SPIN-ON COMPOSITIONS OF SOLUBLE METAL OXIDE CARBOXYLATES AND METHODS OF THEIR USE

FIELD OF INVENTION

The present invention relates to spin-on compositions of organic solvent stable metal oxide carboxylate materials that can be used to prepare a variety of underlayers suitable for photolithographic processes. The metal oxide carboxylate compounds have improved stability. The present invention also relates to processes for preparing such underlayers using the inventive compositions.

BACKGROUND

Metal oxide films are useful in a variety of applications in the semiconductor industry such as, for example, lithographic hardmasks, underlayers for anti-reflective coatings and electro-optical devices.

As an example, photoresist compositions are used in microlithography processes for making miniaturized electronic components such as in the fabrication of computer chips and integrated circuits. Generally, a thin coating of a photoresist composition is applied to a substrate, such as silicon based wafer used for making integrated circuits. The coated substrate is then baked to remove a desired amount of solvent from the photoresist. The baked coated surface of the substrate is then image-wise exposed to actinic radiation, such as, visible, ultraviolet, extreme ultraviolet, electron beam, particle beam and X-ray radiation.

The radiation causes a chemical transformation in the exposed areas of the photoresist. The exposed coating is treated with a developer solution to dissolve and remove either the radiation-exposed or the unexposed areas of the photoresist.

The trend towards the miniaturization of semiconductor devices has led to the use of new photoresists that are sensitive to shorter and shorter wavelengths of radiation and has also led to the use of sophisticated multilevel systems to overcome difficulties associated with such miniaturization.

Absorbing antireflective coatings and underlayers in photolithography are used to diminish problems that result from radiation that reflects from substrates which often are highly reflective. Reflected radiation results in thin film interference effects and reflective notching. Thin film interference, or standing waves, result in changes in critical line width dimensions caused by variations in the total light intensity in the photoresist film as the thickness of the photoresist changes. Interference of reflected and incident exposure radiation can cause standing wave effects that distort the uniformity of the radiation through the thickness. Reflective notching becomes severe as the photoresist is patterned over reflective substrates containing topographical features, which scatter light through the photoresist film, leading to line width variations, and in the extreme case, forming regions with complete loss of desired dimensions. An antireflective coating film coated beneath a photoresist and above a reflective substrate provides significant improvement in lithographic performance of the photoresist. Typically, the bottom antireflective coating is applied on the substrate and cured followed by application of a layer of photoresist. The photoresist is imagewise exposed and developed. The antireflective coating in the exposed area is then typically dry etched using various etching gases, and the photoresist pattern is thus transferred to the substrate.

Underlayers containing high amount of refractory elements can be used as hard masks as well as antireflective coatings. Hard masks are useful when the overlying photoresist is not capable of providing high enough resistance to dry etching that is used to transfer the image into the underlying semiconductor substrate. In such circumstances a material called a hard mask whose etch resistance is high enough to transfer any patterns created over it into the underlying semiconductor substrate. This is made possible because the organic

photoresist is different than the underlying hard mask and it is possible to find an etch gas mixture which will allow the transfer of the image in the photoresist into the underlying hard mask. This patterned hard mask can then be used with appropriate etch conditions and gas mixtures to transfer the image from the hard mask into the semiconductor substrate, a task which the photoresist by itself with a single etch process could not have accomplished.

Multiple antireflective layers and underlayers are being used in new lithographic techniques. In cases where the photoresist does not provide sufficient dry etch resistance, underlayers and/or antireflective coatings for the photoresist that act as a hard mask and are highly etch resistant during substrate etching are preferred. One approach has been to incorporate silicon, titanium, zirconium or other metallic materials into a layer beneath the organic photoresist layer. Additionally, another high carbon content antireflective or mask layer may be placed beneath the metal containing antireflective layer, such as a trilayer of high carbon film/hardmask film/photoresist used to improve the lithographic performance of the imaging process. Conventional hard masks can be applied by chemical vapor deposition, such as sputtering. However, the relative simplicity of spin coating versus the aforementioned conventional approaches makes the development of a new spin-on hard mask or antireflective coating with high concentration of metallic materials in the film very desirable.

Underlayer compositions for semiconductor applications containing metal oxides have been shown to provide dry etch resistance as well as antireflective properties. When higher concentrations of metal oxide are present in the underlayer, improved etch resistance and thermal conductance can be achieved. Conventional metal oxide compositions, however, have been found to be very unstable to moisture in air creating a variety of issues, including shelf life stability, coating problems and performance shortcomings. As well, conventional compositions generally contain non-metal oxide materials such as polymers, crosslinkers and other materials that detract from the metal oxide properties

required for etch resistance and thermal conductivity. Thus there is an outstanding need to prepare spin-on hardmask, antireflective and other underlayers that contain high levels of stable soluble metal oxides which are soluble or colloidally stable.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows examples of precursors useful for the preparation of the current metal oxide dicarboxylates.

Figure 2 shows examples of crosslinking polymers useful for the current compositions.

SUMMARY OF THE DISCLOSURE

The present invention relates to spin-on compositions of organic solvent soluble metal oxide carboxylate materials that can be used to prepare a variety of underlayers suitable for photolithographic processes. The metal oxide carboxylate compounds have improved stability. The present invention also relates to processes for preparing such underlayers using the inventive compositions.

In a first embodiment, disclosed and claimed herein are spin-on compositions comprising at least one metal oxide dicarboxylate, wherein the dicarboxylate is capable of decomposing during heat treatment to give an oligomeric metal oxide film, and an organic solvent into which the metal oxide dicarboxylate is soluble. The carboxylate of the dicarboxylate may be a substituted or unsubstituted, saturated or unsaturated, branched or unbranched C_3 – C_6 carboxylate, such as, for example, a propionate.

In a second embodiment, disclosed and claimed herein are spin-on compositions of the above embodiment, wherein the metal is at least one high refractive metal chosen from Ti, V, Cr, Zr, Nb, Mo, Ru, Rh, Hf, Ta, W, Re, and Ir, such as, for example, the metal oxide may be comprised of zirconium and optionally titanium.

