ACID-ETCH RESISTANT, PROTECTIVE COATINGS

BACKGROUND OF THE INVENTION

Federally Sponsored Research

This invention was made with government support under contract number N66001-08-C-2081 awarded by the Defense Advanced Research Projects Agency of the U.S. Department of Defense. The United States Government has certain rights in the invention.

Related Applications

This application claims the priority benefit of a provisional application entitled SPIN-ON, NON-PHOTOSENSITIVE AND PHOTOSENSITIVE, ACID-ETCH RESISTANT, COATING COMPOSITIONS FORMED FROM CYCLIC OLEFIN COPOLYMERS, Serial No. 61/169,604, filed April 15, 2009, incorporated by reference herein.

Field of the Invention

The present invention is broadly concerned with novel compositions and methods of using those compositions to form protective layers that can protect an underlying wafer during acid etching and other harsh processing conditions. Such protection is useful in the manufacture of microelectronic devices such as those used in microelectromechanical systems (MEMS)

Description of the Prior Art

Deep silicon etching is an essential manufacturing step for all microelectromechanical systems (MEMS). Wet chemical etching in alkaline solutions has dimensional limits due to the differential etch rate of the crystal planes of silicon. Deep reactive etching (DRIE) processes have the ability to etch smaller features with high aspect ratios and can be used for new applications, such as the formation of through-silicon vias (TSVs) for three-dimensional (3-D) integrated circuit fabrication. This technique, however, requires expensive tooling and relatively long process times to complete the manufacturing cycle and still is deficient in meeting dimensional tolerances. New materials and processes are therefore needed to create very-high-aspect-ratio (VHAR), 3-D device features in silicon in a cost-efficient manner and with greater and more precise depth-to-width capabilities than current state-of-art technologies.

Photoelectrochemical (PEC) silicon etching utilize hydrofluoric acid (HF) as the active species to yield a highly controllable and high aspect ratio of greater than 120:1 for standing beams and trench structures within the silicon substrates. PEC deep silicon etching uses a low concentration (2-5%) of HF in water as the etching media, while oxide etching processes usually rely on concentrated aqueous HF (49%) or HF vapor (100%) to achieve suitable etching rates. In either case, masking layers are required to allow selective etching of different regions of the silicon device and/or to protect sensitive areas of the device from the corrosive effects of the etchant. Deposited layers such as silicon nitride, polysilicon, or even a metal mask have been traditionally used for this purpose. However, the need to deposit these layers using chemical vapor deposition (CVD), patterning them, and removing them creates great process flow complexity, which is very expensive and leads to high unit costs.

MEMS devices are increasing in complexity and are finding numerous applications in industrial and consumer products such as cellular phones, micromirrors, radio frequency (RF) devices, microprobes, and pressure sensors. One of the critical processing steps for these devices is release etching. In this step, a sacrificial layer, usually silicon oxide, is removed from certain regions to allow a range of motion of specific features. The thickness of the materials to be removed may vary from a few hundred angstroms to several microns. Because this sacrificial layer is silicon oxide in most cases, MEMS release etching has been historically performed using wet fluorinated chemistries that tend to produce strong surface tension and lead to stiction, resulting in either device malfunction or a reduction in the final product yield.

Recently, it has been demonstrated that using HF vapor for release etching can efficiently circumvent the stiction phenomenon because it substantially eliminates the surface tension that causes the stiction. During HF vapor etching, it is necessary to use masking or protective materials to protect the silicon oxide and metal features from HF attack. Traditionally, inorganic-based films such as silicon nitride (Si_3N_4), alumina (Al_2O_3), SiC, polysilicon, and aluminum were used to provide protection during HF vapor etching, but the effectiveness of their protection against HF attack was very limited due to the nature of the materials. Moreover, such inorganic masking layers require high-temperature deposition techniques, which are often lengthy and complicated. Films have been reported that can survive HF vapor etching processes for only 80 seconds or less, but this limits its practical applications. Some films deposited by chemical

vapor deposition (CVD) can supposedly survive HF vapor etching for longer than 80 seconds, but CVD is an expensive and involved process.

Therefore, the demands placed on newly developed polymeric protective materials are very high. To date, however, there has been little success in using conventional photoresists or other common organic layers for HF etching because the very small HF molecules (~ 0.92 Å in diameter) diffuse through, or in most cases decompose, these protective materials, thus leading to substrate corrosion, etching in protected areas, undercutting, and/or lifting of the masking layer from the edge.

There is a need for new polymeric protective coatings that are resistant to acid etching.

SUMMARY OF THE INVENTION

The present invention provides a method of forming a microelectronic structure. The method comprises providing a substrate having a surface and optionally forming a primer layer on the substrate surface. A protective layer is formed on the primer layer, if present, or on the substrate surface if no primer layer is present, to yield a protected stack. The protective layer is formed from a composition comprising a cycloolefin copolymer dissolved or dispersed in a solvent system. The protected stack is subjected to an acidic etching process.

The invention is also directed towards an article comprising: a substrate having a surface; optionally a primer layer on the substrate surface; and a protective layer on the primer layer, if present, or on the substrate surface if no primer layer is present. The protective layer is formed from a composition comprising a cycloolefin copolymer dissolved or dispersed in a solvent system. The protective layer has first and second sides, with the first side being adjacent the primer layer, if present, or adjacent the substrate surface if no primer layer is present. Furthermore, there is no wafer in contact with the second side of the protective layer.

Finally, the invention also provides a composition useful for forming a protective layer on a substrate, where the composition comprises a cycloolefin copolymer and a photosensitive crosslinking agent dissolved or dispersed in a solvent system.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

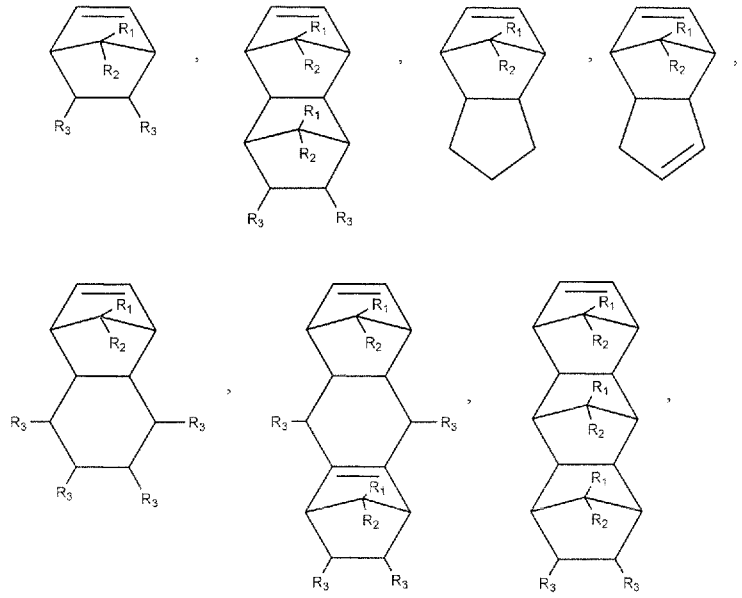
PROTECTIVE LAYER

In more detail, the compositions used to form the inventive protective layers comprise a highly non-polar, hydrophobic, hydrocarbon polymer dispersed or dissolved in a solvent system. The preferred such polymer is a cycloolefin copolymer (COC). Advantageously, the inventive composition is provided in both a non-photosensitive and a photosensitive form, with the latter including a photosensitive crosslinking agent, as discussed in more detail below.

The COC is present in the composition at levels of from about 70% to about 100% by weight, preferably from about 80% to about 95%, and more preferably from about 90% to about 95% by weight, based upon the total weight of solids taken as 100% by weight.

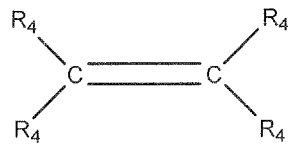
The preferred copolymers are thermoplastic and preferably a high-molecular weight COC. As used herein, "high-molecular weight COC" refers to COCs having a weight average molecular weight (M_w) of from about 50,000 Daltons to about 200,000 Daltons, more preferably from about 70,000 Daltons to about 150,000 Daltons, and even more preferably from about 85,000 to about 100,000. Suitable copolymers also preferably have a glass transition temperature (T_g) of at least about 60°C, more preferably from about 60°C to about 200°C, and most preferably from about 75°C to about 160°C.

Preferred cycloolefin copolymers are comprised of recurring monomers of cyclic olefins and acyclic olefins, or ring-opening polymers based on cyclic olefins. Suitable cyclic olefins for use in the present invention are selected from the group consisting of norbornene-based olefins, tetracyclododecene-based olefins, dicyclopentadiene-based olefins, and derivatives thereof. Derivatives include alkyl (preferably C_1-C_{20} alkyls, more preferably C_1-C_{10} alkyls), alkylidene (preferably C_1-C_{20} alkylidenes, more preferably C_1-C_{10} alkylidenes), aralkyl (preferably C_6-C_{30} aralkyls, more preferably C_6-C_{18} aralkyls), cycloalkyl (preferably C_3-C_{30} cycloalkyls, more preferably C_3-C_{18} cycloalkyls), ether, acetyl, aromatic, ester, hydroxy, alkoxy, cyano, amide, imide, and silyl-substituted derivatives. Particularly preferred cyclic olefins for use in the present invention include those selected from the group consisting of



and combinations of the foregoing, where each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups (preferably C_1-C_{20} alkyls, more preferably C_1-C_{10} alkyls), and each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups (preferably C_6-C_{18} aryls), alkyl groups (preferably C_1-C_{20} alkyls, more preferably C_1-C_{10} alkyls), cycloalkyl groups (preferably C_3-C_{30} cycloalkyl groups, more preferably C_3-C_{18} cycloalkyl groups), aralkyl groups (preferably C_6-C_{30} aralkyls, more preferably C_6-C_{18} aralkyl groups such as benzyl, phenethyl, and phenylpropyl, etc.), ester groups, ether groups, acetyl groups, alcohols (preferably C_1-C_{10} alcohols), aldehyde groups, ketones, nitriles, and combinations thereof.

