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Funktionaaliset vetysilseskioksaanipolymeerit ja niiden käytöt

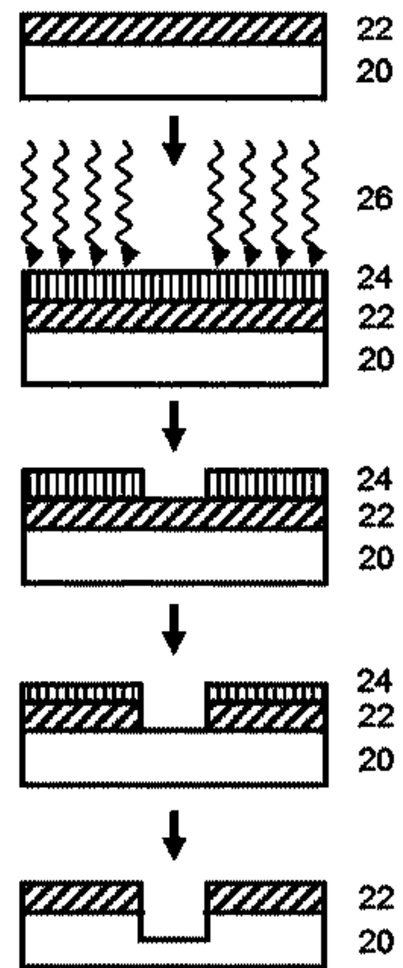
Funktionella vätesilsesqvioxanpolymerer och användningen därav

Functional hydrogen silsesquioxane resins and the use thereof

(57) Tiivistelmä - Sammandrag - Abstract

Hiili-hiili-tyydyttämättömiä sidoksia, halogeenia sekä liukenemista edistäviä aineita sisältävät pinnoitteet puolijohdesubstraattien päällä kuvioinnin muodostamiseksi. Esillä olevat pinnoitteet voidaan tuottaa päällystämällä puolijohdesubstraatteja hiili-hiilityydyttämättömiä sidoksia, halogeenia sekä liukenemista edistäviä aineita sisältävillä poly(vetysilseskvioksaani)-hartsiliuoksilla. Tässä saadaan myös aikaan menetelmä hiilihiili tyydyttämättömiä sidoksia, halogeenia sekä liukenemista edistäviä aineita sisältävällä, poly(vetyseskvioksaanilla) pinnoitettua substraattia käyttämällä säteilyä, jolla on määrätty valon aallonpituus, jolloin menetelmän mukaan säteilytetään pinnoitettu substraatti valittua kuviota pitkin sellaisen säteilytetyn rakenteen muodostamiseksi, jossa on alue, jonka pinnoite on säteilytetty, sekä alue, jonka pinnoite on säteilyttämätön, ja selektiivisesti kehittämällä säteilytetty rakenne poistamalla säteilyttämättömän pinnoitteen oleellisen osuuden poistamiseksi kuvioidun substraatin muodostamiseksi. Keksinnön avulla saadaan aikaan poly(vetysilseskvioksaani)-hartsi, joka sisältää hiili-hiili-tyydyttämättömiä sidoksia, halogeenia ja liukenemista edistävää ainetta, jolloin hiili-hiili-tyydyttämättömän sidoksen, halogeenin ja liukenemista edistävän aineen pitoisuuksien säätämisellä voidaan saada pinnoite, jolla on suuri herkkyys EUV-sovelluksissa.

Carbon-carbon unsaturated bond containing, halogen containing, and solubility-enhancer containing coatings on semiconductor substrates for forming patterns thereon. The present coatings can be produced by coating of semiconductor substrates with carboncarbon unsaturated bond-containing, halogen-containing, and solubility-enhancer containing polyhydrogensilsesquioxane resin solutions. Provided herein is also a method for patterning a carbon-carbon unsaturated bond-containing, 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. The invention allows for obtaining a preselected carbon-carbon unsaturated bond, halogen, and solubility-enhancer content polyhydrogensilsesquioxane resin, and adjustment of the carbon-carbon unsaturated bond, halogen, and solubilityenhancer content will make it possible to obtain a highly sensitive coating for application in EUV.



FUNCTIONAL HYDROGEN SILSESQUIOXANE RESINS AND THE USE THEREOF

FIELD OF THE INVENTION

5 The invention relates to radiation-based methods to perform a patterning step on a substrate using functionalized polyhydrogensilsesquioxane resin coating compositions.

