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(54) Title: SILSESQUOXANE RESIN AND SILYL-ANHYDRIDE COMPOSITION



FIG. 1

(57) Abstract: A silsesquioxane-containing composition comprising a silsesquioxane resin and a silyl-anhydride of formula (II) (see description), products prepared therefrom, photoresist compositions comprising the silsesquioxane-containing composition and a photoacid generator, products prepared therefrom, methods of making and using same, and manufactured articles and semiconductor devices containing same.



SILSESQUIOXANE RESIN AND SILYL-ANHYDRIDE COMPOSITION

TECHNICAL FIELD

[0001] This invention generally relates to a silsesquioxane-containing composition comprising a silsesquioxane resin and a silyl-anhydride, products prepared therefrom, photoresist compositions comprising the silsesquioxane-containing composition and a photoacid generator, products prepared therefrom, methods of making and using same, and manufactured articles and semiconductor devices containing same.

BACKGROUND OF THE RELATED ART

[0002] Critical features of many opto/electronic devices include patterns or integrated circuits (ICs). Patterns and ICs may be made by transferring a pattern from a photoresist layer to a substrate such as a semiconductor material or an electrically conductive metal. The photoresist layer comprises a photoresist composition comprising a light-sensitive material. The pattern in the photoresist layer is formed using photolithography with ultraviolet (UV) light and transferred using etching.

[0003] In order to make new opto/electronic devices more powerful, smaller and faster, these patterns or ICs must be manufactured in smaller and finer feature sizes (finer resolutions). One way to enable finer pattern resolutions is to use shorter wavelengths of light. Trends are shortening the wavelength from 365 nanometers (nm) to 248 nm (KrF) to 193 nm (ArF). Eventually wavelengths may be 157 nm (F2) and/or extreme ultraviolet light (EUV) at 13 nm. A photoresist composition that is useful at a particular wavelength, however, may fail to react at shorter wavelengths. Another way is to form a multilayer resist instead of a single layer resist. As patterns become finer and thus pattern aspect ratios become greater, single layer resists are at risk of collapse. For a given thickness of a photoresist layer, a multilayer resist may enable patterns with higher aspect ratios. Still another way is to formulate a photoresist composition to be chemically amplifiable, which helps counteract weaker responses at shorter wavelengths of light. Typically, a combination of these ways is used.

[0004] A chemically-amplifiable photoresist composition comprises a photoresist polymer that is acid sensitive and a small amount of a photoacid generator. The acid-sensitive photoresist polymer comprises macromolecular chains that bear pendant acid-sensitive groups, sometimes called acid dissociable groups, acid cleavable groups, or acid labile groups. The photoacid generator (PAG) itself is not an acid, but the PAG is a compound that absorbs light of a certain wavelength and produces a product acid *in situ*. Some chemically-amplifiable photoresist compositions may be further formulated with one or more optional additives that

enhance desired properties or inhibit undesired properties of the composition. Examples of such additives are an acid-cleavable dissolution inhibitor, a crosslinking agent (e.g., in negative photoresist compositions), a solvent, a dye, a sensitizer, a stabilizer (e.g., shelf-life stabilizer), an acid-diffusion controlling agent, a coating aid such as a surfactant or an anti-foaming agent, an adhesion promoter, and a plasticizer.

[0005] A variety of incumbent chemically-amplifiable photoresist compositions are known. Some are based on organic polymers comprising acid-sensitive groups. Others are based on organosiloxane polymers comprising acid-sensitive groups. Not all incumbent compositions enable use of shorter wavelengths of light or produce satisfactory patterns.

[0006] Incumbent silsesquioxane resins with acid cleavable groups are mentioned in US 7,261,992 B2 to R. Soorlyakumaran, et al. ("SOORLYAKUMARAN"). SOORLYAKUMARAN mentions, among other things, fluorocarbonol- and/or fluoroacid-functionalized silsesquioxane polymers and copolymers for use in lithographic photoresist compositions. SOORLYAKUMARAN also mention a composition wherein the fluorocarbonol- and/or fluoroacid-functionalized silsesquioxane polymer is a copolymer of a fluorocarbonol-functionalized silsesquioxane monomer and a silsesquioxane monomer substituted with an acid cleavable group. The composition may further comprise additives such as an acid-cleavable dissolution inhibitor, a crosslinking agents, a solvent, dyes, sensitizers, additives used as stabilizers and acid-diffusion controlling agents, coating aids such as surfactants or anti-foaming agents, adhesion promoters, and plasticizers. Examples of the additives used as stabilizers and acid-diffusion controlling agents are compounds with varying basicity. These may include nitrogenous compounds such as aliphatic primary, secondary, and tertiary amines, cyclic amines such as piperidines, pyrimidines, morpholines, aromatic heterocycles such as pyridines, pyrimidines, purines, imines such as diazabicycloundecene, guanidines, imides, amides, and others.

[0007] Incumbent silsesquioxane resins with acid cleavable groups are described in US 7,625,687 B2 to S. Hu, et al. ("HU1"); US 8,088,547 B2 to S. Hu, et al. ("HU2"); US 8,148,043 B2 to S. Hu, et al. ("HU3"); and US 8,524,439 B2 to S. Hu, et al. ("HU4"). HU1, HU2, HU3, and HU4 independently describe, among other things, a silsesquioxane resin that contains (HSiO_{3/2}) units and (RSiO_{3/2}) units wherein R is an acid dissociable group. The acid dissociable group (R) can be described by the formula $-(R^3)_g-L-(R^3)_h-C(R^5)(R^6)---(R^4)_kZ$ or the general formula $-(R^3)_f-L-(R^3)_g-C(R^5)(R^6)---(R^4)_hZ$. HU3 also mentions a silsesquioxane-based composition comprising the silsesquioxane resin and an organic base

additive selected from bulky tertiary amines, imides, amides and polymeric amines. The organic base additive contains an electron-attracting group with the provision that the organic base is not 7-diethylamino-4-methylcoumarin. Some of the organic base additives contain an oxo (=O) group. The composition of HU4 includes 7-diethylamino-4-methylcoumarin. Other additives may be used in the photoresist composition, including one or more of solvents, acid generators, surfactants, dissolution inhibitors, cross-linking agents, sensitizers, halation inhibitors, adhesion promoters, storage stabilizers, anti-foaming agents, coating aids, plasticizers and others.

[0008] Some incumbent resins face challenges to achieving satisfactory structural features and performance. For example, most incumbent silsesquioxane resins have low thermal stability (i.e., low glass transition temperatures, T_g). They also are difficult to configure with other properties including fine pattern resolution, high light sensitivity, and wide process latitude (tolerance for changing process conditions). Some incumbent silsesquioxane resins outgas during UV light exposure (e.g., at 193 nm). Some incumbent composition contain additives that hurt their performance.

[0009] Unrelatedly, WO 2011/111667 A1 to M. Kashio ("KASHIO") mentions a non-resist composition. The composition includes (A) a silane compound copolymer having specific repeating units, (B) an epoxy compound having an isocyanurate skeleton, (C) a curing agent that includes an alicyclic acid anhydride having a carboxyl group, and (D) a silane coupling agent having an acid anhydride structure. Also disclosed is a hardened material formed by hardening the composition and a method for using the composition as an adhesive for an optical element fixing material and as a sealing material for an optical element fixing material. KASHIO's (A) a silane compound copolymer, and composition, is free of a SiH-functional group, including free of a SiH-functional T unit, including a hydrogen silsesquioxane resin.

BRIEF SUMMARY OF THE INVENTION

[0010] Ideally a chemically-amplifiable photoresist composition containing a constituent that is a silsesquioxane resin having acid dissociable groups and a constituent that is a photoacid generator (PAG), must excel in several performance attributes. For example the composition should be radiation sensitive such that after being masked-irradiated with radiation having a suitable wavelength for activating the PAG, it should form a masked-irradiated resist having distinct latent patterns. This means the PAG in the portions of the composition that are exposed to the radiation should readily react to form product acid, and in turn the silsesquioxane resin containing acid sensitive groups in the same portions of the composition should readily react with the product acid to form a product polymer. In contrast, the PAG in

the portions of the composition that are not exposed to the radiation should not form product acid, and thus the silsesquioxane resin containing acid sensitive groups in the same unexposed portions of the composition should not react to form a product polymer. Further, upon being post-exposure baked, both the unexposed portions and the latent image portions of the masked-irradiated resist should exhibit increased adhesion to a substrate or the underlayer, as the case may be, compared to an otherwise corresponding non-invention composition that is free of a silyl functional carboxylic anhydride ("silyl-anhydride") or that contains an unsubstituted carboxylic anhydride instead of the silyl-anhydride. Still further, upon being developed with developer, the resulting post-exposure baked resist should produce a resist image that is a faithful revelation of the former's latent pattern. This means the latent image portions of the post-exposure baked resist should be readily soluble in developer, whereas the unexposed portions of the post-exposure baked resist should remain insoluble in the developer, and adhere robustly to the same substrate or underlayer.

[0011] We have discovered problems with incumbent chemically-amplifiable photoresist compositions containing incumbent adhesion promoters such as unsubstituted carboxylic anhydrides (lacking alkoxysilyl groups), epoxy trialkoxysilanes, methacrylate trialkoxysilanes, isocyanato trialkoxysilanes, and allyl trialkoxysilanes. The incumbent chemically-amplifiable photoresist compositions do not adhere robustly to bare silicon wafers or primed silicon wafers.

[0012] We have discovered a silsesquioxane-containing composition comprising a silsesquioxane resin and a silyl-anhydride of formula (II) (described later) that solves one or more of the aforementioned problems. Embodiments of the present invention include the silsesquioxane-containing composition, products prepared therefrom, photoresist compositions comprising the silsesquioxane-containing composition and a photoacid generator, products prepared therefrom, methods of making and using same, and manufactured articles and semiconductor devices containing same. The silsesquioxane-containing composition may be used to prepare the photoresist composition. The photoresist composition may be used as a layer of a single layer photoresist or as a layer of multilayer photoresist, both in a method of photolithographic patterning. The silsesquioxane-containing composition may also be used in other light related applications other than photolithography such as anti-reflective coatings or optical encapsulants. The silsesquioxane-containing composition may also be used in "dark" applications that do not employ light such as adhesives, coatings, and sealants. The silsesquioxane-containing composition may be used

to make manufactured articles for non-electronics applications and the composition may be used in non-electronic articles and devices.

BRIEF DESCRIPTION OF DRAWINGS

[0013] Certain embodiments of the present invention are illustrated in the accompanying drawings. The drawings preserve same numbers for same elements and features.

[0014] Figure 1 (FIG. 1) is an elevation view of a substrate embodiment.

[0015] FIG. 2 is an elevation view of an underlayer-on-substrate embodiment.

[0016] FIG. 3 is an elevation view of a bilayer resist-on-substrate embodiment.

[0017] FIG. 4 is an elevation view of a masked-irradiated resist-on-substrate embodiment.

[0018] FIG. 5 is an elevation view of a developed resist-on-substrate embodiment.

[0019] FIG. 6 is an elevation view of a plasma-etched resist-on-substrate embodiment.

[0020] FIG. 7 is an elevation view of a halogen-etched substrate embodiment.

[0021] FIG. 8 is an elevation view of a patterned structure embodiment.

[0022] FIG. 9 is a scheme of steps of a process of making a patterned substrate embodiment.

[0023] FIG. 10 is a photograph of an inventive embodiment of a post-exposure baked wafer (primed) after treatment with developer.

[0024] FIG. 11 is a photograph of an inventive embodiment of a post-exposure baked wafer (bare) after treatment with developer.

[0025] FIG. 12L (non-invention) is a photograph of a non-invention embodiment of a post-exposure baked wafer (primed) after treatment with developer.

[0026] FIG. 12R (non-invention) is a photograph of a non-invention embodiment of a post-exposure baked wafer (bare) after treatment with developer.

DETAILED DESCRIPTION OF THE INVENTION

[0027] The Brief Summary and Abstract are incorporated here by reference. This invention is described herein in an illustrative manner by disclosing a plurality of representative, non-limiting embodiments and examples.

[0028] The silsesquioxane-containing composition comprises (A) a silsesquioxane resin of formula (I), described later, and (B) a silyl-anhydride of formula (II), described later. The silyl-anhydride of formula (II) is a silyl-functional carboxylic anhydride. The silsesquioxane-containing composition may consist of constituents (A) and (B) (i.e., 0 optional constituents), or may comprise constituents (A), (B), and 1, 2, 3, or more optional constituents described later (e.g., (C) a photoacid generator and/or (D) a solvent). The silsesquioxane-containing composition may be prepared by mixing together constituents (A) and (B), and, if desired, any

optional constituents. The silsesquioxane-containing composition may be prepared as a 1-part formulation or a multiple part formulation such as a 2-part formulation. The 1-part formulation may appeal to end-users having cold and/or dark storage capacity and/or end-users who wish to avoid mixing multiple parts together just prior to use. The multipart
 5 formulation such as the 2-part formulation may appeal to end-users who lack cold and/or dark storage capacity and/or end-users who wish to mix the multiple parts together just prior to use.

[0029] The photoresist composition comprises the (A) silsesquioxane resin of formula (I), (B) silyl-anhydride of formula (II), and (C) a photoacid generator. The molar amount of the (B) silyl-anhydride of formula (II) may be less than the molar amount of the (C) photoacid
 10 generator in the photoresist composition. The photoresist composition may consist of constituents (A), (B) and (C) (i.e., 0 optional constituents), or may comprise constituents (A), (B), (C), and 1, 2, 3, or more optional constituents described later (e.g., (D) a solvent). The photoresist composition may be prepared by together mixing constituents (A), (B), (C), and any optional constituents. Alternatively, the photoresist composition may be prepared by
 15 mixing the silsesquioxane-containing composition, constituent (C), and any optional constituents. The photoresist composition may be prepared as a 1-part formulation or a multiple part formulation such as a 2-part formulation.

[0030] The silsesquioxane-containing composition and the photoresist composition independently may be prepared as a manufactured article comprising the silsesquioxane-
 20 containing composition or the photoresist composition, respectively. The preparing may comprise shaping the respective composition.

[0031] The silsesquioxane-containing composition and the photoresist composition may be used in an opto/electronic device comprising an opto/electronic component and the silsesquioxane-containing composition or the photoresist composition, respectively. The
 25 opto/electronic component may be an optical component, an electronic component, or a combination optical and electronic component. The silsesquioxane-containing composition and the photoresist composition may be disposed in direct or indirect contact with the opto/electronic component.

[0032] Some embodiments of the invention include the following numbered aspects.