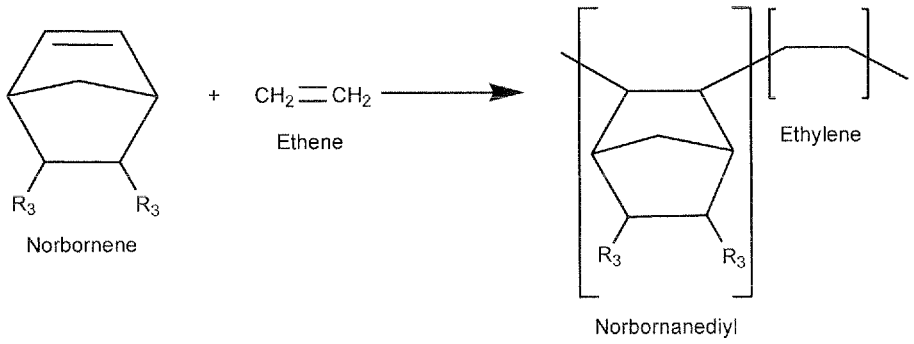
Preferred acyclic olefins are selected from the group consisting of branched and unbranched C_2-C_{20} alkenes (preferably C_2-C_{10} alkenes). More preferably, suitable acyclic olefins for use in the present invention have the structure



where each R_4 is individually selected from the group consisting of -H and alkyl groups (preferably C_1-C_{20} alkyls, more preferably C_1-C_{10} alkyls). Particularly preferred acyclic olefins

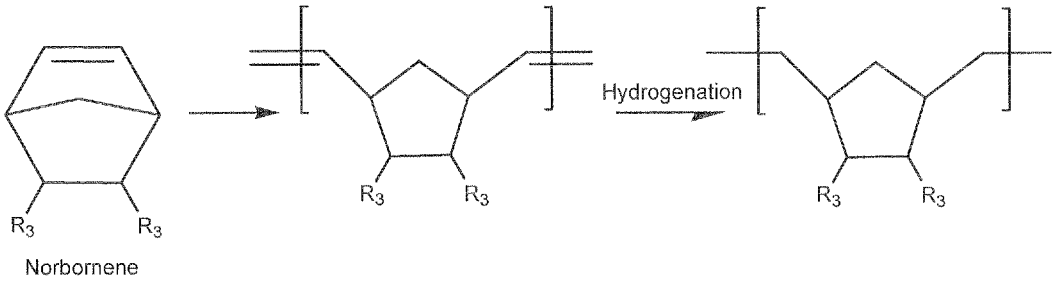
for use in the present invention include those selected from the group consisting of ethene, propene, and butene, with ethene being the most preferred.

Methods of producing cycloolefin copolymers are known in the art. For example, cycloolefin copolymers can be produced by chain polymerization of a cyclic monomer with an acyclic monomer (such as norbornene with ethene as shown below).

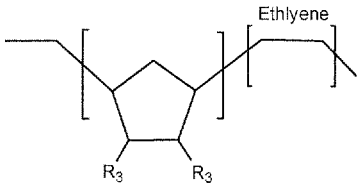


The reaction shown above results in an ethene-norbornene copolymer containing alternating norbornanediyl and ethylene units. Examples of copolymers produced by this method include TOPAS®, produced by Goodfellow Corporation and TOPAS Advanced Polymers, and APEL®, produced by Mitsui Chemicals. A suitable method for making these copolymers is disclosed in U.S. Patent No. 6,008,298, incorporated by reference herein.

Cycloolefin copolymers can also be produced by ring-opening metathesis polymerization of various cyclic monomers followed by hydrogenation as illustrated below.



The polymers resulting from this type of polymerization can be thought of conceptually as a copolymer of ethene and a cyclic olefin monomer (such as alternating units of ethylene and cyclopentane-1,3-diyl as shown below).

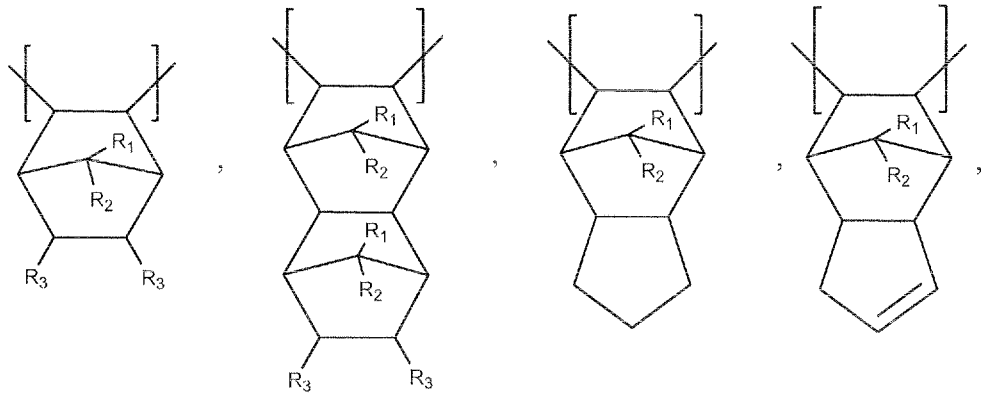


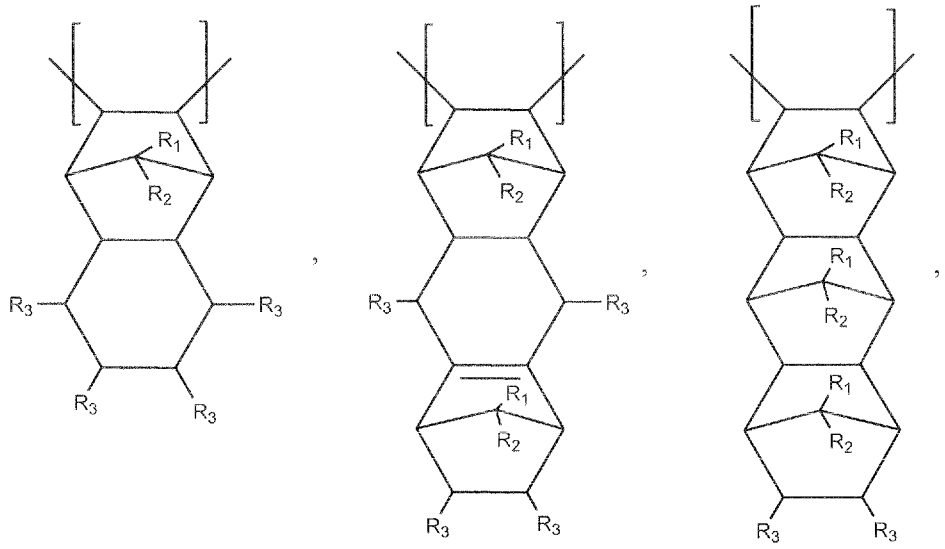
Cyclopentane-1,3-diyl

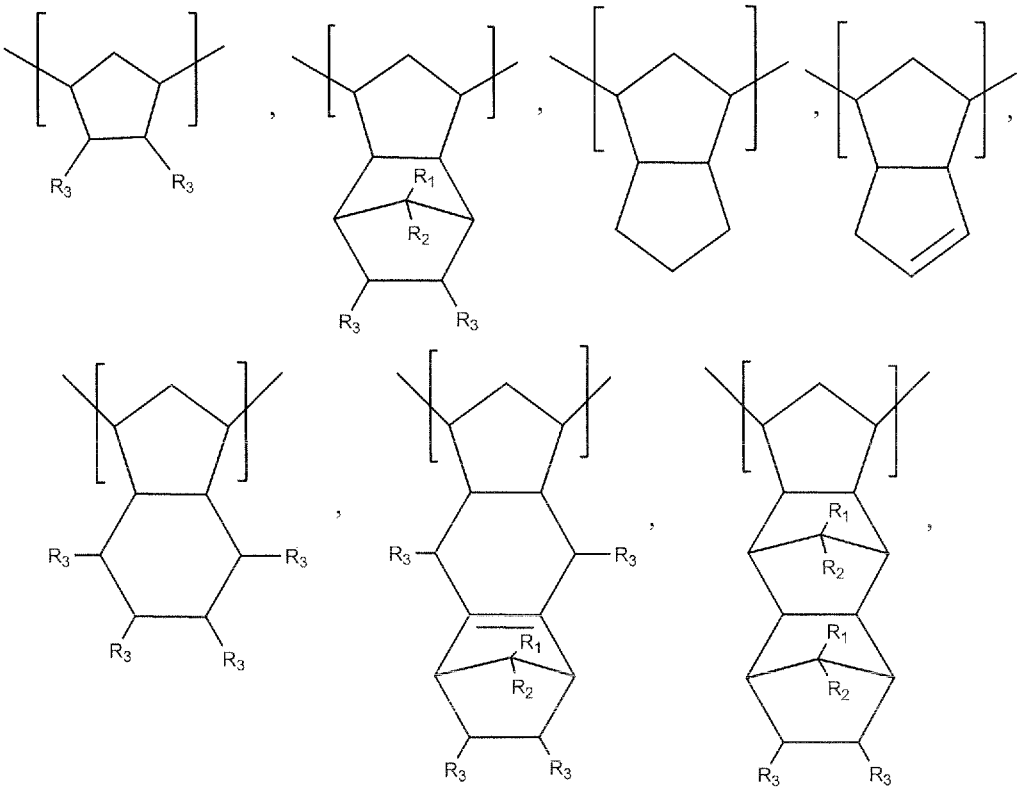
Examples of copolymers produced by this method include ZEONOR® from Zeon Chemicals, and ARTON® from JSR Corporation. A suitable method of making these copolymers is disclosed in U.S. Patent No. 5,191,026, incorporated by reference herein.