In a third embodiment, disclosed and claimed herein are spin-on compositions of the above embodiment, further comprising an organic polymer capable of crosslinking during heat treatment, and wherein the metal oxide dicarboxylate is capable of thermally decomposing to give a film with high metal oxide content.

In a fourth embodiment, disclosed and claimed herein are methods of manufacturing an electronic device comprising, applying a composition of any of the above embodiments to a substrate, and heating the coated substrate. The heating can be from about 200^{O}C to about 500^{O}C for about 30 to about 200 seconds.

In a fifth embodiment, disclosed and claimed herein are methods of the above method embodiments wherein the carboxylate of the dicarboxylate may be a substituted or unsubstituted, saturated or unsaturated, branched or unbranched C_3 – C_6 carboxylate, such as, for example, a propionate.

In a sixth embodiment, disclosed and claimed herein are methods of the above embodiment wherein the metal is at least one high refractive metal chosen from Ti, V, Cr, Zr, Nb, Mo, Ru, Rh, Hf, Ta, W, Re, and Ir, such as, for example, zirconium and optionally titanium.

In a seventh embodiment, disclosed and claimed herein are methods of the above embodiment, wherein the composition further comprises an organic polymer which crosslinks during heat treatment, and wherein the metal oxide dicarboxylate thermally decomposes to give a film with high metal oxide content.

DETAILED DESCRIPTION

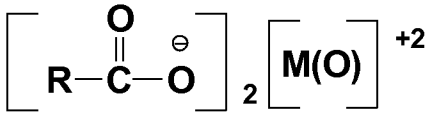
As used herein, the conjunction “and” is intended to be inclusive and the conjunction “or” is not intended to be exclusive unless otherwise indicated. For example, the phrase “or, alternatively” is intended to be exclusive.

As used herein, the term “and/or” refers to any combination of the foregoing elements including using a single element.

As used herein the terms “composition” and “formulation” are used interchangeable and mean the same thing.

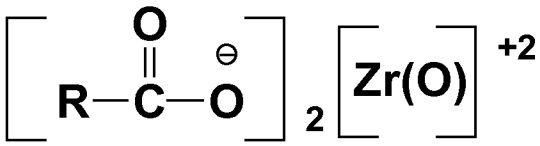
As used herein the phrase “high metal oxide content” means a content higher than about 50% based on weight percentages.

Disclosed and claimed herein are spin-on compositions of metal oxide dicarboxylate materials that are soluble in organic solvents that are typically used in spin-on coating processes. They have been found to be more moisture stable that the currently available materials based on alkoxy metal oxides. The metal oxide dicarboxylates have the following structure:

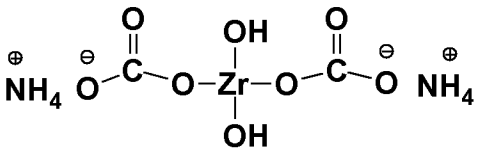


R can be a substituted or unsubstituted, saturated branched or unbranched C_3 – C_6 carboxylate ligand, such as, for example, propanoic or isopropanoic; butanoic, isobutanoic, sec-butanoic, or tert-butanoic; pentanoic or any of the pentanoic isomers; hexanoic or any of the hexanoic isomers. Unsaturated, branched or unbranched, C_3 – C_6 carboxylate ligands may also be used, such as, for example, acrylic, methacrylic, butenoic, pentenoic, hexenoic carboxylates or their isomers. The carboxylates may be substituted with hydroxides, halides, chalcogens, and the like, substituted either in the chain or attached to the chain.

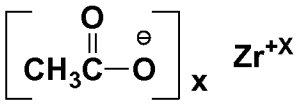
M, in the metal oxide dicarboxylate, is at least one metal chosen from titanium, vanadium, zirconium, tantalum, lead, antimony, thallium, indium, ytterbium, gallium, hafnium, niobium, molybdenum, ruthenium, rhodium, tantalum, rhenium, osmium, iridium, aluminum, magnesium, germanium, tin, iron, cobalt, nickel, copper, zinc, gold, silver, chromium, cadmium, tungsten and platinum. A typical metal oxide dicarboxylates has the following structure:



The metal oxide dicarboxylates are prepared from a number of different precursors, such as, for example, ammonium zirconium carbonate:



or zirconium acetate:



where x is 2-4 and other examples of precursors are listed in Figure 1, such as ammonium zirconium carbonate, zirconium(IV) oxide 2-ethylhexanoate, zirconium (IV) acetylacetonate and zirconium acetate.

In some examples the precursor is at least one colloidally stable nanoparticle with average particle sizes from about 5 nm to about 50 nm, or 5-25 nm or 5-20 nm. Not to be held to theory, it is believed that the metal oxide

nanoparticle precursor reacts with a carboxylic acid or carboxylic acid salt to form a surface layer of metal oxide dicarboxylate surrounding the novel nanoparticle. The resultant carboxylated metal oxide nanoparticle is also stable in the solvent.

More than one metal may be included in the composition depending on the desired properties of the final crosslinked layer. For example, zirconium and titanium may be combined to give a layer with very good etch resistance, thermal conductivity and high refractive index. The amount of each metal in the metal oxide carboxylate in the solution can range from about 5 wt % to about 50 wt % depending on the desired characteristics of the final cured metal oxide layer.

The metal oxide dicarboxylates are soluble in solvents that are typically used in lithographic spin-on processes. Examples of suitable solvents for the current disclosure include ethers, esters, ether esters, ketones and ketone esters and, more specifically, ethylene glycol monoalkyl ethers, diethylene glycol dialkyl ethers, propylene glycol monoalkyl ethers, propylene glycol dialkyl ethers, acetate esters, hydroxyacetate esters, lactate esters, ethylene glycol monoalkylether acetates, propylene glycol monoalkylether acetates, alkoxyacetate esters, (non-)cyclic ketones, acetoacetate esters, pyruvate esters and propionate esters. The aforementioned solvents may be used independently or as a mixture of two or more types. Furthermore, at least one type of high boiling point solvent such as benzylethyl ether, dihexyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, acetonylacetone, caproic acid, capric acid, 1-octanol, 1-nonanol, benzyl alcohol, benzyl acetate, ethyl benzoate, diethyl oxalate, diethyl maleate, γ-butyrolactone, ethylene carbonate, propylene carbonate and phenylcellosolve acetate may be added to the aforementioned solvent.