The invention further relates to one or more hydrolyzed precursors in solutions that can be deposited as functionalized polyhydrogensilsesquioxane to resin coatings that can be
10 patterned with very high resolution directly or by applying a masked radiation and to coated substrates and coatings formed with the precursor solutions before and after patterning.

BACKGROUND

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The industry has transitioned through general exposure tools to defined wavelengths from 436 nm (g-line), 405 nm (h-line), 365 nm (i-line), 248 nm (KrF excimer) and finally 193 nm (ArF excimer) (Okoroanyanwu 2015, Gangnaik et al. 2017, De Simone et al. 2014).

20

The resist material used at 248 nm and 193 nm wavelengths are chemically amplified resists (CAR), whose composition and microstructure has evolved following needs in printing ever finer features on substrates. As a continuation of this trend, extreme ultraviolet (EUV) wavelength of λ =13.5 nm (92 eV) is the major candidate for the next-
25 generation lithography (De Simone et al. 2017).

In the last decade, significant investment has been made in the development of EUV lithography (EUVL) for mass production of integrated circuits. There are various nanolithography techniques including electron beam lithography (EBL), soft lithography,
30 nanoimprint lithography (NIL), photon beam lithography (PBL), or scanning probe lithography proposed to extend the scaling down of the features that can be printed on a two-dimensional surface.

Success of EUVL requires new photoresist materials which all encounter certain benefits
35 and drawbacks. Functional photoresists should provide the RLS characteristics, that is, resolution (R), line-edge roughness (LER), and sensitivity (S) as described by Higgins et al. 2011.

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There are a myriad of different material approaches that have been developed to form patterns using EUVL. On a general level these can be classified in three different categories: organic, silicon based and metal containing resists.

5

Organic resists, often referred as non-CAR resists, can demonstrate sufficient LER but are in great disadvantage due to the need of high doses resulting from poor EUV absorption characteristics. To increase the sensitivity of the resists, CAR materials have been employed. CAR materials on the other hand suffer from poor LER resulting mainly 10 from statistical effects of photon shot noise and photo-acid generator distribution in the CAR.

To address the challenges of both organic type resists, formulations have been prepared with radiation sensitive components included in the resist material. Elements which have 15 high molar absorptivity of 13.5nm EUV photons are metals. Thus, there has been an increasing interest in metal containing resists where the metal is added to other resist materials to improve sensitivity, or the metals have been employed as molecular resists, metal oxide nanoparticle, organometallic precursors or as metal-organic frameworks.

20 Such resists have shown high sensitivity, resolution and thus are being considered as key candidates for future EUVL resists. However, their main disadvantage is that metals are strongly disfavored in fabrication of integrated circuits as they can disrupt the function of transistors, and that LER characteristics require improvement. Furthermore, De Simone et al. and Watanabe note that in EUV scanner, the metal species in metal-containing resists 25 interact with atomic H or radical H^* form metallic hydrides (MxHy) that is a serious risk to optics lifetime. In addition, high LER is a problem in both metal-based and chemically amplified resists (De Simone et al. 2017).

Another disadvantage of CAR is low etch resistance and instability of the pattern 30 (Grigorescu and Hagen 2009). Thus, a CAR requires both a silicon rich middle layer and a carbon rich underlayer for pattern transfer to substrate. Inorganic resins based on metal and silicon have the benefit that the lithographic stack is simplified as the inorganic middle layer is directly patterned by EUVL.

35 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

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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 OF THE INVENTION

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

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

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

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

As further object, the invention 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 invention pertains to a method for patterning a carbon-carbon unsaturated bond and/or halogen-containing bond polyhydrogensilsesquioxane coated

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substrate with radiation of light at a specific wavelength, wherein the wavelength is 13.5nm or less.
As another object, the invention 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 invention 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 invention 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 invention 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 invention 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 invention (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.

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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 invention 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 invention 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.

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Further, the invention provides a method for patterning a functional polyhydrogensilsesquioxane coated substrate with radiation of light at a specific wavelength, wherein the wavelength is 13.5nm or less.

5 Still further, the invention 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 10 the first coating is soluble in aqueous bases.

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

15 Considerable advantages are obtained by the present invention.

The invention 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, 20 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 25 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 invention allows for the controlling of the microstructure of the resin in such way it is 30 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.

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

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Additionally, the use of coatings comprising a functional polyhydrogensilsesquioxane with 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
5 the irradiated coating to the developer.