[0033] Aspect 1. A silsesquioxane-containing composition comprising (A) a silsesquioxane resin and (B) a silyl-anhydride, wherein: the (A) silsesquioxane resin is of formula (I):

$$[\text{HSiO}_{3/2}]_{t1}[\text{Z-L-SiO}_{3/2}]_{t2}[\text{H}(\text{R}^1\text{O})\text{SiO}_{2/2}]_d[(\text{R}^1\text{O})_x\text{SiO}_{(4-x)/2}]_y[\text{R}^2\text{SiO}_{3/2}]_{t3} \quad (\text{I}),$$

 wherein: subscript t1 is a mole fraction of from 0.4 to 0.9; subscript t2 is a mole fraction of from

0.1 to 0.6; subscript d is a mole fraction from 0 to 0.45; subscript x is an integer of 1, 2, or 3; subscript y is a mole fraction from 0 to 0.25; subscript t3 is a mole fraction from 0 to 0.15; the sum of $t_1 + t_2 =$ from ≥ 0.9 to ≤ 1 and the sum of $t_1 + t_2 + d + y + t_3 = 1$; each R^1 is independently H or (C₁-C₆)alkyl; each R^2 is independently HO-L- or HOOC-L-; each L is independently a divalent (C₁-C₂₀)hydrocarbon group that is unsubstituted or substituted with at least 1 substituent independently selected from (C₁-C₃)alkyl, -OH, and a fluorine atom up to and including perfluoro-substitution; and each Z is -OH, -COOH, -O-THP, -OCH(R^{3a})₂, -OC(R^{3b})₃, -COOCH(R^{3a})₂, -COOC(R^{3b})₃, -OCOOCH(R^{3a})₂, or -OCOOC(R^{3b})₃, wherein THP is tetrahydropyran-2-yl; wherein each R^{3a} is independently a (C₁-C₆)alkyl, (C₃-C₁₂)cycloalkyl, (C₆-C₁₀)aralkyl, ((C₁-C₆)alkyl)3SiCH₂CH₂-, or 2 R^{3a} together with the carbon atom to which they are both bonded are a (C₃-C₁₂)cycloalkyl or a (C₆-C₁₂)bicycloalkyl; and wherein each R^{3b} is independently a (C₁-C₆)alkyl, (C₃-C₁₂)cycloalkyl, (C₆-C₁₀)aralkyl, ((C₁-C₆)alkyl)3SiCH₂CH₂-, or 2 R^{3b} together with the carbon atom to which they are both bonded are a (C₃-C₁₂)cycloalkyl or a (C₆-C₁₂)bicycloalkyl and the remaining R^{3b} is independently a (C₁-C₆)alkyl, (C₃-C₁₂)cycloalkyl, (C₆-C₁₀)aralkyl, or ((C₁-C₆)alkyl)3SiCH₂CH₂-, or all 3 R^{3b} together with the carbon atom to which they are all bonded are a (C₇-C₁₂)bicycloalkyl; and the (B) silyl-anhydride is of formula (II): (R⁴O)₃Si-(L¹)_m-C(R⁵)₂-C(=O)-O-C(=O)-R⁶ (II), wherein: each R⁵ is independently H, a (C₁-C₆)alkyl, or a monovalent group of formula -(L²)_n-Si(OR⁴)₃; or both R⁵ are taken together to form a (C₂-C₅)alkane-diyl; or one R⁵ is taken together with R⁶ to form a bond or (C₁-C₄)alkane-diyl, and the remaining R⁵ is independently H, a (C₁-C₆)alkyl, or a monovalent group of formula -(L²)_n-Si(OR⁴)₃; or both R⁵ are taken together with R⁶ to form =CH-; R⁶ is taken together with R⁵ as described above or R⁶ is a (C₁-C₈)hydrocarbyl or a monovalent group of formula -C(R⁷)₂-(L²)_n-Si(OR⁴)₃; subscript m is an integer of 0 or 1; each subscript n is independently an integer of 0 or 1; each R⁴ is independently an unsubstituted (C₁-C₆)alkyl; each L¹ and L² is independently a (C₁-C₈)hydrocarbon-diyl; and each R⁷ is independently H or a (C₁-C₆)alkyl; or both R⁷ are taken together to form a (C₂-C₅)alkane-diyl.

[0034] In embodiments wherein R^5 and R^6 are not taken together, the $-C(R^5)_2C(=O)-O-C(=O)-R^6$ portion of the silyl-anhydride of formula (II) is acyclic. In embodiments wherein one R^5 is taken together with R^6 to form a bond, the $-C(R^5)_2C(=O)-O-C(=O)-R^6$ portion of the silyl-anhydride of formula (II) is a malonic anhydride. In embodiments wherein one R^5 is taken together with R^6 to form a (C_1) alkane-diyl (e.g., CH_2), the $-C(R^5)_2C(=O)-O-C(=O)-R^6$ portion of the silyl-anhydride of formula (II) is a succinic anhydride. In embodiments wherein one R^5 is taken together with R^6 to form a (C_2) alkane-diyl (e.g., CH_2CH_2), the $-C(R^5)_2C(=O)-O-C(=O)-R^6$ portion of the silyl-anhydride of formula (II) is a glutaric anhydride. In embodiments wherein one R^5 is taken together with R^6 to form a (C_3) alkane-diyl (e.g., $CH_2CH_2CH_2$), the $-C(R^5)_2C(=O)-O-C(=O)-R^6$ portion of the silyl-anhydride of formula (II) is an adipic anhydride. In embodiments wherein both R^5 are taken together with R^6 to form $=CH-$, the $-C(R^5)_2C(=O)-O-C(=O)-R^6$ portion of the silyl-anhydride of formula (II) is a maleic anhydride.

[0035] Aspect 2. The silsesquioxane-containing composition of aspect 1 wherein in the (A) silsesquioxane resin: subscript t1 is a mole fraction of from 0.4 to 0.65; subscript t1 is a mole fraction of from 0.65 to 0.9; subscript t2 is a mole fraction of from 0.1 to 0.35; subscript t2 is a mole fraction of from 0.5 to 0.6; subscript d is 0; subscript d is a mole fraction from > 0 to 0.45; subscript x is 1; subscript x is 2; subscript x is 3; subscript y is 0; subscript y is a mole fraction from > 0 to 0.25; subscript t3 is 0; subscript t3 is a mole fraction from > 0 to 0.15; at least one R^1 is H; subscript d is a mole fraction from > 0 to 0.45 or subscript y is a mole fraction from > 0 to 0.25 and at least one R^1 is H; at least one R^1 is independently (C_1-C_6) alkyl; subscript d is a mole fraction from > 0 to 0.45 or subscript y is a mole fraction from > 0 to 0.25 and at least one R^1 is (C_1-C_6) alkyl; at least one R^2 is independently HO-L-; subscript t3 is a mole fraction from > 0 to 0.15 and at least one R^2 is independently HO-L-; at least one R^2 is independently HOOC-L-; subscript t3 is a mole fraction from > 0 to 0.15 and at least one R^2 is independently HOOC-L-; at least one L is independently a divalent (C_1-C_{20}) hydrocarbon group that is unsubstituted; at least one L is independently a divalent (C_6-C_{10}) bicycloalkane group that is unsubstituted; at least one L is a divalent (C_1-C_{20}) hydrocarbon group that is substituted with at least 1 (C_1-C_3) alkyl group; at least one L is a divalent (C_6-C_{10}) bicycloalkane group that is

substituted with at least 1 (C₁-C₃)alkyl group; at least one L is a divalent (C₁-C₂₀)hydrocarbon group that is substituted with at least 1 -OH group; at least one L is a divalent (C₆-C₁₀)bicycloalkane group that is substituted with at least 1 -OH group; at least one L is independently a divalent (C₁-C₂₀)hydrocarbon group that is substituted with at least 1 fluorine atom up to and including perfluoro-substitution; at least one L is independently a divalent (C₆-C₁₀)bicycloalkane group that is substituted with at least 1 fluorine atom up to and including perfluoro-substitution; at least one Z is -OH; at least one Z is -COOH; at least one Z is -O-THP; at least one Z is -OCH(R^{3a})₂; at least one Z is -COOCH(R^{3a})₂; at least one Z is -OCOOCH(R^{3a})₂; at least one Z is -OC(R^{3b})₃; at least one Z is -COOC(R^{3b})₃; at least one Z is -OCOOCH(R^{3b})₃; at least one R^{3a} or R^{3b} is independently a (C₁-C₆)alkyl; at least one R^{3a} or R^{3b} is independently (C₃-C₁₂)cycloalkyl; at least one R^{3a} or R^{3b} is independently (C₆-C₁₀)aralkyl; at least one R^{3a} or R^{3b} is independently ((C₁-C₆)alkyl)₃SiCH₂CH₂-; 2 R^{3a} or 2 R^{3b} together with the carbon atom to which they are both bonded are a (C₃-C₁₂)cycloalkyl or a (C₆-C₁₂)bicycloalkyl; or all 3 R^{3b} together with the carbon atom to which they are all bonded are a (C₇-C₁₂)bicycloalkyl.

[0036] Aspect 3. The silsesquioxane-containing composition of aspect 1 or 2 wherein in the (A) silsesquioxane resin of formula (I) the Z-L- is selected from the following monovalent carboxylic esters: a bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, secondary aliphatic ester; a bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, tertiary aliphatic ester; a bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, secondary aliphatic ester; or a bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, tertiary aliphatic ester.

[0037] Aspect 4. The silsesquioxane-containing composition of aspect 3 wherein Z-L- is selected from the following monovalent carboxylic esters: bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 1',1'-dimethylethyl ester; bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 1',1'-dimethylethyl ester; bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 1'-methylethyl ester; bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 1'-methylethyl ester; bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, adaman-1'-yl ester; bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, adaman-1'-yl ester; bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 3'-methyladaman-1'-yl ester; bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 3'-methyladaman-1'-yl ester; bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 2'-methyladaman-2'-yl ester; bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 2'-methyladaman-2'-yl ester;

bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 2'-ethyladaman-2'-yl ester;
 bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 2'-ethyladaman-2'-yl ester;
 bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, cyclohexyl ester; bicyclo[2.2.1]heptane-6-yl-2-
 carboxylic acid, cyclohexyl ester; bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 1'-
 5 ethylcyclopentyl ester; bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 1'-ethylcyclopentyl ester;
 bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 2'-hydroxy-2',6',6'-
 trimethylbicyclo[3.1.1]heptane-3'-yl ester; and bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 2'-
 hydroxy-2',6',6'-trimethylbicyclo[3.1.1]heptane-3'-yl ester.

[0038] Aspect 5. The silsesquioxane-containing composition of any one of aspects 1 to 4
 10 wherein the (A) silsesquioxane resin of formula (I) has a weight average molecular weight
 (M_w) of 1,000 to 50,000.

[0039] Aspect 6. The silsesquioxane-containing composition of any one of aspects 1 to 5
 wherein in the (B) silyl-anhydride of formula (II): each R^5 is independently H, a (C_1-C_6) alkyl,
 or a monovalent group of formula $-(L^2)_n-Si(OR^4)_3$; at least one R^5 is H; at least one R^5 is a
 15 (C_1-C_6) alkyl; at least one R^5 is a monovalent group of formula $-(L^2)_n-Si(OR^4)_3$; both R^5 are
 taken together to form a (C_2-C_5) alkane-diyl; one R^5 is taken together with R^6 to form a bond
 or (C_1-C_4) alkane-diyl, and the remaining R^5 is independently H, a (C_1-C_6) alkyl, or a
 monovalent group of formula $-(L^2)_n-Si(OR^4)_3$; one R^5 is taken together with R^6 to form a
 bond, and the remaining R^5 is independently H, a (C_1-C_6) alkyl, or a monovalent group of
 20 formula $-(L^2)_n-Si(OR^4)_3$; one R^5 is taken together with R^6 to form a (C_1-C_4) alkane-diyl, and
 the remaining R^5 is independently H, a (C_1-C_6) alkyl, or a monovalent group of formula $-(L^2)_n-$
 $Si(OR^4)_3$; one R^5 is taken together with R^6 to form a (C_1-C_4) alkane-diyl, and the remaining
 R^5 is H; one R^5 is taken together with R^6 to form a (C_1-C_4) alkane-diyl, and the remaining R^5
 is a (C_1-C_6) alkyl; one R^5 is taken together with R^6 to form a (C_1-C_4) alkane-diyl, and the
 25 remaining R^5 is a monovalent group of formula $-(L^2)_n-Si(OR^4)_3$; both R^5 are taken together
 with R^6 to form $=CH-$; R^6 is taken together with R^5 as described above; R^6 is a $(C_1-$
 $C_8)$ hydrocarbyl or a monovalent group of formula $-C(R^7)_2-(L^2)_n-Si(OR^4)_3$; R^6 is a $(C_1-$
 $C_8)$ hydrocarbyl; R^6 is a monovalent group of formula $-C(R^7)_2-(L^2)_n-Si(OR^4)_3$; each R^5 is

independently H or a (C₁-C₆)alkyl and R⁶ is a (C₁-C₈)hydrocarbyl; subscript m is 0; at least one R⁵ is a monovalent group of formula -(L²)_n-Si(OR⁴)₃ and R⁶ is a monovalent group of formula -C(R⁷)₂-(L²)_n-Si(OR⁴)₃; subscript m is 1; at least one subscript n is 0; at least one subscript n is 1; at least one R⁴ is independently an unsubstituted (C₁-C₂)alkyl; at least one R⁴ is independently an unsubstituted (C₃-C₆)alkyl; at least one L¹ and L² is independently a (C₁-C₄)hydrocarbon-diyl; at least one L¹ and L² is independently a (C₁-C₄)alkane-diyl; each of L¹ and L² is independently a (C₁-C₄)alkane-diyl; at least one L¹ and L² is independently a (C₅-C₈)hydrocarbon-diyl; at least one R⁷ is H or a (C₁-C₆)alkyl; at least one R⁷ is H or a (C₁-C₂)alkyl; both R⁷ are taken together to form a (C₂-C₅)alkane-diyl; or both R⁷ are taken together to form a (C₂-C₃)alkane-diyl.

[0040] Aspect 7. The silsesquioxane-containing composition of any one of aspects 1 to 5 wherein the (B) silyl-anhydride of formula (II) is selected from: 2-(3'-triethoxysilyl-propyl)-succinic anhydride; 2,3-bis(3'-triethoxysilyl-propyl)-succinic anhydride; 3-(3'-triethoxysilyl-propyl)-glutaric anhydride; 2,3-bis(3'-triethoxysilyl-propyl)-glutaric anhydride; and 1,1,2,2,3,3-hexamethyl-1,3-bis(ethyl-1',2'-dicarboxylic)-trisiloxane dianhydride.

[0041] Aspect 8. A silsesquioxane-containing composition comprising the silsesquioxane-containing composition of any one of aspects 1 to 7 and (C) a photoacid generator.

[0042] Aspect 9. The silsesquioxane-containing composition of aspect 8, wherein the (C) photoacid generator comprises an onium salt, a halogen-containing compound, a diazoketone compound, a sulfone compound, a sulfonate compound, or a combination of any two or more thereof.

[0043] Aspect 10. The silsesquioxane-containing composition of any one of aspects 1 to 9 independently further comprising one or more constituents (additives): (D) solvent, (E) an acid-diffusion controlling agent, (F) a dye, (G) a halation inhibitor, (H) a plasticizer, (I) a sensitizer, (J) a stabilizer (e.g., storage stabilizer), and (K) a surfactant. In some embodiments the silsesquioxane-containing composition does not contain constituents (D) to (K). In some embodiments the silsesquioxane-containing composition further comprises the (D) solvent, the (E) acid-diffusion controlling agent, or both (D) and (E).

[0044] Aspect 11. A manufactured article comprising the silsesquioxane-containing composition of any one of aspects 1 to 10.

[0045] Aspect 12. A method of making a resist image on a substrate, the method comprising: applying the silsesquioxane-containing composition of any one of aspects 1 to 10 to a surface of a substrate so as to form an applied film thereof on the surface of the substrate, wherein the silsesquioxane-containing composition comprises the (A) silsesquioxane resin, the (B) silyl-anhydride, and (C) a photoacid generator; mask exposing the applied film to radiation to produce an exposed film containing a latent pattern; developing the exposed film to produce a resist image from the latent pattern to give a manufactured article comprising the resist image disposed on the substrate. The substrate may be any article that can receive the silsesquioxane-containing composition and support the applied film thereof. E.g., the substrate may be a semiconductor wafer or an underlayer (e.g., a hardmask or anti-reflective coating). The underlayer may be freestanding or disposed on a semiconductor wafer.

[0046] Aspect 13. The method of making a resist image on a substrate of aspect 12, wherein: the substrate comprises a bare semiconductor wafer; the substrate comprises a primed semiconductor wafer; the substrate comprises a primed semiconductor wafer prepared by priming a bare semiconductor wafer with hexamethyldisilazane; the substrate comprises a semiconductor wafer and the silsesquioxane-containing composition is applied directly on a surface of the semiconductor wafer; the substrate comprises a semiconductor wafer having a surface portion comprising silicon carbide, silicon carbonitride, silicon nitride, silicon oxide, silicon oxynitride, or silicon oxycarbonitride, and the silsesquioxane-containing composition is applied directly on the surface portion of the semiconductor wafer; the substrate comprises an underlayer (e.g., 2 in FIG. 2), such as an antireflective coating (ARC) or a hardmask layer, disposed on a surface of a semiconductor wafer (e.g., 1 in FIG. 2) and the silsesquioxane-containing composition is applied directly on the underlayer (e.g., ARC or the hardmask layer) without being applied directly on the semiconductor wafer (e.g., as in FIG. 3); before the applying step the silsesquioxane-containing composition further comprises (D) a solvent and the applying step comprises spin-coating; the applied film further comprises (D) a solvent and the method further comprises drying the applied film (soft baking) before the mask exposing step; the applied film has a thickness of from 0.01 to 5 micrometers; the radiation is selected from ultraviolet (UV) light, X-ray radiation, e-beam radiation, and extreme ultraviolet (EUV) radiation; the radiation has a wavelength in a range of from 13 nanometers (nm) to 365 nm; the radiation has a wavelength comprising 365 nm, 248 nm, 193 nm, 157 nm, or 13 nm; the developing step comprises contacting the mask exposed film (e.g., 3 in FIG. 4) with a developer comprising an aqueous base; the method further comprises heating the mask exposed film at a temperature from 30 degrees Celsius ($^{\circ}$ C) to 200 $^{\circ}$ C and cooling the mask

exposed film before the developing step and the developing step comprises contacting the cooled mask exposed film with a developer comprising an aqueous base; or the developing step comprises contacting the mask exposed film with a developer comprising aqueous tetramethylammonium hydroxide. The radiation wavelength may comprise 248 nm or 193 nm.