Accordingly, copolymers of the present invention preferably comprise recurring monomers of:

(I):







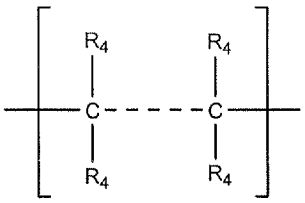
and combinations of the foregoing, where:

each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups (preferably C_1-C_{20} alkyls, more preferably C_1-C_{10} alkyls), and

each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups (preferably C_6-C_{18} aryls), alkyl groups (preferably C_1-C_{20} alkyls, more preferably C_1-C_{10} alkyls), cycloalkyl groups (preferably C_3-C_{30} cycloalkyl groups, more preferably C_3-C_{18} cycloalkyl groups), aralkyl groups (preferably C_6-C_{30} aralkyls, more preferably C_6-C_{18} aralkyl groups, such as benzyl, phenethyl, and phenylpropyl, etc.), ester groups, ether groups, acetyl groups, alcohols (preferably C_1-C_{10} alcohols), aldehyde groups, ketones, nitriles, and combinations thereof;

and

(II):



where:

- - - - - is a single or double-bond; and

each R_4 is individually selected from the group consisting of -H and alkyl groups (preferably C_1-C_{20} alkyls, more preferably C_1-C_{10} alkyls).

The ratio of monomer (I) to monomer (II) within the polymer is preferably from about 5:95 to about 95:5, and more preferably from about 30:70 to about 70:30.

As mentioned above, when a photosensitive version of the composition is desired, a photosensitive crosslinking agent is included in the composition. In this embodiment, the photosensitive crosslinking agent is included at levels of from about 1% to about 15% by weight, preferably from about 2% to about 10% by weight, and more preferably from about 4% to about 6% by weight, based upon the total weight of solids in the composition taken as 100% by weight. It is preferred that the photosensitive crosslinking agent be an azide-based photosensitive crosslinking agent. Suitable examples include those selected from the group consisting of 2,6-bis-(4-azidobenzylidene)-4-methylcyclohexanone, 2,6-bis-(4'-azidobenzal)cyclohexanone, 2,6-bis-(4'-diazidobenzal)-4-methylcyclohexanone, 4,4'-diazidostilbebe, p-phenylenebisazide, 4,4'-diazidobenzophenone, 4,4'-diazidodiphenylmethane, 4,4'-diazidocalcon, 4,4'-diazidodiphenyl, 4,4'-diazido-3,3'-dimethyldiphenyl, and 2,7-diazidofluorene.

The photosensitive embodiment can optionally include a sensitizer, if desired, to increase the photospeed and lithographic performance of the composition. When a sensitizer is included, it is preferably used at levels of from about 0.5% to about 10% by weight, and preferably from about 4% to about 6% by weight, based upon the total weight of solids in the composition taken as 100% by weight. Suitable sensitizers include those selected from the group consisting of carbonyl compounds (e.g., benzophenone, anthraquinone, 1,2-naphthoquinone, 1,4-naphthoquinone, 2-methylanthraquinone, benzanthrone, violanthrone, 9-anthraldehyde, benzil); aromatic hydrocarbon compounds (e.g., anthracene, chrysene); nitro compounds (e.g., nitroaniline, 2-chloro-4-nitroaniline, 5-nitro-2-aminotoluene, tetracyanoethylene); and sulfur compounds (e.g., diphenyl disulfide).

With either embodiment, the composition used to form the inventive protective layers can include additional ingredients, including low-molecular weight cycloolefin copolymer (COC), plasticizers/adhesion promoters, and/or antioxidants.

When a low-molecular weight COC is used in the composition, it is preferably present in the composition at a level of from about 1% to about 99% by weight, more preferably from about 10% to about 50% by weight, and even more preferably from about 20% to about 30% by weight, based upon the total weight of solids in the composition taken as 100% by weight. The term "low-molecular weight COC" is intended to refer to COCs having a weight average molecular weight (M_w) of less than about 15,000 Daltons, preferably less than about 10,000 Daltons, and more preferably from about 500 to about 8,500 Daltons.

Such low-molecular weight COCs also preferably have a T_g of from about 50°C to about 120°C, more preferably from about 60°C to about 90°C, and most preferably from about 60°C to about 70°C. Exemplary low-molecular weight COC resins for use in the present compositions are those sold under the name TOPAS® Toner (M_w 8,000), available from Topas Advanced Polymers.

When a plasticizer/adhesion promoter is included in the composition, it is preferably present at levels of from about 1% to about 10% by weight, and preferably from about 4% to about 6% by weight, based upon the total weight of solids in the composition taken as 100% by weight. Suitable plasticizers/adhesion promoters include those selected from the group consisting of polyisobutylene (preferably about 1,000-40,000 Daltons, more preferably about 1,000-20,000 Daltons, and more preferably about 1,000-10,000 Daltons), terpene, polyterpene resin (SYLVARES™ TR resin from Arizona Chemical), beta-polyterpene resin (SYLVARES™ TR-B resin from Arizona Chemical), styrenated terpene resin (ZONATAC™ NG resin from Arizona Chemical), polymerized rosin resin (SYLVAROS® PR resin from Arizona Chemical), rosin ester resin (EASTOTAC™ resin from Eastman Chemical), cyclo-aliphatic hydrocarbon resin (PLASTOLYN™ resin from Eastman Chemical, ARKON resin from Arakawa Chemical), C5 aliphatic hydrocarbon resins (PICCOTAC™ resin from Eastman Chemical), and hydrogenated hydrocarbon resins (REGALITE™ resin from Eastman Chemical).

The inventive compositions are formed by simply mixing the cycloolefin copolymer and any other ingredients with the solvent system, preferably at room temperature to about 150°C, for time periods of from about 60 minutes to about 720 minutes (until the COC and solvent forms

a solution). The total solids level in the composition should be from about 5% to about 85% by weight, preferably from about 5% to about 60% by weight, and more preferably from about 10% to about 40% by weight, based upon the total weight of the composition taken as 100% by weight. Thus, the composition should comprise from about 15% to about 95% by weight solvent system, preferably from about 40% to about 95% by weight solvent system, and more preferably from about 60% to about 90% by weight solvent system, based upon the total weight of the composition taken as 100% by weight.

The solvent system should have a boiling point of from about 50 to about 280°C, and preferably from about 120 to about 250°C. Suitable solvents include, but are not limited to, hydrocarbon solvents selected from the group consisting of d-limonene, mesitylene, dipentene, pinene, bicyclohexyl, cyclododecene, 1-tert-butyl-3,5-dimethylbenzene, butylcyclohexane, cyclooctane, cycloheptane, cyclohexane, methylcyclohexane, and mixtures thereof.

PRIMER LAYER

Another suitable primer layer comprises a basic polymer dispersed or dissolved in a solvent system. A basic polymer will be one that will have a pH of at least about 7 when dispersed in an aqueous solution at a concentration of about 1% by weight. The basic polymer will preferably comprise recurring monomers that include nitrogen atoms present as part of amine groups (e.g., pyridines). While the polymer could be a copolymer of such amine-containing monomers and a monomer that does not include amine groups, in such instances the amine-containing monomers should be present at levels of at least about 10%, preferably at least about 50%, and more preferably at least about 70%, of the total monomer units present.

Preferred basic polymers include those selected from the group consisting of polyvinyl pyridine, polymelamines, polyethylenimine, triazine-containing copolymers, styrene maleimide resin, poly(4-vinyl pyridine-co-styrene), and poly(2-vinyl pyridine-co-styrene). The basic polymer is present in the composition at levels of from about 1% to about 20% by weight, preferably from about 5% to about 15%, and more preferably from about 7% to about 15% by weight, based upon the total weight of the composition taken as 100% by weight.

Preferred solvent systems for this primer layer include those selected from the group consisting of cyclopentanone, propylene glycol methyl ether acetate ("PGMEA"), methyl ethyl ketone ("MEK"), and methyl isoamyl ketone ("MIAK"). The solvent system is present in the

primer composition at levels of from about 80% to about 99% by weight, preferably from about 85% to about 95%, and more preferably from about 85% to about 93% by weight, based upon the total weight of the composition taken as 100% by weight.

The primer layer compositions are formed by simply mixing the basic polymer with the solvent system, preferably at room temperature to about 150°C, for time periods of from about 60 minutes to about 300 minutes.

APPLICATION PROCESS

The protective layer, either with or without the primer layer, can be applied to any number of substrates (wafers or layers) in need of protection. The substrate will commonly be a thermal oxide substrate, but can also include substrates selected from the group consisting of Si substrates, SiO_2 substrates, Si_3N_4 substrates, SiO_2 on silicon substrates, Si_3N_4 on silicon substrates, glass substrates, quartz substrates, ceramic substrates, semiconductor substrates, and metal substrates.

In embodiments where a primer layer is utilized, the primer composition is spin-applied onto the substrate at speeds of from about 500 to about 5,000 rpm, and preferably from about 1,000 to about 3,000 rpm, for about 30-90 seconds, and preferably for about 60 seconds. The composition is then baked at a temperature of from about 80°C to about 130°C for a time period of from about 60 seconds to about 150 seconds (preferably about 120 seconds) to form the primer layer. It is preferred that the primer layer has an average thickness (as measured by an ellipsometer over 5 different points) of from about 100 nm to about 3,000 nm, and more preferably from about 400 nm to about 1,000 nm.

To form the protective layer, the protective composition is spin coated onto the substrate (or in the primer layer, if utilized) at about 1,000-5,000 rpm, and preferably from about 1,000-2,000 rpm, for about 30-90 seconds, and preferably about 60 seconds. The composition is then baked at a temperature of from about 110°C to about 300°C, and more preferably from about 150°C to about 220°C, for a time period of from about 120 seconds to about 300 seconds (preferably about 180 seconds) to form the protective layer. The average coating thickness after baking (as measured by an ellipsometer over 5 different points) is from about 3,000 nm to about 20,000 nm, and preferably from about 10,000 nm to about 15,000 nm, depending upon the degree of coverage required on the substrate.

In embodiments where the protective layer is photosensitive, the layer can be imaged by exposing it to radiation, such as UV light, with a wavelength of from about 150-500 nm (e.g., about 157 nm, about 248 nm, about 365 nm), preferably in a dose of from about 400 mJ/cm^2 to about 2,500 mJ/cm^2. The coating is then preferably post-exposure baked at a temperature of from about 110°C to about 150°C, and preferably from about 140°C to about 145°C, for a time period of from about 180 seconds to about 300 seconds, and developed with a solvent for a time period of from about 30 seconds to about 120 seconds. Suitable solvents for developing the layer include those selected from the group consisting of d-limonene, mesitylene, dodecene, and isopropyl alcohol ("IPA"). Finally, the coating is baked at about 150°C to about 200°C for about 180 seconds to about 300 seconds.

