methods, components, polymers (such as polysiloxanes), materials, etc. In other instances, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring aspects of the invention.

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. For example, all percentages in the context of mass (such as wt%) refer to mass-percent of the total composition, film or layer, i.e., the mass fraction (wi) of a compound's mass (mi) of the total mass of the composition (mtot), with a denominator of 100 (i.e. (mi / mtot) * 100), unless stated otherwise.

Unless otherwise stated, the term "molecular weight" or "average molecular weight" refers to weight average molecular weight (also abbreviated "MW").

As used herein, the molecular weight has been measured by gel-permeation chromatography using polystyrene standards.

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.

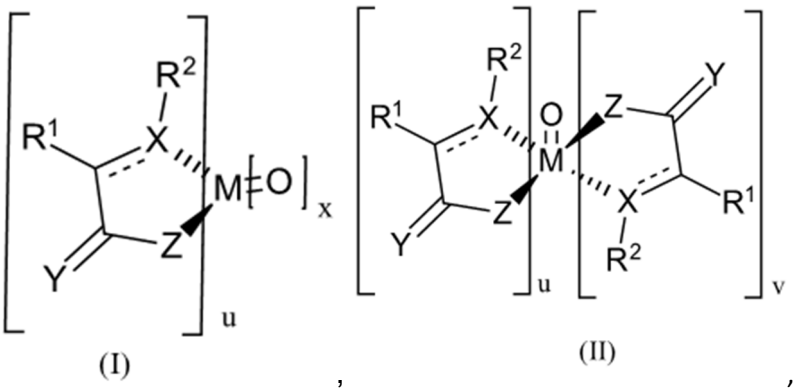
"Optional" or "optionally" denotes that the subsequently described event or circumstance may but need not occur, and that the description includes instances where the event or circumstance occurs and instances in which it does not. The same applies to "optional" or "optionally" in the context of a feature; the subsequently described feature(s) may or may not be included.

The verbs “to comprise” and “to include” are used in this document as open limitations that neither exclude nor require the existence of also un-recited features. “Comprises” or “comprising” denotes that the subsequently described feature(s) or act(s) may but need not include other feature(s) or act(s). The features recited in depending claims are mutually freely combinable unless otherwise explicitly stated. Furthermore, it is to be understood that the use of "a" or "an", i.e., a singular form, throughout this document does not exclude a plurality.

As used herein, the term “about” refers to a value which is ± 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.

Surprisingly it was found that the density of the metal oxide layer (hard mask) obtained with a method as disclosed in the present disclosure is more than 75 % of the density of the corresponding amorphous metal oxide having formula $M(O)_x$, wherein M and x are as defined in in the present disclosure. Further, the Young’s modulus of the hard mask is more than 60 % of the corresponding amorphous metal oxide having formula $M(O)_x$, wherein M and x are as defined in in the present disclosure. Further, the coefficient of thermal expansion is more than 70 % of the corresponding amorphous metal oxide having formula $M(O)_x$, wherein M and x are as defined in in the present disclosure.

In one aspect is provided an organometallic compound of formula (I) or formula (II):



(I) , (II) , wherein

the dotted lines represent optional bonds;

M is a metal selected from the group consisting of Ti, Zr, Hf, Sb, and W, wherein the metal has an oxidation state selected from +3, +4, +5, or +6;

X is a heteroatom selected from the group consisting of O, N, and S;

Y is a heteroatom selected from the group consisting of O, and S;

Z is a heteroatom selected from the group consisting of O, and S;

each R^1 is independently selected from the group consisting of H, and a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms;

each R^2 is independently selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms, and a C_{1-20} -alkoxy;

u and v are each independently selected from integers having a value in the range from 1 to 20; and

x is an integer selected from 1 and 2,

or a metal oxo-cluster thereof.

The terms “metal oxo-cluster” as used herein and hereafter refers to nanostructures composed typically of multiple metal centers that may be linked via bridging oxygen atoms. Metal oxo-clusters (MOCs) can be regarded as units of metal oxides with similar structural and electronic properties. In the present disclosure, the MOCs comprise the organometallic compound of formula (I) or formula (II).

Additionally, or alternatively, the metal-oxo cluster is represented by formula (III):

$M_aO_x(L)_y(R)_u$ (III), wherein

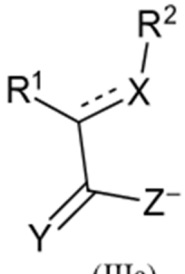
M, u, and x are as defined in the present disclosure;

each L is independently selected from the group consisting of halogen, nitrate, sulfate, hydroxy and C_{1-12}-alkoxy;

a is an integer selected from 1 – 20, preferably selected from 1 – 12;

y is an integer selected from 0 – 20, preferably selected from 1 – 12;

R is a ligand having formula (IIIa):



(IIIa) , wherein

each dotted line, R^1, R^2, X, Y, and Z are as defined in the present disclosure.

It should be understood that “O” of “O_x“ refers to oxygen. Further, R is attached to M, via the Z group of R.

Additionally, or alternatively, the metal-oxo cluster is represented by formula (IIIb):

$M^z_aO_x(L)_y(R)_u$ (IIIb), wherein

z is the oxidation state of M, preferably z is an integer selected from 3 – 6;

M, and x are as defined in the present disclosure; and

a, L, y, R, and u are as defined in the present disclosure;

provided that $u \leq (z - 2x)$.

Additionally, or alternatively, the organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure, wherein

each R^1 is selected from the group consisting of H, and a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms; and

each R^2 is selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms, and a C_{1-20} -alkoxy.

Additionally, or alternatively, the organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure, wherein

the dotted lines represent bonds;

X is N;

Y is a heteroatom selected from the group consisting of O, and S, preferably O; and

Z is a heteroatom selected from the group consisting of O, and S, preferably O.

Additionally, or alternatively, the organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure, wherein

each R^1 is selected from a saturated, linear C_{1-10} -hydrocarbyl; and

each R^2 is selected from a C_{1-20} -alkoxy.

Additionally, or alternatively, the organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure, wherein

the dotted lines represent bonds;

X is N;

Y is O;

Z is O;

each R^1 is selected from a saturated, linear C_{1-10} -hydrocarbyl; and

each R^2 is a C_{1-20} -alkoxy.

Additionally, or alternatively, the organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure, wherein

the dotted lines represent bonds;

X is N;

Y is O;

Z is O;

each R^1 is methyl or ethyl; and

each R^2 is selected from methoxy or ethoxy.

Additionally, or alternatively, the organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure, wherein the organometallic compound has formula (II), formula (III), or formula (IIIb), and at least one R^1 and/or R^2 present in the compound is different from other one(s) of R^1 or the R^2 present in the compound.

Additionally, or alternatively, the organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure, wherein the organometallic compound has formula (II), formula (III), or formula (IIIb), and at least one R^1 present in the compound is different from other one(s) of the R^1 present in the compound.

Additionally, or alternatively, the organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure, wherein the organometallic compound has formula (II), formula (III), or formula (IIIb), and at least one R^2 present in the compound is different from other one(s) of the R^2 present in the compound.