Methods for preparing the metal oxide dicarboxylates are described in the examples below. Generally a precursor is dissolved in a suitable solvent and the acid or salt form of the desired carboxylate is added slowly. In some cases, such

as for example, with the ammonium zirconium carbonate, gaseous by-products are generated which then leave the admixture. The total percent solids in the chosen solvent or solvent blend is between about 1 – about 30% wt/wt, such as, for example, about 2% to about 10% wt/wt.

It has surprisingly been found that the current metal oxide dicarboxylates of the current disclosure decompose during thermal processing to give a highly crosslinked metal oxide layer. Not to be held to theory it is believed that the dicarboxylate decompose at curing temperatures and either evaporate as the carboxylate or as volatile composition products. What remains behind is highly crosslinked metal oxide films.

The compositions of the current disclosure can be coated onto the surface of a substrate such as low dielectric constant materials, silicon, silicon substrates coated with a metal surface, copper coated silicon wafer, copper, aluminum, polymeric resins, silicon dioxide, metals, doped silicon dioxide, silicon nitride, tantalum, polysilicon, ceramics, aluminum/copper mixtures, any of the metal nitrides such as AlN; gallium arsenide and other such Group III/V compounds. The substrate may also be other antireflective coatings or underlayers, such as high carbon underlayers coated over the above mentioned substrates. The substrate may comprise any number of layers made from the materials described above.

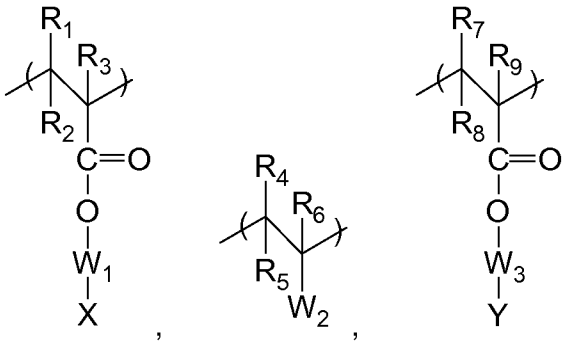
The compositions of the current disclosure are coated on the substrate using techniques well known to those skilled in the art, such as dipping, spin coating, curtain coating, slot coating, spraying and the like. The film thickness of the coating ranges from about 5 nm to about 1000 nm, or about 10 nm to about 520 nm or about 50 to 400 nm. The coated metal oxide dicarboxylate composition is then heated on a hot plate or convection oven at curing temperatures to drive off the carboxylate substituents. The cure temperature may be from about 200°C to about 500°C for about 1 to about 10 minutes, such as, for example, from about 250°C to about 450°C for about 1 to about 2

minutes. The composition may be coated over other layers of antireflective coatings, such as a high carbon (greater than 80% or 85% or 90%) content antireflective coating. Once cooled, other materials can be coated onto the surface of the highly crosslinked metal oxide such as, for example, photoresists.

The metal oxide dicarboxylate compositions of the current disclosure may further contain an organic or inorganic polymer capable of crosslinking during heat treatment, wherein the metal oxide dicarboxylate thermally decomposes while the polymer thermally crosslinks to give a composite film with high metal oxide content.

Polymers such as film forming organic or silicon based polymer are used, such as, for example, polyacrylics, polymethacrylates, and condensation polymers such as polyesters, novolac resins, siloxane resins or organosilsesquioxanes. These polymers may be used alone or in combination with each other depending on the desired properties of the final film after curing. These polymers are generally crosslinking polymer, containing any of a number of the same or different crosslinking substituents, such as, for example, epoxies, hydroxyls, thiols, amines, amides, imides, esters, ethers, ureas, carboxylic acids, anhydrides, and the like. Other examples of crosslinking groups include the glycidyl ether group, glycidyl ester group, glycidyl amino group, methoxymethyl group, ethoxy methyl group, benzyloxymethyl group, dimethylamino methyl group, diethylamino methyl group, dimethylol amino methyl group, diethylol amino methyl group, morpholino methyl group, acetoxymethyl group, benzyloxy methyl group, formyl group, acetyl group, vinyl group and isopropenyl group. Polymers disclosed in US 8,039,201 and incorporated herein by reference may be used.

The polymer of the coating composition can comprise at least one unit of structure (1) comprising a hydrophobic moiety, at least one unit of structure (2) comprising a chromophore moiety, at least one unit of structure (3) comprising a crosslinking moiety (3) and optionally a unit comprising a group capable of crosslinking the polymer, where the structures 1-3 may be represented by,



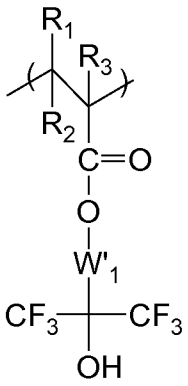
(1) (2) (3)

where, R_1 to R_9 are independently selected from hydrogen and C_1-C_4 alkyl; W_1 is a fully or partially fluorinated group; X is selected from F, H, and OH; W_2 is an organic moiety comprising a chromophore group, and W_3Y comprises a crosslinking moiety. In the polymer, the unit comprising the hydrophobic moiety, W_1, is a fully or partially fluorinated group. W_1 is preferably a nonaromatic group, and may be selected from a fluorinated aliphatic alkylene and partially fluorinated aliphatic alkylene such as a C_1-C_{20} alkylene selected from linear alkylene, branched alkylene, cyclic alkylene and mixtures of these. The alkylene group may be substituted by other functionalities, such as alkoxy and alkyl carboxyl groups. In one embodiment W_1 is not a multicyclic aliphatic alkylene and is also not aromatic and maybe a fully or partially fluorinated C_1-C_{20} alkylene which is selected from linear, branched, monocyclic, and mixture of these. W_1 may be represented by fully or partially fluorinated C_1-C_{20} alkylene, such as fully or partially fluorinated moieties of methylene, ethylene, propylene, isopropylene, butylene, 1-hexylethylene, etc; further such as 3,5 bishexafluromethylene-

hexane. X in structure (1) may be selected from F, H, and OH. In one embodiment X is OH. Further examples of the unit (1) are given in Figure 1. The backbone of the polymer may be an acrylate or a methacrylate.

