and is known to be relatively unstable during processing rendering its industrial adoption limited as described by (Yang et al. 2009).

There are several factors which can facilitate to develop a process suitable for EUVL such as developer temperature, developer concentration and developer composition. Despite the advances in prior art, functional photoresists that provide the RLS characteristics without excessive metal contamination is still being looked for.

SUMMARY

In an aspect of the present disclosure, there is provided a functional polyhydrogensilsesquioxane resist composition for extreme ultraviolet or electron beam lithography comprising at least of 50 mol-% of siloxy repeating units containing a Si-H and up to 30 mol-% of siloxy repeating units having an unsaturated hydrocarbyl radical, wherein the composition is free from photonitiator(s).

In another aspect of the present disclosure, there is provided a method of producing a functional polyhydrogensilsesquioxane resist composition disclosed herein, containing at least SiH moieties and unsaturated hydrocarbyl radicals covalently bound to Si, and optionally hydrocarbon radicals containing halogen, solubility-enhancing moieties.

In a further aspect of the present disclosure, there is provided a method of 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 compound having the general formula III

$$R^3{}_c\text{-}SiR^{21}{}_n\text{-}R^4{}_d \qquad \text{(III)}$$

wherein

R^3 and R^4 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 alkenyl group, an organic group having an epoxy group, an acryloyl group, a methacryloyl 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,
R^{21} represent an alkoxy group, an acyloxy group, or a halogen group,
c is an integer of 0 to 1,

n is an integer of 2 to 4, and
d is an integer of 0 to 2,
wherein the total value of c + n + d may not exceed 4.

In another aspect of the present disclosure, there is provided a method of producing a composition comprising 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 in formula II, with a compound having the general formula IV

$$R^5_e\text{-}SiR^{22}_n\text{-}R^6_f \qquad \text{(IV)}$$

wherein
R^5 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 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,
R^6 is a functional group containing a double or triple bond present in 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 alkoxyalkyl group, an alkoxyaryl group, an acyloxyaryl group, or a combination of them,
R^{22} is an alkoxy group, an acyloxy group, or a halogen group,
e is an integer of 0 to 1,
n is an integer of 1 to 3, and
f is an integer of 0 to 2,
wherein the total value of e + n + f is 4 or less.

In a further aspect of the present disclosure, there is provided a method of producing a composition comprising 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 in formula II, with a compound having the general formula V

$$R^7_g\text{-}SiR^{23}_n\text{-}R^8_h\text{-}X \qquad \text{(V)}$$

wherein
X is a halogen group,

R^7 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 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,

R^8 is a spacer group covalently bound to both X 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 alkenyl group, an alkoxyaryl group, an acyloxyaryl group, or a combination of them,

R^{23} is an alkoxy group, an acyloxy group, or a halogen group,

g is an integer of 0 to 1,

n is an integer of 1 to 3,

h is an integer of 0 to 1, and

wherein the total value of g + n + h is 4 or less.

In another aspect of the present disclosure, there is provided a method of producing a composition comprising 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 in formula II, with a compound having the general formula VI,

$$R^9_i\text{-}SiR^{24}_n\text{-}R^{10}_j\text{-}Z^y_k \qquad \text{(VI)}$$

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

R^9 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 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,

R^{10} 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 alkenyl group, an alkoxyaryl group, an acyloxyaryl group, or a combination of them,

R^{24} is an alkoxy group, an acyloxy group, or a halogen group,

i is an integer of 0 to 1,

n is an integer of 1 to 3, and

j is an integer of 0 to 2,
wherein the total value of i + n + j is 4 or less.

In a further aspect of the present disclosure, there is provided a method of patterning a carbon-carbon unsaturated bond containing, and halogen containing, and solubility-enhancer containing polyhydrogensilsesquioxane 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.

In another aspect of the present disclosure, there is provided a method of forming of a resist film by application of a composition disclosed herein, which is free from any photoinitiator, for forming a resist underlayer film onto a semiconductor substrate and baking the composition.

