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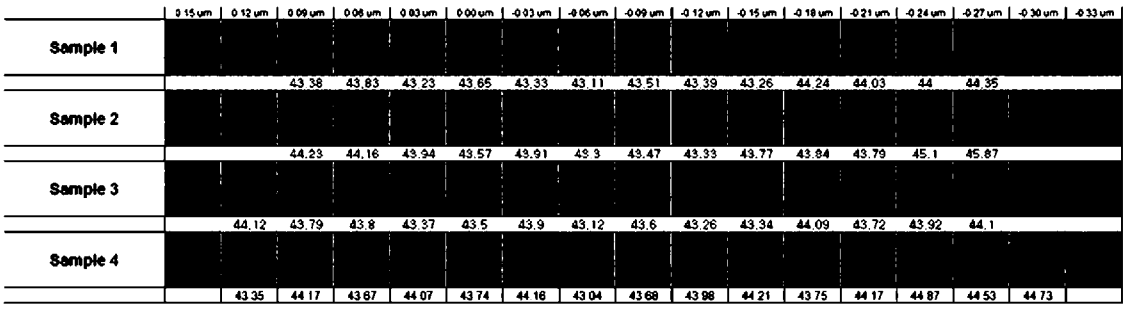
(54) Title: COATING COMPOSITIONS FOR USE WITH AN OVERCOATED PHOTORESIST

FIG. 1



(57) Abstract: Organic coating compositions, particularly antireflective coating compositions for use with an overcoated photoresist, are provided that comprise 1) one or more resins and 2) one or more PDQ compounds that are distinct from the 1) one or more resins.

WO 2018/229554 A2

COATING COMPOSITIONS FOR USE WITH AN OVERCOATED PHOTORESIST

RELATED APPLICATIONS

This application claims the benefit of priority to U.S. Application No. 15/626,872, filed June 19, 2017 which is a continuation application of U.S. Application No. 15624,699, filed June 15, 2017, the entire contents of which are incorporation herein by reference.

FIELD

The present invention relates to compositions and, in particular, antireflective coating compositions (for example, "BARCs"), for use in microelectronic applications. Compositions of the invention comprise one or more substituted photodecomposable quencher compounds.

BACKGROUND

Photoresists are photosensitive films used for the transfer of images to a substrate. A coating layer of a photoresist is formed on a substrate and the photoresist layer is then exposed through a photomask to a source of activating radiation. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of a substrate.

Reflection of activating radiation used to expose a photoresist often poses limits on resolution of the image patterned in the photoresist layer. Reflection of radiation from the substrate/photoresist interface can produce spatial variations in the radiation intensity in the photoresist, resulting in non-uniform photoresist linewidth upon development. Radiation also can scatter from the substrate/photoresist interface into regions of the photoresist where exposure is non-intended, again resulting in linewidth variations.

One approach used to reduce the problem of reflected radiation has been the use of a radiation absorbing layer interposed between the substrate surface and the photoresist coating layer. See U.S. 2016/0187778. See also US2011/0200935; US2012/0258405; and US2015/0346599.

Electronic device manufacturers continually seek increased resolution of a photoresist image patterned over antireflective coating layers.

SUMMARY

We now provide new coating compositions that can be used with overcoated photoresist compositions. In preferred aspects, coating compositions of the invention can function as an effective antireflective layer for an overcoated resist layer.

Preferred coating compositions may comprise 1) one or more resins (sometimes referred to herein as matrix resins) and 2) one or more substituted photodecomposable quencher compounds (PDQ) compounds that are distinct from the 1) one or more resins.

Without being bound by any theory, it is believed that use of a preferred PDQ compound as disclosed herein can minimize migration of photogenerated acid from exposed regions of an overcoated resist layer into unexposed regions of the coated substrate, including unexposed regions at the resist/underlying layer interface. That is, the PDQ in the underlying layer can inhibit undesired flow of photogenerated acid to unexposed regions of the resist and underlying coating layers.

We have found that use of one or more preferred PDGs in an underlying coating composition can provide enhanced lithographic results. See the comparative results set forth in the Examples which follow.

In one aspect, preferred PDQ compounds will react upon exposure to radiation employed to image an overcoated photoresist layer. Exemplary imaging radiation is 193 nm and EUV. In particular, preferred PDQ compounds will react to liberate upon exposure to radiation employed to image an overcoated photoresist layer together with a post-exposure bake (e.g. treatment at 100°C for 30 to 60 seconds), such as by dissociation of an ionic complex (.e. onium salt) to liberate the acidic anion component.

In another aspect, preferred PDQ compounds are non-polymeric compounds. Suitable PDQ compounds may have a molecular weight of less than 3,000, or more typically a molecular weight less than 2500, or less than 2000, or less than 1500, or less than 1000 or less than 800, 700, 600 or 500.

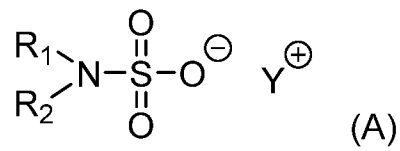
In yet another aspect, preferred PDQ compounds are ionic compounds. Preferred ionic compounds to use as a PDQ compound are onium salts such as sulfonium or iodonium compounds.

In a further aspect, preferred PDQ compounds may have anions having high pKa (e.g. sulfamate having pKa greater than 0 or carboxylate having pKa greater than 3). As referred to herein, pKa values are in aqueous solution at 23° C and can be measured experimentally or calculated, for example using Advanced Chemistry Development (ACD) Labs Software Version 11.02.

Preferred PDQs generate weaker acids than produced by the photoacid generator compounds of an overcoated resist layer. Thus, without being bound by theory, as the strong acid generated by the photoacid generator in the exposed region migrates to the unexposed photoresist bottom region and then photo-destroyable quencher with higher pKa in the unexposed region quenches a strong acid diffused from exposed region. This can result in neutralization of strong acid in the unexposed region.

Thus, in certain preferred aspects, an acidic component of a PDQ in an underlying coating composition will differ in pKa by 0.5, 1, 2, 3 or 4 or more from the acidic component of a photoacid generator compound of an overcoated photoresist composition layer.

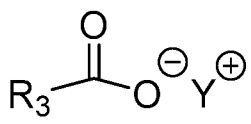
Particularly preferred PDQ compounds may include a formula (A),



(A)

wherein R_1 and R_2 are each independently hydrogen, substituted or unsubstituted alkyl (e.g. C_1-C_{12} alkyl), substituted or unsubstituted cycloalkyl (e.g. C_3-C_{12} cycloalkyl), or substituted or unsubstituted aryl (e.g. 5 to 12 membered aryl or phenyl); and Y is a cation such as a sulfonium cation.

Particularly also preferred PDQ compounds may include a formula (B),



(B)

wherein R_3 is substituted or unsubstituted alkyl (e.g. C_1-C_{12} alkyl), substituted or unsubstituted cycloalkyl (e.g. C_3-C_{12} cycloalkyl), or substituted or unsubstituted aryl (e.g. 5 to 12 membered aryl or phenyl); and Y is a cation such as a sulfonium cation.

In certain preferred aspects, the one or more resins also may comprise one or more PDQ moieties either as pendant groups or integral units of a resin chain.

Coating compositions of the invention also may comprise a crosslinker component that is distinct from the PDQ compound and the resin. In preferred crosslinking compositions, a coating layer of the composition may harden or crosslink upon thermal treatment of 60, 90, 120 or 180 second at 180 °C, 200 °C or 250 °C or more.

For antireflective applications, underlying compositions of the invention also preferably contain a component that comprises chromophore groups that can absorb undesired radiation used to expose the overcoated resist layer from reflecting back into the resist layer. The matrix polymer or substituted PDQ compound may comprise such chromophore groups, or a coating composition may comprise a further component that comprises suitable chromophore groups.

Particularly preferred coating compositions of the invention also may contain a thermal acid (TAG) generator compound that can promote hardening of an applied composition coating layer. Preferred coating compositions may comprise 1) one or more resins (sometimes referred to herein as matrix resins); 2) one or more substituted photodecomposable quencher compounds (PDQ) compounds that are distinct from the 1) one or more resins; and 3) one or more thermal acid generator compounds (TAG) that is distinct form the 1) one or more resins and 2) one or more PDQ compounds. Preferred underlying coating compositions may further comprise a crosslinker component that is distinct from the 1) one or more resins, the 2) one or more PDQ compounds and 3) one or more TAGs.