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

10 **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 shows in a schematic fashion, in side-view, the assembly of a trilayer lithography stack;
Figure 2 shows in a schematic fashion, in side-view, the assembly of a four-layer
15 lithography stack;
Figure 3 shows, in side-view, patterning with carbon-carbon double bond containing polyhydrogensilsesquioxane resin according to one embodiment;
Figure 4 shows schematically the EUV crosslink mechanism of carbon-carbon double bond containing polyhydrogensilsesquioxane of one embodiment;
20 Figures 5a, 5b and 5c show SEM images for e-beam treatment results obtained in a) Comparative Example 1, b) Example 1, and c) Example 2;
Figures 6a, 6b and 6c show SEM images for e-beam treatment results obtained in a) Comparative Example 1, b) Example 2, and c) Example 3;
Figures 7a and 7b show SEM images for e-beam treatment results obtained in a)
25 Comparative Example 1 and b) Example 4;
Figures 8a and 8b show SEM images for e-beam treatment results obtained in a) Example 5 and b) Comparative Example 2;
Figures 9a, 9b and 9c are SEM images showing e-beam result of 22 nm half pitch patterned lines obtained by EUVL using materials in a) Comparative Example 1 exhibiting
30 LER = 3.87 nm, b) Example 6 exhibiting LER = 2.86 nm, and Example 7 exhibiting LER = 2.77 nm; where the applied EUV doses were 77.5 mJ/cm^2, 97.5 mJ/cm^2 and 82.5 mJ/cm^2, respectively;
Figures 10a, 10b and 10c show SEM images for e-beam treatment results obtained in a) Comparative Example 1, b) Example 8, and c) Example 9;
35 Figures 11a, 11b and 11c are SEM images showing e-beam result of 22 nm half pitch patterned lines obtained by EUVL using materials in a) Comparative Example 1 exhibiting LER = 3.87 nm, b) Example 10 exhibiting LER = 2.80 nm, and c) Example 11 exhibiting

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LER = 3.05 nm; where the applied EUV doses were 77.5 mJ/cm^2, 87.5 mJ/cm^2 and 107.5 mJ/cm^2, respectively;

Figures 12a, 12b and 12c are SEM images showing e-beam result of 22 nm half pitch patterned lines obtained by EUVL using materials in a) Comparative Example 1 exhibiting
5 LER = 3.87 nm, b) Example 10 exhibiting LER = 4.96 nm, and Example 11 exhibiting LER = 3.00 nm; where the applied EUV doses were 77.5 mJ/cm^2, 87.5 mJ/cm^2 and 90 mJ/cm^2, respectively.

EMBODIMENTS

10

Embodiments of the present invention relates to a method of manufacturing functional polyhydrogensilsesquioxane resin solutions where in hydrolyzable silicon precursors are subjected to controlled hydrolysis/condensation reactions alone or with suitable other silicon containing precursors.

15

As will appear from the following, the present technology provides carbon-carbon unsaturated bond containing, halogen containing, and solubility-enhancer containing coatings on semiconductor substrates for forming patterns thereon. The present coatings can be produced by coating of semiconductor substrates with carbon-carbon unsaturated
20 bond-containing, halogen-containing, and solubility-enhancer containing polyhydrogensilsesquioxane resin solutions.

Described in more detail are also embodiments comprising methods for patterning a carbon-carbon unsaturated bond-containing, halogen-containing, and solubility-enhancer
25 containing polyhydrogensilsesquioxane coated substrate with radiation of light at a specific wavelength. Typically, embodiments of the method comprise 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
30 coating to form a patterned substrate.

The present materials can be characterized as “functional polyhydrosilsesquioxane resins”. Such materials contain residues derived from organic compounds as well as from inorganic compounds, as will be explained below. Further, the present materials contain
35 silanol groups, i.e. groups exhibiting the connectivity Si-O-H, and other functional groups exhibiting connectivity to Si, typically along its main chain, in particular along its main siloxane chain.

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The term “functional” Is used, for example, for indicating that the novel polyhydrogensilsesquioxane polymers exhibit “functionalities”, i.e. groups capable of reacting. Such functional groups will contribute to the properties of the resins and/or of the coatings prepared from the resins.

More specifically, the functional groups in the present invention related to polyhydrogensilsesquioxane resin relate to hydrocarbyl radical connected to silicon atoms in the resin containing carbon-carbon unsaturated bonds, which when present in even small quantities can greatly improve the pattern formation on a substrate.

