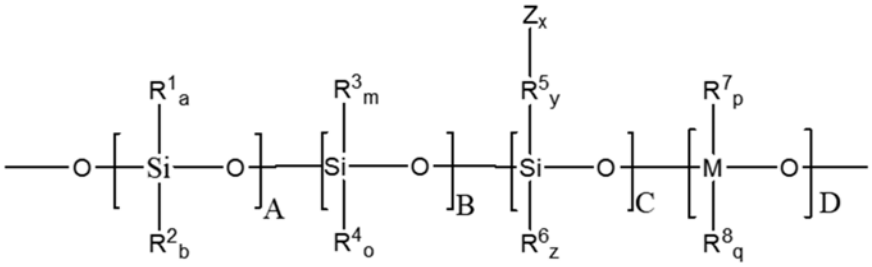
Hydrogen silsesquioxane (HSQ) is a widely utilized negative-type electron-beam and EUVL resist material. Due to its potential for high density patterns, namely, less than 10 nm pitch structures, intensive investigations have been carried out to find an optimum process. However, it suffers from very low sensitivity, requires concentrated developers 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 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 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 measured by FTIR of Si-H to Si-OH being 2:1 to 100:1, which composition is suitable for use in patterning by irradiation, said resin being a polyhydridosilsesquioxane resin having the general formula (I)



(I)

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;

R^1 to R^8 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,

the peak height ratio measured by FTIR of Si-H to Si-OH being 2:1 to 100:1, and which composition is suitable for use in patterning by irradiation.

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 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 an 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.

In a further aspect of the present disclosure, there is provided 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;
- 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 for producing a semiconductor device comprising the steps of

- 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 hydrogen silsesquioxane resin coating compositions.

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

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

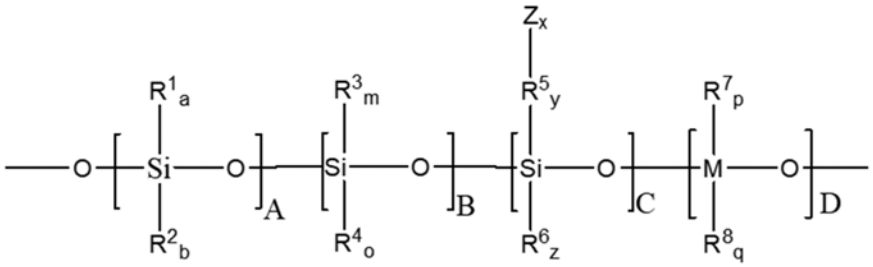
It is a further object of the present disclosure to provide coated substrates comprising radiation sensitive coatings suitable for patterning by radiation of light.

Conventional HSQ resins are free from silanol functionality. In the present disclosure it was surprisingly found that the presence of silanol moieties in an HSQ resin greatly enhances the pattern forming ability of the coatings compared to HSQ resins. As a result, a silanol-containing polyhydridosilsesquioxane of the present kind demonstrates higher sensitivity in EUV lithography compared to those described in literature to date.

It would appear that silanol groups of the resin, present in the film, react with intermediate reactive silicon species generated by EUV from SiH, but this is merely one possible explanation.

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 in a silicon-oxygen network, or silicon-hydrogen (Si-H) and optionally silicon-carbon bonds in a silicon-oxygen-metal network, said resin being a polyhydridosilsesquioxane resin having the general formula (I)



(I)

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;

R^1 to R^8 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,

the peak height ratio measured by FTIR of Si-H to Si-OH being 2:1 to 100:1, and which composition is suitable for use in patterning by irradiation.

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

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 500 to 100,000 g/mol, in particular 1,000 to 50,000 g/mol, measured against polystyrene standards.

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 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.

8. The composition according to any of the preceding claims, comprising silanol containing polyhydridosilsesquioxane 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 polyhydridosilsesquioxane.

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.

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 can be patterned by irradiation.

11. The composition according to claim 10, wherein the coating on the substrate can be patterned by irradiation with radiation of light at a wavelength of 13.5 nm.

12. 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.

13. 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.

14. 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 for forming a resist film onto an 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.

15. 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;
- 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.

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

- 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;
- 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.