Additionally, or alternatively, the organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure, wherein the organometallic compound has formula (II), formula (III), or formula (IIIb), and at least one R^1 present in the compound is different from other one(s) of R^1 present in the compound, and at least one R^2 present in the compound is different from other one(s) of R^2 present in the compound.

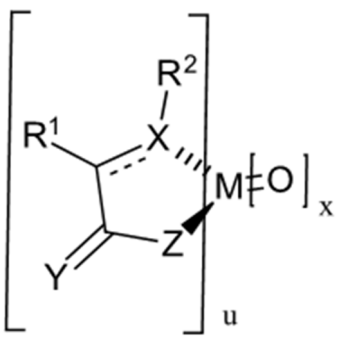
In a second aspect is provided a composition comprising an organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure.

Additionally, or alternatively, the composition further comprises at least one solvent selected form the group consisting of PGME, PGMEA, 2-heptanone, sec-butyl acetate, tert-butyl acetate, iso-propyl acetate, anisole, and NBA, or any combination thereof.

Additionally, or alternatively, the composition is free of particles that have a diameter greater than 10 nm. The diameter may be measured, for example, but not limited to, using an ellipsometer. A person skilled in the art is aware of other techniques to measure the diameter.

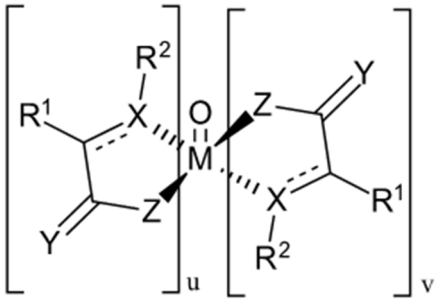
In a third aspect is provided a lithography method comprising:

i) applying an organometallic compound of formula (I) or formula (II)



(I)

,



(II)

, wherein

the dotted lines represent optional bonds;

M is a metal selected from the group consisting of Al, Sn, Zn, Ti, Zr, Hf, Sb, Ta, and W, wherein the metal has an oxidation state selected from +3, +4, +5, or +6;

X, Y, Z, R^1, R^2, u, v, and x are as defined in the present disclosure, or a metal oxo-cluster thereof; or

a composition comprising the organometallic compound, or the metal oxo-cluster thereof, on a substrate, thereby forming a precursor hard mask on the substrate; and

ii) heating the formed precursor hard mask at a temperature below 400 °C, preferably below 250 °C, most preferably below 200 °C, such as at a temperature selected from 60 – 400 °C, 150 – 400 °C, 150 – 250 °C, and 180

– 200 °C, preferably for 1 – 10 min, thereby forming a metal oxide layer on the substrate.

Additionally, or alternatively, M is selected from Ti, Zr, Hf, Sb, and W.

Additionally, or alternatively, each M is independently selected from Ti, Zr, Hf, Sb, and W, preferably each M is selected from Ti, Zr, Hf, Sb, and W.

Additionally, or alternatively, the metal-oxo cluster is represented by formula (III):

$M_aO_x(L)_y(R)_u$ (III), wherein

M is a metal selected from the group consisting of Al, Sn, Zn, Ti, Zr, Hf, Sb, Ta, and W, preferably M is selected from the group consisting of Ti, Zr, Hf, Sb, and W;

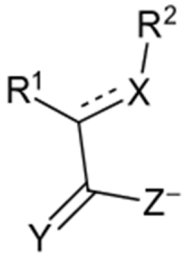
u, and x are as defined in the present disclosure;

each L is independently selected from the group consisting of halogen, nitrate, sulfate, hydroxy and C_{1-12}-alkoxy;

a is an integer selected from 1 – 20, preferably selected from 1 – 12;

y is an integer selected from 0 – 20, preferably selected from 1 – 12;

R is a ligand having formula (IIIa):



(IIIa) , wherein

each dotted line, R^1, R^2, X, Y, and Z are as defined in the present disclosure.

It should be understood that “O” of “O_x“ refers to oxygen. Further, R is attached to M, via the Z group of R.

Additionally, or alternatively, the metal-oxo cluster is represented by formula (IIIb):

$M^z_aO_x(L)_y(R)_u$ (IIIb), wherein

z is the oxidation state of M, preferably z is an integer selected from 3 – 6;

M, and x are as defined in the present disclosure; and

a, L, y, R, and u are as defined in the present disclosure;

provided that $u \leq (z - 2x)$.

Additionally, or alternatively, the organometallic compound, or a metal oxo-cluster thereof, as defined in the present disclosure, wherein

each R^1 is selected from the group consisting of H, and a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms; and

each R^2 is selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms, and a C_{1-20} -alkoxy.

Additionally, or alternatively, the composition further comprises at least one solvent selected form the group consisting of PGME, PGMEA, 2-heptanone, sec-butyl acetate, tert-butyl acetate, iso-propyl acetate, anisole, and NBA, or any combination thereof.

Additionally, or alternatively, the composition is free of particles that have a diameter greater than 10 nm. The diameter may be measured, for example, but not limited to, using an ellipsometer. A person skilled in the art is aware of other techniques to measure the diameter.

Additionally, or alternatively, the metal oxide layer is a hard mask.

Additionally, or alternatively, the metal oxo-cluster is as defined in the present disclosure.

Additionally, or alternatively, in i), the applying the organometallic compound, metal oxo-cluster thereof, or composition is coating a substrate, thereby forming a precursor hard mask on the substrate, preferably the substrate is a semiconductor substrate, such as a semiconductor wafer or glass.

Additionally, or alternatively, the substrate comprises or is essentially made of Si, TiO_2, or GaAs, or is a silicon wafer.

Additionally, or alternatively, in ii), heating comprises heating the formed precursor hard mask first at a temperature selected from 40 – 100 °C, and thereafter heating at a temperature below 350 °C, preferably below 250 °C, most preferably 200 °C or less, such as at a temperature selected from 60 – 350, 100 – 400 °C, 150 – 300 °C, 200 – 250 °C, 150 – 250 °C, and 180 – 200 °C.

Additionally, or alternatively, in ii), heating comprises heating the formed precursor hard mask first to a temperature selected from 40 – 100 °C, and thereafter heating to a temperature below 350 °C, preferably below 250 °C, most preferably 200 °C or less, such as to a temperature selected from 60 – 350, 100 – 400 °C, 150 – 300 °C, 200 – 250 °C, 150 – 250 °C, and 180 – 200 °C.

Additionally, or alternatively, in ii), heating comprises heating the formed precursor hard mask for 0.5 – 20 min, 0.5 – 10 min, 0.5 – 5 min, 1 – 10 min, 1 – 5 min, 0.5 – 2 min, 0.5 – 1.5 min, or 0.5 – 1 min.

Additionally, or alternatively, in ii), heating comprises heating the formed precursor hard mask first at a temperature selected from 40 – 100 °C for 0.5 – 10 min, and thereafter heating at a temperature below 350 °C, preferably below 250 °C, most preferably 200 °C or less, such as at a temperature selected from 60 – 350, 100 – 400 °C, 150 – 300 °C, 200 – 250 °C, 150 – 250 °C, and 180 – 200 °C, for 1 – 10 min.

Additionally, or alternatively, in ii), the formed metal oxide layer is a hard mask, preferably an etch hard mask.

Additionally, or alternatively, the metal oxide layer is a hard mask, preferably an etch hard mask.