Light exposure causes the photosensitive crosslinker to decompose into a nitrene, which is a very active species. The nitrene leads to a hydrogen abstraction reaction, which results in crosslinking at the active hydrogen in the norbornene monomer unit in the COC polymer chains. The photosensitive embodiment of this invention is negative working. Thus, the UV-exposed areas are crosslinked and become insoluble in developers, while the unexposed areas remain soluble and can be washed away by developing to form a pattern in the protective layer. More specifically, the exposed areas become substantially insoluble (e.g., less than about 1% by weight soluble, preferably less than about 0.05% soluble, and more preferably about 0% soluble) in typical solvents/developers such as d-limonene, mesitylene, and IPA.

After the photosensitive protective layer has been developed, the primer layer, if present, can also be developed by an organic solvent such as isopropyl alcohol, cyclopentanone, ethyl lactate, PGMEA, or a 1% HCl solution.

After light exposure and developing for photosensitive embodiments, or after application in non-photosensitive embodiments, the structure is ready to undergo etching by acid etching (e.g., aqueous HF, HF vapor, HF/H_2O vapor, HF/alcohol vapor) or PEC etching. During acid etching, the etchant is contacted with the surface of the protective layer remote from the substrate and primer layer (if present). This can be accomplished by spraying or puddling the etchant on this surface.

Advantageously, the inventive protective systems will experience very little or no acid etchant penetration during these etching processes. Thus, when subjected for about 1-2 hours to etching in an approximately 48% by weight aqueous HF solution having a temperature of

about 20-25 °C, the inventive protective layer will have less than about 0.1 pinholes per cm^2 of substrate, and preferably less than about 0.05 pinholes per cm^2 of substrate, when observed under a microscope at 10X magnification. Furthermore, when subjected for about 1-2 hours to etching with HF vapor having a temperature of about 40-50 °C, a layer immediately below the protective layer (or immediately below the primer layer, if utilized) will experience a thickness loss of less than about 10%, preferably less than about 5%, and even more preferably about 0%.

The same results can be achieved with many acidic etchants, including those selected from the group consisting of HCl, phosphoric acid, HCl/HNO_3, buffered oxide etchant ("BOE"), HF/HNO_3/acetic acid, concentrated H_2SO_4, concentrated HNO_3, and mixtures of the foregoing. Prior art layers typically dissolve, blister, and/or peel relatively quickly in these solutions, and thus lack the protective qualities of the present invention.

EXAMPLES

The following examples set forth preferred methods in accordance with the invention. It is to be understood, however, that these examples are provided by way of illustration and nothing therein should be taken as a limitation upon the overall scope of the invention.

EXAMPLE 1

High-Molecular Weight COC Composition

In this procedure, 20 grams of a high-molecular weight COC (TOPAS® 8007s-04 with a molecular weight of 88,000 Daltons, obtained from Topas Advanced Polymers, Florence, KY) were dissolved in 80 grams of d-limonene (obtained from Florida Chemical Inc., Winter Haven, FL) in a 250-ml amber glass bottle. The resulting solution was filtered through a 0.2-μm Meissner Vangard filter (obtained from Meissner Filtration Products Inc., Camarillo, CA). The solution was spin-coated onto four silicon oxide wafers at 1,000 rpm for 60 seconds, followed by prebaking at 110 °C for 2 minutes and then final baking at 175 °C for 2 minutes. The resulting films had thicknesses of approximately 10.6 μm. Testing was performed by dipping the wafers with the as-formed films in concentrated (48%) or dilute (5%) aqueous HF solutions. The results indicated that the films could withstand HF for a couple of hours. The film was also tested in HF vapor/ethanol vapor carried through nitrogen for 1 hour at 45 °C. The oxide thickness

underneath the films did not change after removing the COC coating, which indicated that the high-molecular-weight COC withstood HF vapor etching in ethanol.

EXAMPLE 2

High- and Low-Molecular Weight COC Composition

In this example, 15 grams of a high-molecular weight COC (TOPAS® 8007s-04) and 15 grams of a low-molecular-weight COC (TOPAS® Toner with a molecular weight of 8,000 Daltons, obtained from Topas Advanced Polymers, Florence, KY) were dissolved in 70 grams of d-limonene in a 250-ml amber glass bottle. The resulting solution was filtered through a 0.2-μm Meissner Vangard filter. The solution was spin-coated onto four silicon wafers at 1,000 rpm for 60 seconds, followed by prebaking at 110°C for 2 minutes and then final baking at 175°C for 2 minutes. The resulting films had thicknesses of approximately 14 μm. Testing was performed by dipping the wafers with the as-formed films in concentrated (48%) or dilute (5%) aqueous HF solutions. Results indicated that the films could withstand HF for 2 hours. The film was then tested in HF vapor/ethanol vapor carried through nitrogen for 1 hour at 45°C. The oxide thickness underneath the films did not change after removing the coating, which indicated that the blended COC coating withstood HF vapor etching in ethanol.

EXAMPLE 3

High-Molecular-Weight COC Composition with a Photosensitive Crosslinking Agent

In this procedure, 19.8 grams of a high-molecular weight COC (TOPAS® 8007s-04) were dissolved in 63.5 grams of mesitylene and 15.9 grams of d-limonene in a 250-ml amber glass bottle, after which 0.8 gram of 2,6-bis-(4-azidobenzylidene)-4-methylcyclohexanone was added. The resulting solution was filtered through a 0.2-μm Meissner Vangard filter. The solution was spin-coated onto four silicon wafers at 3,000 rpm for 60 seconds, followed by prebaking at 110°C for 2 minute. The resulting films were smooth and defect-free and had thicknesses of approximately 3 μm. The films were then subjected to broadband exposure at doses of 400 mJ/cm^2 and higher, followed by a post-exposure bake at 110°C for 3 minutes, which produced clear latent images. The images were developed by either spraying or puddling d-limonene or mesitylene onto the films for 40 seconds followed by rinsing with IPA for 20

seconds and spin-drying at 2,500 rpm for 30 seconds. A final bake was carried out for 2 minutes at 175 °C. No film loss occurred at the exposed portions of the film. Clean and sharp images were achieved with a resolution of 5 μm.

EXAMPLE 4

High-Molecular Weight COC Composition with Plasticizer/Adhesion Promoter and Photosensitive Crosslinking Agent

In this Example, 18.9 grams of a high-molecular weight COC (TOPAS® 8007s-04) and 0.9 gram of polyisobutylene (obtained from Scientific Polymer Products Inc., Ontario, NY) were dissolved in 63.5 grams of mesitylene and 15.9 grams of d-limonene in a 250-ml amber glass bottle, after which 0.8 gram of 2,6-bis-(4-azidobenzylidene)-4-methylcyclohexanone was added. The resulting solution was filtered through a 0.2-μm Meissner Vangard filter. The solution was spin-coated onto four silicon wafers at 3,000 rpm for 60 seconds, followed by prebaking at 110 °C for 2 minutes. The resulting films were smooth and defect-free and had thicknesses of approximately 2.7 μm. The films were subjected to broadband exposure at doses of 400 mJ/cm^2 and higher followed by a post-exposure bake at 110 °C for 3 minutes, which produced clear latent images. The images were developed by either spraying or puddling d-limonene or mesitylene onto the films for 40 seconds followed by rinsing with IPA for 20 seconds and spin-drying at 2,500 rpm for 30 seconds. A final bake was carried out at 175 °C for 2 minutes. No film loss occurred at the exposed portions of the film. Clean and sharp images were achieved with a resolution of 5 μm.

EXAMPLE 5

High-Molecular Weight COC Composition with Plasticizer/Adhesion Promoter and Photosensitive Crosslinking Agent

In this procedure, 18.9 grams of a high-molecular weight COC (TOPAS® 8007s-04) and 0.9 grams of polyisobutylene were dissolved in 63.5 grams of mesitylene and 15.9 grams of d-limonene in a 250-ml amber glass bottle, after which 0.8 gram of 2,6-bis-(4-azidobenzylidene)-4-methylcyclohexanone was added. The resulting solution was filtered through a 0.2-μm Meissner Vangard filter. The solution was spin-coated onto four silicon wafers at 3,000 rpm for 60 seconds. The resulting films were smooth and defect-free and had

thicknesses of approximately 2.7 μm. The films then underwent i-line exposure at doses of 600 mJ/cm^2 and higher followed by a post-exposure bake at 110°C for 3 minutes, which produced clear latent images. The images were developed by either spraying or puddling d-limonene or mesitylene onto the films for 40 seconds followed by rinsing with IPA for 20 seconds and spin-drying at 2,500 rpm for 30 seconds. A final bake was carried out at 175°C for 2 minutes. No film loss occurred at the exposed portions of the film. Clean and sharp images were achieved with a resolution of 5 μm.

EXAMPLE 6

High- and Low-Molecular Weight COC Composition with a Photosensitive Crosslinking Agent

In this Example, 12 grams of a high-molecular-weight COC (TOPAS® 8007s-04) and 12 grams of a low-molecular-weight COC (TOPAS® Toner) were dissolved in 60 grams of mesitylene and 15 grams of d-limonene in a 250-ml amber glass bottle. To make the composition photosensitive, 1 gram of 2,6-bis-(4-azidobenzylidene)-4-methylcyclohexanone was then added. The resulting solution was filtered through a 0.2-μm Meissner Vangard filter. The solution was spin-coated onto four silicon wafers at 3,000 rpm for 60 seconds, followed by prebaking at 110°C for 2 minutes. The resulting films were smooth and defect-free and had thicknesses of approximately 3.1 μm. The films then underwent broadband exposure at doses of 400 mJ/cm^2 and higher, followed by a post-exposure bake at 110°C for 3 minutes, which produced clear latent images. The images were developed by either spraying or puddling d-limonene or mesitylene onto the films for 40 seconds, followed by rinsing with IPA for 20 seconds and spin-drying at 2,500 rpm for 30 seconds. A final bake was carried out at 175°C for 2 minutes. No film loss occurred at the exposed portions of the film. Clean and sharp images were achieved with a resolution of 5 μm.

