

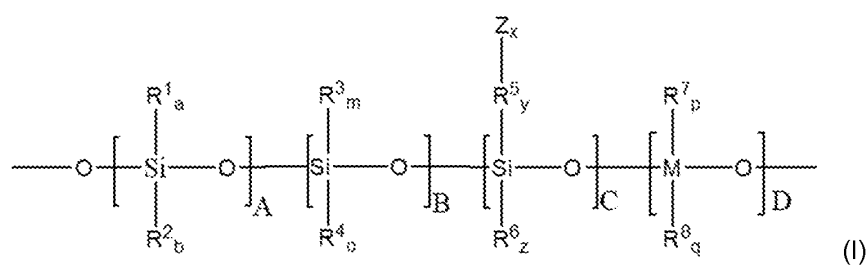
Claims:

1. Hydrogen silsesquioxane resin coating composition, comprising in liquid phase a resin exhibiting silanol (Si-OH) and silicon-hydrogen (Si-H) and optionally silicon-carbon bonds
5 in a silicon-oxygen network, or silicon-hydrogen (Si-H) and optionally silicon-carbon bonds in a silicon-oxygen-metal network, the peak height ratio of Si-H to Si-OH being about 2:1 to 100:1.
2. The composition according to claim 1, having a silicon content of about 35 % by weight
10 or more.
3. The composition according to claim 1 or 2, in which the hydrogen silsesquioxane resin has a Si-H to Si-OH peak height ratio of between 3:1 and 50:1.
- 15 4. The composition according to any of the preceding claims, comprising an at least partially cross-linked, optionally metal containing, organosiloxane polymer in a solvent, said polymer having a molecular weight of about 500 to 100,000 g/mol, in particular about 1,000 to 50,000 g/mol, measured against polystyrene standards.
- 20 5. The composition according to any of the preceding claims, comprising an acid or a latent acid or a base or a latent base, and optionally a latent catalyst.
6. The composition according to any of the preceding claims, wherein the liquid phase is formed by at least one organic solvent for the hydrogen silsesquioxane resin, optionally in
25 mixture with water.
7. The composition according to any of the preceding claims, comprising a metal selected from the group of zirconium, hafnium, aluminium, titanium and tin and combinations thereof.
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8. The composition according to any of the preceding claims, comprising silanol containing polyhydrosilsesquioxane resin solutions obtained by subjecting trifunctional silanes to hydrolysis/condensation reactions with suitable other silicon or metal containing precursors to produce metal and silanol containing polyhydrosilsesquioxane.
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9. The composition according to any of the preceding claims, comprising a siloxane polymer containing SiO moieties, a plurality of reactive sites distributed along the polymer,

and a first SiH portion, a second SiOH portion, and an intermediate aromatic and non-aromatic portion, a fourth portion containing metal-oxygen bonds, wherein the polymer has a molecular weight of from 500 to 50,000 g/mol, and the composition preferably further comprising an acid and/or base catalyst and a solvent.

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10. The composition according to any of the preceding claims, comprising a polyhydridosilsesquioxane resin having the general formula (I)



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wherein

A, B, C, and D each representing an integer independently selected from 1 to 1000;

Z stands for functional group and M stands for a metal atom;

15 R¹ to R⁸ stand for hydrocarbyl radicals; and

a, b, m, o, y, z, p, q and x each independently stand for an integer of 0 to 3.

11. The composition according to any of the preceding claims, which composition is suitable for use in patterning by irradiation, in particular the composition is suitable for the production of a coating formulation that can be cast on substrates, and wherein the coating on the substrate can be patterned by irradiation.

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12. Method of producing a composition containing metal and silanol containing polyhydridosilsesquioxane resin in an organic solution comprising subjecting trifunctional silanes to hydrolysis/condensation reactions with other silicon or metal containing precursors to obtain metal and silanol containing polyhydridosilsesquioxane.

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13. The method according to claim 12, comprising

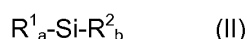
- hydrolyzing a first monomeric hydrogen containing silicon compound having at least two or three hydrolysable groups attached to the silicon with

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- a second monomeric silicon compound having at least zero, one, two or three hydrocarbyl radicals, and at least one hydrolyzable group attached to the silicon atom of the compound, optionally together with at least one of
- a third monomeric silicon compound having at least one functional group and at least one hydrolyzable group attached to the silicon atom of the compound to form a siloxane material, wherein the functional group enhances dissolution to a developer, and
- a fourth compound containing one or more hydrolysable metal oxide precursors, and
- formulating the siloxane material into a stable composition in a suitable solvent system.

14. The method according to claim 12 or 13, wherein the first and second silicon compounds are used at 0–100 mol-%, the third silicon compound at 0–20 mol-%, and the fourth metal compound at 0–50 mol-%. the total amount of the first and second silicon compounds being at least 50 mol-%, in particular at least 60 mol-%, for example at least 70 mol-%.