In use with an overcoated photoresist, a coating composition may be applied on a substrate such as a semiconductor wafer which may have one or more organic or inorganic coating layers thereon. The applied coating layer may be optionally thermally treated prior to overcoating with a photoresist layer. In the case of crosslinking compositions, such thermal treatment may cause hardening including crosslinking of the coating composition layer. Such crosslinking may include hardening and/or covalent-bonding forming reactions between one or more composition components and can modulate water contact angle of the coating composition layer.

Thereafter, a photoresist composition may be applied over the coating composition layer followed by imaging of the applied photoresist composition layer with patterned activating radiation and the imaged photoresist composition layer is developed to provide a photoresist relief image.

A variety of photoresists may be used in combination (i.e. overcoated) with a coating composition of the invention. Preferred photoresists for use with the underlying coating compositions of the invention are chemically-amplified resists, especially positive-tone and negative-tone photoresists that contain one or more photoactive compounds and a resin component that contains units that undergo a deblocking or cleavage reaction in the presence of photogenerated acid.

In certain preferred aspects, the photoresist composition is designed for a negative-tone resist where the light-exposed regions remains after development process, but positive tone development can be also employed to remove the exposed portions of the photoresist layer.

The invention further provides methods for forming a photoresist relief image and novel articles of manufacture comprising substrates (such as a microelectronic wafer substrate) coated with a coating composition of the invention alone or in combination with a photoresist composition.

Other aspects of the invention are disclosed infra.

BRIEF DESCRIPTION OF THE DRAWING

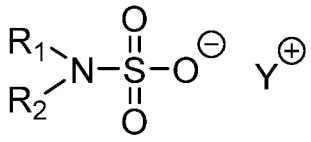
Figure 1 shows scanning electron micrographs of imaged photoresist/underlying coating layer samples and comparative sample.

DETAILED DESCRIPTION

We now provide new organic coating compositions that are particularly useful with an overcoated photoresist layer. As discussed above, preferred coating compositions may comprise 1) a matrix polymer; and 2) one or more PDQ compounds. Preferred coating compositions of the invention may be applied by spin-coating (spin-on compositions) and formulated as a solvent composition. The coating compositions of the invention are especially

useful as antireflective compositions for an overcoated photoresist and/or as planarizing or via-fill compositions for an overcoated photoresist composition coating layer.

Particularly preferred PDQ compounds may have a formula (A),



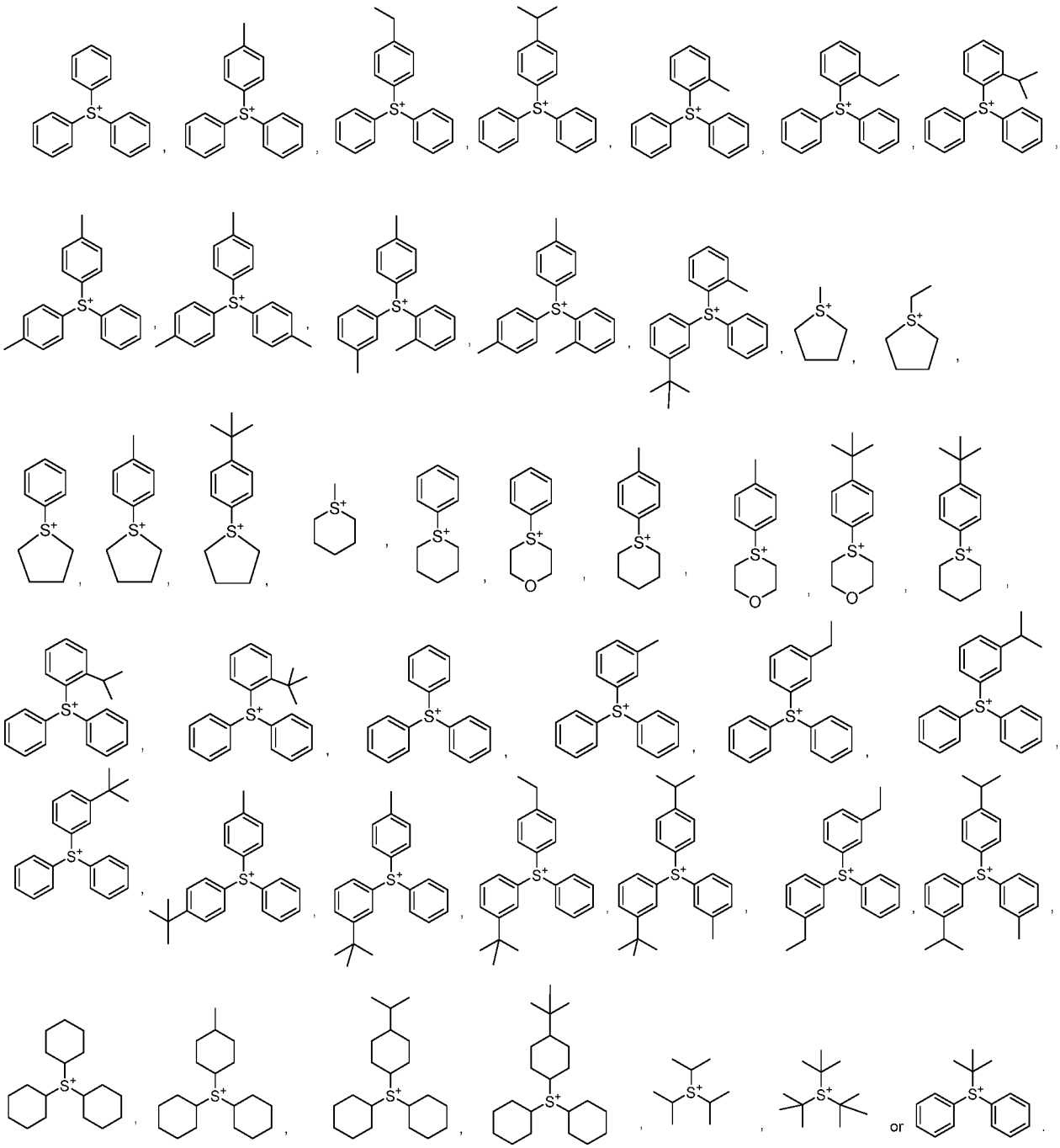
(A)

wherein R_1 and R_2 are each independently hydrogen, substituted or unsubstituted alkyl (e.g. C_1-C_{12} alkyl), substituted or unsubstituted cycloalkyl (e.g. C_3-C_{12} cycloalkyl), or substituted or unsubstituted aryl (e.g. 5 to 12 membered aryl or phenyl); and Y is a cation, such as a sulfonium group.