Embodiments of this invention also related the functional groups in the present invention related to polyhydrogensilsesquioxane resin relate to hydrocarbyl radical connected to silicon atoms in the resin containing halogen atoms, which when present in even small quantities further improve the pattern formation on a substrate by enhancing the absorption of the resin.

More specifically, the functional groups in the present invention related to polyhydrogensilsesquioxane resin relate to hydrocarbyl radical connected to silicon atoms in the resin containing a solubility enhancing group, which when present in even small quantities can greatly improve the pattern formation on a substrate by yielding a better dissolution of non-exposed areas to the developer.

The silicon content of the resins or the coatings is typically at least 30 %, in particular 35 % by weight or more, and can even reach a value of ~52 % by weight.

Generally, there is about 70-99% Si-H groups per repeating unit of the polyhydrogensilsesquioxane resin main chain. In one embodiment, there is, on an average, about 90 to 98% Si-H groups for each unit of the polyhydrogensilsesquioxane resin main chain.

The term “latent” when use in connection to components optionally present in the present compositions refer to a property of being activated during processing of the compositions or of the resin, for example by light. Thus, “latent” catalysts are substances which are in particular activated by light, for example when the resin or composition is exposed to light. Similarly, latent acids and bases in the compositions can be activated when being exposed to light.

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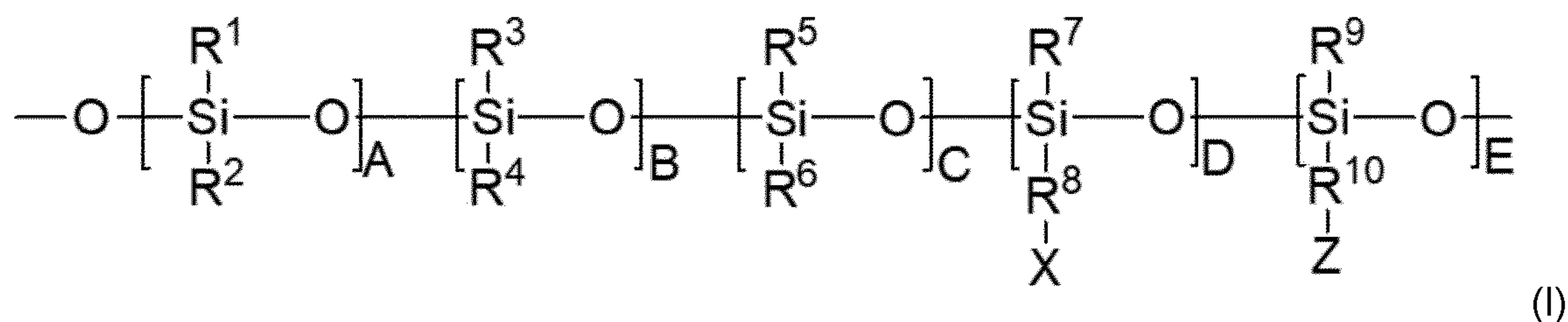
Embodiments of the present invention relates also to the use of the functional polyhydrogensilsesquioxane solutions to cast coatings on semiconductor substrates to form patterns through subsequent bake, irradiation and development steps. In particular, the invention relates to the ability to control the microstructure of the resin in such way it is industrially feasible and solves the drawbacks of prior art. For instance, the invention relates to the ability to control the amount of carbon-carbon unsaturated bond in the polyhydrogensilsesquioxane resin, which is highly desirable to obtain highly sensitive coating for application in EUVL.

According to an embodiment, the present technology relates to a composition suitable for formation of an irradiation curable siloxane layer on a substrate, said composition comprising a siloxane polymer containing SiO moieties, a plurality of reactive sites distributed along the polymer, and a first SiH portion, and an intermediate aromatic and non-aromatic portion, a third organosilicon portion containing a unsaturated bond, a fourth organosilicon portion containing halogen groups, and a fifth organosilicon portion containing a functional group enhancing solubility to developer wherein the polymer has a molecular weight of from 500 to 50000 g/mol, and the composition preferably further comprising an acid and/or base and a solvent.

According to a preferred embodiment, the present invention relates to a composition 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 a patternable and in which the coating is represented by a general formula (I)



(I)

In Formula I, the symbols A, B, C, D and E each represent an integer independently selected from 1 to 1000, Z stands for functional group and X stands for a halogen atom.