5 [0047] Aspect 14. The method of making a resist image on a substrate of aspect 12 or 13, wherein: the substrate comprises a hardmask layer disposed on a surface of a semiconductor wafer and the silsesquioxane-containing composition is applied directly on the hardmask layer without being applied directly on the semiconductor wafer and the method further comprises oxygen (O₂) plasma etching the resist image to etch the hardmask layer by transferring the
10 resist image into the hardmask layer and give a first semiconductor device comprising a bilayer image disposed on the surface of the semiconductor wafer, wherein the bilayer image comprises a resist image layer and a hardmask image layer, and wherein a region of the surface of the semiconductor wafer is covered by the bilayer image and another region of the surface of the semiconductor wafer is uncovered (e.g., as in FIG. 6); or the substrate
15 comprises a hardmask layer disposed on a surface of a semiconductor wafer and the silsesquioxane-containing composition is applied directly on the hardmask layer without being applied directly on the semiconductor wafer and the method further comprises: (i) oxygen (O₂) plasma etching the resist image to etch the hardmask layer by transferring the resist image into the hardmask layer to give a first semiconductor device sequentially comprising a bilayer
20 image disposed on the surface of the semiconductor wafer, wherein the bilayer image comprises a resist image layer and a hardmask image layer, and wherein a region of the surface of the semiconductor wafer is covered by the bilayer image and another region of the surface of the semiconductor wafer is uncovered (e.g., as in FIG. 6); and (ii) halogen etching the uncovered region of the surface of the semiconductor wafer of the first semiconductor
25 device to transfer the bilayer image into the semiconductor wafer by removing the remaining applied film, at least some of the hardmask layer, and some, but not all, of the uncovered region of the semiconductor wafer to give a second semiconductor device comprising a semiconductor image disposed on a basal semiconductor layer. E.g., as in FIG. 7 wherein all of the applied film, some of the hardmask layer, and some, but not all, of the uncovered region
30 of the semiconductor wafer are removed; or as in FIG. 8 wherein all of the applied film, all of the hardmask layer, and some, but not all, of the uncovered region of the semiconductor wafer are removed.

[0048] Aspect 15. A semiconductor device comprising the first or second semiconductor device made by the method of aspect 14.

[0049] Aspect 16. The semiconductor device of aspect 15 comprising the second semiconductor device wherein the semiconductor image of the second semiconductor device has an aspect ratio greater than 5, a rectangular profile, or both.

5 [0050] We present a technical solution to one or more of the aforementioned problems of prior art photoresists. Embodiments of our invention yield resist images that adhere sufficiently to bare silicon wafers and primed silicon wafers.

[0051] Without being bound by theory, we believe that the silyl-anhydride of formula (II) allows the inventive photoresist composition to be radiation sensitive such that after being masked-irradiated with radiation having a suitable wavelength for activating the (C) PAG, it forms a masked-irradiated resist having distinct latent patterns. The (C) PAG in the portions of the photoresist composition that are exposed to the radiation readily react to form product acid, and in turn the silsesquioxane resin of formula (I) in the same portions of the photoresist composition readily reacts with the product acid to cleave its acid dissociable groups and form a product polymer. In contrast, the (C) PAG in the portions of the photoresist composition that are not exposed to the radiation do not form product acid when kept in the dark, and thus the silsesquioxane resin of formula (I) in the same unexposed portions of the photoresist composition do not react to form a product polymer. Further, both the unexposed portions and the latent image portions of the masked-irradiated resist exhibit increased adhesion to a substrate or the underlayer, as the case may be, compared to an otherwise corresponding non-invention composition that is free of the (B) silyl anhydride or that contains an unsubstituted carboxylic anhydride instead of the (B) silyl anhydride. Still further, upon being developed with developer, the resulting post-exposure baked resist produces a resist image that is a faithful revelation of the former's latent pattern. This means the latent image portions of the post-exposure baked resist are readily soluble in developer, whereas the unexposed portions of the post-exposure baked resist should remain insoluble in the developer and adhere robustly to the wafers. The improvements such as better adherence are believed to be due at least in part to the silyl anhydride of formula (II).

[0052] Embodiments of the silsesquioxane-containing composition, including photoresist compositions comprising the (A) silsesquioxane resin of formula (I), the (B) silyl-anhydride of formula (II), and (C) a photoacid generator, may be optically transparent at wavelengths from 13 nm to 365 nm such as 13 nm, 157 nm, 193 nm, or 248 nm. The embodiments may also have adhesion to a semiconductor material or underlayer material such as an ARC or hardcoat material. The embodiments may also be thermally stable, for example if heated in absence of light and from 30° to 250° C for from 1 to 120 minutes. The embodiments further comprising

the (C) photoacid generator are chemically amplifiable during exposure to radiation. The resulting radiation exposed embodiments may be developable in aqueous base such as aqueous tetramethylammonium hydroxide (TMAH_{aq}) such as 2.5 wt% TMAH_{aq}.

[0053] Unless otherwise defined herein, meanings of chemical technology terms used

herein may be found in IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8.

doi:10.1351/goldbook. Terms not defined by IUPAC may be defined in *Hawley's*

CONDENSED CHEMICAL DICTIONARY, 11th edition, N. Irving Sax & Richard J. Lewis, Sr., 1987 (Van Nostrand Reinhold).

[0054] Unless otherwise defined herein, meanings of general terms used herein may be

found here. Alternatively precedes a distinct embodiment. Articles "a", "an", and "the" each refer to one or more. Average molecular mass of a polymer such as weight average

molecular mass or "M_w" is determined using gel permeation chromatography (GPC) with

polystyrene standards. Chemical element or atom, a Group or Groups of chemical elements shall mean those published by IUPAC in the Periodic Table of the Elements, version dated 01 May 2013. Any comparative example is used for illustration purposes only and shall not mean prior art. Cured product such as a cured organosiloxane may have a structure that can be varied depending upon the particular reactants and curing conditions used to make it.

That variability is not unlimited, but is restricted according to the structure of the reactants and curing chemistry and conditions. An example of the invention may be relied upon and provides adequate support for amending claims. Formulation, one-part, means a mixture

containing all the constituents and in proportions needed to produce a cured product. The

one-part formulation may use external factors such as moisture (for condensation curing), heat (for addition curing), or light (for addition curing) to initiate, speed or complete the curing process. Formulation, two-part, means a system that segregates different reactive

constituents into two separate and complementary divisions to prevent premature initiation of curing. For example, a monomer or prepolymer, but not a catalyst, may be included in a

primary part; and a cure catalyst, but not a monomer or prepolymer, may be included in a secondary part. Initiation of curing is achieved by combining the primary part and the

secondary part together to form a one-part formulation. "Free of" or "lacks" means a complete absence of; alternatively not detectable, e.g., using nuclear magnetic resonance

(NMR) spectroscopy (e.g., ^1H -NMR, ^{13}C -NMR, or ^{29}Si -NMR) or Fourier Transform-Infrared (FT-IR) spectroscopy. Invention and inventive shall mean a representative embodiment or aspect, and shall not be interpreted as the entire inventive scope. IUPAC is International Union of Pure and Applied Chemistry (IUPAC Secretariat, Research Triangle Park, North Carolina, USA). Markush group comprises a genus of two or more members. A Markush group of members A and B may be equivalently expressed as: "a member selected from A and B"; "a member selected from the group consisting of A and B"; or "a member A or B".

Each member may independently be a subgenus or species of the genus and may be relied upon individually or collectively in amending claims. May confers a permitted choice, not an

imperative. Operative means functionally capable or effective. Optional(ly) means is absent (or excluded), alternatively is present (or included). Properties are measured using a standard test method and conditions for measuring (e.g., viscosity: 23°C and 101.3 kPa).

Ranges of numbers include endpoints, subranges, and whole and/or fractional values

subsumed therein, except a range of integers does not include fractional values. Any stated

number may be relied upon and provides adequate support for amending claims. Substituted means having, in place of hydrogen, one or more substituents, including per substitution.

Each substituent may independently be a halogen

atom, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{NO}_2$, $-\text{OH}$, $-\text{OR}$, oxo ($=\text{O}$), $-\text{C}\equiv\text{N}$, $-\text{C}(=\text{O})-\text{R}$, $-\text{OC}(=\text{O})\text{R}$, -

$\text{C}(=\text{O})\text{OH}$, $-\text{C}(=\text{O})\text{OR}$, $-\text{SH}$, $-\text{SR}$, $-\text{SSH}$, $-\text{SSR}$, $-\text{SC}(=\text{O})\text{R}$, $-\text{SO}_2\text{R}$, $-\text{OSO}_2\text{R}$, $-\text{SiR}_3$,

or $-\text{Si}(\text{OR})_3$; wherein each R independently is an unsubstituted (C_1 - C_{30})hydrocarbyl,

alternatively (C_1 - C_6)hydrocarbyl. Halogen atom is F, Cl, Br, or I; alternatively F, Cl, or Br;

alternatively F or Cl; alternatively F; alternatively Cl. "Vehicle" means a liquid acting as a

carrier, dispersant, diluent, storage medium, supernatant, or solvent for another material.

[0055] Any compound herein includes all its "isotopic forms", including natural abundance

forms and isotopically-enriched forms. In some aspects, the isotopic form is the natural abundance form, alternatively the isotopically-enriched form. The isotopically-enriched forms may have additional uses, such as medical research or anti-counterfeiting applications, wherein detection of the isotopically-enriched compound is helpful in treatment or detection.

[0056] In some aspects any composition described herein may contain any one or more of

the chemical elements of Groups 1 to 18 of the Periodic Table of the Elements, unless that chemical element has been specifically excluded. Specifically excluded chemical elements may be: (i) at least one chemical element from any one of Groups 2 to 13 and 18, including the lanthanoids and actinoids; (ii) at least one chemical element from any one of the third to

sixth rows of the Periodic Table of the Elements, including the lanthanoids and actinoids; or
(iii) both (i) and (ii), except not excluding Si, O, H, C, N, F, Cl, Br, or I.

[0057] Additional invention embodiments described below.

[0058] In some embodiments the silsesquioxane-containing composition and the photoresist composition independently may be free of an organic polymer such as any epoxy, natural rubber, polyacrylate, polymethacrylate, polyamide, polyester, polyether, polyimide, polyisocyanate, polyisocyanurate, polyolefin, polyphenol, polyurethane, poly(vinyl acetate), poly(vinyl alcohol), or a combination thereof. The organic polymer is a macromolecular material having a backbone that includes carbon atoms and optionally N and/or O atoms and is free of (lacks) a Si atom. Epoxy includes epoxy resin and polyepoxide. In some embodiments the silsesquioxane-containing composition and the photoresist composition independently may be free of an unsubstituted carboxylic anhydride (i.e., an anhydride consisting of C, H and O atoms) such as acetic anhydride and an unsubstituted multicarboxylic anhydride such as an unsubstituted dicarboxylic anhydride such as succinic anhydride and phthalic anhydride, and an unsubstituted tetracarboxylic anhydride such as benzophenone-3,3',4,4'-tetracarboxylic dianhydride. In some embodiments the silsesquioxane-containing composition and the photoresist composition independently may be free of both the organic polymer and the unsubstituted carboxylic anhydride.

[0059] (A) silsesquioxane resin of formula (I):

[0060] The (A) silsesquioxane resin is of formula (I):

$$[\text{HSiO}_{3/2}]_{t1}[\text{Z-L-SiO}_{3/2}]_{t2}[\text{H}(\text{R}^1\text{O})\text{SiO}_{2/2}]_d[(\text{R}^1\text{O})_x\text{SiO}_{(4-x)/2}]_y[\text{R}^2\text{SiO}_{3/2}]_{t3} \quad (\text{I}),$$
 wherein: subscript $t1$ is a mole fraction of from 0.4 to 0.9; subscript $t2$ is a mole fraction of from 0.1 to 0.6; subscript d is a mole fraction from 0 to 0.45; subscript x is an integer of 1, 2, or 3; subscript y is a mole fraction from 0 to 0.25; subscript $t3$ is a mole fraction from 0 to 0.15; the sum of $t1 + t2 =$ from ≥ 0.9 to ≤ 1 and the sum of $t1 + t2 + d + y + t3 = 1$; each R^1 is independently H or $(\text{C}_1\text{-C}_6)\text{alkyl}$; each R^2 is independently HO-L- or HOOC-L- ; each L is independently a divalent $(\text{C}_1\text{-C}_{20})\text{hydrocarbon}$ group that is unsubstituted or substituted with at least 1 substituent independently selected from $(\text{C}_1\text{-C}_3)\text{alkyl}$, $-\text{OH}$, and a fluorine atom up to and including perfluoro-substitution; and each Z is $-\text{OH}$, $-\text{COOH}$, $-\text{O-THP}$, $-\text{OCH}(\text{R}^{3a})_2$, $-\text{OC}(\text{R}^{3b})_3$, $-\text{COOCH}(\text{R}^{3a})_2$, $-\text{COOC}(\text{R}^{3b})_3$, $-\text{OCOOCH}(\text{R}^{3a})_2$, or $-\text{OCOOC}(\text{R}^{3b})_3$, wherein THP is tetrahydropyran-2-yl; wherein each R^{3a} is independently a $(\text{C}_1\text{-C}_6)\text{alkyl}$,

(C₃-C₁₂)cycloalkyl, (C₆-C₁₀)aralkyl, ((C₁-C₆)alkyl)3SiCH₂CH₂-, or 2 R^{3a} together with the carbon atom to which they are both bonded are a (C₃-C₁₂)cycloalkyl or a (C₆-C₁₂)bicycloalkyl; and wherein each R^{3b} is independently a (C₁-C₆)alkyl, (C₃-C₁₂)cycloalkyl, (C₆-C₁₀)aralkyl, ((C₁-C₆)alkyl)3SiCH₂CH₂-, or 2 R^{3b} together with the carbon atom to which they are both bonded are a (C₃-C₁₂)cycloalkyl or a (C₆-C₁₂)bicycloalkyl and the remaining R^{3b} is independently a (C₁-C₆)alkyl, (C₃-C₁₂)cycloalkyl, (C₆-C₁₀)aralkyl, or ((C₁-C₆)alkyl)3SiCH₂CH₂-, or all 3 R^{3b} together with the carbon atom to which they are all bonded are a (C₇-C₁₂)bicycloalkyl. In some embodiments any one of subscripts t₁, t₂, d, x, y, and t₂ and functional groups Z, L, R¹, and R² is as defined above in a dependent numbered aspect.

In some embodiments the (A) silsesquioxane resin is the silsesquioxane resin 1 of the working examples described later.

[0061] (B) Silyl-anhydride:

[0062] The (B) silyl-anhydride is of formula (II): (R⁴O)₃Si-(L¹)_m-C(R⁵)₂-C(=O)-O-C(=O)-R⁶ (II), wherein: each R⁵ is independently H, a (C₁-C₆)alkyl, or a monovalent group of formula -(L²)_n-Si(OR⁴)₃; or both R⁵ are taken together to form a (C₂-C₅)alkane-diyl; or one R⁵ is taken together with R⁶ to form a bond or (C₁-C₄)alkane-diyl, and the remaining R⁵ is independently H, a (C₁-C₆)alkyl, or a monovalent group of formula -(L²)_n-Si(OR⁴)₃; or both R⁵ are taken together with R⁶ to form =CH-; R⁶ is taken together with R⁵ as described above or R⁶ is a (C₁-C₈)hydrocarbonyl or a monovalent group of formula -C(R⁷)₂-(L²)_n-Si(OR⁴)₃; subscript m is an integer of 0 or 1; each subscript n is independently an integer of 0 or 1; each R⁴ is independently an unsubstituted (C₁-C₆)alkyl; each L¹ and L² is independently a (C₁-C₈)hydrocarbon-diyl; and each R⁷ is independently H or a (C₁-C₆)alkyl; or both R⁷ are taken together to form a (C₂-C₅)alkane-diyl. In some embodiments any one of subscripts m and n and groups R⁴ to R⁷ is as defined above in a dependent numbered aspect. In some embodiments the (B) silyl-anhydride is the silyl-anhydride (B-1), (B-2), (B-3), (B-4), or (B-5) of the working examples described later.