In one embodiment of unit (1) of the polymer, X is fluorine and W_1 is a fully or partially fluorinated aliphatic C_1-C_{20} alkylene. Further examples of W_1X are fully fluorinated aliphatic C_1-C_{20} alkanes which are linear, branched, monocyclic or mixtures of these, such as pentafluoropropyl, 2,2,2-trifluoroethyl, and heptafluorobutyl, etc.

In one embodiment, the unit (1) in the polymer of the present novel composition may have the structure,

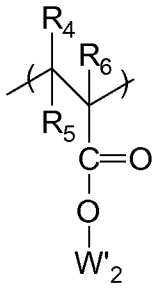


(4)

where, R_1 to R_3 are independently hydrogen and C_1-C_4 alkyl, W'_1 may be selected from a single bond, an alkylene, substituted alkylene, such as a C_1-C_{20} alkylene selected from linear, branched, cyclic and mixtures of these. The alkylene may be substituted with other functionalities such as alkoxy, alkyl carboxyl groups, partially or fully fluorinated alkylene hydroxy groups. Preferably W'_1 is a nonaromatic group, and may be selected from a fluorinated aliphatic alkylene and partially fluorinated aliphatic alkylene such as a C_1-C_{20} alkylene selected from linear alkylene, branched alkylene, monocyclic alkylene and mixtures of these. W'_1 may be represented by fluorinated aliphatic alkylene, partially fluorinated aliphatic alkylene, where the alkylene may be cyclic, linear,

branched or a mixture of these. In another embodiment, W'_1 is selected from C_1-C_{12} linear alkylene, C_1-C_{12} branched alkylene, C_1-C_{12} monocyclic alkylene and mixtures thereof, where the alkylene may be substituted with other functionalities such as alkoxy, alkyl carboxyl groups, and partially or fully fluorinated alkylene hydroxy groups. In yet another embodiment W'_1 is selected from methylene, ethylene, propylene, isopropylene, 1-hexylethylene, and 3-hexafluropropanol-hexane.

In the polymer of the present invention, W_2 in structure (2) is an organic moiety comprising the chromophore group, where the chromophore group is capable of absorbing the radiation used to expose the photoresist coated over the film of the present antireflective coating composition, such as aromatic groups; examples of chromophore groups are unsubstituted phenyl and substituted phenyl, particularly for 193 nm radiation. Other chromophores may also be used, such as unsubstituted naphthyl, substituted naphthyl, unsubstituted anthracyl, and substituted anthracyl for 248 nm radiation. The chromophore group may be substituted with moieties such as hydroxy, esters, ethers, alkyl carboxyl, etc. The chromophore group may be directly linked to the backbone of the polymer or be part of an organic moiety. The organic moiety can be any essentially hydrocarbon moiety comprising carbon and hydrogen, and may additionally contain oxygen. The chromophore group may be attached to the polymer backbone by an ester group. The chromophore group may be attached through a connecting group, where the connecting group may be an ester, alkylene group, alkyeneoxyalkylene group, alkoxy group, etc. Examples of an alkylene group may be C_1-C_{20} alkylene selected from linear, branched, cyclic and mixtures of these. Preferably the connecting group is an aliphatic alkylene or ester. Examples of connecting groups may be methylene, ethylene, propylene, etc. Further examples of W_2 are phenyl methylene, phenyl, naphthyl, methylene naphthyl, anthracyl, methylene anthracyl, etc. An example of structure (2) is structure (2')



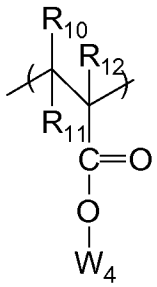
(2')

where R_4 to R_6 are independently hydrogen and C_1-C_4 alkyl, and W'_2 is an chromophore group connected directly or through a C_1-C_{12} alkylene group, where the chromophore group is as described previously. W'_2 may be a chromophore group. Specific examples of W'_2 may be a phenyl group, a substituted phenyl group, benzyl group or a substituted phenyl group. The polymer may be an acrylate or a methacrylate polymer.

In the polymer of the present invention the unit with the crosslinking site is one capable of causing the polymer to be crosslinked, such that it comprises a group which can crosslink the polymer and become a crosslinking site or provide a site where crosslinking with another group can take place. Groups which can crosslink the polymer are for example epoxy groups, methylol groups, uril groups, etc. Groups which can provide a possible crosslinking site useful for reacting with crosslinking groups are hydroxy. Thus Y in structure (3) could be an epoxy, hydroxy, methylol, uril, etc. Epoxy groups are capable of selfcrosslinking the polymer and do not require an external crosslinking compound. One embodiment of Y is epoxy. One embodiment of Y is hydroxy. If Y is hydroxy and the polymer does not contain a crosslinking group within the polymer, then an external crosslinking compound may be added to the composition. The moiety Y may be connected to the ester group through W_3. Preferably W_3 is a nonaromatic group, such as an aliphatic group. W_3 may be an aliphatic alkylene group, aliphatic alkyene ether group, etc. Examples of an alkylene group may be C_1-C_{20} alkylene selected from linear, branched, cyclic and mixtures of these. Examples of W_3 are methylene, ethylene, propylene, butylenes, hexylenes, etc. The

polymer of the present composition may contain unit of structure (1), a unit of structure (2) and one or more types of unit (3). The polymer may contain multiple types of unit (3), such as one unit where Y is hydroxy and one unit where Y is epoxy. Specific examples of W_3Y are methylene epoxy, ethylene epoxy, hexylenemethylene epoxy, etc.