Further, in Formula I each R^1 to R^{10} independently stand for hydrogen or hydrocarbyl radicals, in particular R^1 stands for hydrogen; R^6 stands for hydrocarbyl radicals containing unsaturated moieties; and each R^2 and R^4 to R^{10} independently stands for

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hydrogen or a hydrocarbyl radical. In embodiments, R^1 may stand for hydrogen; R^6 for hydrocarbyl radicals containing unsaturated moieties; and each R^2 to R^5 and R^7-to R^{10} stands for a hydrocarbyl radical.

5 In the present contaxt, the term “unsaturated moieties” stands for structures which exhibit double or triple bonds, in particular between carbon atoms. Such bonds are referred to as “unsaturated bonds”. The unsaturated moieties can contain one or several unsaturated bonds. The unsaturated bonds can be conjugated or non-conjugated.

10 Typically, in one embodiment, an unsaturated moiety contains at least one ethylenically unsaturated bond. Examples of unsaturated moieties include groups or structures containing a double or triple bond, such as an alkylene group, an alkenylene group, a cycloalkylene group, an aryl group, an aralkyl group, a halogenated alkyl or alkylene group, a halogenated aryl group, a halogenated aralkyl group, an alkenyl group, an
15 alkoxyalkyl group, an alkoxyaryl group, an acyloxyaryl group, or a combination of them. Each may, of course, also contain substitutents, typically selected from the group of halides, alkoxy groups, hydroxyl groups, thiol groups, ester groups, oxo groups, ketone groups, carboxylic acid groups, amines and amides.

20 Specific examples of unsaturated moieties include vinyl, vinyl ethers, acrylate, alkacrylate, allyl, norbornylene, and combinations thereof.

Further, unsaturated moieties are examined below in conjunction with the various precursors.

25

“Alkoxy” and “alkyl”, “alkylene”, and “alkenylene” groups are linear or branched groups derived from alkanes comprising 1 to 12 carbon atoms, typically 1 to 10 carbon atoms. In embodiments of the present technology, alkoxy and alkyl are preferably linear or branched groups, in particular lower alkoxy and lower alkyl groups. Such groups contain 1 to 6, in
30 particular 1 to 4 carbon atoms.

“Cycloalkylene” groups comprise at least 3, preferably at least 4, and in particular at least 5 carbon atoms and up to 20 carbon ring atoms.

35 “Aryl” bears the conventional meaning of a functional group or substituent derived from an aromatic ring, usually an aromatic hydrocarbon, such as phenyl and naphthyl or

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antracenyl. The aryl groups typically contain 1 to 5 aromatic rings, which can be fused or partially fused.

The above composition is obtained by hydrolyzing a first monomeric hydrogen containing silicon compound having at least one hydrolysable group attached to the silicon ("Precursor A") with

optionally a second monomeric silicon compound having at least one hydrocarbyl radical, and at least one hydrolyzable group attached to the silicon atom of the compound i.e. "Precursor B"),

a third monomeric silicon compound having at least one functional group containing unsaturated bonds and at least one hydrolyzable group attached to the silicon atom of the compound i.e. "Precursor C"),

optionally a fourth monomeric silicon compound having at least one hydrolysable group and at least one halogen-containing group i.e. "Precursor D")

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 i.e. "Precursor E") and

formulating the siloxane material into a stable composition in a suitable solvent system.

The ratio of the precursors used in the present invention can vary. Precursor 1 can be used in 50-100 mol-%, Precursor 2 can be used in 0-20 mol-%, Precursor 3 can be used in 0.1-20 mol-%, typically 1-10 mol-%, Precursor 4 can be used in 0-20 mol-%, and Precursor 5 can be used in 0-10 mol-%. The siloxane composition can be obtained by carrying out the hydrolysis and condensation in the same reaction vessel or separately in specified portions or each precursor independently.

In one embodiment, the Precursor 1 is used at a molar ratio of 80 to 9:20 to 1 moles of Precursor 3.