[0063] The (B) silyl-anhydride is typically present in the silsesquioxane-containing composition at a concentration from 0.01 part to 5 parts, alternatively from 0.05 part to 4 parts,

alternatively from 0.07 part to 3 parts, alternatively from 0.09 part to 2 parts, all per 100 parts of the (A) silsesquioxane resin.

[0064] (C) Photoacid generator (PAG).

[0065] The photoresist composition comprises one or more (C) photoacid generator. The (C) photoacid generator ("PAG") comprises any compound that is not an acid (not a Brønsted or Lewis acid), but that generates an acid upon exposure to electromagnetic radiation. Thus, a PAG functions as a pro-acid, which is a compound that undergoes a photochemical transformation before exhibiting acidic effects. In some aspects the PAG is an onium salt, a halogen-containing compound, a diazoketone compound, glyoxime derivative, a sulfone compound, a sulfonate compound, or a combination of any two or more of the onium salt, halogen-containing compound, diazoketone compound, sulfone compound, and sulfonate compound. Other useful photoacid generators include those mentioned in US 7,261,992 B2, at column 10, line 57, to column 11, line 9. These include nitrobenzyl esters and s-triazine derivatives, such as the s-triazine derivatives mentioned in US 4,189,323.

[0066] Onium Salts: Examples of onium salts suitable for use as the (C) PAG are iodonium salts, sulfonium salts (including tetrahydrothiophenium salts), phosphonium salts, diazonium salts, and pyridinium salts. Specific examples of onium salts suitable for use as the (C) PAG are listed in US 8,729,148 B2, at column 14, line 40, to column 15, line 4, and tri(4-(4'-acetylphenylthio)-phenyl)sulfonium tetrakis(pentafluorophenyl)borate.

[0067] Halogen-containing Compounds: Examples of halogen-containing compounds suitable for use as the (C) PAG are haloalkyl group-containing hydrocarbon compounds, and haloalkyl group-containing heterocyclic compounds. Specific examples of halogen-containing compounds suitable for use as the (C) PAG are (trichloromethyl)-s-triazine derivatives such as phenylbis(trichloromethyl)-s-triazine, 4-methoxyphenylbis(trichloromethyl)-s-triazine, and 1-naphthylbis(trichloromethyl)-s-triazine, and 1,1-bis(4'-chlorophenyl)-2,2,2-trichloroethane.

[0068] Diazoketone Compounds: Examples of diazoketone compounds suitable for use as the (C) PAG are diazomethane derivatives listed in US 8,729,148 B2, at column 15, lines 4-23, 1,3-diketo-2-diazo compounds, diazobenzoquinone compounds, and diazonaphthoquinone compounds. As specific examples of diazoketone compounds suitable for use as the PAG are 1,2-naphthoquinonediazido-4-sulfonyl chloride, 1,2-naphthoquinonediazido-5-sulfonyl chloride, 1,2-naphthoquinonediazido-4-sulfonate or 1,2-naphthoquinonediazido-5-sulfonate of 2,3,4,4'-tetrahydroxybenzophenone, and 1, 2-naphthoquinonediazido-4-sulfonate or 1,2-naphthoquinonediazido-5-sulfonate of 1,1,1-tris(4'-hydroxyphenyl)ethane.

[0069] Glyoxime Derivatives: Examples of glyoxime derivatives suitable for use as the (C) PAG are listed in US 8,729,148 B2, at column 15, lines 23 to 46.

[0070] Sulfone Compounds: Examples of sulfone compounds suitable for use as the (C) PAG are β -ketosulfone, β -sulfonylsulfone, and α -diazo compounds of these compounds. Specific examples of sulfone compounds are 4-trisphenacylsulfone, mesitylphenacylsulfone, and bis(phenylsulfonyl)methane.

[0071] Sulfonate Compounds: Examples of sulfonate compounds suitable for use as the (C) PAG are alkyl sulfonate, alkylimide sulfonate, haloalkyl sulfonate, aryl sulfonate, and imino sulfonate. Specific examples of sulfonate compounds suitable for use as the (C) PAG are benzointosylate, pyrogallol tris(trifluoromethanesulfonate), nitrobenzyl-9,10-diethoxyanthracene-2-sulfonate, trifluoromethanesulfonylbicyclo[2.2.1] hept-5-ene-2,3-dicarbodiimide, N-hydroxysuccinimidetrifluoromethanesulfonate, and 1,8-naphthalenedicarboxylic acid imido trifluoromethanesulfonate.

[0072] In some embodiments the (C) photoacid generator is diphenyliodoniumtrifluoromethanesulfonate, bis(4-t-butylphenyl)iodonium trifluoromethanesulfonate, bis(4-t-butylphenyl) iodonium nonafluoro-n-butanesulfonate, triphenylsulfonium trifluoromethanesulfonate, triphenylsulfonium nonafluoro-n-butanesulfonate, cyclohexyl-2-oxocyclohexylmethylsulfonium trifluoromethane sulfonate, dicyclohexyl-2-oxocyclohexylsulfonium trifluoromethanesulfonate, 2-oxocyclohexyldimethylsulfonium trifluoromethanesulfonate, 4-hydroxy-1-naphthyldimethylsulfonium trifluoromethanesulfonate, 4-hydroxy-1-naphthyltetrahydrothiophenium trifluoromethanesulfonate, 1-(1'-naphthylacetomethyl) tetrahydrothiophenium trifluoromethanesulfonate, trifluoromethanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-dicarbodiimide, N-hydroxysuccinimidetrifluoromethanesulfonate, or 1,8-naphthalenedicarboxylic acid imido trifluoromethanesulfonate.

[0073] The amount of the (C) photoacid generator to be used in the silsesquioxane-containing composition (e.g., the photoresist composition) may be from 0.01 to 10 parts by weight, alternatively from 0.05 to 7 parts by weight, alternatively from 0.09 part to 2 parts, all per 100 parts by weight of the (A) silsesquioxane resin. If the amount of the photoacid generator is less than 0.01 part by weight of the (A) silsesquioxane resin, sensitivity and developability (difference in solubility in developer solution such as TMAH_{aq} before and after radiation exposure) of the silsesquioxane-containing composition (e.g., the photoresist composition) containing such a low amount may tend to decrease. If the amount of the PAG exceeds 10 parts by weight of the (A) silsesquioxane resin, the silsesquioxane-containing composition

(e.g., the photoresist composition) containing such a large amount may not form a resist pattern having a rounded top or squared top cross-section profile, possibly due to decreased radiation transmittance.

[0074] In some embodiments, the silsesquioxane-containing composition and/or the photoresist composition independently further comprises one or more constituents or additives: (D) a solvent, (E) an acid-diffusion controlling agent (also called a quencher or base quencher), (F) a dye, (G) a halation inhibitor, (H) a plasticizer, (I) a sensitizer, (J) a stabilizer (e.g., storage stabilizer), and (K) a surfactant. Additives (D) to (K) are optional. In some embodiments the silsesquioxane-containing composition and/or the photoresist composition is free of (lacks) additives (D) to (K). In other embodiments the silsesquioxane-containing composition and/or the photoresist composition independently further comprises at least 1, alternatively at least 2, alternatively 3 or more of additives (D) to (K). In some embodiments the silsesquioxane-containing composition and/or the photoresist composition independently further comprises the (D) solvent, the (E) acid-diffusion controlling agent, or both (D) and (E).

[0075] (D) Solvent: In some embodiments the silsesquioxane-containing composition (e.g., the photoresist composition) is free of (lacks) (D) solvent. In some embodiments the silsesquioxane-containing composition (e.g., the photoresist composition) further comprises one or more (D) solvent. The (D) solvent may be used to dissolve, disperse, or dilute the other constituents of the silsesquioxane-containing composition (e.g., the photoresist composition) to give a mixture that can be more easily coated on a substrate in need of coating. Examples of such substrates for photoresist composition are a semiconductor wafer or metal wafer, or an underlayer (e.g., ARC) of a multilayer photoresist sequentially comprising the substrate, the underlayer, and the coating of the photoresist composition (photoresist layer). The underlayer is disposed (sandwiched) between the photoresist layer and the substrate. Examples of (D) solvent are methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), 2-heptanone, methyl pentyl ketone (MAK), cyclopentanone, cyclohexanone, lactate alkyl esters like ethyl lactate, 1,2-propylene glycol monomethyl ether monoacetate (PGMEA), alkylene glycol monoalkyl esters, butyl acetate, 2-ethoxyethanol, and ethyl 3-ethoxypropionate. When present in the silsesquioxane-containing composition (e.g., the photoresist composition), the (D) solvent may be at a concentration of from 50 wt% to 90 wt%, based on total weight of the silsesquioxane-containing composition (e.g., the photoresist composition).

[0076] (E) Acid-diffusion controlling agent: The (E) acid-diffusion controlling agent may be unnecessary in view of (B) the silyl-anhydride. In some embodiments the silsesquioxane-containing composition (e.g., the photoresist composition) is free of (lacks) (E) acid-diffusion

controlling agent. In some embodiments the silsesquioxane-containing composition (e.g., the photoresist composition) further comprises one or more (E) acid-diffusion controlling agent. The (E) acid-diffusion controlling agent may be used in the photoresist composition to inhibit excursion of the acid generated from (C) photoacid generator after exposure of areas of the photoresist composition outside the exposed areas. The (E) acid-diffusion controlling agent may be an aprotic organic base that does not form a covalent bond with a carboxylic anhydride. Examples of (E) acid-diffusion controlling agent are tertiary amines; the examples of the basic compounds found in paragraphs [0306 to 0315] of US 2003/0017415 A1; and the organic base additive mentioned in US 8,148,043 B2 to S. Hu, et al. ("HU3"). Examples of constituent (E) are tertiary arylamines such as 2-(2-amino-phenyl)-isoindole-1,3-dione; 1-((1H-1,2,3-benzotriazol-1-ylmethyl)amino)phenyl)ethanone; 1-((2,3-dimethyl-phenylamino)-methyl)-pyrrolidine-2,5-dione; 1-(2-methyl-4-phenylamino-3,4-dihydro-2H-quinolin-1-yl)-heptan-1-one; 2-((3-fluoro-4-methyl-phenylamino)-methyl)-phenol and N,N-diethylaniline. When present in the silsesquioxane-containing composition (e.g., the photoresist composition), the (E) acid-diffusion controlling agent may be at a concentration of from 0.01 wt% to 10 wt%, based on total weight of the silsesquioxane-containing composition (e.g., the photoresist composition).

[0077] (F) Dye: The (F) dye may be used to adjust optical density of the silsesquioxane-containing composition (e.g., the photoresist composition).

[0078] (G) Halation inhibitor: The (G) halation inhibitor may be used to prevent spreading of the lithographic radiation (light) beyond borders of the directly exposed areas of a photoresist layer of the photoresist composition.

[0079] (H) Plasticizer: The (H) plasticizer may be used to adjust viscosity of the silsesquioxane-containing composition (e.g., the photoresist composition) to enhance its handleability or coatability.

[0080] (I) Sensitizer: The (I) sensitizer may be used to enhance activity of the (C) photoacid generator by absorbing radiation at a first wavelength, and emitting radiation at a second wavelength transferring the emitted radiation to the (C) photoacid generator, wherein the first and second wavelengths may be the same or different.

[0081] (J) Stabilizer: The (J) stabilizer may be used to prolong shelf-life of the silsesquioxane-containing composition (e.g., the photoresist composition), such as by inhibiting oxidative, acid-base, or other degradation reactions therein.

[0082] (K) Surfactant: The (K) surfactant may be used to improve uniformity of a coating of the silsesquioxane-containing composition (e.g., the photoresist composition) on a substrate such as a semiconductor wafer or an underlayer (e.g., ARC) of a multilayer photoresist.

[0083] The silsesquioxane-containing composition and the photoresist composition may
5 contain other or additional optional additives as constituents. The total concentration of all constituents in the silsesquioxane-containing composition and the photoresist composition is 100%.

[0084] In some embodiments the silsesquioxane-containing composition is the photoresist composition. The photoresist composition is a chemically-amplifiable photoresist composition.
10 The photoresist composition may be protected from light having a wavelength shorter than 365 nm until after the photoresist composition has been coated on a substrate and is ready to be masked-irradiated. For example, the photoresist composition may be prepared and coated under an environment consisting essentially of yellow light or red light. After being exposed to light (masked-irradiated), the chemically-amplifiable photoresist composition is converted to a
15 chemically-amplified photoresist composition comprising initially the acid-sensitive photoresist polymer and the product acid. The product acid facilitates cleavage of the acid-sensitive groups of the acid-sensitive photoresist polymer to give a product polymer comprising macromolecular chains that bear pendant acidic groups. The rate of cleavage may be increased by heating the chemically-amplified photoresist composition. After cleavage, the
20 chemically-amplified photoresist composition comprises the product acid and the product polymer. The acid-sensitive photoresist polymer, the PAG, the product acid, and the product polymer are different and distinct compounds.

[0085] When a portion of the chemically-amplifiable photoresist composition is exposed to light and another portion of the chemically-amplifiable photoresist composition is not exposed
25 to light, a composite material is formed comprising a non-exposed region comprising the chemically-amplifiable photoresist composition (unreacted) and a light-exposed region comprising the chemically-amplified photoresist composition (cleavage products). When the chemically-amplifiable photoresist composition is restricted in one dimension and the light exposure is done through a photomask defining a pattern, the composite material is formed in
30 the shape of a sheet or film having a non-exposed region and a patterned light-exposed region, which defines a latent pattern of the chemically-amplified photoresist composition. When the chemically-amplifiable photoresist composition is free of a crosslinker that is reactive with the product polymer, a positive resist image may be formed from the latent pattern by developing the sheet or film of the composite material with a developer (e.g., basic solution

such as an aqueous base). The developer selectively dissolves the light-exposed region without dissolving the non-exposed region, thereby producing the positive resist image, which is defined by the remaining non-exposed region.

[0086] Developer solutions useful for removing the photoresist composition include aqueous solutions comprising water and a base. The base is a chemical compound that is soluble in deionized water to give an aqueous solution having a potential of hydrogen (pH) > 7. This basic chemical compound may be an inorganic chemical compound such as ammonia or a Group 1 or 2 metal hydroxide or carbonate. Alternatively, the basic chemical compound may be an organic chemical compound such as an amine or a basic nitrogen-containing heterocycle. Examples of the base are tetramethylammonium hydroxide (TMAH), choline, sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate, ammonia, ethylamine, propylamine, diethylamine, dipropylamine, triethylamine, methyldiethylamine, ethyldimethylamine, triethanolamine, pyrrole, piperidine, 1,8-diazabicyclo[5.4.0]-7-undecene, and 1,5-diazabicyclo[4.3.0]-5-nonene. When the photoresist composition is formulated for use as a positive photoresist, the exposed areas of a photoresist layer thereof will be soluble in the developer solution and the unexposed areas will be insoluble in the developer solution. Once the exposed photoresist layer (positive photoresist) has been developed with developer solution, the undissolved remainder of the photoresist layer ("pattern") may be washed with water to remove excess developer solution therefrom.