15. The method according to any of claims 12 to 14, comprising hydrolyzing a first silicon compound having the general formula II



wherein

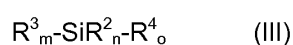
a is an integer of 1 or 2,

b is an integer of 2 or 3,

R^1 denotes a hydrogen atom and

R^2 denotes a hydrolysable group which can independently be selected from hydroxyl, alkoxy, acyloxy and halogen.

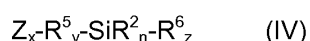
16. The method according to any of claims 12 to 15, comprising producing a copoly(organosiloxane) by hydrolyzing a first silicon compound having the general formula II, wherein the symbols a, b, R^1 and R^2 have the same meaning as above, with a second compound having the general formula III



wherein

- R³ and R⁴ are independently selected from an alkyl group, an aryl group, an aralkyl group, a halogenated alkyl group, a halogenated aryl group, a halogenated aralkyl group, an organic group having an epoxy group, a mercapto group, an alkoxyaryl group, an acyloxyaryl group, an isocyanurate group, a hydroxy group, a cyclic amino group, or a cyano group, or a combination of them, or
- R² and R³ represent an alkoxy group, an acyloxy group, or a halogen group,
- m is an integer of 0 to 1,
- n is an integer of 2 to 4, and
- o is an integer of 0 to 1,
- wherein the total value of m + n + o may not exceed 4.

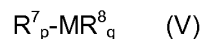
17. The method according to any of claims 12 to 16, comprising producing a composition comprising a copoly(organosiloxane) by hydrolyzing a first silicon compound having the general formula II, wherein the symbols a, b, R¹ and R² have the same meaning as above in formula II, with a second compound having the general formula IV



- wherein
- Z is a group selected from hydroxy, carboxylic acid, mercapto, amine or its salt, or a quaternary ammonium salt facilitating solubility in aqueous developers, and
- R⁵ is a spacer group covalently bound to both Z and Si and can be independently selected from a bivalent group derived from an alkyl group, an aryl group, an aralkyl group, a halogenated alkyl group, a halogenated aryl group, a halogenated aralkyl group, an alkoxyaryl group, an acyloxyaryl group, or a combination of them,
- R⁶ is independently selected from an alkyl group, an aryl group, an aralkyl group, a halogenated alkyl group, a halogenated aryl group, a halogenated aralkyl group, an organic group having an epoxy group, a mercapto group, an alkoxyaryl group, an acyloxyaryl group, a hydroxy group, a cyclic amino group, or a cyano group, or a combination of them,
- R² is an alkoxy group, an acyloxy group, or a halogen group,
- y is an integer of 0 to 2,
- n is an integer of 1 to 3, and
- z is an integer of 0 to 11, and
- wherein the total value of y + n + z is 4 or less.

18. The method according to any of claims 12 to 17, comprising producing a copoly(organosiloxane) by hydrolyzing a first silicon compound having the general formula II, wherein symbols a, b, R¹ and R² have the same meaning as above in formula II, with a second compound having the general formula V

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wherein

R⁷ is independently selected from an alkyl group, an aryl group, an aralkyl group, a halogenated alkyl group, a halogenated aryl group, a halogenated aralkyl group, an alkenyl group, an alkoxyaryl group, an acyloxyaryl group, or a combination of them, M is independently selected from a metal capable of forming precursors that can be hydrolyzed and condensed to metal oxides or metal-oxohydroxides, p is an integer of 0 to 1, with the proviso that M is capable of forming stable carbon metal bonds, q is an integer of a number obtained from M_{ox}-p, wherein M_{ox} is the oxidation state of the metal precursor and p is the number of carbon radicals R⁷ covalently attached to the metal precursor, and R⁸ is an alkoxy group, an acyloxy group, a halogen group, a hydroxy group or an oxygen atom functioning as a linkage to another metal atom; or R⁸ is a bidentate or coordinating ligand of a metal.

19. The method according to any of claims 12 to 18, comprising using HTEOS (HSi(OC₂H₅)₃) or mixture of HTEOS and other trifunctional silanes, which are subjected to a controlled hydrolytic/condensation reaction, for making partially condensed polyhydridosilsesquioxane resins.

20. The method according to claim 19, wherein the trifunctional silanes are typically selected from methyltrimethoxysilane (MTMOS), methyltriethoxysilane (MTEOS), trimethoxyethylsilane (ETMOS) or diethoxydimethylsilane (DMDEOS) or trimethoxyphenylsilane (PhTMOS) or combinations thereof.

21. Method of patterning a metal and silanol containing polyhydridosilsesquioxane coated substrate with radiation of light at a specific wavelength, the method comprising the steps of

- irradiating a coated substrate along a selected pattern to form an irradiated structure with a region of irradiated coating and a region with un-irradiated coating; and
- selectively developing the irradiated structure to remove a substantial portion of the un-irradiated coating to form a patterned substrate.

22. The method according to claim 21, wherein a metal and silanol containing polyhydrosilanesquioxane coated substrate is irradiated with radiation of light at a wavelength between 1 and 200nm.