Additionally, or alternatively, formed metal oxide layer is a middle layer.

Additionally, or alternatively, in ii), the formed metal oxide layer is a hard mask, preferably an etch hard mask, preferably the hard mask is a middle layer, wherein the underlayer is a carbon-based hard mask and the top layer is a photoresist.

Additionally, or alternatively, the method further comprises, after ii), etching, preferably oxygen plasma etching, the formed metal oxide layer to form an etched metal oxide layer, preferably an etched hard mask, preferably the oxygen plasma etching is performed with an O_2 flow rate selected from the range of 25 – 75 sccm, preferably 40 – 60 sccm, more preferably with an O_2 flow rate of 50 sccm; at a pressure selected from the range of 0.3 – 0.9 Pa, preferably 0.4 – 0.8 Pa, more preferably at a pressure of 0.6 Pa; with a RF power selected from the range of 10 – 30 W, preferably 15 – 25 W, more preferably with a RF power of 20 W; with an ICP power selected from the range of 100 – 300 W; preferably 150 – 250 W, more

preferably with an ICP power of 200 W; and with an etch time selected from the range of 10 – 240 s, preferably 10 – 60 s, more preferably with an etch time of 30 s. For those familiar to the art of inductively coupled plasma, or reactive ion etching it is also understood that several other conditions may be applied and the above are provided as reference used in this invention. Other oxidizing gases or mixtures may be used alone or in combination, optionally diluted by inert gases such as argon and helium or the like.

Surprisingly, the formed metal oxide layer, preferably formed hard mask, is an etch resistant metal oxide layer, preferably an etch resistant hard mask. The etch resistant metal oxide layer, preferably the etch resistant hard mask, exhibits during the oxygen plasma etching a thickness loss of less than 5 nm/min, preferably less than 2.5 nm/min.

Surprisingly, the formed etched metal oxide layer, preferably etched hard mask, is an etch resistant hard mask. The oxygen plasma etching of the formed metal oxide layer forms an etch resistant hard mask which exhibits during the oxygen plasma etching a thickness loss of less than 5 nm/min, preferably less than 2.5 nm/min.

Additionally, or alternatively, wherein, in i), the applying the organometallic compound, metal oxo-cluster thereof, or composition is coating on a surface of an organic underlayer film on a semiconductor substrate, thereby forming a precursor hard mask on the surface of the organic underlayer film, preferably the substrate is a semiconductor substrate, such as a semiconductor wafer, and, after ii),

iii) applying a composition for forming a resist underlayer film onto the metal oxide layer, preferably the metal oxide layer is a hard mask, preferably the metal oxide layer is a middle layer, and heating, the applied composition for forming a resist underlayer film to form a resist underlayer film;

iv) applying a composition for a resist onto the formed resist underlayer film to form a resist film;

v) exposing the formed resist film to light or electron beam radiation according to a predetermined pattern to form an exposed resist film;

vi) developing the exposed resist film to obtain a patterned resist film;

vii) etching the resist underlayer film, the metal oxide layer, the organic underlayer film, and the substrate according to a pattern of the obtained patterned resist film to obtain a patterned substrate.

Additionally, or alternatively, the heating is baking.

The exposing the formed resist film to light or electron beam radiation according to a predetermined pattern to form an exposed resist film may be irradiating the formed resist film with light along a predetermined pattern to form an irradiated structure of the resist film with a region of irradiated resist film and a region with un-irradiated resist film. When developing the irradiated structure of the resist film with the region of irradiated resist film and/or the region with un-irradiated resist film a patterned resist film is formed.

Additionally, or alternatively, the method further comprises developing after at least one of the, preferably after each of the, etching the resist underlayer film, the metal oxide layer, the organic underlayer film, and the substrate according to a pattern of the obtained patterned resist film to obtain a patterned substrate

Additionally, or alternatively, the developing is or comprises developing with one or more developers, or combinations thereof. Additionally, or alternatively, the one or more developer is selected from the group consisting of PGME, PGEE, PGPE, and C_{1-10}-alcohols.

In a fourth aspect is provided a metal oxide layer obtainable by a method as defined in the present disclosure.

Additionally, or alternatively, the carbon content of the metal oxide layer is less than 25%, preferably less than 20%, compared to the carbon content of the compound of formula (I), (II), or the oxo-metal cluster in i). Additionally, or alternatively, the carbon content of the metal oxide layer is less than 25%, preferably less than 20%, compared to the carbon content of the compound of formula (I), (II), or the oxo-metal cluster in i) is due to decomposing of the compound of formula (I), (II), or the oxo-metal cluster after heating to 250 °C in ii), preferably after heating to 250 °C at a heating rate of 4 °C/min in air in ii).

Additionally, or alternatively, the char yield of the metal oxide layer is less than 45%, preferably less than 40%, more preferably less than 35%, even more preferably less than 30%, such as 25 – 30%, 25 – 35%, 25 – 40%, or 25 – 45%, preferably when heated to a temperature selected from the range of 475 – 575 °C.

Additionally, or alternatively, the refractive index of the metal oxide layer is 0.2 or less lower, preferably 0.1 or less lower, than the refractive index of the corresponding amorphous metal oxide.

Additionally, or alternatively, the refractive index of the metal oxide layer is 0.2 or less lower, preferably 0.1 or less lower, than the refractive index of the corresponding amorphous metal oxide of formula $M(O)_x$, wherein M and x are as defined in the present disclosure.

Additionally, or alternatively, the metal oxide layer as defined in the present disclosure obtainable by a lithography method as defined in the present disclosure, wherein the lithography method comprises, after ii), etching, preferably oxygen plasma etching, the formed metal oxide layer to form an etched metal oxide layer, preferably wherein the refractive index of the metal oxide layer is 0.1 or less lower, preferably 0.07 or less lower, than the refractive index of the etched metal oxide layer.

Additionally, or alternatively, the refractive index of the metal oxide layer is 0.1 or less lower, preferably 0.07 or less lower, than the refractive index of the etched metal oxide layer obtainable by a lithography method as defined in the present disclosure, wherein the lithography method comprises, after ii), etching, preferably oxygen plasma etching, the formed metal oxide layer to form the etched metal oxide layer.

Additionally, or alternatively, the refractive index of the metal oxide layer is ≤0.1 lower, ≤0.09 lower, ≤0.08 lower, ≤0.06 lower, ≤0.05 lower, ≤0.04 lower, ≤0.03 lower, ≤0.02 lower, or ≤0.01 lower, than the refractive index of the etched metal oxide layer, or the refractive index of the metal oxide layer is the same as the refractive index of the etched metal oxide layer, or the refractive index of the metal oxide layer is ≤0.1 higher, ≤0.05 higher, or ≤0.01 higher, than the refractive index of the etched metal oxide layer.

Additionally, or alternatively, the metal oxide layer is an etched metal oxide layer.

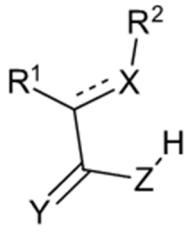
Additionally, or alternatively, the metal oxide layer is an etched metal oxide layer obtainable by a lithography method as defined in the present disclosure, wherein the lithography method comprises, after ii), etching, preferably oxygen plasma etching, the formed metal oxide layer to form the etched metal oxide layer.