[0087] The developer is different than the (B) silyl-anhydride in structure, formulation, function or use, and/or amount. For example, even when the basic chemical compound of the developer is an amine, it typically is not a (B) silyl-anhydride, but an unsubstituted alkyl-containing amine. Further, the developer is a solution of the basic chemical compound in water, whereas the (B) silyl-anhydride and the silsesquioxane-containing composition containing it is substantially free of water (e.g., has from 0 wt% to less than 1 wt% water). Also, the developer is used in the developing step to selectively dissolve the mask exposed region of the mask exposed film of the photoresist composition, while not dissolving the unexposed region of the film. The (B) silyl-anhydride is primarily used in, and just after, the mask exposing step, where it is believed to chemically amplify the mask exposed region of a film of a photoresist composition comprising the (A) silsesquioxane resin, (B) silyl-anhydride, and (C) photoacid generator or a product acid thereof. The product acid is formed *in situ* from the (C) photoacid generator upon exposure of the (C) photoacid generator of the mask exposed region of the film of the photoresist composition to radiation in the mask exposing step. The (B) silyl-anhydride may have additional uses in the photoresist composition such as in steps

other than the mask exposing step such as in the applying, optional drying, developing, and/or optional heating steps. Additionally, the (B) silyl-anhydride may have uses in embodiments of the silsesquioxane-containing composition that are free of the (C) photoacid generator such as a surfactant, adhesion promoter, solvent, stabilizer, or plasticizer. Further, the basic chemical compound is typically present in the developer at a concentration of from 1 to 5 wt%, whereas the (B) silyl-anhydride is typically present in the silsesquioxane-containing composition at a concentration from 0.01 part to 5 parts, alternatively from 0.05 part to 4 parts, alternatively from 0.07 part to 3 parts, all per 100 parts of the (A) silsesquioxane resin.

[0088] The pattern may then be transferred to an underlying substrate. In bilayer photoresists, the transferring comprises transferring the pattern through the underlayer (e.g., ARC or hardcoat layer) onto the substrate (e.g., silicon or metal). In single layer photoresist, there is no underlayer and the pattern is transferred directly onto the substrate. Typically, the pattern is transferred via etching with reactive ions such as oxygen, plasma, or oxygen/sulfur dioxide plasma. Etching methods are well known in the art.

[0089] Another embodiment is a process for generating a resist image on a substrate or on an underlayer disposed on a substrate. In some embodiments the process comprises the steps of: (a) coating a substrate with a photoresist composition comprising constituents (A) to (C), and typically also constituent (D) solvent, to form a resist-coated substrate comprising an applied film of the photoresist composition on the substrate; (b) mask exposing (imagewise exposing) the applied film to, or mask irradiating with, radiation (e.g., 248 nm, 193 nm, or 157 nm) to produce a mask-irradiated resist comprising an exposed film containing a latent pattern; and (c) developing the exposed film of the mask-irradiated resist to produce a resist image from the latent pattern to give a developed resist. The developed resist is a manufactured article comprising the resist image disposed on the substrate. In other embodiments the process comprises the steps of: (a) coating an underlayer, which is pre-disposed on a substrate, with a resist composition comprising constituents (A) to (C), and typically also constituent (D) solvent, to form a bilayer on the substrate, wherein the bilayer comprises an applied film of the resist composition disposed on the underlayer; (b) mask exposing (imagewise exposing) the applied film to radiation to produce an exposed film containing a latent pattern; and (c) developing the exposed film to produce a resist image from the latent pattern to give a manufactured article comprising the resist image disposed on the substrate.

[0090] Suitable substrates are ceramic, metallic or semiconductive, and preferred substrates are silicon-containing, including, for example, silicon dioxide, silicon nitride, silicon oxynitride, silicon carbide, and silicon oxycarbide.

5 [0091] The underlayer may be a hardcoat layer (e.g., an organic hardcoat layer) or an anti-reflective coating (ARC). The underlayer is formed on the substrate prior to the coating step of forming the film of the resist composition. Typically, the underlayer is composed of is comprised of a material that is highly light absorbing at the imaging wavelength used in the mask exposing step and is chemically compatible with the resist composition. Typical underlayer materials are crosslinked poly(4-hydroxystyrene), polyesters, polyacrylates, 10 polymethacrylates, fluorinated polymers, and cyclic-olefin polymers. E.g., diazonaphthoquinone (DNQ) or novolak.

[0092] Prior to step (a) coating, typically, the surface of the underlayer or the substrate, as the case may be, is cleaned before the resist composition is applied or coated thereon. Suitable cleaning procedures are known in the art. The resist composition may be coated on the 15 underlayer or directly on the substrate, as the case may be, using techniques such as spin-coating, spray coating, or doctor blading. Typically, the resist film comprises the (D) solvent and is dried (soft baked) before the applied film (after drying) is exposed to radiation in the mask exposing step. The drying or soft baking step may comprise heating the resist film to a temperature in the range of 30° to 200° C, typically from 80° to 140° C, for a short period of time (e.g. 20 to 90 seconds), typically on the order of approximately 1.0 minute. The resulting 20 dried film has a thickness of 0.01 to 5.0 micrometers (μm), alternatively 0.02 to 2.5 μm , alternatively 0.05 to 1.0 μm , and alternatively 0.10 to 0.20 μm .

[0093] In step (b) mask exposing, the applied film (e.g., dried applied film) is exposed to radiation through a mask designed to create a latent pattern in the mask exposed film. The 25 latent pattern is suitable for ultimately giving a patterned semiconductor device having a predetermined pattern. The radiation may be UV, X-ray, e-beam, or EUV. The EUV may have a wavelength of 13 nm. Typically, the radiation is UV radiation having a wavelength of 157 nm to 365 nm (e.g., 157 nm or 193 nm). Suitable radiation sources include mercury, mercury/xenon, and xenon lamps. A particular radiation source is a KrF excimer laser or a F₂ 30 excimer laser. At longer wavelength radiation is used, e.g., 365 nm, a sensitizer may be included in the photoresist composition to enhance absorption of the radiation. Satisfactory exposure of the photoresist composition is typically achieved by irradiating the applied film with from 10 to < 100 millijoules per square centimeter of surface area of the applied film (mJ/cm^2), alternatively from 10 to 50 mJ/cm^2 of radiation.

[0094] In the (b) mask exposing step, the radiation is absorbed by the photoacid generator in the mask exposed regions of the exposed film of the photoresist composition to generate a product acid *in situ* therein. After the photoresist composition has been exposed to radiation, the resulting exposed film is typically heated to a temperature in the range of 30° C. to 200°

5 C. for a short period of time, on the order of approximately 1 minute. When the photoresist composition is a positive photoresist, the product acid causes cleavage of the acid dissociable groups (e.g., the Z group in formula (I)) of the (A) silsesquioxane resin that is present in the photoresist composition, thereby forming a latent pattern having developer-soluble regions in the exposed film.

10 [0095] In step (c) developing step, the exposed film is contacted with a suitable developer to produce a resist image from the latent pattern of the exposed film. The composition of the developer is described earlier. In the positive photoresist film, the exposed regions of the photoresist will be soluble in developer ("developer-soluble"), and the (c) developing step dissolves the exposed regions in the developer and leaves behind the unexposed regions of

15 the exposed positive photoresist film in the form of a generated image or pattern. After the exposed film has been developed and the generated image or pattern has been formed, typically the remaining resist film ("pattern") is washed with water to remove any residual developer.

[0096] The generated image or pattern obtained from step (c) and optional washing step may

20 then be transferred directly into the substrate or through the underlayer into the substrate, as the case may be. Typically, the pattern is transferred by etching with reactive ions such as a molecular oxygen plasma and/or a molecular oxygen/sulfur dioxide plasma. Suitable techniques and machines for forming the plasma include systems such as electron cyclotron resonance (ECR), helicon, inductively coupled plasma, (ICP) and transmission-coupled

25 plasma (TCP).

[0097] Thus the photoresist composition may be used in the foregoing photolithographic patterning method or process to manufacture patterned structures. Examples of patterned structures that can be made are metal wiring lines, holes or vias as conduits for electrical contacts, insulation sections (e.g., damascene trenches or shallow trench isolation), trenches

30 for capacitor structures, and other structures that may be used to manufacture integrated circuit devices.

[0098] Some embodiments include a resist-coated wafer comprising a layer of the photoresist composition disposed on a semiconductor wafer. The photoresist composition may be directly contacting the semiconductor wafer or the resist-coated wafer may further comprise an

underlayer disposed between the layer of the photoresist composition and the semiconductor wafer. The underlayer may be formed by coating the semiconductor wafer with an underlayer composition. The semiconductor wafer may be a bare wafer when it is coated with the photoresist composition or an underlayer composition, as the case may be. Alternatively, the semiconductor wafer may be a primed wafer made by pre-treating a bare semiconductor wafer with a primer. The pre-treating may comprise chemical vapor deposition of a primer. The primer may comprise any compound effective for enhancing adhesion of the photoresist layer or the underlayer, as the case may be, to the semiconductor wafer. For example, the primer compound may be hexamethyldisilazane.

[0099] Some embodiments include a soft baked wafer prepared by heating the resist coated wafer for a brief period of time (e.g., 30 to 120 seconds, e.g., 45 to 90 seconds, or 50 to 70 seconds, e.g., 60 seconds) at a temperature of from 80° to 140° C (e.g., 90° to 120° C, e.g., 100° or 110° C). The soft baked wafer comprises a soft baked resist layer disposed on the semiconductor wafer or on an underlayer, which is disposed on the semiconductor wafer.

[00100] Some embodiments include a masked-irradiated wafer prepared by exposing the resist coated wafer or the soft baked wafer to radiation including, e.g., 248 nm, 193 nm, 157 nm using a dose of from 10 to 75 millijoules per square centimeter (mJ/cm^2) surface area of the resist-coated wafer or soft baked wafer. In some embodiments the radiation is dosed at from 15 to 55 mJ/cm^2 , alternatively from 20 to 50 mJ/cm^2 , alternatively from 23 to 45 mJ/cm^2 . The masked-irradiated wafer comprises a masked-irradiated resist layer disposed on the semiconductor wafer or on an underlayer, which is disposed on the semiconductor wafer. The masked-irradiated resist layer contains a latent pattern.

[00101] Some embodiments include a post-exposure baked wafer prepared by heating the masked-irradiated wafer for a brief period of time (e.g., 30 to 120 seconds, e.g., 45 to 90 seconds, or 50 to 70 seconds, e.g., 60 seconds) at a temperature of from 80° to 140° C (e.g., 90° to 120° C, e.g., 100° or 110° C). The post-exposure baked wafer comprises a post-exposure baked resist layer disposed on the semiconductor wafer or on an underlayer, which is disposed on the semiconductor wafer. The post-exposure baked resist layer contains a latent pattern.

[00102] Some embodiments include a developed resist prepared by contacting the masked-irradiated wafer or the post-exposure baked wafer with a developer so as to remove some of the masked-irradiated resist material or some of the post-exposure baked resist material without removing other portions of the material so as to form a resist pattern or image.

The developer may comprise an aqueous base solution for positive resist formulations of the photoresist composition. The positive resist formulation comprises constituents (A) to (C). The developed resist comprises a developed resist layer disposed on the semiconductor wafer or on an underlayer, which is disposed on the semiconductor wafer. The developed resist layer
5 contains a resist pattern or resist image. The resist pattern or image may contain vertical features having cross-section profiles characterized by Field Emission Scanning Electron Microscope (FE-SEM) as having rounded corner tops or squared corner tops.

[00103] Some embodiments include a rinsed resist prepared by rinsing excess developer from the developed resist. Excess developer may cling to the developed resist and
10 may be removed by rinsing the developed resist with a rinsing agent such as a volatile organic solvent. The rinsed resist comprises a rinsed resist layer disposed on the semiconductor wafer or on an underlayer, which is disposed on the semiconductor wafer. The rinsed resist layer contains a resist pattern or resist image. The resist pattern or image may contain vertical features having cross-section profiles characterized by FE-SEM as having rounded corner
15 tops or squared corner tops.

[00104] Some embodiments include an etched resist prepared by etching the developed resist or rinsed resist with an etching agent using an anisotropic etching technique. The etching agent may comprise a molecular oxygen plasma, a halogen plasma, or a sequential application of a molecular oxygen plasma followed by a halogen plasma. In some
20 embodiments the etched resist is a molecular oxygen plasma etched resist. In other embodiments the etched resist is a halogen plasma etched resist. In other embodiments the etched resist is a sequential molecular oxygen plasma etched followed by halogen plasma etched resist. The molecular oxygen plasma etched resist comprises an etched resist layer disposed on the semiconductor wafer or on a molecular oxygen plasma etched underlayer,
25 which is disposed on the semiconductor wafer. The halogen plasma etched resist layer contains a halogen plasma etched underlayer disposed on a patterned structure comprising a patterned semiconductor wafer.

[00105] Some embodiments include a patterned structure prepared by removing the etched resist layer from the patterned semiconductor wafer.

30 **[00106]** Some embodiments are illustrated in the accompanying drawings.

[00107] FIG. 1 is an elevation view of a substrate. In FIG. 1 substrate 1 is an article in need of coating. Examples of the substrate 1 are wafers and sheets. The substrate 1 may be composed of a semiconductor material. The semiconductor material may be based on silicon, germanium, or compounds of gallium. For example, the semiconductor material may be

gallium arsenide or gallium nitride. Alternatively, the semiconductor material may be polycrystalline silicon, monocrystalline silicon, or silicon carbide. The substrate 1 may be a homogeneous material or may have two or more layers (not shown). For example, the substrate 1 may have a basal layer and a surface layer on the basal layer. The basal layer
5 may be composed of the semiconductor material and may host the surface layer. The surface layer may be composed of a doped material or a compound of the semiconductor material. Examples of the compound of silicon that may be used as the compound of the semiconductor material are silicon nitride, silicon oxide, silicon carbonitride, silicon oxycarbide, silicon oxynitride, and silicon oxycarbonitride. The surface layer may be formed by doping a surface
10 of a semiconductor material (e.g., vapor deposition of a dopant), by treating a surface of a semiconductor material (e.g., oxidizing), or by depositing a suitable material on a semiconductor material (e.g., vapor deposition).

[00108] FIG. 2 is an elevation view of an underlayer-on-substrate. In FIG. 2, underlayer-on-substrate 10 comprises underlayer 2 disposed on substrate 1. Underlayer 2 may be an
15 example of the surface layer of the embodiment of substrate 1 having a basal layer and surface layer. Alternatively, underlayer 2 may be distinct and separate from substrate 1. For example, underlayer 2 may be an anti-reflective coating (ARC) layer or a hardmask layer. Underlayer 2 may be deposited on substrate 1 by any suitable deposition process such as spin-coating.

[00109] FIG. 3 is an elevation view of a bilayer resist-on-substrate. In FIG. 3, bilayer resist-on-substrate 20 comprises bilayer resist 26 disposed on substrate 1. Bilayer resist 26 is composed of photoresist composition 3 disposed on underlayer 2. Photoresist composition 3
20 may be deposited on underlayer 2 by any suitable deposition process such as spin-coating. Photoresist composition 3 may be an embodiment of the present photoresist composition, which is a chemically-amplifiable photoresist composition comprising the (A) silsesquioxane resin, (B) silyl-anhydride, and (C) photoacid generator.

[00110] FIG. 4 is an elevation view of a masked-irradiated resist-on-substrate. In FIG. 4, masked-irradiated resist-on-substrate 30 comprises photoresist composition 3 disposed on underlayer 2 disposed on substrate 1, wherein photoresist composition 3 contains latent
30 pattern 4. Photoresist composition 3 may be an embodiment of the present chemically-amplifiable photoresist composition comprising constituents (A), (B), and (C). Initially, latent pattern 4 comprises a chemically-amplified photoresist composition comprising constituents (A) and (B), and a product acid of a light-facilitated reaction of constituent (C). Then the chemically-amplified photoresist composition of latent pattern 4 undergoes a reaction of constituent (A) silsesquioxane resin and the product acid to give a product polymer. The

product polymer is formed by a cleavage reaction of the acid dissociable groups of constituent (A). The cleavage reaction is enabled and enhanced (amplified) by the product acid. If desired, the cleavage reaction may be further enhanced by post exposure baking of the masked-irradiated resist-on-substrate 30. After the formation of the product polymer is complete, the masked-irradiated resist-on-substrate 30 is ready for a subsequent step such as developing.

[00111] FIG. 5 is an elevation view of a developed resist-on-substrate. In FIG. 5, developed resist-on-substrate 40 comprises photoresist composition 3 disposed on underlayer 2 disposed on substrate 1. Photoresist composition 3 defines a resist image containing trenches 5. The trenches 5 are volumetric spaces (trenches) from which the latent pattern 4 of the masked-irradiated resist-on-substrate 30 (see FIG. 4) have been removed via a developing step, thereby exposing portions of underlayer 2.