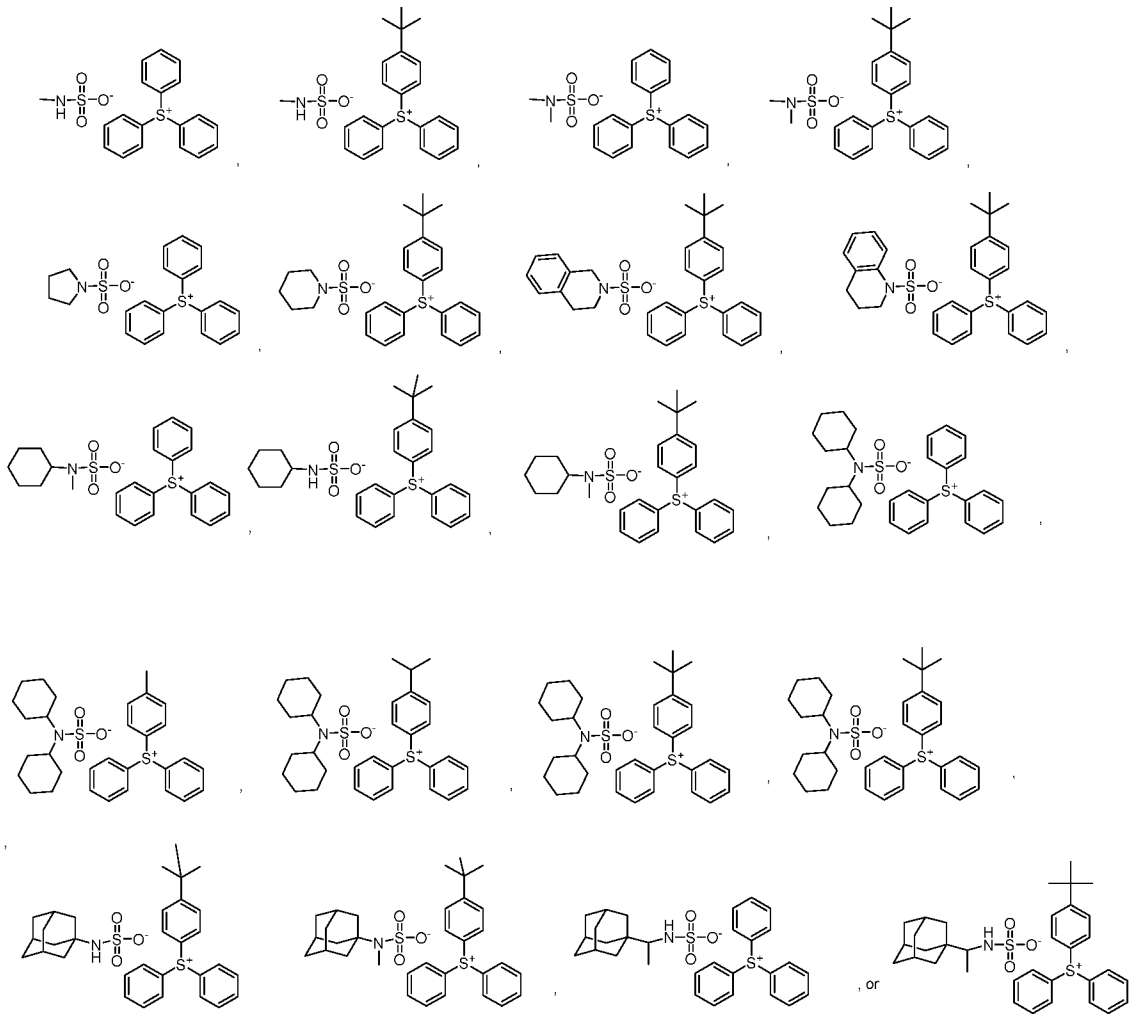
Preferred R_1 and R_2 are independently hydrogen or C_1-C_4 alkyl which may be optionally substituted with methyl, ethyl, cyclohexyl, cyclopentyl and adamantyl. Other preferred R_1 and R_2 are independently C_3-C_{12} cycloalkyl, such as cyclohexyl, cyclopentyl and adamantyl.

Preferred Y is a sulfonium cation that has C_1-C_{12} alkyl, 2-8 membered heteroalkyl, C_3-C_{12} cycloalkyl, 5-12 membered heterocycloalkyl, or 5-12 membered aryl (e.g. phenyl, naphthyl, or anthracenyl), each of which is optionally substituted with C_1-C_3 alkyl or C_3-C_{12} cycloalkyl. Other preferred Y is a sulfonium cation having with phenyl, cyclopentyl, cyclohexyl, adamantyl, methyl, ethyl, propyl, butyl, t-butyl, or isopropyl, each of which is optionally substituted with linear or branched C_1-C_4 alkyl such as methyl, ethyl, propyl, butyl, t-butyl, or isopropyl. Further preferred Y includes a 5-6 membered heterocycloalkyl which is formed by a sulfur atom together with alkyl substituents.

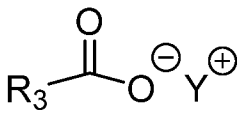
Exemplary preferred anion Y may include:



Exemplary PDQ compound having a formula (A) may include:



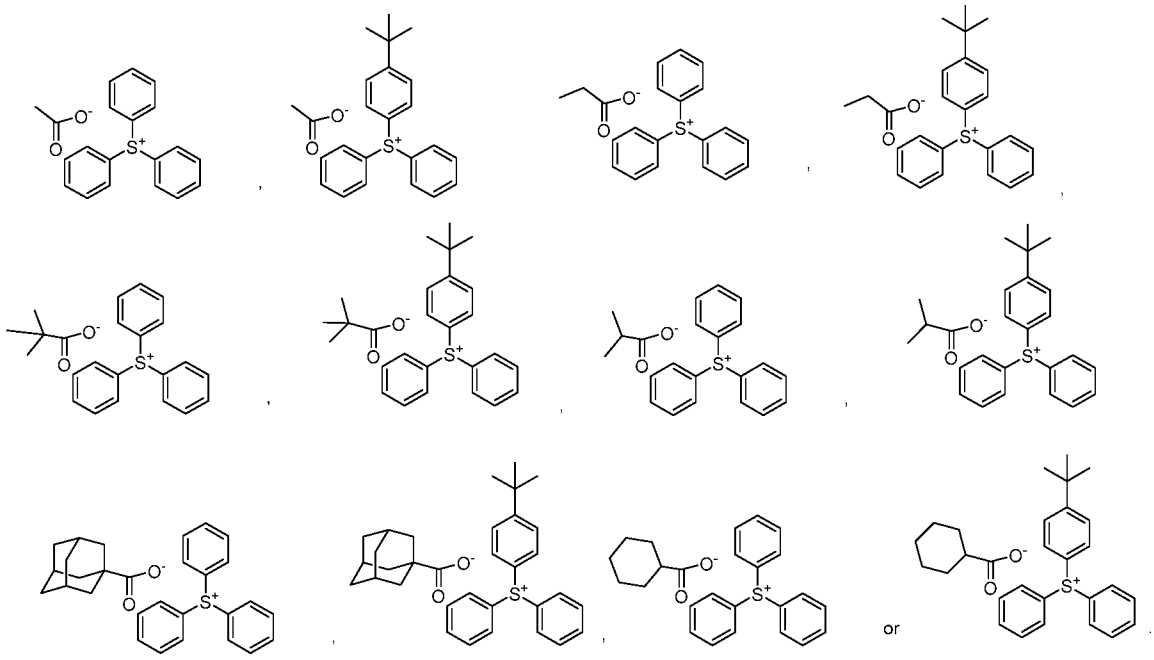
Particularly also preferred PDQ compounds may include a formula (B),



(B)

wherein R_3 is substituted or unsubstituted alkyl (e.g. C_1-C_{12} alkyl), substituted or unsubstituted cycloalkyl (e.g. C_3-C_{12} cycloalkyl), or substituted or unsubstituted aryl (e.g. 5 to 12 membered aryl or phenyl); and Y is described herein. Preferred R_3 may include C_1-C_4 alkyl, which may be linear or branched and optionally substituted. Other preferred R_3 is C_3-C_{12} cycloalkyl, such as cyclohexyl, cyclopentyl and adamantyl, or is phenyl, which may be optionally substituted.

Exemplary PDQ compound having a formula (B) may include:



PDQ compounds are commercially available or can be readily synthesized. See the examples which follow.

As referred to herein, suitable heteroalkyl groups include optionally substituted C_1-C_{20} alkoxy, optionally substituted alkylthio preferably having 1 to about 20 carbon atoms; optionally substituted alkylsulfinyl preferably 1 to about 20 carbon atoms; optionally substituted alkylsulfonyl preferably having 1 to about 20 carbon atoms; and optionally substituted alkylamine preferably having 1 to about 20 carbon atoms.

Various materials and substituents that are "optionally substituted" may be suitably substituted at one or more available positions by e.g. halogen (F, Cl, Br, I); nitro; hydroxy; amino; alkyl such as C_{1-4}alkyl; alkenyl such as C_{2-8} alkenyl; alkylamino such as C_{1-8} alkylamino; carbocyclic aryl such as phenyl, naphthyl, anthracenyl, etc; and the like.

Preferably, the one or more resins and one or more substituted PDQ compounds are distinct materials, i.e. the one or more resins and the one or more substituted PDQ compounds are not covalently linked.

One or more substituted PDQ compounds are suitably present in a coating composition in an amount of from 0.1 weight percent to 10, 15, 20, 30, 40 or more weight

percent based on weight of total solids of a coating composition, more typically from 1, 2, or 3 weight percent to 5, 10, 15, or 20 or more weight percent based on weight of total solids of a coating composition. Total solids as referred to herein

A variety of resins may serve as the matrix polymer of an underlying coating composition.