Additionally, or alternatively, the oxygen plasma etching is performed with an O_2 flow rate selected from the range of 25 – 75 sccm, preferably 40 – 60 sccm, more preferably with an O_2 flow rate of 50 sccm; at a pressure selected from the range of 0.3 – 0.9 Pa, preferably 0.4 – 0.8 Pa, more preferably at a pressure of 0.6 Pa; with a RF power selected from the range of 10 – 30 W, preferably 15 – 25 W, more preferably with a RF power of 20 W; with an ICP power selected from the range of 100 – 300 W; preferably 150 – 250 W, more preferably with an ICP power of 200 W; and with an etch time selected from the range of 10 – 240 s, preferably 10 – 60 s, more preferably with an etch time of 30 s. Additionally, or alternatively, the oxygen plasma etching is performed with an O_2 flow rate of 50 sccm; at a pressure of 0.6 Pa; with a RF power of 20 W; with an ICP power of 200 W; and with an etch time of 30 s.

In a fifth aspect is provided a use of a compound, oxo-metal cluster thereof, or composition as defined in the present disclosure for the preparation of a hard mask, in the preparation of an optical element, optically active device, or optical or semiconductor device.

In a sixth aspect is provided a method for the preparation of a compound of formula (I) or formula (II), or an oxo-metal cluster thereof, as defined in the present disclosure, wherein the method comprises:

i) providing a reaction composition comprising a compound of formula (V):



(V) , wherein

the dotted line, X, Y, Z, R^1, and R^2 are as defined in the present disclosure; and

ii) providing a salt of X, or a hydrate thereof, wherein X is as defined in the present disclosure;

iii) reacting the compound of formula (V) with the salt of X, or a hydrate thereof,

to obtain the compound of formula (I) or formula (II), or the oxo-metal cluster thereof.

Additionally, or alternatively, the compound of formula (V) is 2-(methoxyimino)propanoic acid.

Additionally, or alternatively, the compound of formula (V) is 2-(methoxyimino)propanoic acid, and the salt of X, or a hydrate thereof, is selected from titanium tetrachloride, titanyl sulfate, titanium tetra(C_{1-15}-alkoxide), zirconium tetrachloride, zirconyl chloride octahydrate, zirconium propoxide, hafnium butoxide, hafnium tetrachloride, hafnium oxychloride octahydrate, and tungsten di-oxo dichloride (WO_2Cl_2).

Additionally, or alternatively, in iii), reacting the compound of formula (V) with the salt of X, or a hydrate thereof, comprises mixing the compound of formula (V) with the salt of X, or a hydrate thereof, to obtain a reaction composition; and optionally heating or cooling the reaction composition at a predetermined temperature.

Additionally, or alternatively, the mixing the compound of formula (V) with the salt of X, or a hydrate thereof, comprises mixing the compound of formula (V) with the salt of X, or a hydrate thereof, in at least one solvent, to obtain the reaction composition, optionally the reaction composition further comprises an acid or a base.

Additionally, or alternatively, the at least one solvent is selected from the group consisting of methanol, methylene chloride, ethyl acetate, propanol, dichloromethane, ethylene glycol dimethyl ether, water, or a mixture thereof; and the optional acid and base are selected from triethylamine, and HCl.

Additionally, or alternatively, the method comprises heating or cooling the reaction composition at a predetermined temperature selected from -5 – 120 °C.

In a seventh aspect is provided an optical element, optically active device or optical or semiconductor device obtainable by a method as defined in the present disclosure.

Additionally, or alternatively, the optical element, optically active device or optical or semiconductor device is a patterned substrate comprising a substrate and a first coating, wherein the substrate comprises a surface and the first coating is attached to selected regions of the surface and absent at other regions of the surface, wherein the first coating comprises or is a metal oxide layer, preferably a hard mask, obtainable by a method as defined in the present disclosure, and the thickness loss

of the metal oxide layer, preferably the hard mask, is 5 nm/min or less during etching the metal oxide layer, preferably the hard mask, as defined in the present disclosure or in ashing process.

In certain embodiments, the present invention relates to the use of organometallic compound of formula (I) or formula (II), or a metal oxo-cluster thereof described in the present disclosure in the formation of patterns on a semiconductor substrate, as illustrated in Figures 1 and 2.

Thus, in a process of the present kind, typically a surface of a substrate 10 is coated 11 with an organic underlayer 12, followed by coating 13 and curing of an inorganic middle layer 14, which typically consist of a high silicon containing material. On top of this, a photoresist (resist film) 16 is coated 15. After exposing 18 the formed resist film 16 to light or electron beam radiation, e.g., irradiation 18 using 193 nm wavelength of light a pattern is formed and developed (not shown) to form a patterned resist film 16a. Such a combination of layers is frequently described in the literature as a ‘tri-layer’ stack, referring to the number of layers.

Subsequent pattern transfer etch processes (with optional developing(s)) can be applied to transfer the pattern formed on the photoresist (patterned resist film 16a) to the substrate 10 (Figure 1). Therefore, a patterned inorganic middle layer 14a, a patterned organic underlayer 12a, and a patterned substrate 10a, such as a patterned semiconductor substrate 10a, may be obtained. It is worth noting that the stack of various layers used in lithography can be higher than 3.

Another combination of layers is a four-layer stack (Figure 2), comprising substrate 10, inorganic middle layer 14 or a metal oxide layer (hard mask) 14, an organic bottom anti-reflective layer 17, and a photoresist (resist film) 16. For the four-layer stack, an organic underlayer 12 has first been applied on the substrate 10, followed by coating, thereby forming a precursor hard mask (not shown), and curing the formed precursor hard mask to form an inorganic middle layer 14, which typically consist of a high silicon containing material, but according to the present invention, the inorganic middle layer 14 is a metal oxide layer (hard mask) 14 obtained from the organometallic compound or composition as disclosed in the present disclosure (not shown in the figure). On top of this, an organic bottom anti-reflective layer 17 is applied prior to a photoresist (resist film) 16 which completes the four-layer stack (Figure 2).

After application by spin coating or other suitable deposition methods for liquids, a prebake step may be applied to remove, at least partially, the solvents and volatile compounds which are included in the coating material. This is beneficial to avoid contamination in the manufacturing equipment. Prebake can be done at different temperatures and times depending on the boiling temperature of the solvents and volatile components. Usually, prebake can be done at 60 – 120 °C for a period of 30 seconds to no more than 30 minutes.

After the drying or prebake step, exposure of the coating to EUV light, electron beam or similar exposure method (18) through an optionally used mask is used to generate the patterns on the substrate. The dose needed to generate patterns is at minimum 5 mJ/cm^2 and at maximum 200 mJ/cm^2.

Development is carried out to remove the exposed or unexposed region, thus obtaining designed pattern. During the development step, exposed or non-exposed regions of, for example, the photoresist (resist film) 16 dissolves in the developer, forming a patterned resist film 16a.

The following non-limiting examples illustrate embodiments.

EXAMPLES

Methods

E-beam lithography was carried out on a Vistec tool. The formulations are 1.3% solid content. The formulations were spin coated on silicon wafers via a spin coater with a spinning speed of 1500 rpm for 30 seconds. Soft bake was then carried out on a hot plate at temperature of 80 °C for 1 minute. The e-beam doses were varied from 100 to 20000 μC/cm^2 at 100 kV and current of 1 nA. The development step was carried out by immersing the film in various organic developers (such as PGME, PGEE, PGPE, alcohols) for 10 s. The patterned film was then rinsed with the same solvent for 5 s and finally dried with nitrogen gas.