In a further aspect of the present disclosure, there is provided 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 disclosed herein, 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.

In another aspect of the present disclosure, there is provided a method of producing a semiconductor device, comprising:

- forming an organic underlayer film on a semiconductor substrate;
- applying the composition disclosed herein, 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;
- 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.

It is an object of the present disclosure to provide novel functional polyhydrogensilsesquioxane resin coating compositions.

It is another object of the present disclosure to provide methods of producing novel functional hydrogen silsesquioxane resins.

It is a third object of the present disclosure to provide methods for patterning of functional polyhydrogensilsesquioxane coated substrates with radiation of light.

It is a further object of the present disclosure to provide coated substrates comprising radiation sensitive coatings suitable for patterning by radiation of light or electron beams.

As further object, the present disclosure pertains to a method for patterning a carbon-carbon unsaturated bond and/or halogen-containing bond containing polyhydrogensilsesquioxane 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. The coated substrate generally comprises a coating used for pattern formation that comprises a silicon-oxygen network with silicon-carbon bonds and silicon-hydrogen and/or with carbon-carbon unsaturated bond and/or halogen-containing bonds.

As a one more object, the present disclosure pertains to a method for patterning a carbon-carbon unsaturated bond and/or halogen-containing bond polyhydrogensilsesquioxane coated substrate with radiation of light at a specific wavelength, wherein the wavelength is 13.5 nm or less.

Claims:

1. A functional polyhydrogensilsesquioxane resist composition for extreme ultraviolet or electron beam lithography comprising at least of 50 mol-% of siloxy repeating units containing a Si-H and up to 30 mol-% of siloxy repeating units having an unsaturated hydrocarbyl radical, wherein the composition is free from photonitiator(s).

2. The composition according to claim 1, having a silicon content of more than 35 % by weight.

3. The composition according to any of the preceding claims, comprising an at least partially cross-linked 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.

4. The composition according to any of the preceding claims, wherein the liquid phase is formed by at least one organic solvent for the functional polyhydrogensilsesquioxane resin, optionally in mixture with water.

5. The composition according to any of the preceding claims, comprising a functional polyhydrogensilsesquioxane resin solutions obtained by subjecting di- or trifunctional silanes to hydrolysis/condensation reactions with other hydrolysable silicon containing precursor(s) to form a functional polyhydrogensilsesquioxane.

6. The composition according to claim 5~~6~~, wherein the other, e.g. di- or trifunctional, silicon precursor contains organic radicals containing one or more halogen atoms.

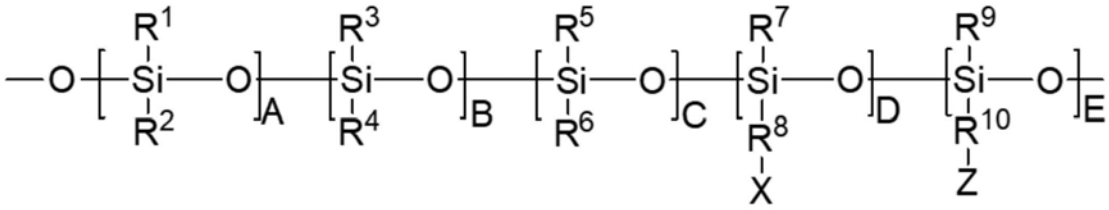
7. The composition according to claim 6, wherein the other, e.g. di- or trifunctional silicon precursor contains organic radicals that bear functionalities making the polymer, in particular organosiloxane polymer, more soluble into alkaline developer solutions.

~~8. The composition according to any of the preceding claims, wherein the composition is free from photonitiator(s).~~

8~~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 organosilicon portion containing an unsaturated

hydrocarbyl radical, and an intermediate siloxy (SiO) portion that optionally is independently selected from non-functional and halogen containing hydrrocarbyl radicals 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.