Particularly preferred matrix resins of coating compositions of the invention may comprise polyester linkages. Polyester resins can be readily prepared by reaction of one or more polyol reagents with one or more carboxy-containing (such as a carboxylic acid, ester, anhydride, etc.) compounds. Suitable polyol reagents include diols, glycerols and triols such as e.g. diols such as diol is ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, butane diol, pentane diol, cyclobutyl diol, cyclopentyl diol, cyclohexyl diol, dimethylolcyclohexane, and triols such as glycerol, trimethylolethane, trimethylolpropane and the like.

Matrix resins of coating compositions of the invention may comprise a variety of additional groups such as cyanurate groups, as disclosed in U.S. Patent 6852421 and 8501383.

Particularly preferred matrix resins of coating compositions of the invention may comprise one or more one or more cyanurate groups and polyester linkages.

As discussed, for antireflective applications, suitably one or more of the compounds reacted to form the resin comprise a moiety that can function as a chromophore to absorb radiation employed to expose an overcoated photoresist coating layer. For example, a phthalate compound (e.g. a phthalic acid or dialkyl phthalate (i.e. di-ester such as each ester having 1-6 carbon atoms, preferably a di-methyl or ethyl phthalate) may be polymerized with an aromatic or non-aromatic polyol and optionally other reactive compounds to provide a polyester particularly useful in a coating composition employed with a photoresist imaged at sub-200 nm wavelengths such as 193 nm. An PDQ compound also may be polymerized with one or more polyols to provide a resin useful in the present underlying coating compositions. Resins to be used in compositions with an overcoated photoresist imaged at sub-300 nm wavelengths or sub-200 nm wavelengths such as 248 nm or 193 nm, a naphthyl compound may be polymerized, such as a naphthyl compound containing one or two or more carboxyl substituents e.g. dialkyl particularly di-C_{1-6}alkyl

naphthalenedicarboxylate. Reactive anthracene compounds also are preferred, e.g. an anthracene compound having one or more carboxy or ester groups, such as one or more methyl ester or ethyl ester groups.

The compound that contains a chromophore unit also may contain one or preferably two or more hydroxy groups and be reacted with a carboxyl-containing compound. For example, a phenyl compound or anthracene compound having one, two or more hydroxyl groups may be reacted with a carboxyl-containing compound.

Additionally, underlying coating compositions that are employed for antireflective purposes may contain a material that contains chromophore units that is separate from a resin component that provides water contact angle modulation (e.g. a resin that contains photoacid-labile groups and/or base-reactive groups. For instance, the coating composition may comprise a polymeric or non-polymeric compound that contains phenyl, anthracene, naphthyl, etc. units. It is often preferred, however, that the one or more resins that provide water contact angle modulation also contain chromophore moieties.

Preferably matrix resins of underlying coating compositions of the invention will have a weight average molecular weight (Mw) of about 1,000 to about 10,000,000 daltons, more typically about 2,000 to about 100,000 daltons, and a number average molecular weight (Mn) of about 500 to about 1,000,000 daltons. Molecular weights (either Mw or Mn) of the polymers of the invention are suitably determined by gel permeation chromatography.

The matrix polymer will be the major solids component of an underlying coating composition in many preferred embodiments. For instance, the matrix polymer suitably may be present from 50 to 99.9 weight percent based on total solid content of a coating composition, more typically from 80 to 95 weight percent based total solid content of a coating composition. As referred to herein, solids of a coating composition refer to all materials of the coating composition except solvent carrier.

As mentioned, preferred underlying coating compositions of the invention can be crosslinked, e.g. by thermal and/or radiation treatment. For example, preferred underlying coating compositions of the invention may contain a separate crosslinker component that can crosslink with one or more other components of the coating composition. Generally preferred crosslinking coating compositions comprise a separate crosslinker component.

A variety of crosslinkers may be employed, including those crosslinkers disclosed in European Application 542008. For example, suitable coating composition crosslinkers include amine-based crosslinkers such as melamine materials, including melamine resins such as manufactured by Cytec Industries and sold under the tradename of Cymel 300, 301, 303, 350, 370, 380, 1116 and 1130. Glycolurils are particularly preferred including glycolurils available from Cytec Industries. Benzoquanamines and urea-based materials also will be suitable including resins such as the benzoquanamine resins available from Cytec Industries under the name Cymel 1123 and 1125, and urea resins available from Cytec Industries under the names of Powderlink 1174 and 1196. In addition to being commercially available, such amine-based resins may be prepared e.g. by the reaction of acrylamide or methacrylamide copolymers with formaldehyde in an alcohol-containing solution, or alternatively by the copolymerization of N-alkoxymethyl acrylamide or methacrylamide with other suitable monomers.

A crosslinker component of a coating composition of the invention in general is present in an amount of between about 5 and 50 weight percent of total solids (all components except solvent carrier) of the coating composition, more typically in an amount of about 5 to 25 weight percent total solids.

As discussed, particularly preferred coating compositions of the invention also may contain a thermal acid (TAG) generator compound. Thermal-induced crosslinking of the coating composition by activation of the thermal acid generator is generally preferred. As discussed, an underlying coating composition layer may be suitably applied on a substrate surface thermally treated to activate i.e. generate liberated acid from the TAG and harden or crosslink one or more composition components. Thereafter, a photoresist layer may be applied over the hardened underlying layer.

Suitable thermal acid generator compounds for use in a coating composition include ionic or substantially neutral thermal acid generators, e.g. an ammonium arenesulfonate salt (e.g. toluene sulfonic acid ammonium salt), for catalyzing or promoting crosslinking during curing of an antireflective composition coating layer. Typically one or more thermal acid generators are present in an coating composition in a concentration from about 0.1 to 10 percent by weight of the total of the dry components

of the composition (all components except solvent carrier), more preferably about 0.5 to 2 percent by weight of the total dry components.

Coating compositions of the invention, particularly for reflection control applications, also may contain additional dye compounds that absorb radiation used to expose an overcoated photoresist layer. Other optional additives include surface leveling agents, for example, the leveling agent available under the tradename Silwet 7604, or the surfactant FC 171 or FC 431 available from the 3M Company.

Underlying coating compositions of the invention also may contain other materials such as a photoacid generator, including a photoacid generator as discussed for use with an overcoated photoresist composition. See U.S. Patent 6261743 for a discussion of such use of a photoacid generator in an antireflective composition.

To make a liquid coating composition of the invention, the components of the coating composition are dissolved in a suitable solvent such as, for example, one or more oxyisobutyric acid esters particularly methyl-2-hydroxyisobutyrate, ethyl lactate or one or more of the glycol ethers such as 2-methoxyethyl ether (diglyme), ethylene glycol monomethyl ether, and propylene glycol monomethyl ether; solvents that have both ether and hydroxy moieties such as methoxy butanol, ethoxy butanol, methoxy propanol, and ethoxy propanol; methyl 2-hydroxyisobutyrate; esters such as methyl cellosolve acetate, ethyl cellosolve acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether acetate and other solvents such as dibasic esters, propylene carbonate and gamma-butyro lactone. The concentration of the dry components in the solvent will depend on several factors such as the method of application. In general, the solid content of an underlying coating composition varies from about 0.5 to 20 weight percent of the total weight of the coating composition, preferably the solid content varies from about 0.5 to 10 weight of the coating composition.

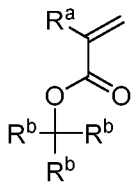
Exemplary photoresist systems

Photoresists for use with an underlying coating composition typically comprise a polymer and one or more acid generators. Generally preferred are positive-tone resists and the resist polymer has functional groups that impart alkaline aqueous solubility to the resist composition. For example, preferred are polymers that comprise polar functional groups such as hydroxyl or carboxylate, or acid-labile groups that can liberate such polar moieties

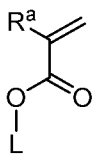
upon lithographic processing. Preferably the polymer is used in a resist composition in an amount sufficient to render the resist developable with an aqueous alkaline solution.