EUV lithography: Formulation of 1.5 – 2 % solid content was spin coated on silicon wafers via a spin coater with a spinning speed of 1500 rpm for 30 seconds. Soft bake was then carried out on a hot plate at temperature of 40-80 °C (depending upon the resist) for 1 minute. The film samples after soft bake were irradiated with a XIL-II EUV tool. The doses were varied from 2 to 200 mJ/cm^2. The development

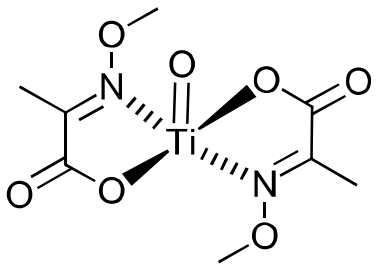
step was carried out by immersing the film in various organic developers (such as PGME, PGEE, PGPE, alcohols) for 10 s. The patterned film was then rinsed with the same solvent for 5 s and finally dried with nitrogen gas.

SYNTHESIS OF COMPOUNDS (PRECURSORS FOR METAL HARD MASKS)

Below are the typical synthetic procedures used for the preparation of precursors of metal hard masks.

TITANIUM HARD MASK PRECURSORS

Example 1: *Titanium oxy di(methoxyiminopropanoate)*



To prepare a ca. 12.4 mM solution, 2.35 g of titanium tetrachloride was added to 150 mL acetone dropwise. The reaction was exothermic and the solution slowly turned yellow. To this solution, 6.7 g of ammonium methoxyimino-propanoate was added. The yellow colour of the solution slowly started to fade. The reaction was allowed to continue for 24 h. The solution was filtered and the filtrate was subjected to rotary evaporation to remove acetone. The obtained gel was dissolved in 7.5 mL dichloromethane and the compound was precipitated in hexane. It was dried at 50 °C for 18 h. Yield of the product titanium oxy di(methoxyiminopropanoate (titanium bis[2-(methoxyimino)propionate] oxide) was nearly quantitative, 96 %. The compound was characterized by NMR, FTIR, and TGA.

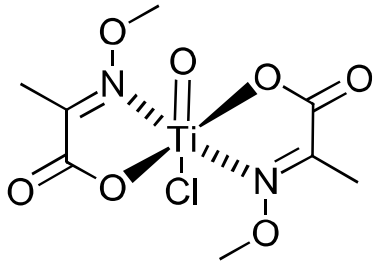
The same synthesis can also be carried out by bubbling ammonia gas in a mixture of titanium tetrachloride and 2-(methoxyimino)propanoic acid in an organic solvent.

The above precursor can also be synthesized by reacting titanyl sulfate with 2-(methoxyimino)propanoic acid in 1:2 molar ratio in the presence of a base with reflux in methanol.

Thermogravimetric analysis (TGA) studies of this compound show that the mass loss starts close to 100 °C and finishes around 225 °C. The TGA analyses were performed by heating the compound to 600 °C and measuring mass loss of the

compound. Within the range 100 – 225 °C the maximum mass loss of the compound seems to occur. Thereafter a minor mass loss is obtained leading to the formation of amorphous TiO_2 (obtained ceramic mass = 27.7%; calculated ceramic mass = 26.9%). These results indicate that a precursor hard mask of this compound decomposes when heating it and the carbon content of the thus formed hard mask is lower compared to the precursor hard mask, due to the heating of the precursor hard mask.

Comparative Example 2: *Titanium oxo-chloro di(methoxyiminopropionate)*



To prepare a ca. 19.6 mM solution, 3.71 g of titanium tetrachloride was added to 150 mL dichloromethane. To this solution, 9.16 g of 2-(methoxyimino)propanoic acid was added. The colour of the solution turned yellow. The reaction was allowed to continue for 18 h. The solution was subjected to rotary evaporation to remove dichloromethane. A pale yellow solid was formed. The obtained solid was dissolved in 7.5 mL dichloromethane and the compound was precipitated in hexane. It was dried at 35 C for 18 h. Yield of the product titanium oxo-chloro di(methoxyiminopropanoate (titanium bis[2-(methoxyimino)propanoate] chloride oxide) was 7.32 g, 73 %. The compound was characterized by NMR, FTIR, and TGA.

ZIRCONIUM HARD MASK PRECURSORS

Example 3: *Zirconium oxy hydroxy methoxyiminopropanoate*

To prepare a ca. 8.8 mM solution, 2.06 g of zirconium tetrachloride was added to 150 mL acetone portion wise. The reaction was exothermic and the solution slowly turned pale yellow. To this solution, 4.74 g of ammonium methoxyimino-propanoate was added. The yellow colour of the solution slowly started to fade. The reaction was allowed to continue for 24 h. The solution was filtered and the filtrate was subjected to rotary evaporation to remove acetone. The obtained gel was dissolved in 7.5 mL dichloromethane and the compound was precipitated in hexane. It was

dried at 38 °C for 18 h. Yield of the compound zirconium oxy hydroxy methoxyiminopropanoate (zirconium 2-(methoxyimino)propanoate oxide) was nearly quantitative, 95 %. The compound was characterized by NMR, FTIR, and TGA.

The same synthesis can also be carried out by bubbling ammonia gas in a mixture of zirconium tetrachloride and 2-(methoxyimino)propanoic acid in an organic solvent.

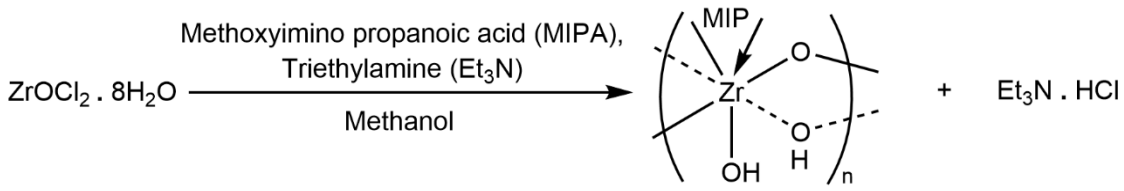
TGA studies of this compound were performed as described in Example 1 and show that the mass loss starts close to 60 °C and finishes around 250 °C. Maximum mass loss seems to occur in this range. At slightly higher temperature, the formation of amorphous ZrO_2 is obtained (obtained ceramic mass = 33.5%; calculated ceramic mass = 35.7%). These results indicate that a precursor hard mask of this compound decomposes when heating it and the carbon content of the thus formed hard mask is lower compared to the precursor hard mask, due to the heating of the precursor hard mask.

Example 4: *Poly(zirconyl di(methoxyiminopropanoate))*

To prepare a ca. 30 mM solution, 9.66 g of zirconyl chloride octahydrate was dissolved in 100 mL methanol. The solution was cooled down to 5 °C in an ice bath. Separately, 2-(methoxyimino)propanoic acid (7.02 g) was dissolved in 10 mL methanol to give a ca. 60 mM solution. This led the solution cold to touch. To this, 8.36 mL of triethylamine was added. The solution was slowly warmed. This mixture was immediately added dropwise to the cold solution of zirconyl chloride octahydrate. After the addition, the solution was slowly warmed to the room temperature and allowed to stir for 2 h during which the solution slowly became cloudy.