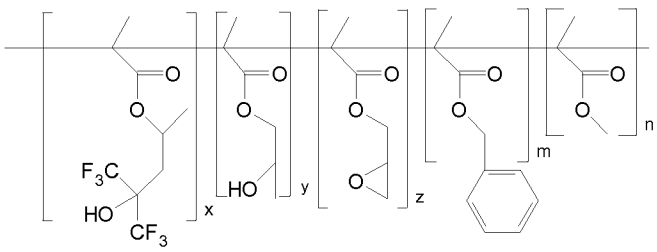
The polymer present in the novel composition may comprise additional (meth)acrylate monomeric units, such as in structure (5).



(5)

where R_{10}-R_{12} are independently selected from hydrogen and C_1-C_4 alkyl, W_4 is C_1-C_{10} alkyl, C_1-C_{10} alkyleneetheralkyl, substituted C_1-C_{10} alkyl, and substituted C_1-C_{10} alkyleneetheralkyl. The substitution may be alkoxy, alkylcarboxyl, alkylester, etc.

In one embodiment of the polymer, the polymer comprises the units shown in structure (6),



(6)

where x, y, z, m and n are mole% of the monomeric units shown, x can range from about 1-50 mole%, preferably about 5-30 mole%; y can range from about 0-50 mole%, preferably about 5-50 mole%; z can range from about 0-50 mole%; m can range from about 5-50 mole% and n can range from about 0-50 mole%, providing y and/or z is greater than 1 mole%.

The polymer, when used, is less than about 80% based on solids, such as, for example, less than 50% based on solids. Crosslinking additives may also be present between 15 – 40% based on solids. Other additives typical of coating additive may be added, such as, for example, wetting agents, surfactants, anti-foam agent, thixotropic agents and the like.

The compositions of the current disclosure contain about 1 weight% to about 30 weight% of the metal oxide dicarboxylate based on total composition, or about 2-15 weight%, or about 3-10 weight%. The cured metal film has a metal content in the range of about 10 to about 85 weight% after 200 – 300^{O}C for about 60-120 seconds, or about 10 to about 70 weight%, or about 30 to about 65%, or about 40 to about 65 weight% or about 40 to about 60 weight % based on the total weight of the cured film. In particular, cured zirconium or titanium oxide films formed from the novel composition have a metal content in the range of about 10 to about 70 weight% after 200 – 300^{O}C for about 60-120 seconds, or about 20 to about 70 weight%, or about 40 to about 60 weight% or about 20 to about 70 weight%.

The cured metal oxide film can be removed using a stripping agent, including, for example, 85% phosphoric acid, 3% HF, 10% TMAH, 10% hydrogen peroxide and aqueous alkaline peroxides. Stripping time ranges from about 30 seconds to about 120 seconds at about room temperature to about 70^{O}C depending on the film curing conditions. Other stripping processes may be

employed in conjunction with processing conditions of the cured metal oxide film. For example, when the film is cured at a lower temperature or a shorter time, the stripper may be diluted, the time may be shortened and/or the temperature of stripping may be reduced.

The metal oxide dicarboxylates of the current disclosure, their compositions and methods of use can be used to prepare lithographic antireflective layer. Sufficient chromophore groups are present, and the refractive indices of the underlayer n (refractive index) can range from about 1.8 to about 2.2 and k (extinction coefficient) can range from about 0.1 to about 0.5 at 193 nm exposure wavelength.

The refractive indices of the polymer or composition, n (refractive index) and k (extinction coefficient) are parameters which relate to the complex refractive index $n_{c,}$ are defined as follows,

$n_c = n - jk$

(Handbook of Semiconductor Manufacturing Technology Edited by Yoshio Nishi et al, Marcel Dekker Inc, 2000 page 205).

The novel coatings are useful as a hard mask. The n and k values can be calculated using an ellipsometer, such as the J. A. Woollam WVASE VU-32™ Ellipsometer. The exact values of the optimum ranges for k and n are dependent on the exposure wavelength used and the type of application. Typically for 193 nm the preferred range for k is about 0.1 to about 0.6, and for 248 nm the preferred range for k is about 0.15 to about 0.8, however, other exposure wavelengths such as, for example DUV and beyond DUV can be used and the compositions tuned to work in conjunction with them, as shown in Table 2, below.

The photoresist compositions are applied over the cured novel coating by such processes as spin coating, and the like, as described herein. After coating, the solvent is removed to a level wherein the coating can be properly exposed. In some cases a residual of 5% solvent may remain in the coating while in other

cases less than 1% is required. Drying can be accomplished by hot plate heating, convection heating, infrared heating and the like. The coating is imagewise exposed with actinic radiation through a mark containing a desired pattern. A film of photoresist is coated on top of the underlayer coating and baked to substantially remove the photoresist solvent. An edge bead remover may be applied after the coating steps to clean the edges of the substrate using processes well known in the art.

Photoresists can be any of the types used in the semiconductor industry, provided the photoactive compound in the photoresist and the antireflective coating substantially absorb at the exposure wavelength used for the imaging process. Photoresists useful for immersion lithography are preferred. Typically, photoresists suitable for imaging with immersion lithography may be used, where such photoresists have a refractive index higher than 1.85 and also are hydrophobic having water contact angle in the range of 75° to 95°.

