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.

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 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.

As another object, the present disclosure pertains to a coated substrate comprising a radiation sensitive coating having an average thickness of no more than about 5 microns and a thickness variation of no more than about 50% from the average at any point along the coating, the coating comprising a silicon-oxygen network with silicon-carbon bonds and silicon-hydrogen and/or with carbon-carbon unsaturated bond and/or halogen-containing bonds.

Another object of the present disclosure pertains to 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 network with silicon-carbon bonds and silicon-hydrogen and/or carbon-carbon unsaturated bond and/or halogen-containing bonds. Alternatively, the first coating is soluble in at least some organic liquids, or the first coating is soluble in aqueous bases.

As an additional object, the present disclosure pertains to a precursor solution comprising an organic liquid and from about 0.001M to about 1M carbon-carbon unsaturated bond compared to Si-H or Si-R in silicon-oxygen network silicon-carbon bonds and silicon-hydrogen, and the precursor solution having a viscosity from about 0.5 centipoises (cP) to about 150 cP. The organic liquid can have a flash point of at least 10 °C and a vapor pressure at 20° C of less than about 10 kPa.

As one more object, the present disclosure pertains to 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 network with silicon-carbon bonds and silicon-hydrogen and/or with carbon-carbon unsaturated bonds, and has an etch rate in an oxygen plasma or ashing process lower than 50nm/min.

One last object of the present disclosure is the ability to alter the solubility of the coating comprising silicon-oxygen network with silicon-carbon bonds and silicon-hydrogen and/or with carbon-carbon unsaturated bond and/or halogen-containing bonds by methods of copolymerization of precursors either restricting or facilitating the solubility of the coating to a developer.

Conventional HSQ resins are free from silanol functionality. In our co-pending disclosure (FI patent application 20185677) it is shown that the presence of silanol moieties in an HSQ resin enhances the pattern forming ability of the coatings compared to HSQ resins.

As a result, a silanol-containing polyhydrogensilsesquioxane demonstrates higher sensitivity in EUV lithography compared to those described in literature to date.

Further, provided herein are polyhydrogensilsesquioxane resins having a network with silicon-carbon bonds and silicon-hydrogen in combination with carbon-carbon unsaturated bond(s), halogen-containing bond(s), and solubility enhancing groups or combinations thereof.

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 such as unsaturated bonds or halogen atoms further enhances the sensitivity of the resin and enables a wider process margin or window.

Similarly, silicon containing precursors containing functional groups that enhances solubility in aqueous developers can further improve pattern formation and compounds to a wider process margin.

These solutions can be used for producing cast silanol-containing functional 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 silicon-oxygen network with functional silicon-carbon bonds and silicon-hydrogen and/or with silanol bonds.

The present disclosure further provides a method for patterning a functional polyhydrogensilsesquioxane coated substrate with radiation of light at a specific wavelength or electron beams, 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 functional polyhydrogensilsesquioxane coated substrate with radiation of light at a specific wavelength, wherein the wavelength is 13.5 nm 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 functional polyhydrogensilsesquioxane 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.

The present disclosure described herein addresses key challenges in patterning of sub 20nm features. In addition, materials described offer high oxygen plasma etch resistance making the simplification of the lithographic stack possible. Additionally, to our surprise, the use of coatings comprising a polyhydrogensilsesquioxane resin network with silicon-carbon bonds and silicon-hydrogen present in combination with carbon-carbon unsaturated bond and/or halogen-containing bond and/or solubility enhancing group 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.

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 functional polyhydrogensilsesquioxane resin composition can be adjusted to impart higher sensitivity and wider process window, which is highly desirable to obtained highly sensitive coating for application in EUVL.

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.