EXAMPLE 7

High- and Low-Molecular Weight COC Composition with Plasticizer/Adhesion Promoter and Photosensitive Crosslinking Agent

In this procedure, 11.4 grams of a high-molecular-weight COC (TOPAS® 8007s-04) and 11.4 grams of a low-molecular-weight COC (TOPAS® Toner) were dissolved in 60 grams of

mesitylene and 15 grams of d-limonene along with 1.2 grams of polyisobutylene in a 250-ml amber glass bottle. To make the composition photosensitive, 1 gram of 2,6-bis-(4-azidobenzylidene)-4-methylcyclohexanone was added. The resulting solution was filtered through a 0.2-μm Meissner Vangard filter. The solution was spin-coated onto four silicon wafers at 3,000 rpm for 60 seconds, followed by prebaking at 110°C for 2 minutes. The resulting films were smooth and defect-free and had thicknesses of approximately 3.1 μm. The films were subjected to broadband exposure at doses of 600 mJ/cm^2 and higher, followed by a post-exposure bake at 110°C for 3 minutes, which produced clear latent images. The images were developed by either spraying or puddling d-limonene or mesitylene onto the films for 40 seconds followed by rinsing with IPA for 20 seconds and spin-drying at 2,500 rpm for 30 seconds. A final bake was carried out at 175°C for 2 minutes. No film loss occurred at the exposed portions of the film. Clean and sharp images were achieved with a resolution of 5 μm.

EXAMPLE 8

High- Molecular Weight COC Composition with Plasticizer/Adhesion Promoter and Photosensitive Crosslinking Agent

In this procedure, 45.6 grams of a high-molecular-weight COC (TOPAS® 8007s-04) were dissolved in 121.6 grams of mesitylene and 30.4 grams of d-limonene along with 2.4 grams of polyisobutylene, all in a 250-ml amber glass bottle. In order to make the composition photosensitive, 1.92 grams of 2,6-bis-(4-azidobenzylidene)-4-methylcyclohexanone were then added. The resulting solution was filtered through a 0.2-μm Meissner Vangard filter. This solution was filtered through a 0.2-μm Meissner Vangard filter, after which it was spin-coated onto silicon wafers at 1,200 rpm to form smooth and defect-free films having thicknesses of approximately 13 μm. The films were subjected to broadband exposure at doses of 2,000 mJ/cm^2 and higher, followed by a post exposure bake at 145°C for 5 minutes, which produced clear latent images. The images were then developed by either spraying or puddling using d-limonene/dodecence (9/1; v/v) with about 5% film loss in the thickness of the exposed portions. A final bake was carried out at 175°C for 5 minutes. Clean and sharp images were achieved with a resolution of 20 μm.

EXAMPLE 9

Bilayer System with High-Molecular Weight COC

Layer and Poly(4-Vinyl Pyridine) Layer

In this Example, 14 grams of basic polymer poly(4-vinyl pyridine) (Poly4-VP, obtained from Sigma Aldrich Inc, St. Louis, MO) were dissolved in 186 grams of cyclopentanone (obtained from Alfa Aesar Inc, Ward Hill, MA) in a 250-ml amber glass bottle. Next, 139.65 grams of a high-molecular-weight COC (TOPAS® 8007s-04) and 40.35 grams of a low-molecular-weight COC (TOPAS® Toner) were dissolved in 420 grams of d-limonene in a 1-liter amber glass bottle. Both solutions were separately filtered through a 0.2-μm Meissner Vangard filter. The solution of Poly(4-VP) was spin-coated onto four blanket thermal oxide wafers at 1,200 rpm followed by baking at 110 °C for 2 minutes to produce thin films having a thickness of approximately 400 nm. Next, the solution of COC blends was spin-coated onto the Poly(4-VP) thin films at 2,100 rpm followed by baking at 110°C for 3 minutes and 175°C for 3 minutes to produce thin films having a thickness of approximately 15 μm.

Testing was performed by dipping the wafers with the as-formed films in concentrated (48%) or dilute (5%) aqueous HF solutions. Results indicated that the films could withstand HF for a couple of hours without blisters being formed during etching. The films were also tested in HF vapor/ethanol vapor carried through nitrogen for 1 hour at 45°C in either mild (i.e., a thermal oxide etch rate of 100 Å/min) or medium (i.e., a thermal oxide etch rate of 350 Å/min) conditions. No film degradation, blistering, or dislocation, and no edge attacking were observed after HF vapor etching. Moreover, the oxide thickness beneath the films did not change after removing the COC and Poly(4-VP) coatings, which demonstrated the effectiveness of this bilayer structure at resisting the HF vapor etching.

EXAMPLE 10

Bilayer System with High- and Low-Molecular Weight

COC Layer and Poly(4-Vinyl Pyridine) Layer

In this Example, 14 grams of basic polymer poly(4-vinyl pyridine) (Poly4-VP) were dissolved in 186 grams of cyclopentanone in a 250-ml amber glass bottle. Next, 139.65 grams of a high-molecular-weight COC (TOPAS® 8007s-04) and 40.35 grams of a low-molecular-weight COC (TOPAS® Toner) were dissolved in 420 grams of d-limonene in a

1-liter amber glass bottle. Both solutions were separately filtered through a 0.2-μm Meissner Vangard filter. The solution of Poly(4-VP) was spin-coated onto four patterned, thermal oxide silicon wafers (625 μm x 625 μm square) at 1,200 rpm, followed by baking at 110°C for 2 minutes to produce thin films having thicknesses of approximately 400 nm. Next, the solution of COC blends was spin-coated onto the Poly(4-VP) thin films at 2,100 rpm followed by baking at 110°C for 3 minutes and 175°C for 3minutes to produce thin films having thicknesses of approximately 15 μm.

Testing was performed by dipping the wafers with the as-formed films in concentrated (48%) or dilute (5%) aqueous HF solutions. Results indicated that the films could withstand HF for a couple of hours without blisters forming during etching. The films were tested in HF vapor/ethanol vapor carried through nitrogen for 1 hour at 45°C at either mild (i.e., a thermal oxide etch rate of 100 Å/min) or medium (i.e., a thermal oxide etch rate of 350 Å/min) conditions. No film degradation, blistering, or dislocation was observed. Furthermore, no edge attacking or square oxide attacking was observed over the oxide square surface after HF vapor etching. Finally, the oxide thickness of the oxide square patterns did not change after removing the COC and Poly(4-VP) coatings, which demonstrated the effectiveness of this bilayer structure at resisting the HF vapor etching.

EXAMPLE 11

Bilayer System with High- and Low-Molecular Weight COC Layer and Poly(4-Vinyl Pyridine) Layer

In this procedure, 14 grams of basic polymer poly(4-vinyl pyridine) (Poly4-VP) were dissolved in 186 grams of cyclopentanone in a 250-ml amber glass bottle. Next, 139.65 grams of a high-molecular-weight COC (TOPAS® 8007s-04) and 40.35 grams of a low-molecular-weight COC (TOPAS® Toner) were dissolved in 420 grams of d-limonene in a 1-liter amber glass bottle. Both solutions were separately filtered through a 0.2-μm Meissner Vangard filter. The solution of Poly(4-VP) was spin-coated onto four blanket thermal oxide silicon wafers at 1,200 rpm, followed by baking at 110°C for 2 minutes to produce thin films having thicknesses of approximately 400 nm. The solution of COC blends was then spin-coated onto the Poly(4-VP) thin films at 3,900 rpm followed by baking at 110°C for 3 minutes and 175°C for 3minutes to produce thin films having a thickness of approximately 10 μm.

Testing was performed by dipping the wafers with the as-formed films in concentrated (48%) or dilute (5%) aqueous HF solutions. The results indicated that the films could withstand HF for a couple of hours without blisters forming during etching. The films were then tested in HF vapor/ethanol vapor carried through nitrogen for 1 hour at 45 °C at either mild (i.e., a thermal oxide etch rate of 100 Å/min) or medium (i.e., a thermal oxide etch rate of 350 Å/min) conditions. No film degradation or dislocation, and no edge attacking were observed after HF vapor etching. Moreover, the oxide thickness below the films did not change after removing the COC and Poly(4-VP) coatings, which demonstrated the effectiveness of this bilayer structure at resisting the HF vapor etching.

EXAMPLE 12

Bilayer System with High- and Low-Molecular Weight COC Layer and Poly(4-Vinyl Pyridine) Layer

In this Example, 14 grams of basic polymer poly(4-vinyl pyridine) were dissolved in 186 grams of cyclopentanone in a 250-ml amber glass bottle. Next, 139.65 grams of a high-molecular-weight COC (TOPAS® 8007s-04) and 40.35 grams of a low-molecular-weight COC (TOPAS® Toner) were dissolved in 420 grams of d-limonene in a 1-liter amber glass bottle. Both solutions were separately filtered through a 0.2-μm Meissner Vangard filter. The solution of Poly(4-VP) was spin-coated onto four patterned thermal oxide silicon wafers (625 μm x 625 μm square) at 1,200 rpm, followed with baking at 110 °C for 2 minutes to produce thin films having thicknesses of approximately 400 nm. The solution of COC blends was spin-coated onto the Poly(4-VP) thin films at 2,100 rpm, followed with baking at 110 °C for 3 minutes and 175 °C for 3minutes to produce thin films having thicknesses of approximately 10 μm.

Testing was performed by dipping the wafers with the as-formed films in concentrated (48%) or dilute (5%) aqueous HF solutions. The results indicated that the films could withstand HF for a couple of hours without blisters forming during etching. The films were then tested in HF vapor/ethanol vapor carried through nitrogen for 1 hour at 45 °C at both mild (i.e., a thermal oxide etch rate of 100 Å/min) and medium (i.e., a thermal oxide etch rate of 350 Å/min) conditions. No film degradation, blistering, or dislocation was observed. Additionally, no edge attacking or square oxide attacking was observed over the oxide square surface after HF vapor etching. Finally, the oxide thickness of the oxide square patterns did not change after removing

the COC and Poly(4-VP) coatings, which demonstrated the effectiveness of this bilayer structure at resisting the HF vapor etching.