To date, there are several major deep ultraviolet (uv) exposure technologies that have provided significant advancement in miniaturization, and have actinic radiation of 250 nm to 10 nm, such as 248 nm, 193 nm, 157 and 13.5 nm. Chemically amplified photoresist are often used. Photoresists for 248 nm have typically been based on substituted polyhydroxystyrene and its copolymers/onium salts, such as those described in US 4,491,628 and US 5,350,660. On the other hand, photoresists for exposure at 193 nm and 157 nm require non-aromatic polymers since aromatics are opaque at this wavelength. US 5,843,624 and US 6,866,984 disclose photoresists useful for 193 nm exposure. Generally, polymers containing alicyclic hydrocarbons are used for photoresists for exposure below 200 nm. Alicyclic hydrocarbons are incorporated into the polymer for many reasons, primarily since they have relatively high carbon to hydrogen ratios which improve etch resistance, they also provide transparency at low wavelengths and they have relatively high glass transition temperatures. US 5,843,624 discloses polymers for photoresist that are obtained by free radical polymerization of maleic anhydride and unsaturated

cyclic monomers. Any of the known types of 193nm photoresists may be used, such as those described in US 6,447,980 and US 6,723,488, and incorporated herein by reference. Two basic classes of photoresists sensitive at 157 nm, and based on fluorinated polymers with pendant fluoroalcohol groups, are known to be substantially transparent at that wavelength. One class of 157 nm fluoroalcohol photoresists is derived from polymers containing groups such as fluorinated-norbornenes, and are homopolymerized or copolymerized with other transparent monomers such as tetrafluoroethylene (US 6,790,587, and US 6,849,377) using either metal catalyzed or radical polymerization. Generally, these materials give higher absorbencies but have good plasma etch resistance due to their high alicyclic content. More recently, a class of 157 nm fluoroalcohol polymers was described in which the polymer backbone is derived from the cyclopolymerization of an asymmetrical diene such as 1,1,2,3,3-pentafluoro-4-trifluoromethyl-4-hydroxy-1,6-heptadiene (US 6,818,258) or copolymerization of a fluorodiene with an olefin (US 6,916,590). These materials give acceptable absorbance at 157 nm, but due to their lower alicyclic content as compared to the fluoro-norbornene polymer, have lower plasma etch resistance. These two classes of polymers can often be blended to provide a balance between the high etch resistance of the first polymer type and the high transparency at 157 nm of the second polymer type. Photoresists that absorb extreme ultraviolet radiation (EUV) of 13.5nm are also useful and are known in the art. Thus photoresists absorbing in the range of about 12 nm to about 250 nm are useful. The novel coatings can also be used in process with nanoimprinting and e-beam resists.

After the coating process, the photoresist is imagewise exposed. The exposure may be done using typical exposure equipment. The exposed photoresist is then developed in an aqueous developer to remove the treated photoresist. The developer is preferably an aqueous alkaline solution

comrising, for example, tetramethylammonium hydroxide (TMAH), typically 2.38 weight% TMAH. The developer may further comprise surfactant(s). An optional heating step can be incorporated into the process prior to development and after exposure.

The process of coating and imaging photoresists is well known to those skilled in the art and is optimized for the specific type of photoresist used. The photoresist patterned substrate can then be dry etched with an etching gas or mixture of gases, in a suitable etch chamber to remove the exposed portions of the underlayers and optional other antireflective coatings. Various etching gases are known in the art for etching underlayer coatings, such as those comprising O_2, CF_4, CHF_3, Cl_2, HBr, SO_2, CO, etc. In one embodiment, the article comprises a semiconductor substrate with a high carbon antireflective film, over which the novel metal layer is coated. A photoresist layer is coated above this. The photoresist is imaged as disclosed above and the metal underlayer is dry etched using gases comprising fluorocarbons. After the metal underlayer is etched, the high carbon film can be dry etched using oxygen or oxygen mixtures. Advantageously the novel metal layer may be removed using a stripper which is a chemical solution, as described herein.

Each of the documents referred to above are incorporated herein by reference in its entirety, for all purposes. The following specific examples will provide detailed illustrations of the methods of producing and utilizing compositions of the present invention. These examples are not intended, however, to limit or restrict the scope of the invention in any way and should not be construed as providing conditions, parameters or values which must be utilized exclusively in order to practice the present invention.

EXAMPLES

The refractive index (n) and the extinction coefficient (k) values of the carbon hard mask antireflective coating in the Examples below were measured on a J. A. Woollam VASE32 ellipsometer.

The molecular weight of the polymers was measured on a Gel Permeation Chromatograph using a Water 2695 Alliance Separation Module, or equivalent equipped with a Waters Dual Wavelength UV Detector, Model 2487, or equivalent and a Waters Differential Refractometer, Model 2414, Dectector equivalent, a Shodex Columns set as follows: one Shodex GPC KF-801 (1.5 x 10^3) column, Two Shodex GPC KF-802 (5 x 10^3) columns and one Shodex GPC KF-804 (4 x 10^5) column. The mobile phase was UV stabilized THF HPLC grade and the molecular weight standard was as set of polystyrene standards supplied by American Standards Corporation and Millipore Corporation or equivalent.

The TGA analysis was done using a Perkin Elmer-TGA7-Thermogravimeteric Analyser in the presence of oxygen from 50-900ºC.

Composition Example 1

20.0g of Zirconium oxide propionate from Gelest Inc., Morrisville PA was placed into a reaction vessel and 180g of propylene glycol monomethyl ether acetate (PGMEA) was added. After shaking over night the formulation was filtered through a 0.2µm filter.

Composition Example 2

18.0g of ammonium zirconium carbonate (20 wt%ZrO_2) from Aldrich Chemical Company, St. Louis, MO, was placed in a reaction vessel and 18gms of propionic acid was slowly added dropwise. While adding these acids, ammonia and carbon

dioxide gases were released. When the reaction was completed, it formed a foam type white solid compound. 30gms of PGMEA was then added. After shaking for 2 to 3 hours the formulation was filtered by 0.2µm filter.

Composition Example 3

20gms of ZrO_2 nanoparticle solution (20 wt%) stabilized with acetate ions obtained from Nyacol Nano Technology, Inc., Ashland, MA, (average particle size of around 5-10nm, initial pH of the solution was 3.5) was placed in a reaction vessel. 10gms of acrylic acid was added dropwise under constant stirring. 30gms of a 70/30 blend of PGMEA and propylene glycol monomethyl ether (PGME) was added. After 4 to 5 hrs of shaking, the formulation was filtered using a 0.2um filter.

