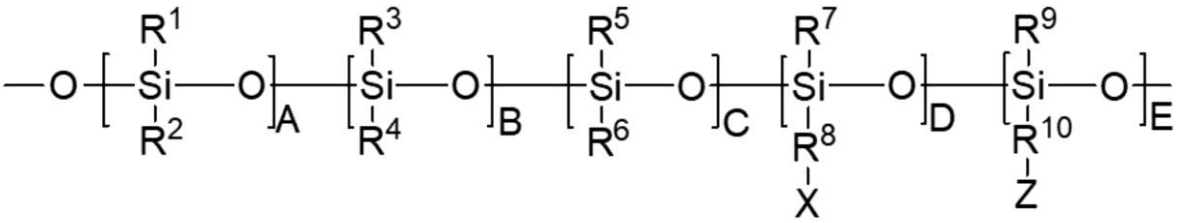
and is known to be relatively unstable during processing rendering its industrial adoption limited as described by (Yang et al. 2009).

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, and 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,

wherein the composition is free from photoinitiator(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 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.

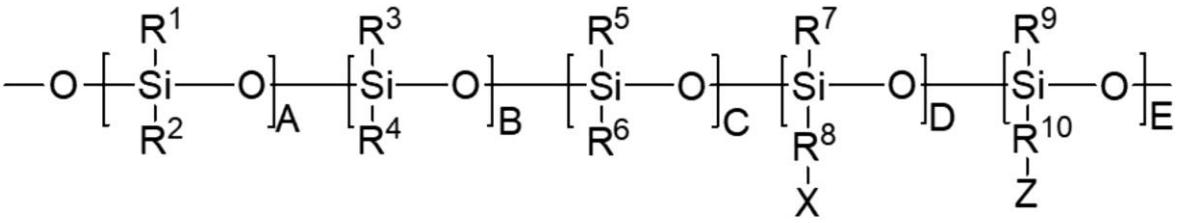
It is a further object of the present disclosure to provide coated substrates comprising radiation sensitive coatings suitable for patterning by radiation of light or electron beams.

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, and 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,
wherein the composition is free from photoinitiator(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 500 to 100,000 g/mol, in particular 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 the functional polyhydrogensilsesquioxane.

6. The composition according to claim 5, 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, 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.

9. 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.

10. Method of producing a functional polyhydrogensilsesquioxane resist composition according to any of claims 1 to 9, containing at least SiH moieties and unsaturated hydrocarbyl radicals covalently bound to Si, and optionally hydrocarbon radicals containing halogen, solubility-enhancing moieties.

11. The method according to claim 10, 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,

- 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,
- 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.

12. The method according to claim 10 or 11, 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-%".

13. The method according to any of claims 10 to 12, 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.

14. The method according to any of claims 10 to 13, 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.

15. The method according to any of claims 10 to 14, 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.

16. The method according to any of claims 10 to 15, 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.

17. The method according to any of claims 10 to 16, comprising adding to the obtained polyhydrogensilsesquioxane resins or the coating solutions radical inhibitors or antioxidants.

18. The method according to any of claims 10 to 17, comprising adding to the obtained polyhydrogensilsesquioxane resins or the coating solutions stabilizers which prevent the aging of the polyhydrogensilsesquioxane resins.

19. The method according to claim 18, wherein the stabilizers are typically selected from at least one dicarboxylic acids, typically maleic acid, malonic acid, or succinic acid.

20. A method of forming of a resist film by application of a composition according to any of claims 1 to 9, which is free from any photoinitiator, for forming a resist underlayer film onto a semiconductor substrate and baking the composition.

21. 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 9 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.

22. 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 9 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.

23. A method according to claim 21 or 22, 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).