~~10~~9. The composition according to any of the preceding claims, comprising a functional polyhydrogensilsesquioxane resin having the general formula (I)



(I)

wherein

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

X stands for a halogen atom;

Z stands for functional group enhancing solubility to alkaline developers;

R^1 stands for hydrogen;

R^6 stands for a hydrocarbyl radical containing unsaturated moieties; and

each R^2 to R^5 and R^7 to R^{10} independently stands for hydrogen or hydrocarbyl radical, in particular hydrocarbyl radical.

~~11~~10. The composition according to any of the preceding claims, which composition is suitable for the production of a coating formulation that can be cast on substrates, and wherein the coating on the substrate optionally is capable of being patterned by irradiation directly or using a mask.

~~12~~11. Method of producing a functional polyhydrogensilsesquioxane resist composition according to any of claims 1 to ~~11~~10, containing at least SiH moieties and unsaturated hydrocarbyl radicals covalently bound to Si, and optionally hydrocarbon radicals containing halogen, solubility-enhancing moieties.

~~13~~12. The method according to claim ~~12~~11, comprising

- hydrolyzing a first monomeric hydrogen containing silicon compound having at least two, optionally at least three hydrolysable groups attached to the silicon with
- optionally 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 is unsaturated, ~~and~~
- optionally a fourth 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 containing halogen atom, and
- optionally a fifth 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 formulating the siloxane material into a composition, in particular a stable composition, in a solvent system.

~~14~~13. The method according to claim ~~12~~ 11 or ~~13~~12, wherein a first monomeric hydrogen compound is used in 50-100 mol-%, a second monomeric silicon compound is used in 0-20 mol-%, a third monomeric silicon compound is used in 0.1-20 mol-%, and a fourth monomeric silicon compound is used in 0-20 mol-%"~~the first and second silicon compounds are used at 0–100 mol-%, the third silicon compound at 0–30 mol-%, and the fourth compound at 0–20 mol-%, the total amount of the first and second silicon compounds being at least 30 mol-%, in particular at least 60 mol-%, for example at least 70 mol-%~~.

~~15~~14. The method according to any of claims ~~12~~ 11 to ~~14~~13, comprising hydrolyzing a first silicon compound having the general formula II

$$R^1{}_a\text{-Si-}R^2{}_b \qquad \text{(II)}$$

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 is independently selected from hydroxyl, alkoxy, acyloxy and halogen.

~~16~~15. A method of ~~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 compound having the general formula III

$$R^3{}_c\text{-}SiR^{21}{}_n\text{-}R^4{}_d \qquad \text{(III)}$$

wherein

R^3 and R^4 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 alkenyl group, an organic group having an epoxy group, an acryloyl group, a methacryloyl 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,
R^{21} represent an alkoxy group, an acyloxy group, or a halogen group,
c is an integer of 0 to 1,
n is an integer of 2 to 4, and
d is an integer of 0 to 2,
wherein the total value of c + n + d may not exceed 4.

~~17~~16. A method of ~~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, R^1 and R^2 have the same meaning as above in formula II, with a compound having the general formula IV

$$R^5{}_e\text{-}SiR^{22}{}_n\text{-}R^6{}_f \qquad \text{(IV)}$$

wherein
R^5 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 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,

R^6 is a functional group containing a double or triple bond present in 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 alkoxyalkyl group, an alkoxyaryl group, an acyloxyaryl group, or a combination of them,

R^{22} is an alkoxy group, an acyloxy group, or a halogen group,

e is an integer of 0 to 1,

n is an integer of 1 to 3, and

f is an integer of 0 to 2,

wherein the total value of e + n + f is 4 or less.

~~18~~17. A method of ~~The method according to any of claims 12 to 17, comprising~~ producing a composition comprising 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 in formula II, with a compound having the general formula V

$$R^7{}_g\text{-}SiR^{23}{}_n\text{-}R^8{}_h\text{-}X \qquad (V)$$

wherein

X is a halogen group,

R^7 is independently selected from an alkyl group, an aryl group, an aralkyl group, ap halogenated alkyl group, a halogenated aryl group, a halogenated aralkyl group, an alkenyl 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,

R^8 is a spacer group covalently bound to both X~~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 alkenyl group, an alkoxyaryl group, an acyloxyaryl group, or a combination of them,

R^{23} is an alkoxy group, an acyloxy group, or a halogen group,

g is an integer of 0 to 1,

n is an integer of 1 to 3,

h is an integer of 0 to 1, and

wherein the total value of g + n + h is 4 or less.