Composition Example 4

15 gms of zirconium acetate solution in diluted acetic acid(16wt% Zr) obtained from Aldrich Chemical Company was placed in a reaction vessel and 10gms of acrylic acid was added under constant stirring. 25gms of ArF thinner was then added. After 4-5 hrs shaking the solution was filtered with 0.2µm filter.

Composition Example 5

4 gms of ethylene glycol and 20 gms of zirconium acetate solution in diluted acetic acid(16wt% Zr) from Aldrich Chemical Company were added to a reaction vessel and slowly heated to remove the water from the solution, increasing the viscosity of the precursor and ultimately forming a gel. 2 gms of acrylic acid was added followed by 40gms PGMEA.

Composition Example 6

20.0g of Zirconium oxide propionate from Gelest Inc., Morrisville PA was placed into a reaction vessel and 180g of PGMEA was added. After shaking overnight the formulation was filtered through a 0.2µm filter. 22.2g of a 10% solution of the polymer of Example 9 in ArF Thinner was added to give a composition with a 90/10 proportion of metal oxide to polymer and filtered again through a 0.2µm filter.

Composition Example 7

20.0g of Zirconium oxide propionate from Gelest Inc., Morrisville PA was placed into a reaction vessel and 180g of PGMEA was added. After shaking overnight the formulation was filtered through a 0.2µm filter. 50.0g of a 10% solution of the polymer of Example 9 in ArF Thinner was added to give a composition with a 80/20 proportion of metal oxide to polymer and filtered again through a 0.2µm filter.

Composition Example 8

20.0g of Zirconium oxide propionate from Gelest Inc., Morrisville PA was placed into a reaction vessel and 180g of PGMEA was added. After shaking overnight the formulation was filtered through a 0.2µm filter. 85.7g of a 10% solution of the polymer of Example 9 in ArF Thinner was added to give a composition with a 70/30 proportion of metal oxide to polymer and filtered again through a 0.2µm filter.

Polymer synthesis Example 9

9.7 g of 1,1,1-trifluoro-2-trifluoromethyl-2-hydroxy-4-pentyl methacrylate, 5.8 g of benzyl methacrylate, 5.1 g of 2-hydroxyethyl methacrylate and 6.4 g of glycidyl methacrylate, were mixed with in 120 g of tetrahydrofuran (THF) solvent. The polymerization reaction took place in the presence of 1.0 g of

azobisisobutyronitrile (AIBN) at 75°C under nitrogen for 20 hrs. After cooling down to room temperature, the reaction mixture was precipitated in deionized (DI) water. The white polymer solid was washed and dried under vacuum at 45°C with a yield of 26.5 g (99%). The M_W of polymer measured by GPC was 19,000.

Evaluation of Resistance to Solvents and Developer

Propyleneglycol monomethylether acetate/propyleneglycol monomethylether (PGMEA/PGME) 70:30 solvent was dispensed on the silicon wafer coated with materials from Composition Examples 1, 6, 7 and 8 at indicated temperatures in Table 1. Nitrogen blowing was used to remove the solvent after 60 seconds. No significant film losses were observed. Similar experiments were performed with developer 2.38 % wt/wt tetramethyl ammonium hydroxide (TMAH). The films from Table 1 and Table 2 showed good resistance to developer.

TABLE 1: Soak Test of Films in Various Solvents

Composition	Cure parameters	Soak Solvent (60 sec)	Result
Example 1	250°C/120 sec	TMAH 70/30 PGMEA/PGME Ethyl lactate	All passed
Example 6	240°C/ 60 sec		
Example 7	240°C/ 60 sec		
Example 8	240°C/ 60 sec		

Evaluation of the Refractive Index (n) and Extinction coefficient (k)

The n and k values can be calculated using an ellipsometer, such as the J. A. Woollam WVASE VU-32™ Ellipsometer. The exact values of the optimum ranges for k and n are dependent on the exposure wavelength used and the type of application. Typically for 193 nm the preferred range for k is about 0.1 to about

0.6, and for 248 nm the preferred range for k is about 0.15 to about 0.8, however, other exposure wavelengths such as, for example DUV and beyond DUV can be used and the compositions tuned to work in conjunction with them, as shown in Table 2, below.

TABLE 2: Refractive Index (n) and Extinction Coefficient (k) of Composition Examples

Composition	Cure Temp	Film Thickness (Å)	n@ 193nm	k@ 193nm	n@ 248nm	k@ 248nm	n@ 633nm	k@ 633nm
Example 1	250°C/120sec	260.82	2.0633	0.28212	1.7633	0.0003	1.5811	0.001
Example 6	240°C/60sec	496.61	2.0040	0.22040	1.7294	0	1.578	0
Example 7	240°C/60sec	433.52	1.9534	0.22186	1.6912	0	1.5544	0
Example 8	240°C/60sec	551.23	1.9114	0.22123	1.668	0	1.5397	0

Evaluation of the Bulk Etch Resistance

The bulk etch resistance of the cured films in Table 3 were carried out using CF_4 etchant. The coatings were subjected to the etchant for 60 or 40 seconds at a power of 500 watts and base pressure of 137 Pa. The etch rates were based on the average of 2 wafers.

TABLE 3: Bulk Etch Resistance of examples in CF_4

Formulation	Initial Film Thickness (Å)	Change in Film Thickness (Å)	Etch Rate Å/sec
Example 1	4033	120.5 (60 sec)	6.03
Example 7	4759	47 (60 sec)	2.35
Example 3	2136	109 (40 sec)	2.72
Example 2	1977	135 (40 sec)	3.36

Evaluation of the Bulk Etch Resistance

The bulk etch resistance of the cured films with materials from Example 1, at 250^{O}C/120 sec. bake, were carried out using different gases, under the condition of 2 Pa/Chamber 500W/ Platen 200W/ 40 sccm Cl_2/ 4 sccm CF_4/ 25sccm Ar/ 266Pa He.Back Pressure /20deg C Electrode Temp using ULVAC NE5000N from ULVAC Technologies, Inc. 401 Griffin Brook Drive, Methuen, MA.