The present invention is particularly well suited for the production of compositions comprises a poly(organosiloxane) obtained by hydrolyzing a first silicon compound having the general formula II

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

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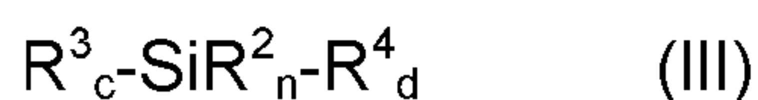
In the composition, a is an integer of 1 or 2 while b is an integer of 2 or 3. R^1 denotes a hydrogen atom and R^2 denotes a hydrolysable group which can independently be selected from hydroxyl, alkoxy, acyloxy and halogen. In the meaning of “halogen”, each of the hydrolysable groups preferably and independently stands for chlorine, iodine, fluorine, or bromine. In the meaning of “alkoxy”, each of the hydrolysable groups preferably and independently stands for methoxy, ethoxy, n-propoxy, i-propoxy, butoxy, sec-butoxy, tert-butoxy. In the meaning of “acyloxy”, each of the hydrolysable groups preferably and independently stands for acetoxy, acryloxy, or methacryloxy. Specific examples of such precursors are triethoxysilane (HTEOS), trimethoxysilane (HTMOS), diethoxysilane and trichlorosilane. In some cases R2 may also be a organic radical, such as methyl, ethyl, propyl, vinyl. Specific examples of such precursors include as methyldimethoxysilane, methyldiethoxysilane, methyldichlorosilane, vinyldimethoxysilane, vinyldiethoxysilane and vinyldichlorosilane.

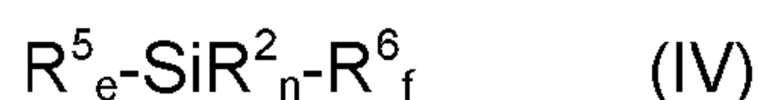
The present invention also relates to the compositions comprising a copoly(organosiloxane) obtained by hydrolyzing the first silicon compound having the general formula II, with a precursor having the general formula III



$$R^3{}_c\text{-}SiR^2{}_n\text{-}R^4{}_d \qquad \text{(III)}$$

Wherein R^3 and R^4 can be 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, an isocyanurate group, a hydroxy group, a cyclic amino group, or a cyano group, or a combination of them. R2 and R3 may also be an alkoxy group, an acyloxy group, or a halogen group. c is an integer of 0 to 1, and n is an integer of 2 to 4, and d is an integer of 0 to 1, wherein the total value of m + n + o may not exceed 4.

The present invention further relates to the compositions comprising a copoly(organosiloxane) obtained by hydrolyzing the first silicon compound having the general formula II, with a precursor having the general formula IV



$$R^5{}_e\text{-}SiR^2{}_n\text{-}R^6{}_f \qquad \text{(IV)}$$

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

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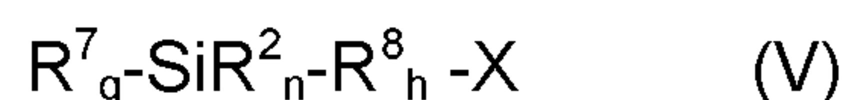
alkenyl group, an organic group having an epoxy group, a mercapto group, an alkoxyaryl group, an acyloxyaryl group, a hydroxy group, a cyclic amino group, or a cyano group, or a combination of them, R^6 is a functional group containing a double or triple bond present in an alkyl group, an aryl group, 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^2 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.

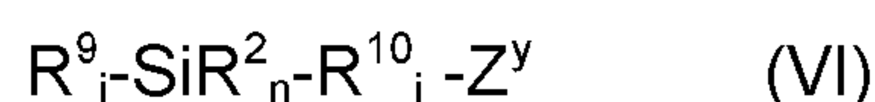
The present invention finally relates to the compositions comprising a copoly(organosiloxane) obtained by hydrolyzing the first silicon compound having the general formula II, with a precursor having the general formula V



$$R^7_g\text{-}SiR^2_n\text{-}R^8_h\text{-}X \qquad (V)$$

wherein X is a halogen group, R^7 is independently selected from an alkyl group, an aryl group, an aralkyl group, 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^2 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, and h is an integer of 0 to 1, and wherein the total value of g + n + h is 4 or less. In the structure of Formula (V), h denotes the value that the spacer group R^8 can encompass and must be equal or greater to 1.

The present invention finally relates to the compositions comprising a copoly(organosiloxane) obtained by hydrolyzing the first silicon compound having the general formula II, with a precursor having the general formula VI



$$R^9_i\text{-}SiR^2_n\text{-}R^{10}_j\text{-}Z^y \qquad (VI)$$

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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^2 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, and wherein the total value of i + n + j is 4 or less. In the structure of Formula (VI), j denotes the value that the spacer group R^{10} can encompass and must be equal or greater to 1.