~~19~~18. A method of ~~The method according to any of claims 12 to 18, comprising~~ producing a composition comprising 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 in formula II, with a compound having the general formula VI,

$$R^9{}_i\text{-}SiR^{24}{}_n\text{-}R^{10}{}_j\text{-}Z^y{}_k \qquad (VI)$$

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

R^9 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 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,

R^{10} 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 alkenyl group, an alkoxyaryl group, an acyloxyaryl group, or a combination of them,

R^{24} is an alkoxy group, an acyloxy group, or a halogen group,

i is an integer of 0 to 1,

n is an integer of 1 to 3, and

j is an integer of 0 to 2,

wherein the total value of i + n + j is 4 or less. ~~In the structure of Formula (IV), k denotes the value that the spacer group R3 can encompass and must be equal or greater to 1.~~

~~20~~19. The method according to any of claims ~~12~~ 11 to ~~19~~18, comprising 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 in formula II, with at least one second compound according to one of general formulas III to VI, and with at least one third compound according to one of general formulas III to VI, said third compound being different from said second compound.

~~21~~20. The method according to any of claims ~~12~~ 11 to ~~20~~19, comprising 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 in formula II, with at least one second compound according to one of general formulas III to VI, with at least one third compound according to one of general formulas III to VI, and with at least one fourth and optionally at least one fifth compound according to one of general formulas III to VI, said third, fourth and optionally

fifth compounds being different from said second compound and optionally mutually different.

~~22~~21. The method according to any of claims ~~12~~ 11 to ~~21~~20, comprising using HTEOS ($HSi(OC_2H_5)_3$) and a silicon precursor containing unsaturated hydrocarbyl radicals or HTEOS ($HSi(OC_2H_5)_3$) and a silicon precursor containing unsaturated hydrocarbyl radicals in a mixture of other hydrolyzable silanes, which are subjected to a, preferably controlled, hydrolytic/condensation reaction, for making partially condensed polyhydrogensilsesquioxane resins.

~~23~~22. The method according to any of claims ~~12~~ 11 to ~~22~~21, comprising adding to the obtained polyhydrogensilsesquioxane resins or the coating solutions radical inhibitors or antioxidants.

~~24~~23. The method according to any of claims ~~12~~ 11 to ~~23~~22, comprising adding to the obtained polyhydrogensilsesquioxane resins or the coating solutions stabilizers which prevent the aging of the polyhydrogensilsesquioxane resins.

~~25~~24. The method according to the claim ~~24~~23, wherein the stabilizers are typically selected from at least one dicarboxylic acids, typically maleic acid, malonic acid, or succinic acid.

~~26~~25. Method of patterning a carbon-carbon unsaturated bond containing, and halogen containing, and solubility-enhancer containing polyhydrogensilsesquioxane 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.

~~27~~26. The method according to claim ~~26~~25, wherein a coated substrate is irradiated with radiation of light at a wavelength in the ultraviolet, in particular extreme ultraviolet wavelength range, such as at 1 to 200 nm, in particular 13.5 nm.

~~28~~27. The method according to claim ~~26~~ 25 or ~~27~~26, wherein a carbon-carbon unsaturated bond containing, and halogen containing, and solubility-enhancer containing polyhydrogensilsesquioxane coated substrate is irradiated with radiation of light at a wavelength between 1 and 200 nm.