TABLE 4: Bulk Etch Resistance in different gases

Gas	Etch Rate nm/min
CF_4	53.0
O_2/N_2/Air	65.3
Cl_2/Ar/CF_4	46.2
Cl_2/O_2	29.7

Determination of Metal% in cured films

The metal % wt/wt in the cured metal oxide films were measured by elemental analysis and TGA weight loss measurement. The results from two methods were consistent. The metal content in the film from Example 1 was 60 weight% after 200^{O}C for about 60-120 seconds film heating.

Lithographic evaluation Example 1

The performance of the Zr metallic anti-reflective coating formulation was evaluated using AZ® 2110P photoresist (product of AZ Electronic Materials USA Corp., Somerville, NJ). A silicon wafer was coated with Composition Example 1 and baked at 240°C for 60 seconds to form a 200 nm thick film. Then using AZ® EXP AX2110P photoresist film of 160 nm was coated on top and baked at 100°C for 60 seconds. The wafer was then imaged using a 193 nm Nikon 306D

exposure tool with a Numerical Aperture (NA) of 0.85, with Y-Dipole Illumination of 0.85 outer sigma, and 0.55 inner sigma. The exposed wafer was then baked at 110°C for 60 seconds and developed using AZ® 300MIF developer (TMAH) (product of AZ Electronic Materials USA Corp., Somerville, NJ) for 30 seconds. The top down and cross-section patterns when observed under scanning electron microscope showed no significant collapse in the process window. Pattern profile was observed at Line/Space 81.67nm 1:1 with photospeed of 36 mJ/cm^2.

Lithographic evaluation Example 2

The performance of the Zr metallic anti-reflective coating formulation was evaluated using AZ® 2110P photoresist (product of AZ Electronic Materials USA Corp., Somerville, NJ). A silicon wafer was coated with Formulation from Example 1 and baked at 350°C for 120 seconds to form a 200 nm thick film. Then using AZ® EXP AX2110P photoresist film of 160 nm was coated on top and baked at 100°C for 60 seconds. The wafer was then imaged using a 193 nm Nikon 306D exposure tool with a Numerical Aperture (NA) of 0.85, with Y-Dipole Illumination with a 0.85 outer sigma, and 0.55 inner sigma. The exposed wafer was then baked at 110°C for 60 seconds and developed using AZ® 300MIF developer (TMAH) for 30 seconds. The top down and cross-section patterns when observed under scanning electron microscope showed no significant collapse in the process window. Pattern profile was observed at Line/Space 80 nm, 160 nm pitch photospeed of 30 mJ/cm^2.

We claim:

1. A spin-on composition comprising at least one metal oxide dicarboxylate and an organic solvent, where the metal oxide dicarboxylate is soluble or colloidally stable in the solvent, and wherein the metal oxide dicarboxylate is capable of decomposing during heat treatment to give a cured metal oxide film.

2. The composition of claim 1, wherein the carboxylate of the dicarboxylate is selected from a group consisting of a substituted C_3 – C_6 carboxylate, unsubstituted C_3 – C_6 carboxylate, saturated C_3 – C_6 carboxylate, unsaturated C_3 – C_6 carboxylate, branched C_3 – C_6 carboxylate and unbranched C_3 – C_6 carboxylate, and is probably propionate.

3. The composition of claim 1 or 2, wherein the metal in the metal oxide dicarboxylate is at least one high refractive metal selected from Ti, V, Cr, Zr, Nb, Mo, Ru, Rh, Hf, Ta, W, Re, and Ir.

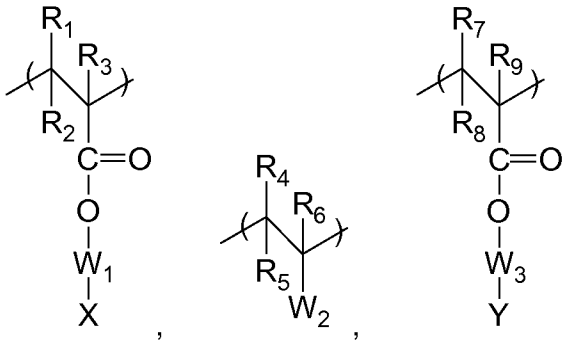
4. The composition of one of claims 1 to 3, wherein the metal oxide dicarboxylate is a nanoparticle.

5. The composition of one of claims 1 to 4, wherein the metal oxide dicarboxylate is zirconium oxide dicarboxylate or titanium oxide dicarboxylate.

6. The composition of one of claims 1 to 5, further comprising at least one polymer selected from a group consisting of an organic polymer, an inorganic polymer, and mixtures thereof.

7. The composition of claim 6, where the polymer can comprise at least one unit of structure (1) comprising a hydrophobic moiety, at least one unit of structure (2) comprising a chromophore moiety, at least one unit of structure (3) comprising a crosslinking moiety (3) and optionally a unit comprising a group

capable of crosslinking the polymer, where the structures 1-3 may be represented by,



(1) (2) (3)

where R_1 to R_9 are independently selected from hydrogen and C_1-C_4 alkyl; W_1 is a fully or partially fluorinated group; X is selected from a group consisting of F, H, and OH; W_2 is an organic moiety comprising a chromophore group, and W_3 Y comprises a crosslinking site.

8. A method of manufacturing an electronic device comprising:

a. applying a composition of one of claims 1 to 7 to form a metal oxide dicarboxylate film, and

b. heating the coated substrate, thereby forming a cured metal oxide film.

9. The method of claim 8, wherein the metal content of the metal oxide film after the heating step is in the range of 10 to 85 weight%.

10. The method of claim 8 or 9, wherein a photoresist film is formed above the metal film.

11. The method of one of claims 8 to 10, wherein the photoresist film is imaged with radiation in the range of about 12 nm to about 250 nm and developed to form a pattern.

12. The method of one of claims 8 to 11, where the heating step is in the range of 200ºC to 500 ºC.

13. The method of one of claims 8 to 12, where the metal is zirconium or titanium.

14. The method of one of claims 8 to 13, wherein the metal content of the metal oxide film after the heating step is in the range of 10 to 70 weight%.