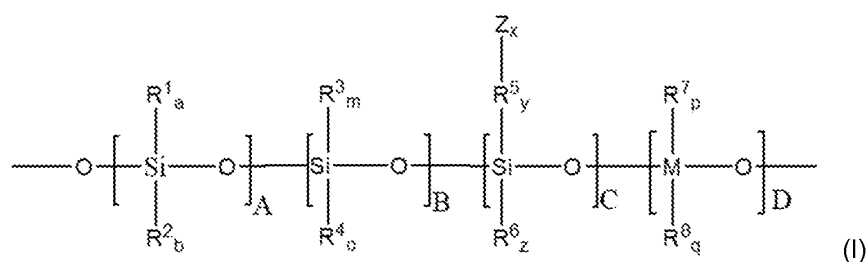
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23. The method according to claim 22, wherein a metal and silanol containing polyhydrosilanesquioxane coated substrate is irradiated with radiation of light at a wavelength of 13.5 nm..

24. The method according to any of claims 21 to 23, , wherein the coating comprises a siloxane polymer containing SiO moieties, a plurality of reactive sites distributed along the polymer, and a first SiH portion, a second SiOH portion, and an intermediate aromatic and non-aromatic portion, a fourth portion containing metal-oxygen bonds, wherein the polymer has a molecular weight of from 500 to 50000 g/mol.

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25. The method according to any of claims 21 to 24, wherein the coating comprises a polyhydrosilanesquioxane resin having the general formula (I)



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wherein

A, B, C, and D each representing an integer independently selected from 1 to 1000;

Z stands for functional group and M stands for a metal atom;

30 R¹ to R⁸ stand for hydrocarbyl radicals; and

a, b, m, o, y, z, p, q and x each independently stand for an integer of 0 to 3.

26. The method according to any of claims 21 to 25, comprising patterning a substrate, comprising:

- irradiating a coated substrate along a selected pattern to form an irradiated structure with a region of irradiated coating and a region with un-irradiated coating, wherein the coated substrate comprises a coating having an average thickness from about 5 nm to about 400 nm and that comprises a Si-O-Si network with Si-H and Si-OH bonds in material structures;
- heating the irradiated structure at a temperature from about 45° C. to about 200° C. for 0.1 minutes to about 30 minutes to form an annealed irradiated structure; and
- selectively developing the annealed irradiated structure to remove a substantial portion of the un-irradiated coating to form a patterned substrate.

27. The method of any of claims 21 to 26, wherein the irradiated structure has an irradiated coating that is insoluble in aqueous base and non-irradiated coating soluble in aqueous base such that the irradiated structure can be subjected to negative tone imaging.

28. The method of any of claims 21 to 27, comprising patterning a substrate comprising a substrate with a surface and a coating at selected regions along the surface and absent at other regions along the surface, said coating comprising a silicon-oxygen, or silicon-oxygen-metal network with silicon-carbon bonds and silicon-hydrogen and/or with silanol bonds, the coating being soluble in organic liquids or in aqueous bases.

29. A method of forming of a resist film by application of a composition according to any of claims 1 to 11 for forming a resist underlayer film onto a semiconductor substrate and baking the composition.

30. A method for producing a semiconductor device, comprising:

- applying a resist underlayer film or several underlayer films onto a semiconductor substrate and baking the composition to form one or more resist underlayer films;
- applying a composition according to any of claims 1 to 11 as a resist onto one or more resist underlayer films to form a resist film;
- exposing the resist film to light;
- after the light exposure, developing the resist film to form a resist pattern;
- etching the resist underlayer film using the resist pattern; and

- fabricating the semiconductor substrate using the resist film thus patterned and the resist underlayer film thus patterned.

31. A method of producing a semiconductor device, comprising:

- 5 – forming an organic underlayer film on a semiconductor substrate;
- applying the composition according to any of claims 1 to 11 for forming a resist film onto the organic underlayer film and baking the composition to form a resist film;
- exposing the resist film to light;
- 10 – after the light exposure, developing the resist film to form a resist pattern;
- etching the resist underlayer film using the resist pattern;
- etching the organic underlayer film using the resist underlayer film thus patterned; and
- 15 – fabricating the semiconductor substrate using the organic underlayer film thus patterned.

32. A method of producing a semiconductor device, the method comprising:

- applying a resist underlayer film or several underlayer films onto a semiconductor substrate and baking the composition to form one or more resist underlayer films;
- 20 – applying a composition according to any of claims 1 to 11 as a resist onto one or more resist underlayer films to form a resist film;
- exposing the resist film to light;
- after the light exposure, developing the resist film to form a resist pattern;
- 25 – etching the resist underlayer film using the resist pattern; and
- fabricating the semiconductor substrate using the resist film thus patterned and the resist underlayer film thus patterned.

33. A method for producing a semiconductor device comprising the steps of

- 30 – forming an organic underlayer film on a semiconductor substrate;
- applying the composition according to any of claims 1 to 11 for forming a resist film onto the organic underlayer film and baking the composition to form a resist film;
- exposing the resist film to light;
- 35 – after the light exposure, developing the resist film to form a resist pattern;
- etching the resist underlayer film using the resist pattern;

- etching the organic underlayer film using the resist underlayer film thus patterned; and
- fabricating the semiconductor substrate using the organic underlayer film thus patterned.