Acid generators are also suitably used with polymers that comprise repeat units containing aromatic groups, such as optionally substituted phenyl including phenol, optionally substituted naphthyl, and optionally substituted anthracene. Optionally substituted phenyl (including phenol) containing polymers are particularly suitable for many resist systems, including those imaged with EUV and e-beam radiation. For positive-acting resists, the polymer also preferably contains one or more repeat units that comprise acid-labile groups. For example, in the case of polymers containing optionally substituted phenyl or other aromatic groups, a polymer may comprise repeat units that contain one or more acid-labile moieties such as a polymer that is formed by polymerization of monomers of an acrylate or methacrylate compound with acid-labile ester (e.g. t-butyl acrylate or t-butyl methacrylate). Such monomers may be copolymerized with one or more other monomers that comprise aromatic group(s) such as optionally phenyl, e.g. a styrene or vinyl phenol monomer.

Preferred monomers used for the formation of such polymers include: an acid-labile monomer having the following formula (V), a lactone-containing monomer or polarity control monomer of the following formula (VI), or a combination comprising at least one of the foregoing monomers:



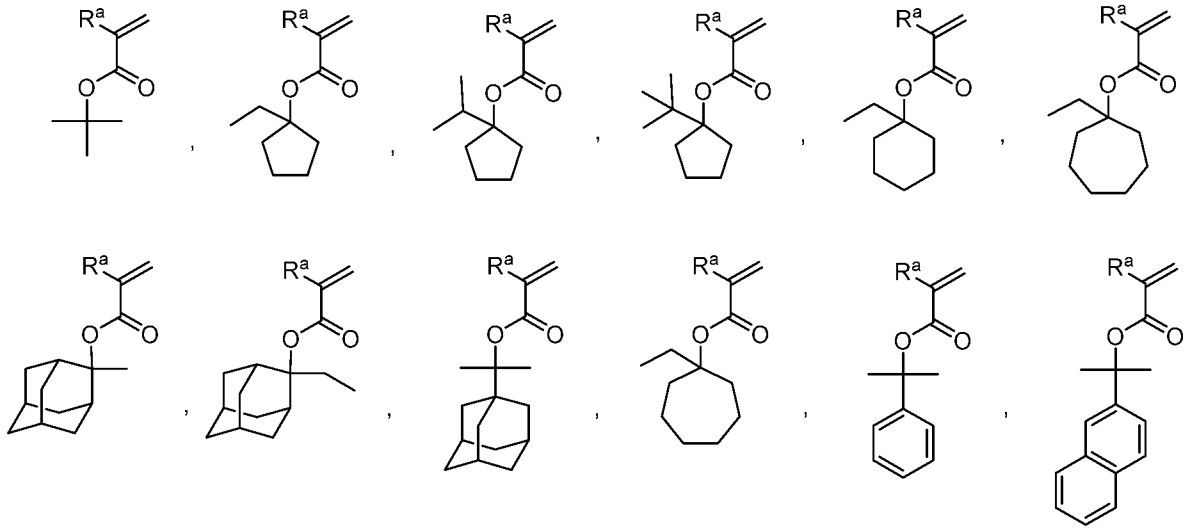
(V)



(VI)

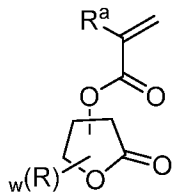
wherein each R^a is independently H, F, -CN, C_{1-10} alkyl, or C_{1-10} fluoroalkyl. In the acid-deprotectable monomer of formula (V), R^b is independently C_{1-20} alkyl, C_{3-20} cycloalkyl, C_{6-20} aryl, or C_{7-20} aralkyl, and each R^b is separate or at least one R^b is bonded to an adjacent R^b to form a cyclic structure. In lactone-containing monomer of formula (VI), L is a monocyclic, polycyclic, or fused polycyclic C_{4-20} lactone-containing group.

Exemplary acid-deprotectable monomers include but are not limited to:



or a combination comprising at least one of the foregoing, wherein R^a is H, F, -CN, C_{1-6} alkyl, or C_{1-6} fluoroalkyl.

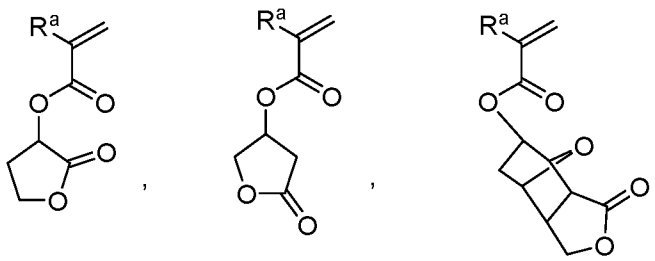
Suitable lactone monomers may be of the following formula (IX):



(IX)

wherein R^a is H, F, -CN, C_{1-6} alkyl, or C_{1-6} fluoroalkyl, R is a C_{1-10} alkyl, cycloalkyl, or heterocycloalkyl, and w is an integer of 0 to 5. In formula (IX), R is attached directly to the lactone ring or commonly attached to the lactone ring and/or one or more R groups, and the ester moiety is attached to the lactone ring directly, or indirectly through R.

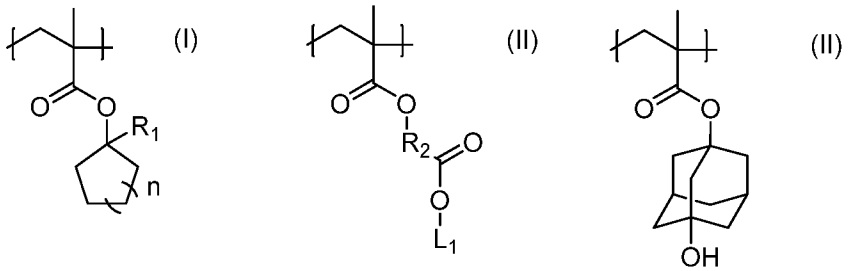
Exemplary lactone-containing monomers include:



or a combination comprising at least one of the foregoing monomers, wherein R^a is H, F, -CN, C_{1-10} alkyl, or C_{1-10}fluoroalkyl.

Specifically suitable polymers that have acid-labile deblocking groups for use in a positive-acting chemically-amplified photoresist of the invention have been disclosed in European Patent Application 0829766A2 (polymers with acetal and ketal polymers) and European Patent Application EP0783136A2 (terpolymers and other copolymers including units of 1) styrene; 2) hydroxystyrene; and 3) acid labile groups, particularly alkyl acrylate acid labile groups.

Additional preferred resins for use in photoresists to be imaged at sub-200 nm, such as at 193 nm, comprises units of the following general formulae (I), (II) and (III):



wherein: R_1 is a (C_1-C_3)alkyl group; R^2 is a (C_1-C_3)alkylene group; Li is a lactone group; and n is 1 or 2.

Polymers for use in photoresists of the invention may suitably vary widely in molecular weight and polydisperity. Suitable polymers include those that have an M_w, of from about 1,000 to about 50,000, more typically about 2,000 to about 30,000 with a molecular weight distribution of about 3 or less, more typically a molecular weight distribution of about 2 or less.

Preferred negative-acting compositions of the invention comprise a mixture of materials that will cure, crosslink or harden upon exposure to acid, and two or more acid generators as disclosed herein. Preferred negative acting compositions comprise a polymer binder such as a phenolic or non-aromatic polymer, a crosslinker component and a photoactive component of the invention. Such compositions and the use thereof have been disclosed in European Patent Applications 0164248 and U.S. Patent No. 5,128,232 to

Thackeray et al. Preferred phenolic polymers for use as the polymer binder component include novolaks and poly(vinylphenol)s such as those discussed above. Preferred crosslinkers include amine-based materials, including melamine, glycolurils, benzoguanamine-based materials and urea-based materials. Melamine-formaldehyde polymers are often particularly suitable. Such crosslinkers are commercially available, e.g. the melamine polymers, glycoluril polymers, urea-based polymer and benzoguanamine polymers, such as those sold by Cytec under tradenames Cymel 301, 303, 1170, 1171, 1172, 1123 and 1125 and Beetle 60, 65 and 80.

Particularly preferred photoresists of the invention may be used in immersion lithography applications. See, for example, U.S. 7968268 to Rohm and Haas Electronic Materials for a discussion of preferred immersion lithography photoresists and methods.

Photoresists of the invention also may comprise a single acid generator or a mixture of distinct acid generators, typically a mixture of 2 or 3 different acid generators, more typically a mixture that consists of a total of 2 distinct acid generators. The photoresist composition comprises an acid generator employed in an amount sufficient to generate a latent image in a coating layer of the composition upon exposure to activating radiation. For example, the acid generator will suitably be present in an amount of from 1 to 20 wt% based on total solids of the photoresist composition.