[00112] FIG. 6 is an elevation view of a plasma-etched resist-on-substrate. In FIG. 6, plasma-etched resist-on-substrate 50 comprises photoresist composition 3 disposed on underlayer 2 disposed on substrate 1. Photoresist composition 3 and underlayer 2 together define a bilayer image containing trenches 6. The trenches 6 are volumetric spaces from which portions of underlayer 2 that were exposed as shown in FIG. 5 have been removed via a plasma etching step, thereby exposing portions of substrate 1. Trenches 6 may have an aspect ratio greater than 5. The plasma etching step may comprise oxygen (O₂) plasma.

[00113] FIG. 7 is an elevation view of a halogen-etched substrate. In FIG. 7, halogen-etched substrate 60 comprises a remainder of underlayer 2 disposed on a remainder of substrate 1. The remainder of underlayer 2 and remainder of substrate 1 together define a transferred pattern comprising trenches 7. The trenches 7 are volumetric spaces from which portions of substrate 1 that were exposed as shown in FIG. 6 have been removed via an etching step such as a halogen etching step, thereby creating trenches 7 in substrate 1. A halogen etching step may comprise a plasma of a chlorofluorocarbon. The chlorofluorocarbon may be trichlorofluoromethane (CCl₃F), dichlorodifluoromethane (CCl₂F₂), dichlorofluoromethane (HCCl₂F), chlorodifluoromethane (HCCIF₂), chlorotrifluoromethane (CCIF₃), chlorofluoromethane (H₂CCIF), and combinations of any two or more thereof.

[00114] FIG. 8 is an elevation view of a patterned structure. In FIG. 8, patterned structure 70 is free of the remainder of underlayer 2 shown in FIG. 7. Patterned structure 70 may comprise metal wiring lines, holes or vias as conduits for electrical contacts, insulation sections (e.g., damascene trenches or shallow trench isolation), trenches for capacitor structures, and other structures that may be used to manufacture integrated circuit devices.

[00115] FIG. 9 is a scheme of certain steps of a process of making a patterned structure. In FIG. 9, the process comprises steps (A) to (F) and, optionally, step (G). An embodiment of the process of FIG. 9 is described here with reference to using a positive photoresist composition. In some embodiments the positive photoresist composition comprises constituents (A) to (C), and is free of (lacks) constituent (H) crosslinker. Step (A) comprises coating an underlayer composition on a substrate to give an underlayer-on-substrate (e.g., underlayer-on-substrate 10 of FIG. 2). Step (B) comprises coating a positive photoresist composition on the underlayer-on-substrate to give a bilayer resist-on-substrate (e.g., bilayer resist-on-substrate 20 of FIG. 3). Step (C) comprises selectively irradiating (e.g., through a photomask) a portion of the bilayer resist-on-substrate without irradiating another portion thereof to give a masked-irradiated resist-on-substrate (e.g., masked-irradiated resist-on-substrate 30 of FIG. 4). Step (C) may further comprise soft baking the masked-irradiated resist-on-substrate prior to step (D). Step (D) comprises contacting the masked-irradiated resist-on-substrate with a developer (e.g., an aqueous base) to give a developed resist (e.g., developed resist 40 of FIG. 5). In this embodiment the developed resist would lack the masked-irradiated resist portions of the positive photoresist composition (e.g., the latent pattern 4 portions shown in FIG. 4 would be removed) and would retain the non-irradiated portions of the positive photoresist composition (e.g., would retain the non-irradiated portions of photoresist composition 3 of FIG. 4). Step (D) may further comprise rinsing excess developer from the developed resist, and drying the rinsed developed resist prior to step (E). The rinsing agent may comprise purified water. Step (E) comprises plasma etching the developed resist to give a plasma-etched resist (e.g., plasma-etched resist 50 of FIG. 6). Step (F) comprises halogen etching the plasma-etched resist to give a halogen-etched substrate (e.g., halogen-etched substrate 60 of FIG. 7). Step (G) is optional. Step (G) comprises removing any remainder of bilayer resist material without removing any or removing only insignificant substrate material to give a positively patterned structure (e.g., patterned structure 70 of FIG. 8). Step (G) may comprise halogen etching and may be done by extending the time period for conducting step (F). The etching steps comprise any suitable anisotropic etching technique such as deep reactive ion-etching.

[00116] FIG. 10 is a photograph of an inventive embodiment of a post-exposure baked wafer (primed) after treatment with TMAH_{aq} developer. The post-exposure baked wafer (primed) was formed by applying a coating of the photoresist composition to an HMDS-primed silicon wafer, soft baking the coating, mask-irradiating the coating, post exposure baking the coating, and then dipping the post-exposure baked wafer in 2.37 wt% aqueous TMAH for 60

seconds at 23° C. The (B) silyl-anhydride of the photoresist composition was 2-(3'-triethoxysilyl-propyl)-succinic anhydride. As shown in FIG. 10, the inventive photoresist composition produced a post-exposure baked wafer (primed) having a resist image that exhibited excellent adhesion to the HMDS-primed silicon wafer.

5 [00117] FIG. 11 is a photograph of an inventive embodiment of a post-exposure baked wafer (bare) after treatment with TMAH_{aq} developer. The post-exposure baked wafer (bare) was prepared in the same manner as for that of FIG. 10 except wherein a bare silicon wafer was used instead of the HMDS-primed silicon wafer. As shown in FIG. 11, the inventive photoresist composition produced a post-exposure baked wafer (bare) having a resist image that exhibited good adhesion to the bare silicon wafer.

10 [00118] FIG. 12L (left image; non-invention) is a photograph of a non-invention embodiment of a post-exposure baked wafer (primed) after treatment with TMAH_{aq} developer. The post-exposure baked wafer (primed) was prepared in the same manner as for that of FIG. 10 except wherein no (B) silyl-anhydride was used. That is, no 2-(3'-triethoxysilyl-propyl)-succinic anhydride was used. As shown in FIG. 12L, the non-invention photoresist composition that did not contain a (B) silyl-anhydride produced a post-exposure baked wafer (primed) having a resist image that exhibited poor adhesion to the HMDS-primed silicon wafer.

15 [00119] FIG. 12R (right image; non-invention) is a photograph of a non-invention embodiment of a post-exposure baked wafer (bare) after treatment with TMAH_{aq} developer. The post-exposure baked wafer (bare) was prepared in the same manner as for that of FIG. 12L except wherein a bare silicon wafer was used instead of the HMDS-primed silicon wafer. As shown in FIG. 12R, the non-invention photoresist composition that did not contain a (B) silyl-anhydride produced a post-exposure baked wafer (bare) having a resist image that exhibited terrible adhesion to the bare silicon wafer.

20 [00120] The invention is further illustrated by, and an invention embodiment may include any combinations of features and limitations of, the non-limiting examples thereof that follow. Ambient temperature is about 23° C. unless indicated otherwise.

[00121] ²⁹Si-NMR instrument and solvent: a Varian 400 MHz Mercury spectrometer was used. C₆D₆ was used as the solvent.

30 [00122] ¹H-NMR instrument and solvent: a Varian 400 MHz Mercury spectrometer was used. C₆D₆ was used as the solvent.

[00123] Preparation 1: synthesis of a hydrogen silsesquioxane (HSQ) resin: mixed concentrated sulfuric acid and fuming sulfur trioxide with toluene to give a solution of

toluenesulfonic acid monohydrate (TSAM) in toluene. To 100 grams (g) of the solution of TSAM was added dropwise a solution of trichlorosilane (10 g; 0.075 mole) in toluene (50 g) with stirring under nitrogen gas atmosphere. After the addition, the resulting mixture was washed at least three times with deionized (DI) water, and the resulting organic phase was rotary evaporated under reduced pressure to remove some of the solvent, thereby giving a mixture of HSQ resin in toluene and having a solid content of from 5 to 25 wt%.

[00124] Silyl-anhydride (B-1): a silyl-anhydride of formula (II) that is 2-(3'-triethoxysilyl-propyl)-succinic anhydride.

[00125] Silyl-anhydride (B-2): a silyl-anhydride of formula (II) that is 2,3-bis(3'-triethoxysilyl-propyl)-succinic anhydride.

[00126] Silyl-anhydride (B-3): a silyl-anhydride of formula (II) that is 3-(3'-triethoxysilyl-propyl)-glutaric anhydride.

[00127] Silyl-anhydride (B-4): a silyl-anhydride of formula (II) that is 2,3-bis(3'-triethoxysilyl-propyl)-glutaric anhydride.

[00128] Silyl-anhydride (B-5): a silyl-anhydride of formula (II) that is 1,1,2,2,3,3-hexamethyl-1,3-bis(ethyl-1',2'-dicarboxylic)-trisiloxane dianhydride.

[00129] Photoacid generator (C-1): IRGACURE 290 TPC, which is a of 20 wt% tri(4-(4'-acetylphenylthio)-phenyl)sulfonium tetrakis(pentafluorophenyl)borate (4-(4'-MeCO-C₆H₄S)-Ph)₃S⁺ B(C₆F₅)₄⁻), 62 wt% 3-ethyl-3-oxetanemethanol, and 18 wt% propylene carbonate; available from BASF Corporation.

[00130] Inventive Examples (IEx.) 1a to 1d: synthesis of a constituent (A-1): silsesquioxane resin 1 of formula (I) and solvent exchanged products thereof. To a 50:50 w/w solution of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 1,1-dimethylethyl ester (0.1 mole) in anhydrous toluene was added platinum(0) 1,3-diethylenyl-1,1,3,3-tetramethyldisiloxane complex. To the resulting mixture was slowly added under a nitrogen gas atmosphere the mixture of hydrogen silsesquioxane resin of Preparation 1 (containing about 0.33 mole of HSQ resin). After addition was complete, the resulting mixture was refluxed for 8 hours while stirring. Progress of the resulting hydrosilylation reaction was monitored by ¹H-NMR for complete disappearance of peaks for the olefinic hydrogen atoms of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 1,1-dimethylethyl ester to give a mixture of silsesquioxane resin 1 in toluene (IEx. 1a). Once the peaks disappeared, the toluene of the reaction mixture was solvent exchanged with 1,2-propylene glycol monomethyl ether monoacetate (PGMEA), ethyl lactate (EL), or methyl isobutyl ketone (MIBK) to give a mixture of silsesquioxane resin 1 in PGMEA

(IEx. 1b), a mixture of silsesquioxane resin 1 in EL (IEx. 1c), or a mixture of silsesquioxane resin 1 in MIBK (IEx. 1d), respectively. The mixtures of IEx. 1a to 1d contained from 4 to 45 wt% of the silsesquioxane resin 1 in the ad rem solvent. E.g., the mixture of IEx. 1b contained 20 wt% silsesquioxane resin 1 in PGMEA.

5 **[00131]** IEx. 2a: synthesis of photoresist composition. Added 2 g photoacid generator (C-1) and 2 g silyl-anhydride (B-1) to 100 g of the mixture of IEx. 1b to give the photoresist composition of IEx. 2a.

10 **[00132]** IEx. 2b to 2e: (Prophetic) synthesis of photoresist compositions. In separate experiments, replicate the procedure of IEx. 2a except use the silyl-anhydride (B-2), (B-3), (B-4), or (B-5) instead of the silyl-anhydride (B-1) to give the photoresist composition of IEx. 2b, 2c, 2d, or 2e, respectively.

15 **[00133]** IEx. 3a-1 and 3a-2: preparation of resist-coated wafers. In separate experiments in a clean room, spin-coated the photoresist composition of IEx. 2a onto either a HMDS-primed silicon wafer (primed, 15 cm diameter) or a bare silicon wafer (bare, 15 cm diameter) to give a resist-coated wafer of IEx. 3a-1 or 3a-2, respectively. ("Bare" means the silicon wafer did not contain an underlayer and was not pretreated with a primer.) Each resist-coated wafer comprised a resist layer disposed directly on the wafer. Each resist layer had a thickness of 5,000 angstroms (Å).

20 **[00134]** IEx. 3b-1 to 3e-1 and 3b-2 to 3e-2 (prophetic): preparation of resist-coated wafers. Replicate the procedure of IEx. 3a-1 except use the photoresist composition of IEx. 2b, 2c, 2d, or 2e instead of the photoresist composition of IEx. 2a to give the resist-coated wafers (primed) of IEx. 3b-1 to 3e-1, respectively. Replicate the procedure of IEx. 3a-2 except use the photoresist composition of IEx. 2b, 2c, 2d, or 2e instead of the photoresist composition of IEx. 2a to give the resist-coated wafers (bare) of IEx. 3b-2 to 3e-2, respectively.

25 **[00135]** IEx. 4a-1 and 4a-2: preparation of soft baked resists. In separate experiments in a clean room, the resist-coated wafers of IEx. 3a-1 and 3a-2 were heated for 60 seconds at a temperature of 120° C, and then cooled to give the soft baked resists of IEx. 4a-1 and 4a-2, respectively.

30 **[00136]** IEx. 4b-1 to 4e-1 and 4b-2 to 4e-2 (prophetic): preparation of soft baked resists. Replicate the procedure of IEx. 4a-1 except use the resist-coated wafer of IEx. 3b-1, 3c-1, 3d-1, or 3e-1 instead of the resist-coated wafer of IEx. 3a-1 to give the soft baked resists of IEx. 4b-1 to 4e-1, respectively. Replicate the procedure of IEx. 4a-2 except use the resist-coated wafer of IEx. 3b-2, 3c-2, 3d-2, or 3e-2 instead of the resist-coated wafer of IEx. 3a-2 to give the soft baked resists of IEx. 4b-2 to 4e-2, respectively.

[00137] IEx. 5a-1 and 5a-2: preparation of masked-irradiated resists. In separate experiments in a clean room, the soft baked resists of IEx. 4a-1 and IEx. 4a-2 were placed in a mask aligner under a photomask with lines having widths of 5 μm to 100 μm , and the soft baked resists were exposed through the photomasks to broadband ultraviolet radiation (including 248 nm) exposure dose (100%) to 200 millijoules to give the masked-irradiated resists of IEx. 5a-1 and 5a-2, respectively.

[00138] IEx. 5b-1 to 5e-1 and 5b-2 to 5e-2 (prophetic): preparation of masked-irradiated resists. Replicate the procedure of IEx. 5a-1 except use the soft baked resists of IEx. 4b-1, 4c-1, 4d-1, or 4e-1 instead of the soft baked resist of IEx. 4a-1 to give the masked-irradiated resists of IEx. 5b-1 to 5e-1, respectively. Replicate the procedure of IEx. 5a-2 except use the soft baked resist of IEx. 4b-2, 4c-2, 4d-2, or 4e-2 instead of the soft baked resist of IEx. 4a-2 to give the masked-irradiated resists of IEx. 5b-2 to 5e-2, respectively.

[00139] IEx. 6a-1 and 6a-2: preparation post-exposure baked resists. In separate experiments in a clean room, the masked-irradiated resists of IEx. 5a-1 and IEx. 5a-2 were heated for 60 seconds at a temperature of 120° C, and then cooled to give the post exposure baked resists of IEx. 6a-1 and 6a-2, respectively.

[00140] IEx. 6b-1 to 6e-1 and 6b-2 to 6e-2 (prophetic): preparation of post-exposure baked resists. Replicate the procedure of IEx. 6a-1 except use the masked-irradiated resists of IEx. 5b-1, 5c-1, 5d-1, or 5e-1 instead of the masked-irradiated resist of IEx. 5a-1 to give the post-exposure baked resists of IEx. 6b-1 to 6e-1, respectively. Replicate the procedure of IEx. 6a-2 except use the masked-irradiated resist of IEx. 5b-2, 5c-2, 5d-2, or 5e-2 instead of the masked-irradiated resist of IEx. 5a-2 to give the post-exposure baked resists of IEx. 6b-2 to 6e-2, respectively.

[00141] IEx. 7a-1 and 7a-2: preparation of developed resists. In separate experiments (outside a clean room), conducted using a single puddle process without pre-wetting, the post-exposure baked resists of IEx. 6a-1 and IEx. 6a-2 were developed in 2.38 wt% aqueous TMAH solution for 60 seconds at a temperature of 23° C to give the developed resists of IEx. 7a-1 and 7a-2, respectively. The developed resists of IEx. 7a-1 and 7a-2 contained resist patterns or images exhibiting trenches.