EXAMPLE 13

Bilayer System with High- and Low-Molecular Weight COC Layer and Poly(2-Vinyl Pyridine-Co-Styrene) Layer

In this procedure, 6 grams of a basic polymer poly(2-vinyl pyridine-co-styrene) (Poly(2-VP-co-St), obtained from Sigma Aldrich Inc, St. Louis, MO) were dissolved in 194 grams of cyclopentanone in a 250-ml amber glass bottle. Next, 139.65 grams of a high-molecular-weight COC (TOPAS® 8007s-04) and 40.35 grams of a low-molecular-weight COC (TOPAS® Toner) were dissolved in 420 grams of d-limonene in a 1-liter amber glass bottle. Both solutions were filtered through a 0.2-μm Meissner Vangard filter. The solution of Poly(2-VP-co-St) was spin-coated onto four thermal oxide silicon wafers at 1,000 rpm to produce thin films having thicknesses of approximately 210 nm, followed by baking at 110°C for 2 minutes. The solution of COC blends was spin-coated onto the Poly(2-VP-co-St) thin films at 1,500 rpm to produce thin films having thicknesses of approximately 20 μm, followed by baking at 110°C for 3 minutes and 175°C for 3minutes.

Testing was performed by dipping the wafers with the as-formed films in concentrated (48%) or dilute (5%) aqueous HF solutions. The results indicated that the films could withstand HF for a couple of hours without blisters being formed during etching. The films were then tested in HF vapor/ethanol vapor carried through nitrogen for 1 hour at 45°C under mild conditions (i.e., a thermal oxide etch rate of 100 Å/min). The films were blistered, dislocated and damaged after HF vapor etching. This demonstrated the difference in etching behavior when using Poly(2-VP-co-St) instead of Poly(4-VP).

EXAMPLE 14

Bilayer System with Photosensitive High-Molecular Weight COC Layer and Poly(4-Vinyl Pyridine) Layer

In this Example, 14 grams of basic polymer poly(4-vinyl pyridine) (Poly4-VP) were dissolved in 186 grams of cyclopentanone in a 250-ml amber glass bottle. In a different 250-ml amber glass bottle, 45.6 grams of a high-molecular-weight COC (TOPAS® 8007s-04) were

dissolved in 121.6 grams of mesitylene and 30.4 grams of d-limonene along with 2.4 grams of polyisobutylene. In order to make the composition photosensitive, 1.92 grams of 2,6-bis-(4-azidobenzylidene)-4-methylcyclohexanone were then added. Both solutions were separately filtered through a 0.2-μm Meissner Vangard filter. The solution of Poly(4-VP) was spin-coated onto silicon wafers at 1,200 rpm, followed by baking at 110°C for 2 minutes to produce thin films having thicknesses of approximately 400 nm. The solution of photosensitive COC was then spin-coated onto the Poly(4-VP) thin films at 1,200 rpm, followed by baking at 110°C for 5 minutes to produce thin films having thicknesses of approximately 13 μm.

The films were then subjected to broadband exposure at doses of 2,000 mJ/cm^2 and higher, followed by a post exposure bake at 145°C for 5 minutes, which produced clear latent images. The photosensitive COC coating was developed by either spraying or puddling with d-limonene/dodecence (9/1; v/v), resulting in about a 5% film loss at the exposed portions of the film. A final bake was carried out at 175°C for 3 minutes. The Poly(4-VP) layer can be developed by either an organic solvent (e.g. IPA, cyclopentanone, PGMEA, ethyl lactate, mixtures of the foregoing) or 1% HCl solution to yield clean and sharp images with a resolution of 20 μm.

EXAMPLE 15

Bilayer System with Photosensitive High--Molecular Weight COC Layer and Poly(4-Vinyl Pyridine) Layer

In this Example, 14 grams of basic polymer poly(4-vinyl pyridine) (Poly4-VP) were dissolved in 186 grams of cyclopentanone in a 250-ml amber glass bottle. In a different 250-ml amber glass bottle, 45.6 grams of a high-molecular-weight COC (TOPAS® 8007s-04) were dissolved in 121.6 grams of mesitylene and 30.4 grams of d-limonene along with 2.4 grams of polyisobutylene. In order to make the composition photosensitive, 1.92 grams of 2,6-bis-(4-azidobenzylidene)-4-methylcyclohexanone were then added. Both solutions were filtered through a 0.2-μm Meissner Vangard filter. The solution of Poly(4-VP) was spin-coated onto four patterned thermal oxide silicon wafers (625 μm x 625 μm square) at 1,000 rpm, followed by baking at 110°C for 2 minutes to produce thin films having thicknesses of approximately 600 nm. The solution of photosensitive COC was then spin-coated onto the Poly(4-VP) thin films at 1,250 rpm, followed by baking at 110°C for 5 minutes to produce thin films having

thicknesses of approximately 12.5 μm. The films were then subjected to broadband flood exposure at doses of 2,000 mJ/cm^2 and higher, followed by a post exposure bake at 145°C for 5 minutes and a final bake at 175°C for 3 minutes.

Testing was performed by dipping the wafers with the as-formed films in concentrated (48%) or dilute (5%) aqueous HF solutions. The results indicated that the films could withstand HF for a couple of hours without blisters forming during etching. The films were then tested in HF vapor/ethanol vapor carried through nitrogen for 1 hour at 45°C under mild (i.e., a thermal oxide etch rate of 100 Å/min) or medium (i.e., a thermal oxide etch rate of 350 Å/min) conditions. No film degradation, blistering, or dislocation, and no edge attacking were observed after HF vapor etching. Moreover, the oxide thickness underneath the films did not change after removing the photo-crosslinked COC and Poly(4-VP) coatings by Nanostrip®, which demonstrated the effectiveness of this bilayer structure at resisting the HF vapor etching.

We Claim:

1. A method of forming a microelectronic structure, said method comprising:

providing a substrate having a surface;

optionally forming a primer layer on said substrate surface;

forming a protective layer on said primer layer, if present, or on said substrate surface if no primer layer is present, to yield a protected stack, said protective layer being formed from a composition comprising a cycloolefin copolymer dissolved or dispersed in a solvent system; and

subjecting said protected stack to an acidic etching process.

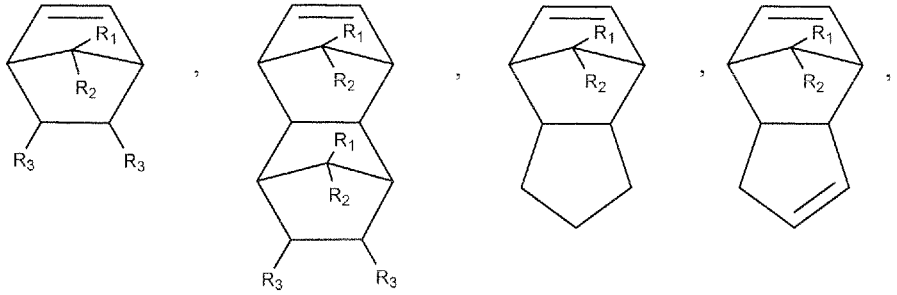
2. The method of claim 1, further comprising subjecting said protected step to further processing steps prior to subjecting said stack to said acidic etching process.

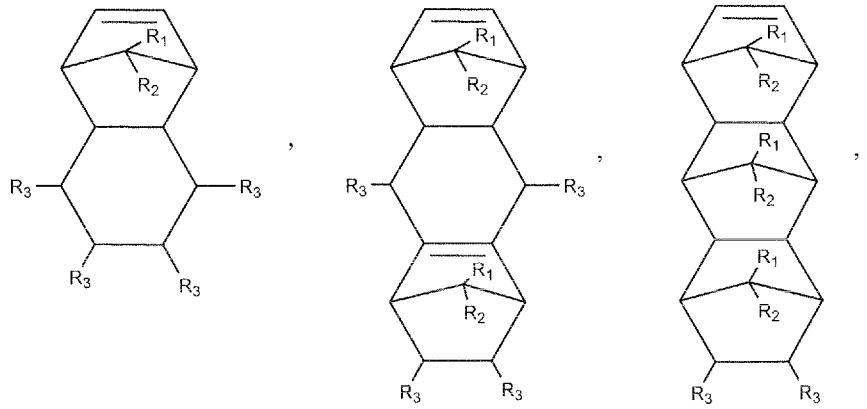
3. The method of claim 1, further comprising exposing said protective layer to broadband UV radiation.

4. The method of claim 3, wherein said protective layer is photosensitive and said exposing yields exposed portions of said protective layer, said exposed portions comprising a crosslinked cycloolefin copolymer.

5. The method of claim 1, wherein said acidic etching process comprises etching with an etchant selected from the group consisting of aqueous HF, HF vapor, HF/H_2O vapor, HF/alcohol vapor, HCl, phosphoric acid, HCl/HNO_3, buffered oxide etchant ("BOE"), HF/HNO_3/acetic acid, concentrated H_2SO_4, concentrated HNO_3, and mixtures of the foregoing.

