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.

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.

Further, it has been found that the addition of functionalized groups further enhanced the sensitivity of the polyhydrogensilsesquioxane resin. Addition of silicon containing precursors containing functional groups enhances solubility in aqueous developers also improves the sensitivity of the resin.

A still further finding is that in some examples the use of metal oxide compounds either as part of the hydrolysis mixture or added separate as additives or as nanoparticles improves the sensitivity of the resin.

Thus, the present disclosure provides a solution of a hydrogen silsesquioxane resin, comprising an organic liquid and from about 0.001M to about 1M silanol compared to Si-H or Si-R in silicon-oxygen network, or silicon-oxygen-metal with silicon-carbon bonds and silicon-hydrogen.

Metal and silanol containing polyhydridosilsesquioxane resin solutions of the present kind can be produced by subjecting trifunctional silanes to hydrolysis/condensation reactions with other silicon or metal containing precursors to obtain metal and silanol containing polyhydridosilsesquioxane.

These solutions can be used for producing cast silanol-containing organic-inorganic hybrid coatings on semiconductor substrates for forming patterns thereon.

The present disclosure also provides a coated substrate comprising a radiation sensitive coating, comprising a silicon-oxygen, or silicon-oxygen-metal network with silicon-carbon bonds and silicon-hydrogen and/or with silanol bonds.

The present disclosure further provides a method for 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.

Further, the present disclosure provides a method for patterning a metal and silanol containing polyhydridosilsesquioxane coated substrate with radiation of light at a specific wavelength, wherein the wavelength is 13.5nm or less.

Still further, the present disclosure provides a patterned substrate comprising a substrate with a surface and a first coating at selected regions along the surface and absent at other regions along the surface. Generally, the first coating comprises a silicon-oxygen, or silicon-oxygen-metal network with silicon-carbon bonds and silicon-hydrogen and/or with silanol bonds. Alternatively, the first coating is soluble in at least some organic liquids, or the first coating is soluble in aqueous bases.

More specifically, the present disclosure is characterized by what is stated in the characterizing part of the independent claims.

Considerable advantages are obtained by the present disclosure.

Thus, the present solutions can be used to cast coatings on semiconductor substrates to form patterns through subsequent bake, irradiation and development steps. In particular, the present disclosure allows for the controlling of the microstructure of the resin in such way it is industrially feasible and solves the drawbacks of prior art. For instance, the silanol content in the metal and silanol containing polyhydridosilsesquioxane resin can be adjusted, which is highly desirable to obtained highly sensitive coating for application in EUVL.

Further, the solubility of the coating comprising silicon-oxygen, or silicon-oxygen-metal network with silicon-carbon bonds and silicon-hydrogen and/or with silanol bonds can be modified by copolymerization of precursors either restricting or facilitating the solubility of the coating to a developer.

The present disclosure described herein addresses key RLS challenges, and in addition offers high oxygen plasma etch resistance making the simplification of the lithographic stack possible.

Additionally, the use of coatings comprising a silicon-oxygen, or silicon-oxygen-metal network with silicon-carbon bonds and silicon-hydrogen and/or with silanol bonds permits the use of industry standard 2.38 wt-% TMAH solutions to develop the patterns with means to engineer the solubility characteristics of the irradiated coating to the developer.

In an important example, the present disclosure provides siloxanes that can be patterned by irradiation.

Further features and advantages of the present technology will appear from the following detailed discussion of examples.

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, 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.

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.

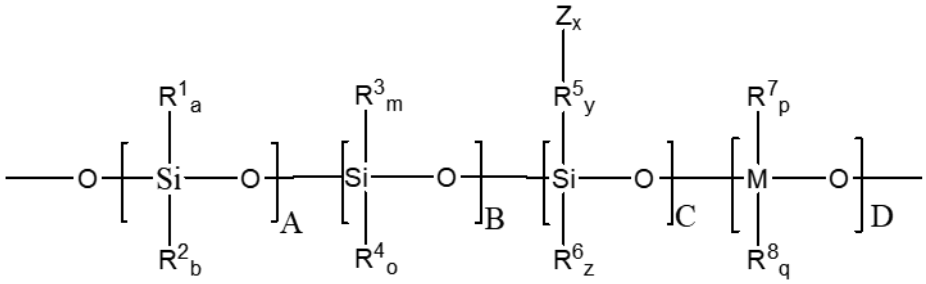
7. The composition according to any of the preceding claims, comprising a metal selected from the group of zirconium, hafnium, aluminium, titanium and tin and combinations thereof.

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, comprising 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.

11. 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.

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.