[00142] IEx. 7b-1 to 7e-1 and 7b-2 to 7e-2 (prophetic): preparation of developed resists. Replicate the procedure of IEx. 7a-1 except use the post exposure baked resist of IEx. 6b-1, 6c-1, 6d-1, or 6e-1 instead of the post-exposure baked resist of IEx. 6a-1 to give the developed resists of IEx. 7b-1 to 7e-1, respectively. Replicate the procedure of IEx. 7a-2 except use the

post-exposure baked resist of IEx. 6b-2, 6c-2, 6d-2, or 6e-2 instead of the post-exposure baked resist of IEx. 6a-2 to give the developed resists of IEx. 7b-2 to 7e-2, respectively.

[00143] IEx. 8a-1 and 8a-2: characterizations of the developed resists. Each of the developed resists of IEx. 7a-1 and 7a-2 were imaged with a digital camera to obtain the photographic images shown in FIG. 10 and 11.

[00144] As shown by the photographic images in FIGs. 10 and 11 the inventive post-exposure baked resists of IEx. 6a-1 and 6a-2 produced developed resists of IEx. 7a-1 and 7a-2, respectively, that have resist images that are faithful revelations of the former's latent pattern and that adhered to the bare and primed silicon wafers. The latent image portions of the post-exposure baked resists of IEx. 6a-1 and 6a-2 were readily soluble in developer, whereas the unexposed portions of the post-exposure baked resists of IEx. 6a-1 and 6a-2 were insoluble in the developer and adhered robustly to the wafers.

[00145] If desired, the developed resists of IEx. 7a-1 to 7e-1 and 7a-2 to 7e-2 may be rinsed with a rinse agent to remove excess developer and give corresponding rinsed resists.

The rinsed resists may be etched using an etching agent such as molecular oxygen plasma and/or halogen-containing plasma and an anisotropic etching technique to give corresponding etched resists. The etched resists may be further etched using an etching agent such as halogen-containing plasma and an anisotropic etching technique to give corresponding patterned structures. The patterned structures comprise a patterned silicon wafer and are free of the photoresist composition or the aforementioned products prepared therefrom.

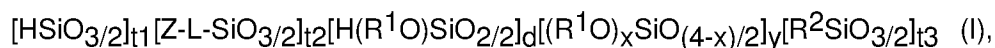
[00146] The below claims are incorporated by reference here, and the terms "claim" and "claims" are replaced by the term "aspect" or "aspects," respectively. Embodiments of the invention also include these resulting numbered aspects.

CLAIMS

What is claimed is:

1. A silsesquioxane-containing composition comprising (A) a silsesquioxane resin and (B) a silyl-anhydride, wherein:

the (A) silsesquioxane resin is of formula (I):



wherein:

- subscript $t1$ is a mole fraction of from 0.4 to 0.9;
 subscript $t2$ is a mole fraction of from 0.1 to 0.6;
 subscript d is a mole fraction from 0 to 0.45;
 subscript x is an integer of 1, 2, or 3;
 subscript y is a mole fraction from 0 to 0.25;
 subscript $t3$ is a mole fraction from 0 to 0.15;
 the sum of $t1 + t2 =$ from ≥ 0.9 to ≤ 1 and the sum of $t1 + t2 + d + y + t3 = 1$;
 each R^1 is independently H or $(\text{C}_1\text{-C}_6)\text{alkyl}$;
 each R^2 is independently HO-L- or HOOC-L-;
 each L is independently a divalent $(\text{C}_1\text{-C}_{20})\text{hydrocarbon}$ group that is unsubstituted or substituted with at least 1 substituent independently selected from $(\text{C}_1\text{-C}_3)\text{alkyl}$, -OH, and a fluorine atom up to and including perfluoro-substitution; and
 each Z is -OH, -COOH, -O-THP, $-\text{OCH}(\text{R}^{3a})_2$, $-\text{OC}(\text{R}^{3b})_3$, $-\text{COOCH}(\text{R}^{3a})_2$, $-\text{COOC}(\text{R}^{3b})_3$, $-\text{OCOOCH}(\text{R}^{3a})_2$, or $-\text{OCOOC}(\text{R}^{3b})_3$,
 wherein THP is tetrahydropyran-2-yl;
 wherein each R^{3a} is independently a $(\text{C}_1\text{-C}_6)\text{alkyl}$, $(\text{C}_3\text{-C}_{12})\text{cycloalkyl}$, $(\text{C}_6\text{-C}_{10})\text{aralkyl}$, $((\text{C}_1\text{-C}_6)\text{alkyl})_3\text{SiCH}_2\text{CH}_2-$, or 2 R^{3a} together with the carbon atom to which they are both bonded are a $(\text{C}_3\text{-C}_{12})\text{cycloalkyl}$ or a $(\text{C}_6\text{-C}_{12})\text{bicycloalkyl}$; and
 wherein each R^{3b} is independently a $(\text{C}_1\text{-C}_6)\text{alkyl}$, $(\text{C}_3\text{-C}_{12})\text{cycloalkyl}$, $(\text{C}_6\text{-C}_{10})\text{aralkyl}$, $((\text{C}_1\text{-C}_6)\text{alkyl})_3\text{SiCH}_2\text{CH}_2-$; or 2 R^{3b} together with the carbon atom

to which they are both bonded are a (C₃-C₁₂)cycloalkyl or a (C₆-C₁₂)bicycloalkyl and the remaining R^{3b} is independently a (C₁-C₆)alkyl, (C₃-C₁₂)cycloalkyl, (C₆-C₁₀)aralkyl, or ((C₁-C₆)alkyl)₃SiCH₂CH₂-; or all 3 R^{3b} together with the carbon atom to which they are all bonded are a (C₇-C₁₂)bicycloalkyl; and

the (B) silyl-anhydride is of formula (II): (R⁴O)₃Si-(L¹)_m-C(R⁵)₂-C(=O)-O-C(=O)-R⁶ (II), wherein:

each R⁵ is independently H, a (C₁-C₆)alkyl, or a monovalent group of formula -(L²)_n-Si(OR⁴)₃; or both R⁵ are taken together to form a (C₂-C₅)alkane-diyl; or one R⁵ is taken together with R⁶ to form a bond or (C₁-C₄)alkane-diyl, and the remaining R⁵ is independently H, a (C₁-C₆)alkyl, or a monovalent group of formula -(L²)_n-Si(OR⁴)₃; or both R⁵ are taken together with R⁶ to form =CH-;

R⁶ is taken together with R⁵ as described above or R⁶ is a (C₁-C₈)hydrocarbonyl or a monovalent group of formula -C(R⁷)₂-(L²)_n-Si(OR⁴)₃;

subscript m is an integer of 0 or 1;

each subscript n is independently an integer of 0 or 1;

each R⁴ is independently an unsubstituted (C₁-C₆)alkyl;

each L¹ and L² is independently a (C₁-C₈)hydrocarbon-diyl; and

each R⁷ is independently H or a (C₁-C₆)alkyl; or both R⁷ are taken together to form a (C₂-C₅)alkane-diyl.

2. The silsesquioxane-containing composition of claim 1 wherein in the (A) silsesquioxane resin:

subscript t1 is a mole fraction of from 0.4 to 0.65;

subscript t1 is a mole fraction of from 0.65 to 0.9;

subscript t2 is a mole fraction of from 0.1 to 0.35;

subscript t2 is a mole fraction of from 0.5 to 0.6;

subscript d is 0;

subscript d is a mole fraction from > 0 to 0.45;

subscript x is 1;

subscript x is 2;
subscript x is 3;
subscript y is 0;
subscript y is a mole fraction from > 0 to 0.25;
5 subscript t3 is 0;
subscript t3 is a mole fraction from > 0 to 0.15;
at least one R¹ is H;
subscript d is a mole fraction from > 0 to 0.45 or subscript y is a mole fraction from
> 0 to 0.25 and at least one R¹ is H;
10 at least one R¹ is independently (C₁-C₆)alkyl;
subscript d is a mole fraction from > 0 to 0.45 or subscript y is a mole fraction from
> 0 to 0.25 and at least one R¹ is (C₁-C₆)alkyl;
at least one R² is independently HO-L-;
subscript t3 is a mole fraction from > 0 to 0.15 and at least one R² is independently
15 HO-L-;
at least one R² is independently HOOC-L-;
subscript t3 is a mole fraction from > 0 to 0.15 and at least one R² is independently
HOOC-L-;
at least one L is independently a divalent (C₁-C₂₀)hydrocarbon group that is
20 unsubstituted;
at least one L is independently a divalent (C₆-C₁₀)bicycloalkane group that is
unsubstituted;
at least one L is a divalent (C₁-C₂₀)hydrocarbon group that is substituted with at
least 1 (C₁-C₃)alkyl group;
25 at least one L is a divalent (C₆-C₁₀)bicycloalkane group that is substituted with at
least 1 (C₁-C₃)alkyl group;
at least one L is a divalent (C₁-C₂₀)hydrocarbon group that is substituted with at
least 1 -OH group;
at least one L is a divalent (C₆-C₁₀)bicycloalkane group that is substituted with at
30 least 1 -OH group;

at least one L is independently a divalent (C₁-C₂₀)hydrocarbon group that is substituted with at least 1 fluorine atom up to and including perfluoro-substitution;

at least one L is independently a divalent (C₆-C₁₀)bicycloalkane group that is substituted with at least 1 fluorine atom up to and including perfluoro-substitution;

5 at least one Z is -OH;

at least one Z is -COOH;

at least one Z is -O-THP;

at least one Z is -OCH(R^{3a})₂;

at least one Z is -COOCH(R^{3a})₂;

10 at least one Z is -OCOOCH(R^{3a})₂;

at least one Z is -OC(R^{3b})₃;

at least one Z is -COOC(R^{3b})₃;

at least one Z is -OCOOOC(R^{3b})₃;

at least one R^{3a} or R^{3b} is independently a (C₁-C₆)alkyl;

15 at least one R^{3a} or R^{3b} is independently (C₃-C₁₂)cycloalkyl;

at least one R^{3a} or R^{3b} is independently (C₆-C₁₀)aralkyl;

at least one R^{3a} or R^{3b} is independently ((C₁-C₆)alkyl)₃SiCH₂CH₂-;

2 R^{3a} or 2 R^{3b} together with the carbon atom to which they are both bonded are a (C₃-C₁₂)cycloalkyl or a (C₆-C₁₂)bicycloalkyl; or

20 all 3 R^{3b} together with the carbon atom to which they are all bonded are a (C₇-C₁₂)bicycloalkyl.

3. The silsesquioxane-containing composition of claim 1 or 2 wherein in the (A) silsesquioxane resin of formula (I) the Z-L- is selected from the following monovalent
25 carboxylic esters: a bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, secondary aliphatic ester; a bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, tertiary aliphatic ester; a bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, secondary aliphatic ester; or a bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, tertiary aliphatic ester.

4. The silsesquioxane-containing composition of claim 3 wherein Z-L- is selected from the following monovalent carboxylic esters:

- bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 1',1'-dimethylethyl ester;
 bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 1',1'-dimethylethyl ester;
 5 bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 1'-methylethyl ester;
 bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 1'-methylethyl ester;
 bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, adaman-1'-yl ester;
 bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, adaman-1'-yl ester;
 bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 3'-methyladaman-1'-yl ester;
 10 bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 3'-methyladaman-1'-yl ester;
 bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 2'-methyladaman-2'-yl ester;
 bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 2'-methyladaman-2'-yl ester;
 bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 2'-ethyladaman-2'-yl ester;
 bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 2'-ethyladaman-2'-yl ester;
 15 bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, cyclohexyl ester;
 bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, cyclohexyl ester;
 bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 1'-ethylcyclopentyl ester;
 bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 1'-ethylcyclopentyl ester;
 20 bicyclo[2.2.1]heptane-5-yl-2-carboxylic acid, 2'-hydroxy-2',6',6'-
 trimethylbicyclo[3.1.1]heptane-3'-yl ester; and
 bicyclo[2.2.1]heptane-6-yl-2-carboxylic acid, 2'-hydroxy-2',6',6'-
 trimethylbicyclo[3.1.1]heptane-3'-yl ester.

5. The silsesquioxane-containing composition of any one of claims 1 to 4 wherein the (A)
 25 silsesquioxane resin of formula (I) has a weight average molecular weight (M_w) of 1,000 to 50,000.

6. The silsesquioxane-containing composition of any one of claims 1 to 5 wherein in the (B) silyl-anhydride of formula (II):

- 30 each R^5 is independently H, a (C_1-C_6) alkyl, or a monovalent group of formula
 $-(L^2)_n-Si(OR^4)_3$;
 at least one R^5 is H;
 at least one R^5 is a (C_1-C_6) alkyl;

at least one R^5 is a monovalent group of formula $-(L^2)_n-Si(OR^4)_3$;

both R^5 are taken together to form a (C_2-C_5) alkane-diyl;

one R^5 is taken together with R^6 to form a bond or (C_1-C_4) alkane-diyl, and the remaining R^5 is independently H, a (C_1-C_6) alkyl, or a monovalent group of formula $-(L^2)_n-Si(OR^4)_3$;

one R^5 is taken together with R^6 to form a bond, and the remaining R^5 is independently H, a (C_1-C_6) alkyl, or a monovalent group of formula $-(L^2)_n-Si(OR^4)_3$;

one R^5 is taken together with R^6 to form a (C_1-C_4) alkane-diyl, and the remaining R^5 is independently H, a (C_1-C_6) alkyl, or a monovalent group of formula $-(L^2)_n-Si(OR^4)_3$;

one R^5 is taken together with R^6 to form a (C_1-C_4) alkane-diyl, and the remaining R^5 is H;

one R^5 is taken together with R^6 to form a (C_1-C_4) alkane-diyl, and the remaining R^5 is a (C_1-C_6) alkyl;

one R^5 is taken together with R^6 to form a (C_1-C_4) alkane-diyl, and the remaining R^5 is a monovalent group of formula $-(L^2)_n-Si(OR^4)_3$;

both R^5 are taken together with R^6 to form $=CH-$;

R^6 is taken together with R^5 as described above;

R^6 is a (C_1-C_8) hydrocarbyl or a monovalent group of formula $-C(R^7)_2-(L^2)_n-Si(OR^4)_3$;

R^6 is a (C_1-C_8) hydrocarbyl;

R^6 is a monovalent group of formula $-C(R^7)_2-(L^2)_n-Si(OR^4)_3$; subscript m is 0;

each R^5 is independently H or a (C_1-C_6) alkyl and R^6 is a (C_1-C_8) hydrocarbyl;

at least one R^5 is a monovalent group of formula $-(L^2)_n-Si(OR^4)_3$ and R^6 is a monovalent group of formula $-C(R^7)_2-(L^2)_n-Si(OR^4)_3$;

subscript m is 1;
 at least one subscript n is 0;
 at least one subscript n is 1;
 at least one R⁴ is independently an unsubstituted (C₁-C₂)alkyl;
 at least one R⁴ is independently an unsubstituted (C₃-C₆)alkyl;
 at least one L¹ and L² is independently a (C₁-C₄)hydrocarbon-diyl;
 at least one L¹ and L² is independently a (C₁-C₄)alkane-diyl;
 each of L¹ and L² is independently a (C₁-C₄)alkane-diyl;
 at least one L¹ and L² is independently a (C₅-C₈)hydrocarbon-diyl;
 at least one R⁷ is H or a (C₁-C₆)alkyl;
 at least one R⁷ is H or a (C₁-C₂)alkyl;
 both R⁷ are taken together to form a (C₂-C₅)alkane-diyl; or
 both R⁷ are taken together to form a (C₂-C₃)alkane-diyl.

7. The silsesquioxane-containing composition of any one of claims 1 to 5 wherein the (B) silyl-anhydride of formula (II) is selected from:

2-(3'-triethoxysilyl-propyl)-succinic anhydride;
 2,3-bis(3'-triethoxysilyl-propyl)-succinic anhydride;
 3-(3'-triethoxysilyl-propyl)-glutaric anhydride;
 2,3-bis(3'-triethoxysilyl-propyl)-glutaric anhydride; and
 1,1,2,2,3,3-hexamethyl-1,3-bis(ethyl-1',2'-dicarboxylic)-trisiloxane dianhydride.

8. A silsesquioxane-containing composition comprising the silsesquioxane-containing composition of any one of claims 1 to 7 and (C) a photoacid generator, wherein the (C) photoacid generator comprises an onium salt, a halogen-containing compound, a diazoketone compound, a glyoxime derivative, a sulfone compound, a sulfonate compound, or a combination of any two or more thereof.