After the completion of the reaction, methanol was removed from the mixture using a rotary evaporator. 75 mL THF was added to the resultant dry powder and shaken. The solution was filtered using a PTFE filter (pore size = 0.45 µm) and added dropwise to vigorously stirred hexane (250 mL) leading to the formation of an off-white precipitate. Hexane was decanted and the collected precipitate was dried in vacuum for 2 h. Without being bound to any theories, the reaction between zirconyl

chloride octahydrate and 2-(methoxyimino)propanoic acid (MIPA) with triethylamine in methanol may be shown as presented below (MIP = methoxyiminopropanoate):



Here the zirconium atom is chelated to the MIP ligand.

HAFNIUM HARD MASK PRECURSORS

Example 5: *Hafnium oxy hydroxy methoxyiminopropionate*

To prepare a ca. 6 mM solution, 1.92 g of hafnium tetrachloride was added to 150 mL acetone portion wise. The reaction was exothermic and the solution slowly turned faint yellow. To this solution, 3.32 g of ammonium methoxyimino-propanoate was added. The reaction was allowed to continue for 24 h. The solution was filtered and the filtrate was subjected to rotary evaporation to remove acetone. The obtained gel was dissolved in 5 mL dichloromethane and the compound was precipitated in hexane. It was dried at 38 °C for 19 h. Yield of the product hafnium oxy hydroxy methoxyiminopropionate was nearly quantitative, 2.57 g, 98 %. The compound was characterized by NMR, FTIR, and TGA.

The same synthesis can also be carried out by bubbling ammonia gas in a mixture of hafnium tetrachloride and 2-(methoxyimino)propanoic acid in an organic solvent.

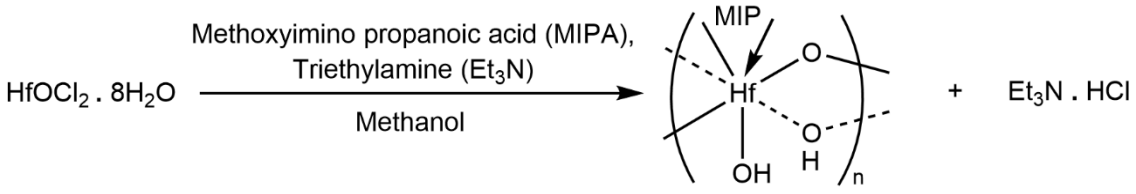
TGA studies of this compound were performed as described in Example 1 and show that the mass loss starts close to 50 °C and finishes around 250 °C. Maximum mass loss seems to occur in this range. At slightly higher temperature, the formation of amorphous HfO_2 is obtained (obtained ceramic mass = 43.3%; calculated ceramic mass = 48.6%). These results indicate that a precursor hard mask of this compound decomposes when heating it and the carbon content of the thus formed hard mask is lower compared to the precursor hard mask, due to the heating of the precursor hard mask.

Example 6: *Poly(hafnyl di(methoxyiminopropionate))*

To prepare a ca. 15 mM solution, 6.14 g of hafnium oxychloride octahydrate was dissolved in 50 mL methanol. The solution was cooled down to 5 °C in an ice bath.

Separately, 2-(methoxyimino)propanoic acid (3.5 g) was dissolved in 10 mL methanol to give a ca. 30 mM solution. This led the solution cold to touch. To this, 4.18 ml of triethylamine was added. The solution slowly warmed. This mixture was immediately added dropwise to the cold solution of hafnium oxychloride octahydrate. After the addition, the solution was slowly warmed to the room temperature and allowed to stir for 2 h during which the solution slowly became cloudy.

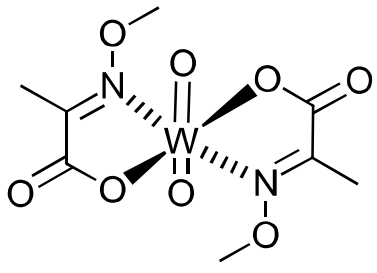
After the completion of the reaction, methanol was removed from the mixture using a rotary evaporator. 50 mL THF was added to the resultant dry powder and shaken. The solution was centrifuged and the clear supernatant liquid was collected. This was added dropwise to vigorously stirred hexane (250 mL) leading to the formation of an off-white precipitate. Hexane was decanted and the collected precipitate was dried in vacuum for 2 h. Without being bound to any theories, the reaction between hafnium oxychloride octahydrate and MIPA with triethylamine in methanol may be shown as presented below (MIP = methoxyiminopropanoate):



Here hafnium atom is chelated to 2-(methoxyimino) propanoate (MIP) ligand.

TUNGSTEN HARD MASK PRECURSORS

Example 7: *Tungsten di-oxo di(methoxyiminopropionate)*



This compound (tungsten bis[2-(methoxyimino)propanoate] dioxide) can be prepared by reacting tungsten di-oxo dichloride (WO_2Cl_2) with 2-(methoxyimino)propanoic acid in 1:2 molar ratio in dichloromethane in the presence of ethylene glycol dimethylether and a base.

ETCH PERFORMANCE AND FILM PROPERTIES OF THE METAL HARD MASKS

Refractive index (RI) and etch performance in O_2 of the metal hard masks were tested at different bake temperatures.

Process conditions

The compounds were coated on 6-inch bare Si wafers and soft baked at 80 °C for 2 minutes, whereafter cured at 200, 250 or 300 °C for 5 minutes. The film thickness and RI (at 633 nm) are measured by Woollam M2000D. Etch rate in O_2 of the metal oxide hard masks (also disclosed as “metal oxide layer” and “hard mask”) disclosed in the present disclosure is obtained by Sentech SI500 with the parameters of 50 sccm O_2 flow rate, Pressure 0.6 Pa, RF power 20 W, ICP power 200 W and 30 seconds of etch time. The film thickness and RI after etching are measured to calculate the etch rate.

Results are shown in tables 1 – 3 below.

Table 1. Hard mask etching results of hard mask of TiO_x obtained from titanium oxy di(methoxyiminopropionate) as a hard mask precursor from Example 1.

Bake temperature (°C)	**Thickness[a] before etch (nm)**	**Etch rate in O_2 (nm/min)**	**RI before etch**	**RI after etch**
200	23.20	2.20	1.97	2.04
250	21.59	2.01	2.03	2.06
300	20.42	1.27	2.06	2.11

[a] Thickness refers to the thickness of the formed hard mask (metal oxide layer, TiO_x) after curing and before etch.

Remaining mass after baking at different temperatures of hard masks obtained from titanium oxy di(methoxyiminopropionate) as a hard mask precursor from Example 1, for 3 min were determined: after baking at 200 °C: 34.0 %, after baking at 300 °C: 20.0 %; after baking at 350 °C: 19.1 %; and after baking at 400 °C: 18.4 %.

Table 2. Hard mask etching results of hard mask of ZrO_x obtained from zirconium oxy hydroxy methoxyiminopropionate as a hard mask precursor from Example 3.