6. The method of claim 1, wherein said cycloolefin copolymer is formed from the polymerization of a cyclic olefin selected from the group consisting of





and combinations of the foregoing,

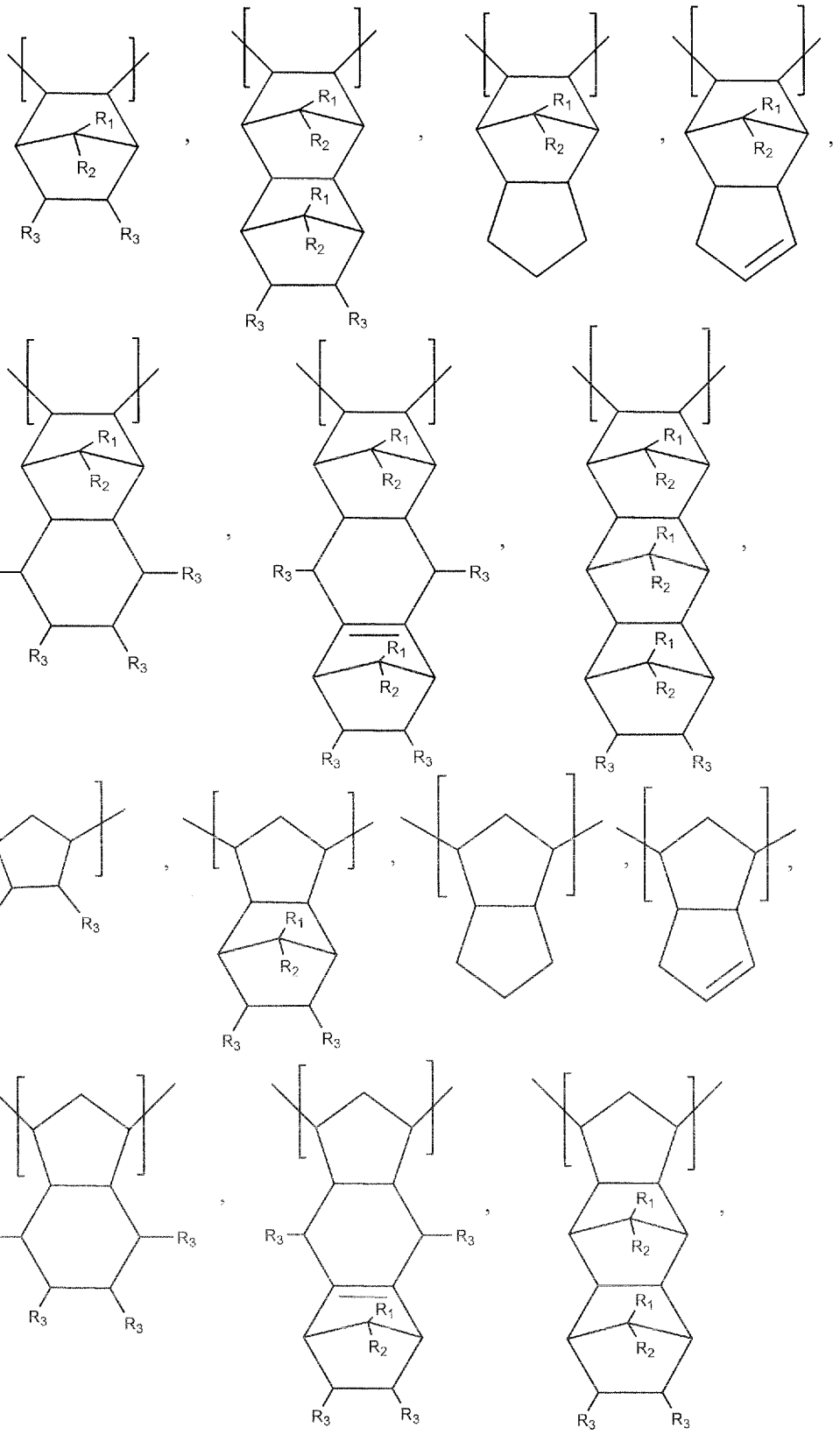
where:

each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups; and

each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups, cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof.

7. The method of claim 1, wherein said cycloolefin copolymer comprises recurring monomers of:

(I):



and combinations of the foregoing,

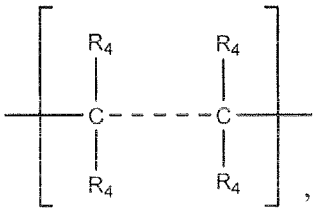
where:

each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups; and

each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups, cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof;

and

(II):



,

where:

- - - - - is a single or double-bond; and

each R_4 is individually selected from the group consisting of -H and alkyl groups.

8. The method of claim 1, wherein a primer layer is formed on said substrate surface.

9. The method of claim 8, wherein said primer layer is formed from composition comprising a basic polymer in a solvent system.

10. The method of claim 9, wherein said basic polymer is selected from the group consisting of polyvinyl pyridine, polymelamines, polyethylenimine, triazine-containing copolymers, styrene maleimide resin, poly(4-vinyl pyridine-co-styrene), and poly(2-vinyl pyridine-co-styrene).

11. The method of claim 1, wherein said substrate is selected from the group consisting of thermal oxide substrates, Si substrates, SiO_2 substrates, Si_3N_4 substrates, SiO_2 on silicon substrates, Si_3N_4 on silicon substrates, glass substrates, quartz substrates, ceramic substrates, semiconductor substrates, and metal substrates.

12. An article comprising:

a substrate having a surface;

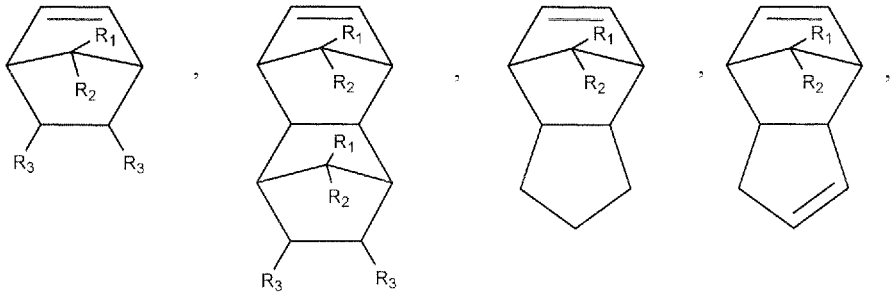
optionally a primer layer on said substrate surface; and

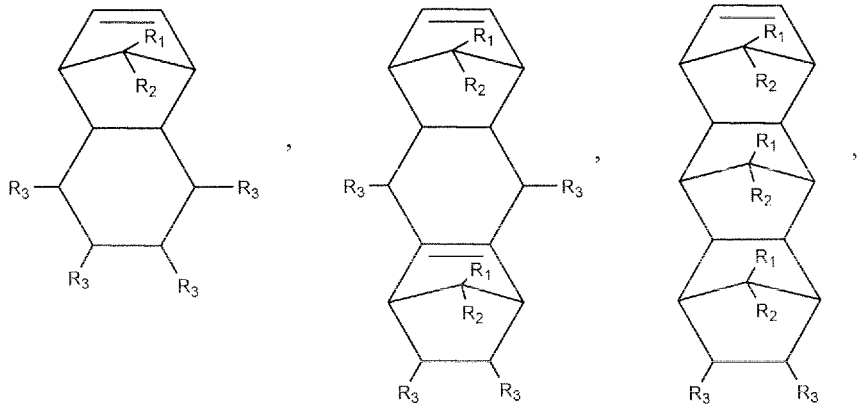
a protective layer on said primer layer, if present, or on said substrate surface if no primer layer is present, said protective layer being formed from a composition comprising a cycloolefin copolymer dissolved or dispersed in a solvent system,

wherein said protective layer has first and second sides, said first side being adjacent said primer layer, if present, or adjacent said substrate surface if no primer layer is present, there being no wafer in contact with said second side.

13. The article of claim 12, wherein said substrate is selected from the group consisting of thermal oxide substrates, Si substrates, SiO_2 substrates, Si_3N_4 substrates, SiO_2 on silicon substrates, Si_3N_4 on silicon substrates, glass substrates, quartz substrates, ceramic substrates, semiconductor substrates, and metal substrates.

14. The article of claim 12, wherein said cycloolefin copolymer is formed from the polymerization of a cyclic olefin selected from the group consisting of





and combinations of the foregoing,

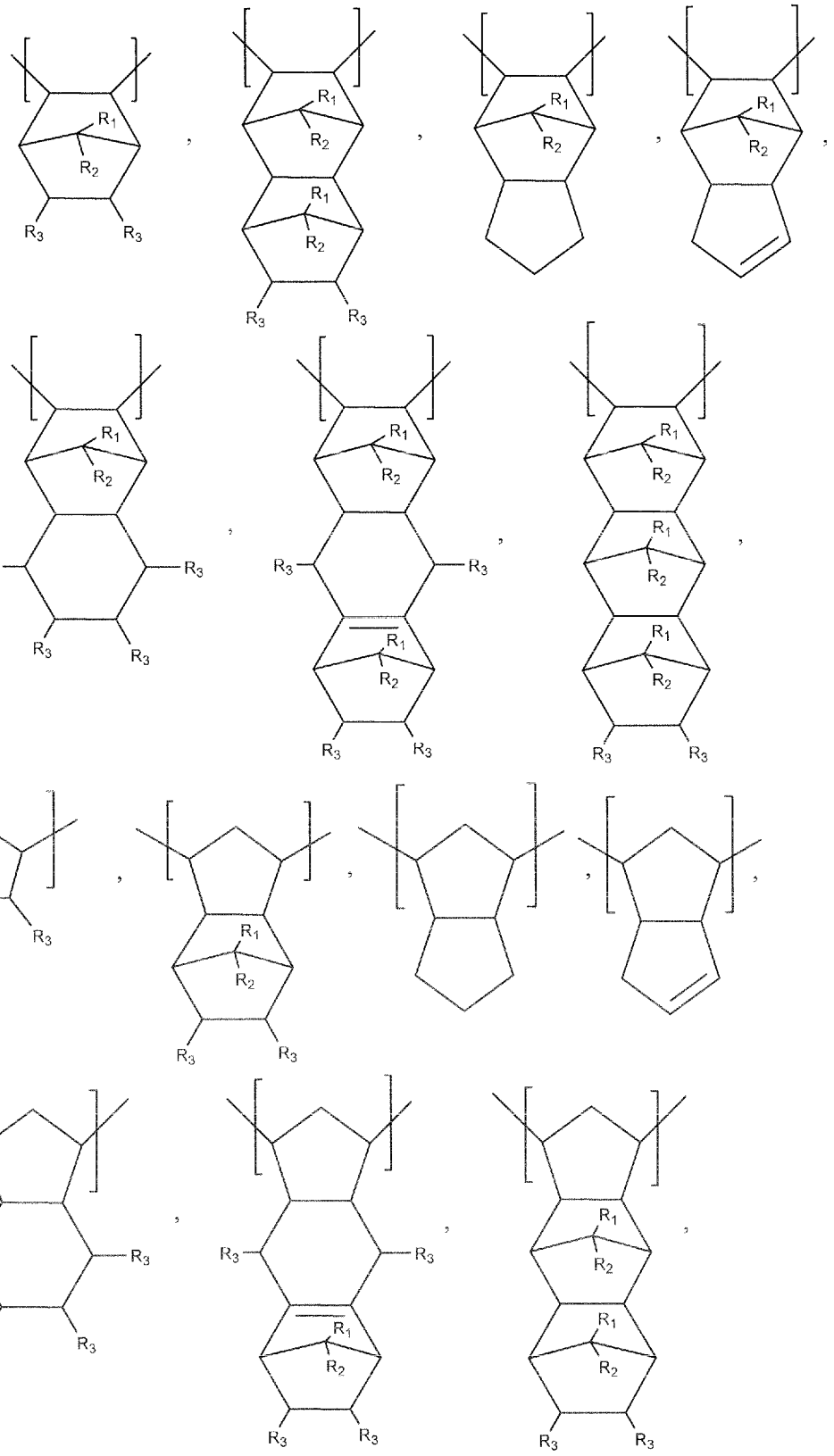
where:

each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups; and

R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups , cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof.