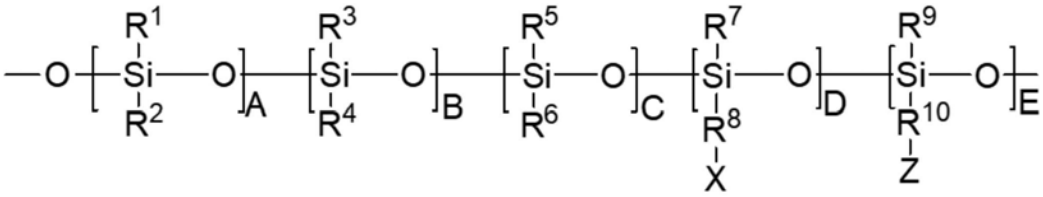
~~29~~28. The method according to claim ~~28~~27, wherein a carbon-carbon unsaturated bond containing, and halogen containing, and solubility-enhancer containing polyhydrogensilsesquioxane coated substrate is irradiated with radiation of light at a wavelength of 13.5 nm.

~~30~~39. The method according to any of claims ~~26~~ 25 to ~~29~~28, 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 intermediate aromatic and non-aromatic portion, a third portion containing carbon-carbon unsaturated bond selected from methacrylate, acrylate, norbornene, or combinations thereof, a fourth portion containing halogen, a fifth portion selected from hydroxy, carboxylic acid, mercapto, amine or its salt, or a quaternary ammonium salt facilitating solubility in aqueous developers wherein the polymer has a molecular weight of from 500 to 50000 g/mol.

~~31~~30. The method according to any of claims ~~26~~ 25 to ~~30~~29, wherein the coating comprises a

polyhydrogensilsesquioxane resin having the general formula (I)



(I)

wherein

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

X stands for a halogen atom;

Z stands for functional group enhancing solubility to alkaline developers;

R^1 stands for hydrogen;

R^6 stands for a hydrocarbyl radical containing unsaturated moieties; and

each R^2 to R^5 and R^7 to R^{10} independently stands for hydrogen or hydrocarbyl radical, in particular hydrocarbyl radical.

~~32~~31. The method according to any of claims ~~26~~ 25 to ~~31~~30, 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 carbon-carbon unsaturated bond 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.

~~33~~32. The method of any of claims ~~26~~ 25 to ~~32~~31, 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.

~~34~~33. The method of any of claims ~~26~~ 25 to ~~33~~ 32 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 network with silicon-carbon bonds and silicon-hydrogen and~~/or~~ with carbon-carbon unsaturated bonds, the coating being soluble in organic liquids or in aqueous bases.

~~35~~34. The method according to any of claims ~~26~~ 25 to ~~34~~33, wherein patterning is carried out in the absence of any photoinitiator.

~~36~~35. The method according to any of claims ~~26~~ 25 to ~~35~~34, comprising

- providing a polyhydrogensilsesquioxane resist composition comprising at least of 50 mol-% of siloxy repeating units containing a Si-H and up to 30 mol-% of siloxy repeating units having an unsaturated hydrocarbyl radical, the composition having a silicon content of more than 35 % by weight,
- forming the composition into a layer or a coating on a substrate; and
- patterning it, in the absence of a photoinitiator, by extreme ultraviolet beam lithography using radiation of light at a wavelength between 1 and 200 nm or at a

wavelength of 13.5 nm, wherein the composition preferably contains carbon-carbon unsaturated bonds and halogen and ~~optionally~~ a solubility-enhancer.

~~37~~36. A method of forming of a resist film by application of a composition according to any of claims 1 to ~~11~~10, which is free from any photoinitiator, for forming a resist underlayer film onto a semiconductor substrate and baking the composition.

~~38~~37. 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~~ 10 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.

~~39~~38. A method of producing a semiconductor device, comprising:

- forming an organic underlayer film on a semiconductor substrate;
- applying the composition according to any of claims 1 to ~~11~~ 10 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;
- 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.

~~40~~39. A method according to any of claims ~~38~~ 37 or ~~39~~38, wherein the resist film is exposed to light in the ultraviolet or, in particular in the extreme ultraviolet wavelength range, for example in the range from 1 to 200 nm, in particular about 13.5 nm (92 eV).

~~41. The method according to any of claims 38 to 40, wherein the composition according to any of claims 1 to 11 is free from a photoinitiator.~~