Bake temperature (°C)	**Thickness[a] before etch (nm)**	**Etch rate in O_2 (nm/min)**	**RI before etch**	**RI after etch**
200	40.13	3.93	1.77	1.78
250	35.65	2.23	1.81	1.81
300	32.74	1.09	1.84	1.85

[a] Thickness refers to the thickness of the formed hard mask (metal oxide layer, ZrO_x) after curing and before etch.

Remaining mass after baking at different temperatures of hard masks obtained from zirconium oxy hydroxy methoxyiminopropionate as a hard mask precursor from Example 3, for 3 min were determined: after baking at 205 °C: 41.7 %, after baking at 300 °C: 36.1 %; and after baking at 350 °C: 34.1 %.

Table 3. Hard mask etching results of hard mask of HfO_x obtained from hafnium oxy hydroxy methoxyiminopropionate as a hard mask precursor from Example 5.

Bake temperature (°C)	**Thickness[a] before etch (nm)**	**Etch rate in O_2 (nm/min)**	**RI before etch**	**RI after etch**
200	29.62	4.11	1.71	1.70
250	27.03	2.72	1.74	1.74
300	24.11	1.39	1.76	1.76

[a] Thickness refers to the thickness of the formed hard mask (metal oxide layer, HfO_x) after curing and before etch.

Remaining mass after baking at different temperatures of hard masks obtained from hafnium oxy hydroxy methoxyiminopropionate as a hard mask precursor from Example 5, for 3 min were determined: after baking at 209 °C: 47.3 %, after baking at 300 °C: 42.4 %; and after baking at 350 °C: 40.8 %.

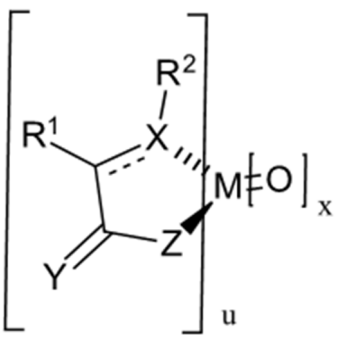
Although the exemplary embodiments of the present disclosure are described herein, it should be noted that any various changes and modifications could be made in the embodiments of the present disclosure, without departing from the scope of legal protection which is defined by the appended claims. In the appended claims, the word "comprising" does not exclude other elements, steps or operations, and the indefinite article "a" or "an" does not exclude a plurality. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage.

INDUSTRIAL APPLICABILITY

Generally, the present technology can be used in the semiconductor industry. For example, the present technology can be used for achieving complex circuitry in microelectronic devices in particular using lithographic processes, such as photolithographic processes.

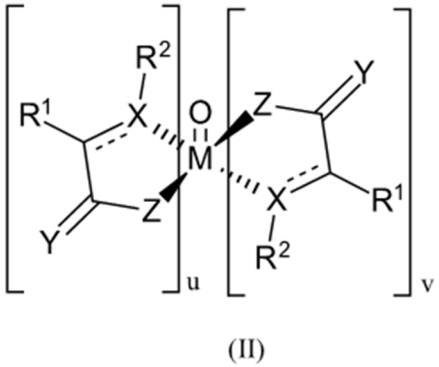
Claims:

1. An organometallic compound of formula (I) or formula (II):



(I)

,



(II)

, wherein

the dotted lines represent optional bonds;

M is a metal selected from the group consisting of Ti, Zr, Hf, Sb, and W, wherein the metal has an oxidation state selected from +3, +4, +5, or +6;

X is a heteroatom selected from the group consisting of O, N, and S;

Y is a heteroatom selected from the group consisting of O, and S;

Z is a heteroatom selected from the group consisting of O, and S;

each R^1 is independently selected from the group consisting of H, and a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms;

each R^2 is independently selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms, and a C_{1-20} -alkoxy;

u and v are each independently selected from integers having a value in the range from 1 to 20; and

x is an integer selected from 1 and 2,

or a metal oxo-cluster thereof.

2. The metal oxo-cluster as claimed in claim 1, wherein the metal-oxo cluster is represented by formula (III):

$M_aO_x(L)_y(R)_u$ (III), wherein

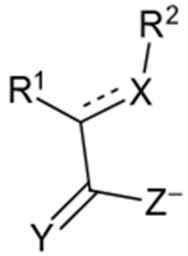
M, u, and x are as defined in claim 1;

each L is independently selected from the group consisting of halogen, nitrate, sulfate, hydroxy and C_{1-12}-alkoxy;

a is an integer selected from 1 – 20;

y is an integer selected from 0 – 20;

R is a ligand having formula (IIIa):



(IIIa) , wherein

each dotted line, R^1, R^2, X, Y, and Z are as defined in claim 1.

3. The metal oxo-cluster as claimed in claim 1 or 2, wherein the metal-oxo cluster is represented by formula (IIIb):

$M^z_aO_x(L)_y(R)_u$ (IIIb), wherein

z is the oxidation state of M, preferably z is an integer selected from 3 – 6;

M, and x are as defined in claim 1; and

a, L, y, R, and u are as defined in claim 2;

provided that $u \leq (z - 2x)$.

4. The organometallic compound, or a metal oxo-cluster thereof, as claimed in any of the preceding claims, wherein

each R^1 is selected from the group consisting of H, and a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms; and

each R^2 is selected from the group consisting of H, a saturated or unsaturated, linear, branched or cyclic C_{1-20} -hydrocarbyl, optionally containing one or more hetero atoms, and a C_{1-20} -alkoxy.

5. The organometallic compound, or a metal oxo-cluster thereof, as claimed in any of the preceding claims, wherein

the dotted lines represent bonds;

X is N;

Y is a heteroatom selected from the group consisting of O, and S, preferably O; and

Z is a heteroatom selected from the group consisting of O, and S, preferably O.

6. The organometallic compound, or a metal oxo-cluster thereof, as claimed in any of the preceding claims, wherein

each R^1 is selected from a saturated, linear $C_{1\text{-}10}$ -hydrocarbyl; and

each R^2 is selected from a $C_{1\text{-}20}$ -alkoxy.

7. The organometallic compound, or a metal oxo-cluster thereof, as claimed in any of the preceding claims, wherein

the dotted lines represent bonds;

X is N;

Y is O;

Z is O;

each R^1 is selected from a saturated, linear $C_{1\text{-}10}$ -hydrocarbyl; and

each R^2 is a $C_{1\text{-}20}$ -alkoxy.

8. The organometallic compound, or a metal oxo-cluster thereof, as claimed in any of the preceding claims, wherein

the dotted lines represent bonds;

X is N;

Y is O;

Z is O;

each R^1 is methyl or ethyl; and

each R^2 is selected from methoxy or ethoxy.

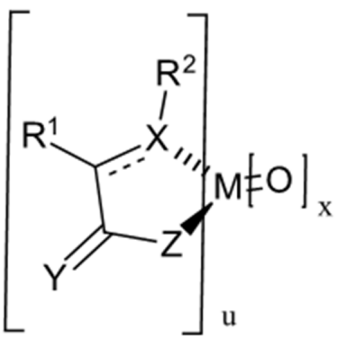
9. The organometallic compound, or a metal oxo-cluster thereof, as claimed in any of the preceding claims, wherein the organometallic compound has formula (II), formula (III), or formula (IIIb), and at least one R^1 and/or R^2 present in the compound is different from other one(s) of R^1 or the R^2 present in the compound.

10. A composition comprising an organometallic compound, or a metal oxo-cluster thereof, as defined in any of the preceding claims.