15. The article of claim 12, wherein cycloolefin copolymer comprises recurring monomers of:

(I):



and combinations of the foregoing,

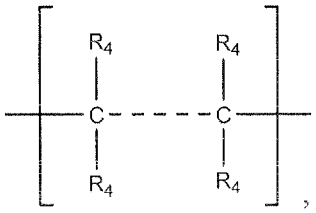
where:

each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups; and

each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups, cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof;

and

(II):



where:

- - - - - is a single or double-bond; and

each R_4 is individually selected from the group consisting of -H and alkyl groups.

16. The article of claim 12, wherein said protective layer is photosensitive.

17. The article of claim 12, further comprising an acidic etchant on said second side.

18. The article of claim 17, said acidic etchant selected from the group consisting of aqueous HF, HF vapor, HF/H_2O vapor, HF/alcohol vapor, HCl, phosphoric acid, HCl/HNO_3, buffered oxide etchant ("BOE"), HF/HNO_3/acetic acid, concentrated H_2SO_4, concentrated HNO_3, and mixtures of the foregoing.

19. The article of claim 12, wherein said article includes a primer layer on said substrate surface.

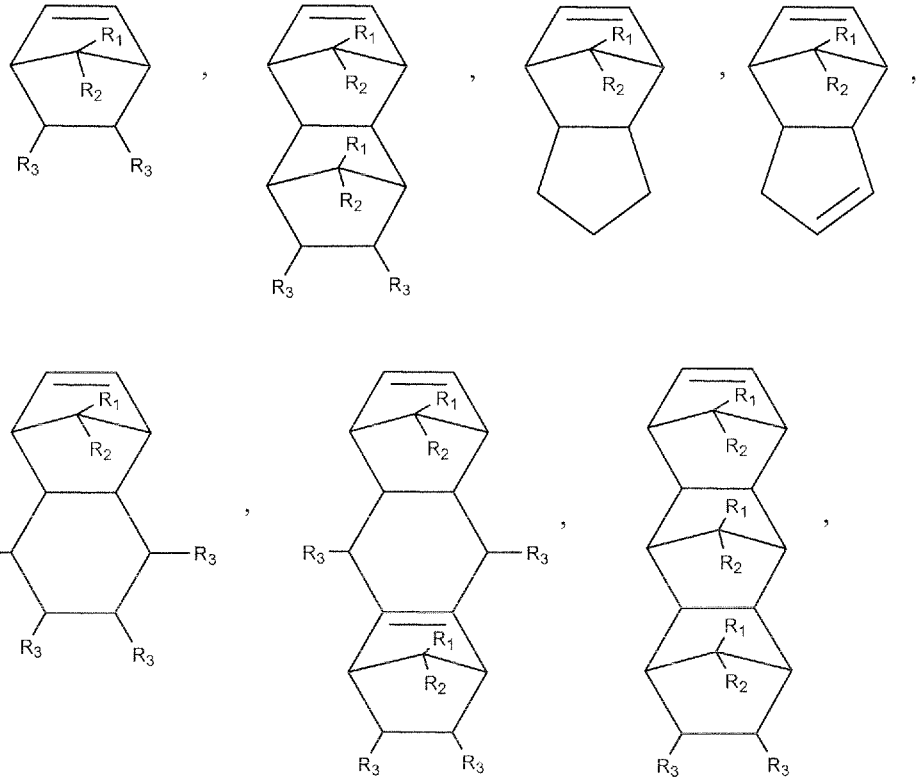
20. The article of claim 19, wherein said primer layer is formed from a composition comprising a basic polymer in a solvent system.

21. The article of claim 20, wherein said basic polymer is selected from the group consisting of polyvinyl pyridine, polymelamines, polyethylenimine, triazine-containing copolymers, styrene maleimide resin, poly(4-vinyl pyridine-co-styrene), and poly(2-vinyl pyridine-co-styrene).

22. A composition useful for forming a protective layer on a substrate, said composition comprising a cycloolefin copolymer and a photosensitive crosslinking agent dissolved or dispersed in a solvent system.

23. The composition of claim 22, wherein said photosensitive crosslinking agent is selected from the group consisting of 2,6-bis-(4-azidobenzylidene)-4-methylcyclohexanone, 2,6-bis-(4'-azidobenzal)cyclohexanone, 2,6-bis-(4'-diazidobenzal)-4-methylcyclohexanone, 4,4'-diazidostilbebe, p-phenylenebisazide, 4,4'-diazidobenzophenone, 4,4'-diazidodiphenylmethane, 4,4'-diazidocalcon, 4,4'-diazidodiphenyl, 4,4'-diazido-3,3'-dimethyldiphenyl, and 2,7-diazidofluorene.

24. The composition of claim 22, said cycloolefin copolymer being formed from the polymerization of a cyclic olefin selected from the group consisting of



and combinations of the foregoing,

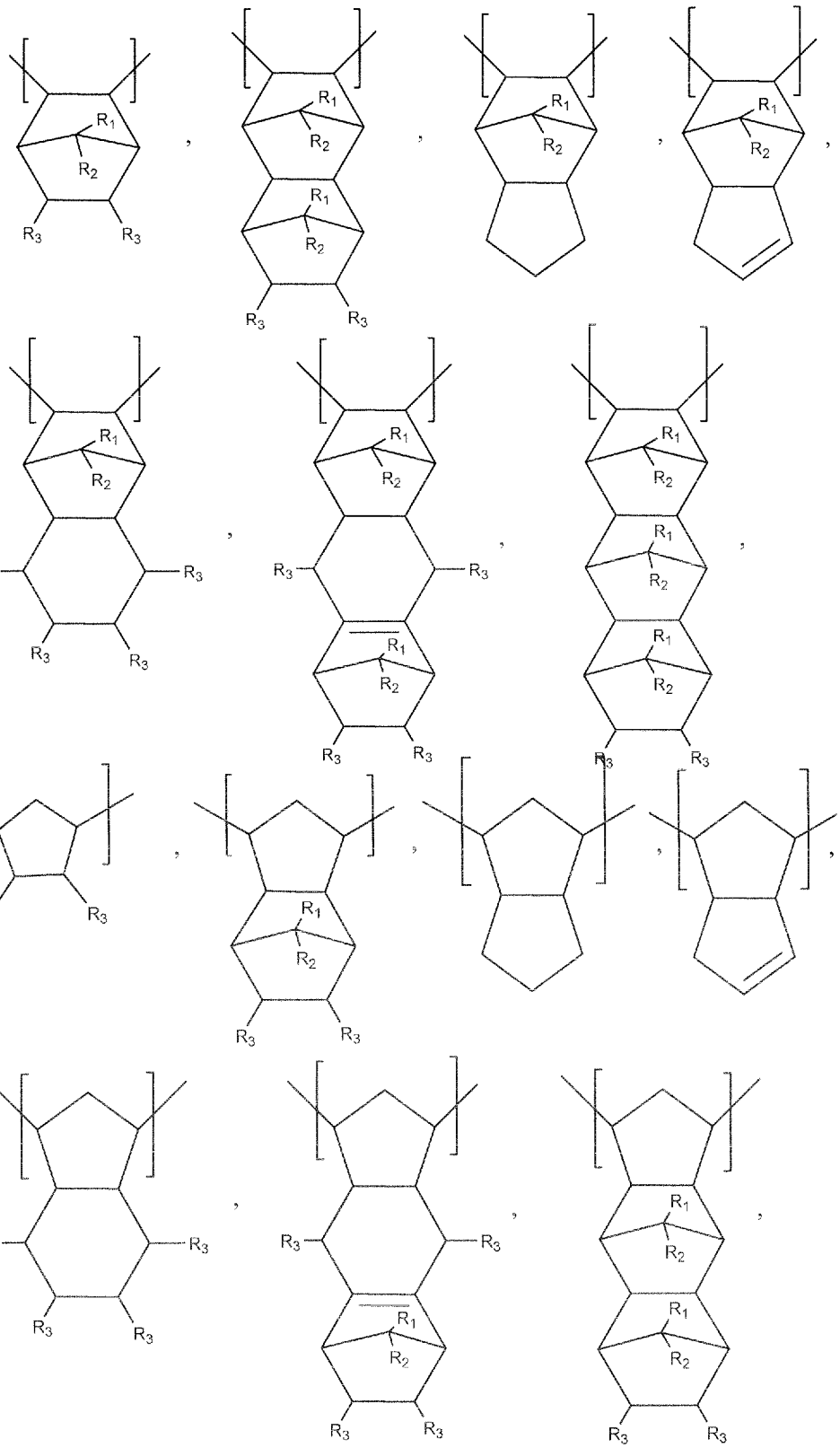
where:

each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups; and

each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups, cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof.

25. The composition of claim 22, wherein said cycloolefin copolymer comprises recurring monomers of:

(I):



and combinations of the foregoing,

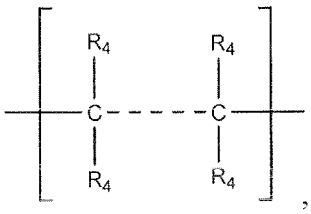
where:

each R_1 and R_2 is individually selected from the group consisting of -H, and alkyl groups; and

each R_3 is individually selected from the group consisting of -H, substituted and unsubstituted aryl groups, alkyl groups, cycloalkyl groups, aralkyl groups, ester groups, ether groups, acetyl groups, alcohols, aldehyde groups, ketones, nitriles, and combinations thereof;

and

(II):



,

where:

- - - - - is a single or double-bond; and

each R_4 is individually selected from the group consisting of -H and alkyl groups.