Suitable acid generators are known in the art of chemically amplified photoresists and include, for example: onium salts, for example, triphenylsulfonium trifluoromethanesulfonate, (p-tert-butoxyphenyl)diphenylsulfonium trifluoromethanesulfonate, tris(p-tert-butoxyphenyl)sulfonium trifluoromethanesulfonate, triphenylsulfonium p-toluenesulfonate; nitrobenzyl derivatives, for example, 2-nitrobenzyl-p-toluenesulfonate, 2,6-dinitrobenzyl-p-toluenesulfonate, and 2,4-dinitrobenzyl-p-toluenesulfonate; sulfonic acid esters, for example, 1,2,3-tris(methanesulfonyloxy)benzene, 1,2,3-tris(trifluoromethanesulfonyloxy)benzene, and 1,2,3-tris(p-toluenesulfonyloxy)benzene; diazomethane derivatives, for example, bis(benzenesulfonyl)diazomethane, bis(p-toluenesulfonyediazomethane; glyoxime derivatives, for example, bis-O-(p-toluenesulfony1)-α-dimethylglyoxime, and bis-O-(n-butanesulfony1)-α-dimethylglyoxime; sulfonic acid ester derivatives of an N-hydroxyimide

compound, for example, N-hydroxysuccinimide methanesulfonic acid ester, N-hydroxysuccinimide trifluoromethanesulfonic acid ester; and halogen-containing triazine compounds, for example, 2-(4-methoxypheny1)-4,6-bis(trichloromethyl)-1,3,5-triazine, and 2-(4-methoxynaphthyl)-4,6-bis(trichloromethyl)-1,3,5-triazine.

As referred to herein, acid generators can produce an acid when exposed to activating radiation, such as EUV radiation, e-beam radiation, 193 nm wavelength radiation or other radiation sources. Acid generator compounds as referred to herein also may be referred to as photoacid generator compounds.

Photoresists of the invention also may contain other materials. For example, other optional additives include actinic and contrast dyes, anti-striation agents, plasticizers, speed enhancers and sensitizers. Such optional additives typically will be present in minor concentration in a photoresist composition.

Alternatively, or in addition, other additives may include quenchers that are non-photo-destroyable bases, such as, for example, those based on hydroxides, carboxylates, amines, imines, and amides. Preferably, such quenchers include C_{1-30} organic amines, imines, or amides, or may be a C_{1-30} quaternary ammonium salt of a strong base (e.g., a hydroxide or alkoxide) or a weak base (e.g., a carboxylate). Exemplary quenchers include amines such as tripropylamine, dodecylamine, tris(2-hydroxypropyl)amine, oltetrakis(2-hydroxypropyl)ethylenediamine; aryl amines such as diphenylamine, triphenylamine, aminophenol, and 2-(4-aminopheny1)-2-(4-hydroxyphenyl)propane, a hindered amine such as diazabicycloundecene (DBU) or diazabicyclononene (DBN), or ionic quenchers including quaternary alkyl ammonium salts such as tetrabutylammonium hydroxide (TBAH) or tetrabutylammonium lactate.

Surfactants include fluorinated and non-fluorinated surfactants, and are preferably nonionic. Exemplary fluorinated non-ionic surfactants include perfluoro C_4 surfactants such as FC-4430 and FC-4432 surfactants, available from 3M Corporation; and fluorodiols such as POLYFOX PF-636, PF-6320, PF-656, and PF-6520 fluorosurfactants from Omnova.

The photoresist further includes a solvent generally suitable for dissolving, dispensing, and coating the components used in a photoresists. Exemplary solvents include anisole, alcohols including ethyl lactate, 1-methoxy-2-propanol, and 1-ethoxy-2 propanol, esters including n-butylacetate, 1-methoxy-2-propyl acetate, methoxyethoxypropionate,

ethoxyethoxypropionate, ketones including cyclohexanone and 2-heptanone, and a combination comprising at least one of the foregoing solvents.

Lithographic processing

In use, a coating composition of the invention is applied as a coating layer to a substrate by any of a variety of methods such as spin coating. The coating composition in general is applied on a substrate with a dried layer thickness of between about 0.02 and 0.5 μm, preferably a dried layer thickness of between about 0.04 and 0.20 μm. The substrate is suitably any substrate used in processes involving photoresists. For example, the substrate can be silicon, silicon dioxide or aluminum-aluminum oxide microelectronic wafers. Gallium arsenide, silicon carbide, ceramic, quartz or copper substrates may also be employed. Substrates for liquid crystal display or other flat panel display applications are also suitably employed, for example glass substrates, indium tin oxide coated substrates and the like. Substrates for optical and optical-electronic devices (e.g. waveguides) also can be employed.

Preferably the applied coating layer is cured before a photoresist composition is applied over the underlying coating composition. Cure conditions will vary with the components of the underlying coating composition. Particularly the cure temperature will depend on the specific acid or acid (thermal) generator that is employed in the coating composition. Typical cure conditions are from about 80°C to 225°C for about 0.5 to 5 minutes. Cure conditions preferably render the coating composition coating layer substantially insoluble to the photoresist solvent as well the developer solution to be used.

After such curing, a photoresist is applied above the surface of the applied coating composition. As with application of the bottom coating composition layer(s), the overcoated photoresist can be applied by any standard means such as by spinning, dipping, meniscus or roller coating. Following application, the photoresist coating layer is typically dried by heating to remove solvent preferably until the resist layer is tack free. Optimally, essentially no intermixing of the bottom composition layer and overcoated photoresist layer should occur.

The resist layer is then imaged with activating radiation such as 248 nm, 193 nm or EUV radiation through a mask in a conventional manner. The exposure energy is sufficient to effectively activate the photoactive component of the resist system to produce a patterned

image in the resist coating layer. Typically, the exposure energy ranges from about 3 to 300 mJ/cm^2 and depending in part upon the exposure tool and the particular resist and resist processing that is employed. The exposed resist layer may be subjected to a post-exposure bake if desired to create or enhance solubility differences between exposed and unexposed regions of a coating layer. For example, negative acid-hardening photoresists typically require post-exposure heating to induce the acid-promoted crosslinking reaction, and many chemically amplified positive-acting resists require post-exposure heating to induce an acid-promoted deprotection reaction. Typically post-exposure bake conditions include temperatures of about 50°C or greater, more specifically a temperature in the range of from about 50°C to about 160°C.

The photoresist layer also may be exposed in an immersion lithography system, i.e. where the space between the exposure tool (particularly the projection lens) and the photoresist coated substrate is occupied by an immersion fluid, such as water or water mixed with one or more additives such as cesium sulfate which can provide a fluid of enhanced refractive index. Preferably the immersion fluid (e.g., water) has been treated to avoid bubbles, e.g. water can be degassed to avoid nano bubbles.

References herein to "immersion exposing" or other similar term indicates that exposure is conducted with such a fluid layer (e.g. water or water with additives) interposed between an exposure tool and the coated photoresist composition layer.

The exposed photoresist layer is then treated with a suitable developer capable of selectively removing portions of the film to form a photoresist pattern. In a negative tone development process, unexposed regions of a photoresist layer can be selectively removed by treatment with a suitable nonpolar solvent. See U.S. 2011/0294069 for suitable procedures for negative tone development. Typical nonpolar solvents for negative tone development are organic developers, such as a solvent chosen from ketones, esters, hydrocarbons, and mixtures thereof, e.g. acetone, 2-hexanone, 2-heptanone, methyl acetate, butyl acetate, and tetrahydrofuran. Photoresist materials used in the NTD process preferably form a photoresist layer that can form a negative image with organic solvent developer or a positive image with aqueous base developer such as tetraalkylammonium hydroxide solution. Preferably, the NTD photoresist is based on a polymer having acid

sensitive (deprotectable) groups which, when deprotected, form carboxylic acid groups and/or hydroxyl groups.