Specific examples of precursor (III) include but are not limited to tetramethoxysilane, tetrachlorosilane, tetraacetoxysilane, tetraethoxysilane, tetra-n-propoxysilane, tetraisopropoxysilane, tetra-n-butoxysilane, methyltrimethoxysilane, methyltriethoxysilane, methyltrichlorosilane, methyltriacetoxysilane, methyltripropoxysilane, methyltributoxysilane, methyltriphenoxysilane, methyltribenzyloxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, phenyltrimethoxysilane, phenyltrichlorosilane, phenyltriacetoxysilane, phenyltriethoxysilane, γ-mercaptopropyltrimethoxysilane, γ-mercaptopropyltriethoxysilane, β-cyanoethyltriethoxysilane, dimethyldimethoxysilane, phenylmethyldimethoxysilane, dimethyldiethoxysilane, dipropyldiethoxysilane, diphenyldimethoxysilane, phenylmethyldiethoxysilane, dimethyldiacetoxysilane, γ-mercaptopropylmethyldimethoxysilane, γ-mercaptomethyldiethoxysilane, glycidoxymethyltrimethoxysilane, glycidoxymethyltriethoxysilane, α-glycidoxyethyltrimethoxysilane, α-glycidoxyethyltriethoxysilane, β-glycidoxyethyltrimethoxysilane, β-glycidoxyethyltriethoxysilane, α-glycidoxypropyltrimethoxysilane, α-glycidoxypropyltriethoxysilane, β-glycidoxypropyltrimethoxysilane, β-glycidoxypropyltriethoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropyltriethoxysilane, γ-glycidoxypropyltripropoxysilane, γ-glycidoxypropyltributoxysilane, γ-glycidoxypropyltriphenoxysilane, α-glycidoxybutyltrimethoxysilane, α-glycidoxybutyltriethoxysilane, β-glycidoxybutyltriethoxysilane, γ-glycidoxybutyltrimethoxysilane, γ-glycidoxybutyltriethoxysilane, δ-glycidoxybutyltrimethoxysilane, δ-glycidoxybutyltriethoxysilane, (3,4-

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epoxycyclohexyl)methyltrimethoxysilane, (3,4-epoxycyclohexyl)methyltriethoxysilane, β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, β-(3,4-epoxycyclohexyl)ethyltriethoxysilane, β-(3,4-epoxycyclohexyl)ethyltripropoxysilane, β-(3,4-epoxycyclohexyl)ethyltributoxysilane, β-(3,4-epoxycyclohexyl)ethyltriphenoxysilane, γ-(3,4-
5 epoxycyclohexyl)propyltrimethoxysilane, γ-(3,4-epoxycyclohexyl)propyltriethoxysilane, δ-(3,4-epoxycyclohexyl)butyltrimethoxysilane, δ-(3,4-epoxycyclohexyl)butyltriethoxysilane, glycidoxymethylmethyldimethoxysilane, glycidoxymethylmethyldiethoxysilane, α-glycidoxyethylmethyldimethoxysilane, α-glycidoxyethylmethyldiethoxysilane, β-glycidoxyethylmethyldimethoxysilane, β-glycidoxyethylethyldimethoxysilane, α-
10 glycidoxypropylmethyldimethoxysilane, α-glycidoxypropylmethyldiethoxysilane, β-glycidoxypropylmethyldimethoxysilane, β-glycidoxypropylethyldimethoxysilane, γ-glycidoxypropylmethyldimethoxysilane, γ-glycidoxypropylmethyldiethoxysilane, γ-glycidoxypropylmethyldipropoxysilane, γ-glycidoxypropylmethyldibutoxysilane, γ-glycidoxypropylmethyldiphenoxysilane, γ-glycidoxypropylethyldimethoxysilane, γ-
15 glycidoxypropylethyldiethoxysilane, γ-glycidoxypropylvinyldimethoxysilane, γ-glycidoxypropylvinyldiethoxysilane, and phenylsulfonylaminopropyltriethoxysilane.