9. The silsesquioxane-containing composition of any one of claims 1 to 8 independently further comprising one or more constituents: (D) a solvent or (E) an acid-diffusion controlling agent.

5 10. A manufactured article comprising the silsesquioxane-containing composition of any one of claims 1 to 9.

11. A method of making a resist image on a substrate, the method comprising:

10 applying the silsesquioxane-containing composition of any one of claims 1 to 9 to a surface of a substrate so as to form an applied film thereof on the surface of the substrate, wherein the silsesquioxane-containing composition comprises the (A) silsesquioxane resin, the (B) silyl-anhydride, and (C) a photoacid generator;
mask exposing the applied film to radiation to produce an exposed film containing a latent pattern;
15 developing the exposed film to produce a resist image from the latent pattern to give a manufactured article comprising the resist image disposed on the substrate.

12. The method of making a resist image on a substrate of claim 11, wherein:

20 the substrate comprises a bare semiconductor wafer;
the substrate comprises a primed semiconductor wafer;
the substrate comprises a primed semiconductor wafer prepared by priming a bare semiconductor wafer with hexamethyldisilazane;
the substrate comprises a semiconductor wafer and the silsesquioxane-containing composition is applied directly on a surface of the semiconductor wafer;
25 the substrate comprises a semiconductor wafer having a surface portion comprising silicon carbide, silicon carbonitride, silicon nitride, silicon oxide, silicon oxynitride, or silicon oxycarbonitride, and the silsesquioxane-containing composition is applied directly on the surface portion of the semiconductor wafer;
the substrate comprises an underlayer disposed on a surface of a semiconductor
30 wafer and the silsesquioxane-containing composition is applied directly on the underlayer without being applied directly on the semiconductor wafer;
before the applying step the silsesquioxane-containing composition further comprises (D) a solvent and the applying step comprises spin-coating;

the applied film further comprises (D) a solvent and the method further comprises drying the applied film (soft baking) before the mask exposing step;

the applied film has a thickness of from 0.01 to 5 micrometers;

the radiation is selected from ultraviolet (UV) light, X-ray radiation, e-beam radiation, and extreme ultraviolet (EUV) radiation;

the radiation has a wavelength in a range of from 13 nanometers (nm) to 365 nm;

the radiation has a wavelength comprising 365 nm, 248 nm, 193 nm, 157 nm, or 13 nm;

the developing step comprises contacting the mask exposed film with a developer comprising an aqueous base;

the method further comprises heating the mask exposed film at a temperature from 30 degrees Celsius (° C) to 200° C and cooling the mask exposed film before the developing step and the developing step comprises contacting the cooled mask exposed film with a developer comprising an aqueous base; or

the developing step comprises contacting the mask exposed film with a developer comprising aqueous tetramethylammonium hydroxide.

13. The method of making a resist image on a substrate of claim 11 or 12, wherein:

the substrate comprises a hardmask layer disposed on a surface of a semiconductor wafer and the silsesquioxane-containing composition is applied directly on the hardmask layer without being applied directly on the semiconductor wafer and the method further comprises oxygen (O₂) plasma etching the resist image to etch the hardmask layer by transferring the resist image into the hardmask layer and give a first semiconductor device comprising a bilayer image disposed on the surface of the semiconductor wafer, wherein the bilayer image comprises a resist image layer and a hardmask image layer, and wherein a region of the surface of the semiconductor wafer is covered by the bilayer image and another region of the surface of the semiconductor wafer is uncovered; or

the substrate comprises a hardmask layer disposed on a surface of a semiconductor wafer and the silsesquioxane-containing composition is applied directly on the hardmask layer without being applied directly on the semiconductor wafer and the method further comprises: (i) oxygen (O₂) plasma etching the resist image to etch the hardmask layer by transferring the resist image into the hardmask layer to give a first semiconductor device sequentially comprising a bilayer image disposed on the

5 surface of the semiconductor wafer, wherein the bilayer image comprises a resist image layer and a hardmask image layer, and wherein a region of the surface of the semiconductor wafer is covered by the bilayer image and another region of the surface of the semiconductor wafer is uncovered; and (ii) halogen-containing etching the uncovered region of the surface of the semiconductor wafer of the first semiconductor device to transfer the bilayer image into the semiconductor wafer by removing the remaining applied film, at least some of the hardmask layer, and some, but not all, of the uncovered region of the semiconductor wafer to give a second semiconductor device comprising a semiconductor image disposed on a basal semiconductor layer.

10 14. A semiconductor device comprising the first or second semiconductor device made by the method of claim 13.

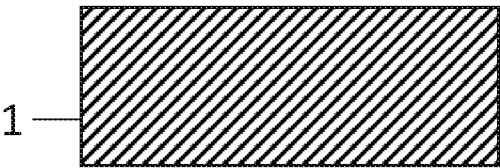


FIG. 1

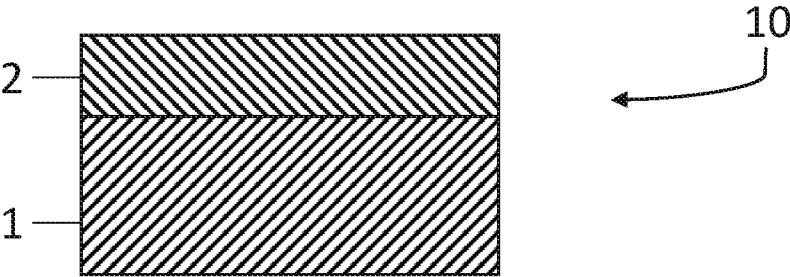


FIG. 2

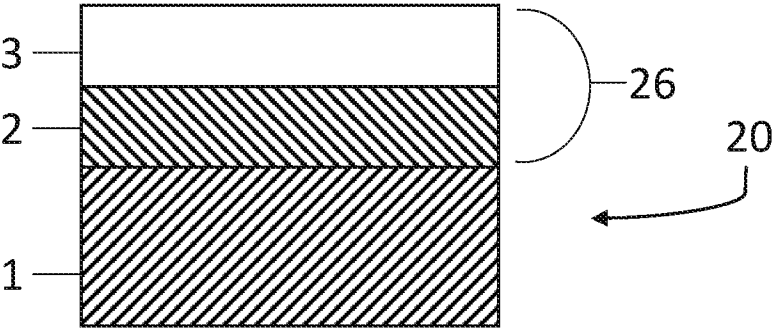


FIG. 3

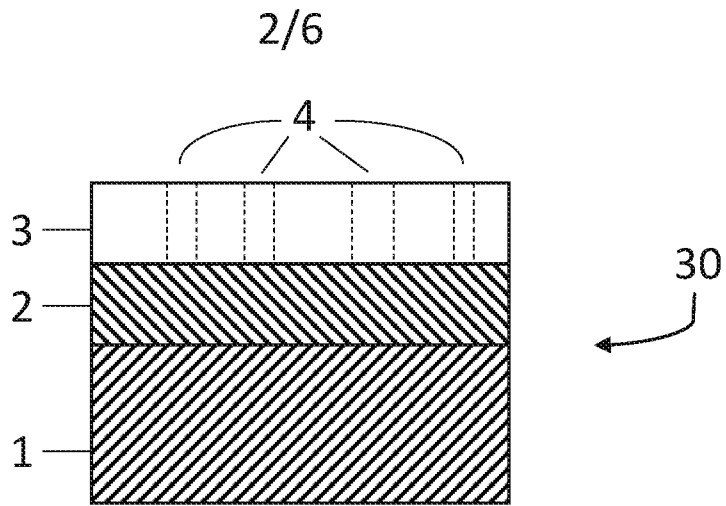


FIG. 4

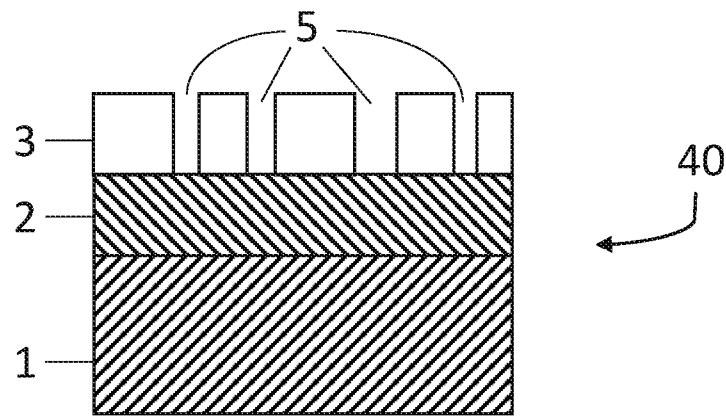


FIG. 5

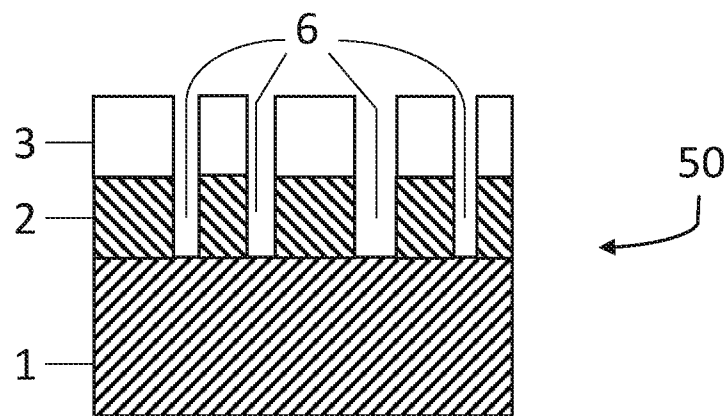


FIG. 6

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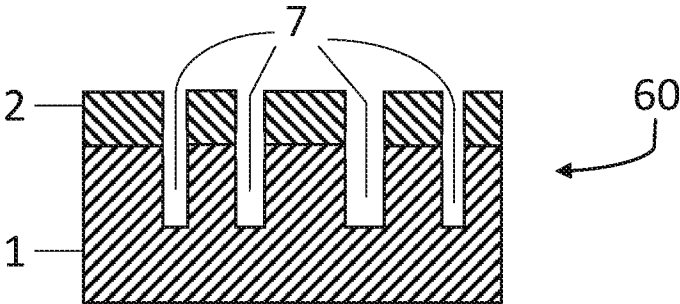


FIG. 7

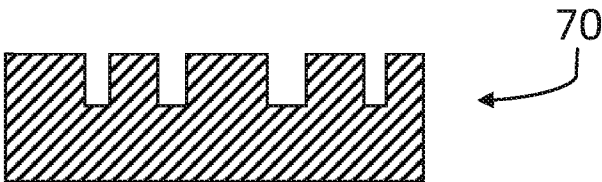


FIG. 8

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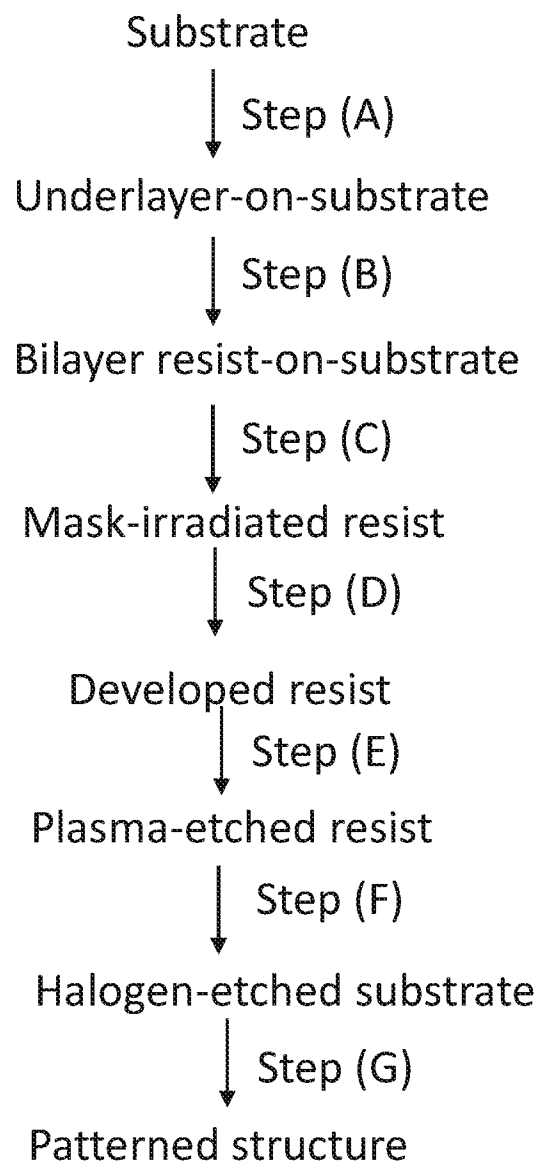


FIG. 9

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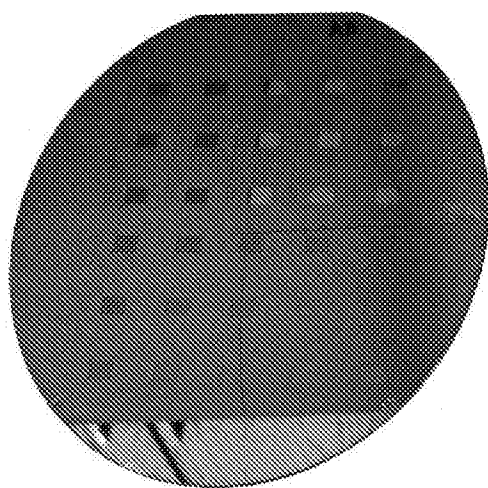


FIG. 10

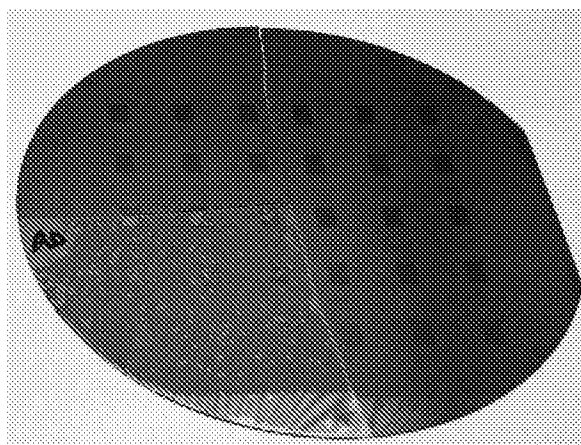
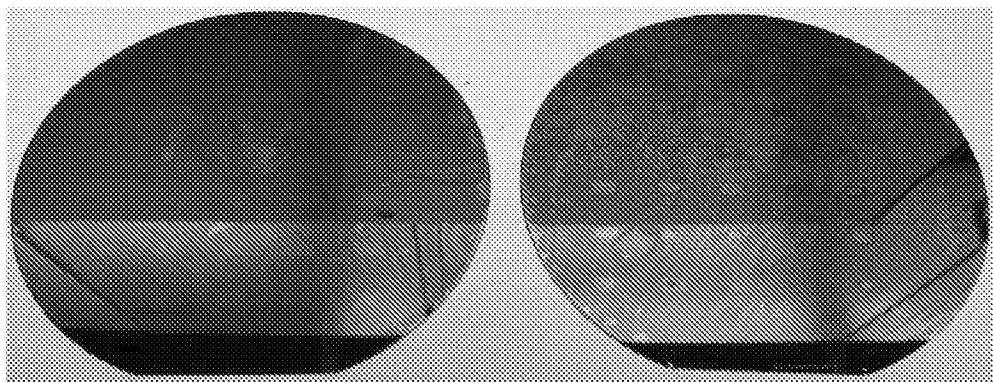


FIG. 11

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FIGs 12L
(non-invention)

FIGs 12R
(non-invention)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/029808

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07F7/18 C07F7/21 C08K5/04 C08L83/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07F C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/163652 A1 (TAJIMA AKIO [JP] ET AL) 25 June 2009 (2009-06-25) claim 10; paragraph [0072]-[0073]; paragraph [0032]	1-14
A	JP 2007 326988 A (CHISSO CORP) 20 December 2007 (2007-12-20) claims 1,8-10	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search

6 July 2017

Date of mailing of the international search report

17/07/2017

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Authorized officer

Bourghida, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/029808

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2009163652	A1	25-06-2009	NONE	

JP 2007326988	A	20-12-2007	NONE	