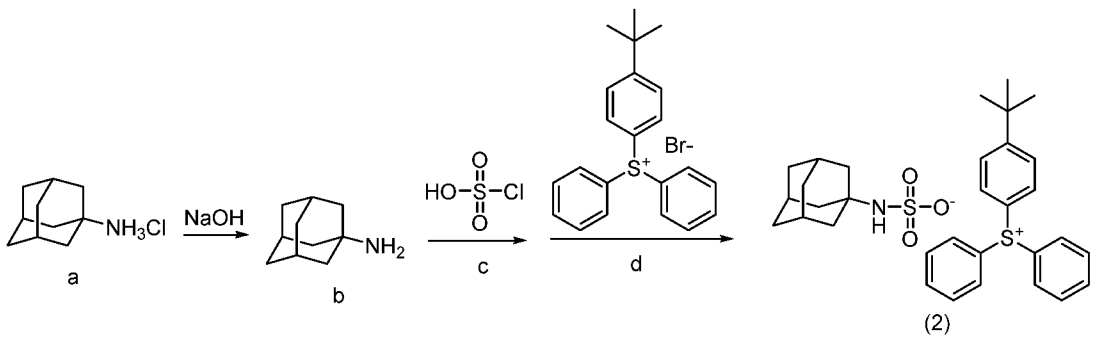
Alternatively, development of the exposed photoresist layer can be accomplished by treating the exposed layer to a suitable developer capable of selectively removing the exposed portions of the film (where the photoresist is positive tone) or removing the unexposed portions of the film (where the photoresist is crosslinkable in the exposed regions, i.e., negative tone)Preferably, the photoresist is positive tone based on a polymer having acid sensitive (deprotectable) groups which form carboxylic acid groups when deprotected, and the developer is preferably a metal-ion free tetraalkylammonium hydroxide solution, such as, for example, aqueous 0.26 N tetramethylammonium hydroxide. A pattern forms by developing.

The developed substrate may then be selectively processed on those substrate areas bared of photoresist, for example, chemically etching or plating substrate areas bared of photoresist in accordance with procedures well known in the art. Suitable etchants include a hydrofluoric acid etching solution and a plasma gas etch such as an oxygen plasma etch. A plasma gas etch removes the underlying coating layer.

The following non-limiting examples are illustrative of the invention.

Examples 1-2: PDQ syntheses

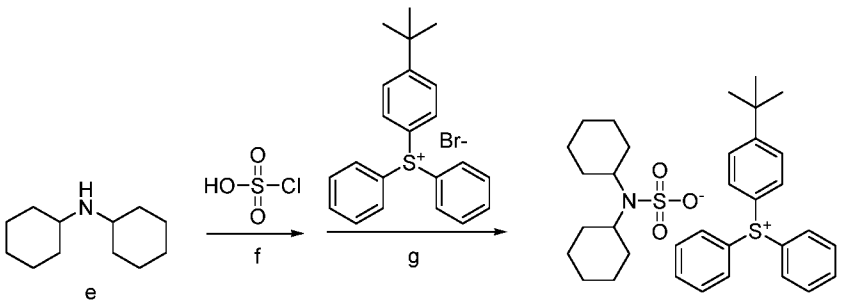
Example 1:



To a mixture of 75.0 parts of a compound (a) (Tokyo Industrial Chemistry, Co., Ltd.), 600 parts of chloroform, 240 parts of 10% aqueous sodium hydroxide solution is added. The resultant mixture is stirred at room temperature for 1 hour, and then the organic layer is separated and dried. 106 parts of triethylamine is added to the filtered organic layer. The resultant mixture is cooled to −10° C., and 51.2 parts of compound (c) is added followed

with stirring at room temperature for 1 hour. A compound of formula (d) is then added following by overnight stirring and then aqueous extraction. The organic layer obtained is concentrated under reduced pressure. The solid is purified to provide compound (2).

Example 2



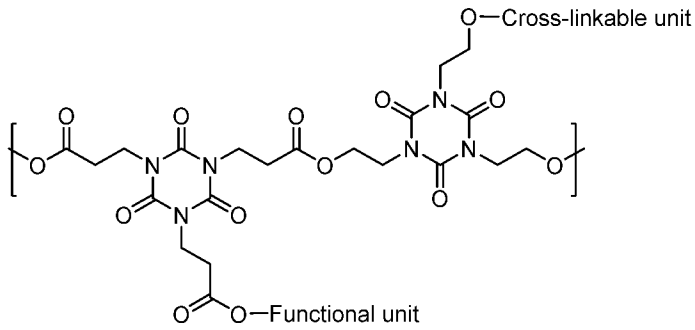
To a mixture of 2.2 parts of a compound (e) (Tokyo Industrial Chemistry, Co., Ltd.) and 50 parts of chloroform, 2.8 parts of triethylamine is added. The mixture is cooled to -10°C, and 1.6 parts of compound (f) added followed by stirring at room temperature. 4.0 parts of compound (g) is then added to the reaction mixture followed by overnight stirring and then aqueous extraction. The obtained organic layer is concentrated under reduced pressure. The solid is purified to provide compound (4).

Examples 3-6: Preparation of underlying coating compositions

Four different underlying coating composition (compositions of Examples 3, 4, 5, and 6 respectively) were prepared by admixing the materials (polymer, crosslinker, TAG, PDQ, solvent) of the type and amount specified in Table 1 immediately below. The structures of the polymer, crosslinker, TAG, PDQ and solvent of each of the compositions of Examples 3-6 follow Table 1. In each of Examples 3-6, the same the polymer, crosslinker, TAG and solvent and amounts thereof were used. The only difference in the Examples is the PDQ and amount thereof used (in Example 3, no PDQ was present). All weight percents (wt.%) listed in Table 1 are based on total solids of the coating compositions (total solids are all materials of the composition except solvent).

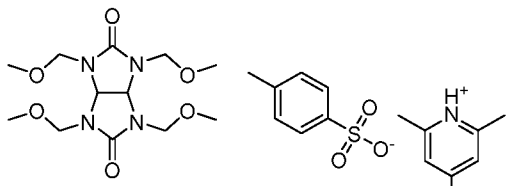
Table 1. Sample formulation

	Polymer	Crosslinker	TAG	PDQ	Solid content	Solvent ratio PGMEA:HBM
Example 3	95.8 wt.%	3 wt.%	1.2 wt.%	-	1.3 wt.%	70:30
Example 4	94.0 wt.%	3 wt.%	1.2 wt.%	(1) 1.8 wt.%	1.3 wt.%	70:30
Example 5	93.1 wt.%	3 wt.%	1.2 wt.%	(2) 2.7 wt.%	1.3 wt.%	70:30
Example 6	93.3 wt.%	3 wt.%	1.2 wt.%	(3) 2.2 wt.%	1.3 wt.%	70:30



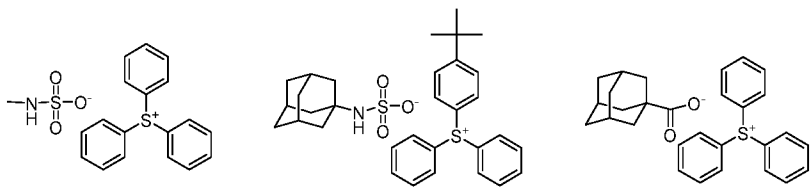
Polymer

Structure of polymer of each of Examples 3-6.



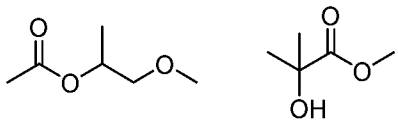
X-linker TAG

Structure of crosslinker and TAG of Examples 3-6



(1) (2) (3)

Strucutres of specified PDQs of Examples 4, 5 and 6.



PGMEA HBM

Solvent of each of Examples 3-6.

Example 7: Lithographic evaluation

The coating compositions of each of Examples 3 through 6 were each spin-coated on 4cm x 4cm wafers that had been previously coated with a 65 nm crosslinked organic layer sold under the tradename AR46 by Dow Chemical. The wafers that were coated with the compositions of Examples 3-6 were then baked at 215 °C for one minute using mini coating machine. The BARC coating thickness after bake was 22 nm. A commercially available chemically-amplified photoresist composition was then spin coated over each of the samples having coating layers of Examples 3-6. The applied photoresist layers were soft-baked at 110°C for 50 second, imaged through a mask with 193 nm radiation and then post-exposure baked at 95°C for 60 seconds.