11. The composition as claimed in claim 10, wherein the composition further comprises at least one solvent selected form the group consisting of PGME, PGMEA, 2-heptanone, sec-butyl acetate, tert-butyl acetate, iso-propyl acetate, anisole, and NBA.

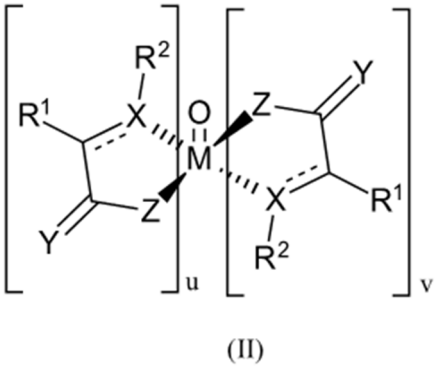
12. A lithography method comprising:

i) applying an organometallic compound of formula (I) or formula (II)



(I)

,



(II)

, wherein

the dotted lines represent optional bonds;

M is a metal selected from the group consisting of Al, Sn, Zn, Ti, Zr, Hf, Sb, Ta and W, wherein the metal has an oxidation state selected from +3, +4, +5, or +6;

X, Y, Z, R^1, R^2, u, v, and x are as defined in any of claims 1 – 9, or a metal oxo-cluster thereof; or

a composition comprising the organometallic compound, or the metal oxo-cluster thereof, on a substrate, thereby forming a precursor hard mask on the substrate; and

ii) heating the formed precursor hard mask at a temperature below 400 °C, thereby forming a metal oxide layer on the substrate.

13. The lithography method as claimed in claim 12, wherein the metal oxo-cluster is as defined in any of claims 2 – 9.

14. The lithography method as claimed in claim 12 or 13, wherein, in i), the applying the organometallic compound, metal oxo-cluster thereof, or composition is coating a substrate, thereby forming a precursor hard mask on the substrate, preferably the substrate is a semiconductor substrate, such as a semiconductor wafer or glass.

15. The lithography method as claimed in any of claims 12 – 14, wherein, the substrate comprises or is essentially made of Si, TiO_2, or GaAs, or is a silicon wafer.

16. The lithography method as claimed in any of claims 12 – 15, wherein, in ii), heating comprises heating the formed precursor hard mask first at a temperature selected from 40 – 100 °C for 0.5 – 10 min, and thereafter heating at a temperature below 350 °C for 1 – 10 min.

17. The lithography method as claimed in any of claims 12 – 16, wherein, in ii), the formed metal oxide layer is an etch hard mask.

18. The lithography method as claimed in any of claims 10 – 17, wherein the method further comprises, after ii), etching the formed metal oxide layer to form an etched metal oxide layer.

19. The lithography method as claimed in any of claims 12 – 18, wherein, in i), the applying the organometallic compound, metal oxo-cluster thereof, or composition is coating on a surface of an organic underlayer film on a semiconductor substrate, thereby forming a precursor hard mask on the surface of the organic underlayer film, preferably the substrate is a semiconductor substrate, such as a semiconductor wafer, and, after ii),

iii) applying a composition for forming a resist underlayer film onto the metal oxide layer, and heating the applied composition for forming a resist underlayer film to form a resist underlayer film;

iv) applying a composition for a resist onto the formed resist underlayer film to form a resist film;

v) exposing the formed resist film to light or electron beam radiation according to a predetermined pattern to form an exposed resist film;

vi) developing the exposed resist film to obtain a patterned resist film;

vii) etching the resist underlayer film, the metal oxide layer, the organic underlayer film, and the substrate according to a pattern of the obtained patterned resist film to obtain a patterned substrate.

20. A metal oxide layer obtainable by a method as defined in any of claims 10 – 19.

21. The metal oxide layer as claimed in claim 20, wherein the carbon content of the metal oxide layer is less than 25% compared to the carbon content of the compound of formula (I), (II), or the oxo-metal cluster in i).

22. The metal oxide layer as claimed in any of claims 20 – 21, wherein the char yield of the metal oxide layer is less than 45%.

23. The metal oxide layer as claimed in any of claims 20 – 22, wherein the refractive index of the metal oxide layer is 0.2 or less lower than the refractive index of the corresponding amorphous metal oxide.

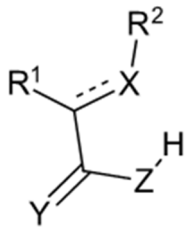
24. The metal oxide layer as claimed in any of claims 20 – 23, wherein the refractive index of the metal oxide layer is 0.1 or less lower than the refractive index of the etched metal oxide layer obtainable by the method as defined in claim 18.

25. The metal oxide layer as claimed in any of claims 20 – 24, wherein the thickness loss of the metal oxide layer is 5 nm/min or less during etching the metal oxide layer.

26. Use of a compound, oxo-metal cluster thereof, or composition as defined in any of claims 1 – 11 for the preparation of a hard mask, in the preparation of an optical element, optically active device, or optical or semiconductor device.

27. A method for the preparation of a compound of formula (I) or formula (II), or an oxo-metal cluster thereof, as defined in any of claims 1 – 11, wherein the method comprises:

i) providing a reaction composition comprising a compound of formula (V):



(V)

, wherein

the dotted line, X, Y, Z, R^1, and R^2 are as defined in any of claims 1 – 11; and

ii) providing a salt of X, or a hydrate thereof, wherein X is as defined in any of claims 1 – 11;

iii) reacting the compound of formula (V) with the salt of X, or a hydrate thereof,

to obtain the compound of formula (I) or formula (II), or the oxo-metal cluster thereof.

28. The method as claimed in claim 27, wherein the compound of formula (V) is 2-(methoxyimino)propanoic acid, and the salt of X, or a hydrate thereof, is selected from titanium tetrachloride, titanyl sulfate, titanium tetra(C_{1-15}-alkoxide), zirconium tetrachloride, zirconyl chloride octahydrate, zirconium propoxide, hafnium butoxide, hafnium tetrachloride, hafnium oxychloride octahydrate, and tungsten di-oxo dichloride (WO_2Cl_2).

29. The method as claimed in any of claims 27 – 28, wherein, in iii), reacting the compound of formula (V) with the salt of X, or a hydrate thereof, comprises mixing the compound of formula (V) with the salt of X, or a hydrate thereof, to obtain a reaction composition; and optionally heating or cooling the reaction composition at a predetermined temperature.

30. The method as claimed in claim 29, wherein the mixing the compound of formula (V) with the salt of X, or a hydrate thereof, comprises mixing the compound of formula (V) with the salt of X, or a hydrate thereof, in at least one solvent, to obtain the reaction composition, optionally the reaction composition further comprises an acid or a base.

31. The method as claimed in claim 30, wherein the at least one solvent is selected from the group consisting of methanol, methylene chloride, ethyl acetate, propanol, dichloromethane, ethylene glycol dimethyl ether, water, or a mixture thereof; and the optional acid and base are selected from triethylamine, and HCl.

32. The method as claimed in any of claims 27 – 31, wherein the method comprises heating or cooling the reaction composition at a predetermined temperature selected from -5 – 120 °C.

33. An optical element, optically active device or optical or semiconductor device obtainable by a method as defined in any of claims 12 – 19.