The images samples were then treated with 0.26 N TMAH aqueous developer. Lithographic results are set forth in Table 2 below. The coated systems that had a PDQ in the underlying coating compositions shows better results including wider focus latitude (FL) margin with improved pattern collapse performance. Figure 1 further shows scanning electron micrographs of the imaged and developed samples. As designated in Figure 1, Sample 1 is the sample imaged with the Example 3 coating composition; Sample 2 is the sample imaged with the Example 4 coating composition; Sample 3 is the sample imaged with the Example 5 coating composition; and Sample 4 is the sample imaged with the Example 6 coating composition;

Table 2. Lithographic results

	Imaged sample with Example 3 coating composition	Imaged sample with Example 4 coating composition	Imaged sample with Example 5 coating composition	Imaged sample with Example 6 coating composition
Eop [mJ/ cm2]	22.7	22.9	23.0	22.8
EL [%]	17.6	17.1	17.7	17.5
FL margin [nm]	360	360	390	420

What is claimed is:

1. A method for forming a photoresist relief image, comprising:

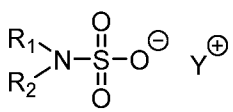
a) applying on a substrate a layer of a coating composition comprising: 1) a resin; and 2) a PDQ compound; and

b) applying a layer of a photoresist composition above the coating composition layer.

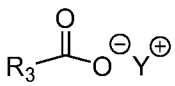
2. The method of claim 1, wherein the PDQ compound has a sulfamate anion or carboxylate anion.

3. The method of claim 2, wherein the PDQ compound comprising an anion having a pKa greater than 0.

4. The method of claim 1 wherein the PDQ compound has a structure of the following Formula (A) or (B):



(A)



(B)

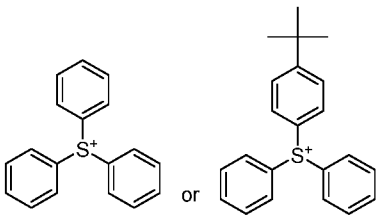
wherein:

R_1 and R_2 are each independently hydrogen, substituted or unsubstituted C_1-C_{12} alkyl, substituted or unsubstituted C_3-C_{12} cycloalkyl, or substituted or unsubstituted phenyl;

R_3 is substituted or unsubstituted C_1-C_{12} alkyl, substituted or unsubstituted C_3-C_{12} cycloalkyl, or substituted or unsubstituted phenyl; and

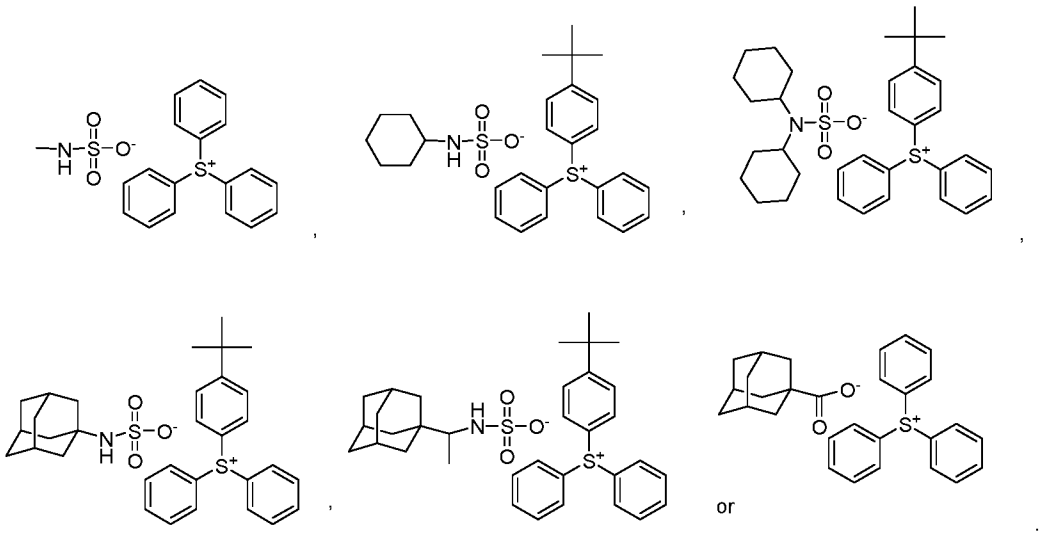
Y is a cation.

5. The method of claim 4, wherein Y is:



6. The method of claim 4 or 5, wherein R_1 and R_2 are independently hydrogen, methyl, cyclohexyl, adamantyl or C_1-C_3 alkyl substituted with adamantyl and/or R_3 is adamantyl.

7. The method of any one of claims 1 through 6, wherein the PDQ compound is:



8. The method of any one of claims 1 through 7, wherein the resin comprises isocyanurate groups.

9. The method of any one of claims 1 through 8 wherein the coating composition further comprises 1) a crosslinker component and/or 2) a themeral acid generator compound that are each distinct from the PDQ compound and the resin.

10. A coated substrate comprising:

a substrate having thereon:

a) a coating composition comprising:

1) a resin; and

2) a PDQ compound; and

b) a layer of a photoresist composition above the coating composition layer.

11. A coating composition for use with an overcoating photoresist composition, the coating composition comprising:

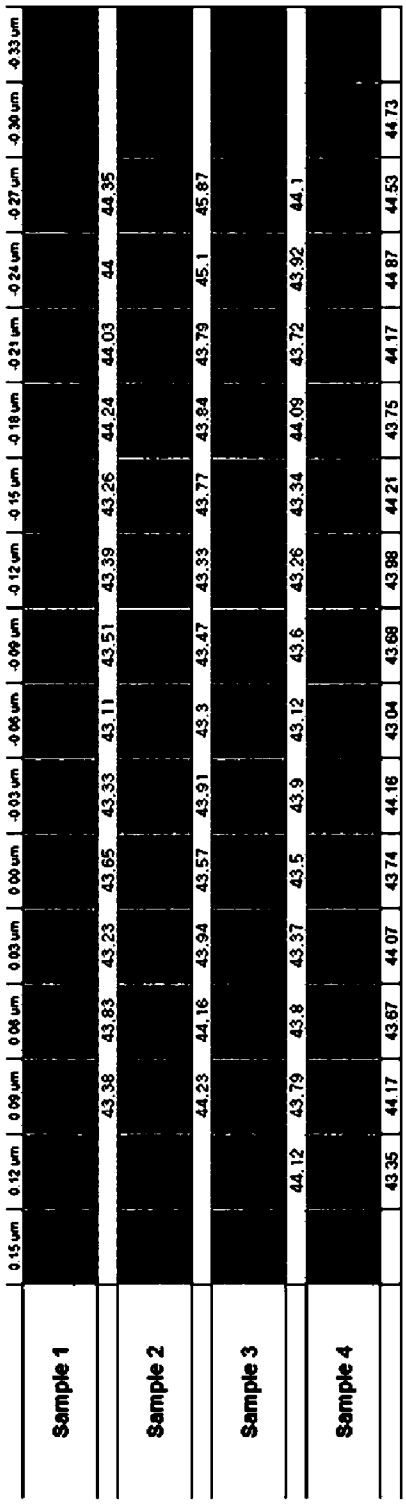
1) a resin; and

2) a PDQ compound.

12. The coating composition of claim 11 wherein the PDQ compound comprises a sulfamate anion or carboxylate anion.

13. The coating composition of claim 11 or 12 wherein the coating composition further comprises 1) a crosslinker component and/or 2) a themeral acid generator compound that are each distinct from the PDQ compound and the resin.

FIG. 1



	0.15 µm	0.12 µm	0.09 µm	0.06 µm	0.03 µm	0.00 µm	-0.03 µm	-0.06 µm	-0.09 µm	-0.12 µm	-0.15 µm	-0.18 µm	-0.21 µm	-0.24 µm	-0.27 µm	-0.30 µm	-0.33 µm
Sample 1			43.38	43.83	43.23	43.65	43.33	43.11	43.51	43.39	43.26	44.24	44.03	44	44.35		
Sample 2			44.23	44.16	43.94	43.57	43.91	43.3	43.47	43.33	43.77	43.84	43.79	45.1	45.87		
Sample 3		44.12	43.79	43.8	43.37	43.5	43.9	43.12	43.6	43.26	43.34	44.09	43.72	43.92	44.1		
Sample 4		43.35	44.17	43.67	44.07	43.74	44.16	43.04	43.68	43.98	44.21	43.75	44.17	44.87	44.53	44.73	