Specific examples of precursor (IV) vinyltrimethoxysilane, vinyltrichlorosilane, vinyltriacetoxysilane, vinyltriethoxysilane, methylvinyldimethoxysilane,
20 methylvinyldiethoxysilane,dimethylvinylmethoxysilane allyltrimethoxysilane, allyltrichlorosilane, allyltriacetoxysilane, allyltriethoxysilane, allylmethyldimethoxysilane, allylmethyldiethoxysilane, 3-butenyltrimethoxysilane,styrylethyltriethoxysilane, styrylethyltrimethoxysilane, γ-methacryloxypropyltrimethoxysilane, γ-methacryloxypropylmethyldimethoxysilane, γ-methacryloxypropylmethyldiethoxysilane,
25 (methacryloxymethyl)methyldiethoxysilane, (methacryloxymethyl)methyldimethoxysilane, methacryloxymethyltriethoxysilane, methacryloxymethyltrimethoxysilane, methacryloxypropyltrichlorosilane, methacryloxypropyltriethoxysilane, methacryloxypropyltriisopropoxysilane, 3-acrylamidopropyltrimethoxysilane, acryloxymethyltrimethoxysilane, 3-acryloxypropyltrimethoxysilane, 3-
30 acryloxypropylmethyldimethoxysilane, 3-acryloxypropylmethyldiethoxysilane, 3-acryloxypropyldimethylmethoxysilane, 3-acryloxypropyldimethylethoxysilane, acrylamidopropyltriethoxysilane, acrylamidopropyltrichlorosilane, (acryloxymethyl(phenylethyl)trimethoxysilane, methacrylamidopropyltriethoxysilane, methacrylamidopropyltrichlorosilane, [2-(3-cyclohexenyl)ethyl]trimethoxysilane, [2-(3-
35 cyclohexenyl)ethyl]triethoxysilane, [2-(3-cyclohexenyl)ethyl]trichlorosilane, [2-(3-cyclohexenyl)ethyl]methyldimethoxysilane, [2-(3-cyclohexenyl)ethyl]methyldichlorosilane (5-bicyclo[2.2.1]hept-2-enyl)triethoxysilane, (5-bicyclo[2.2.1]hept-2-enyl)trimethoxysilane,

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(5-bicyclo[2.2.1]hept-2-enyl)methyldiethoxysilane, (5-bicyclo[2.2.1]hept-2-enyl)ethyldiethoxysilane, (5-bicyclo[2.2.1]hept-2-enyl)dimethylmethoxysilane, (5-bicyclo[2.2.1]hept-2-enyl)trichlorosilane, (5-bicyclo[2.2.1]hept-2-enyl)methyldichlorosilane, (5-bicyclo[2.2.1]hept-2-enyl)dimethylchlorosilane,

5

Specific examples of precursor (V) chloromethyltrimethoxysilane, chloromethylmethyldichlorosilane, chloromethylmethyldimethoxysilane, chloromethyltrichlorosilane, chloromethyltriethoxysilane, 2-chloroethylmethyldimethoxysilane, 2-chloroethylmethyldichlorosilane, 2-
10 chloroethyltrimethoxysilane, 2-chloroethyltrichlorosilane, -chloroethylmethyldimethoxysilane, 2-chloroethylmethyldichlorosilane, 3-chloropropyltrimethoxysilane, 3-chloropropyltriethoxysilane, 3-chloropropyltriacetoxysilane, chloromethyltrimethoxysilane, chloromethyltriethoxysilane, 3-chloropropylmethyldimethoxysilane, 3-chloropropylmethyldiethoxysilane,
15 bis(chloromethyl)dichlorosilane, bis(chloromehyl)methylchlorosilane, bis(chloromehyl)dimethoxysilane, bis(chloromehyl)methylmethoxysilane, bis(chloromehyl)diethoxysilane, bis(chloromehyl)methylethoxysilane, bis(3-chloropropyl)dichlorosilane, chlorophenylmethyldimethoxysilane, chlorophenyltrimethoxysilane, chlorophenyltriethoxysilane, chlorophenyltrichlorosilane,
20 ((chloromethyl)phenylethyl)methyldimethoxysilane, ((chloromethyl)phenylethyl)trimethoxysilane and similar compounds where chloro groups is replaced with equivalent bromo or iodo compounds. Specific examples in addition to above: 4-bromobutyltrimethoxysilane, 4-bromobutyltrichlorosilane, 2-bromoethyltrimethoxysilane, 5-bromopentyltrimethoxysilane,
25 bromophenyltrimethoxysilane, Examples of precursor (V) also include linear, branched, cyclic and aromatic and alkylaromatic compounds where multiple hydrogen atoms are replaced with a halogen atoms. Specific examples of these include trifluoropropyltrimethoxysilane, trifluoropropylmethyldimethoxysilane, trifluoropropyltriethoxysilane, nonafluorohexyltrimethoxysilane,
30 nonafluorohexylmethyldimethoxysilane 1,2-dibromoethyltrimethoxysilane, 1,2-dibromoethyltrichlorosilane, pentafluorophenyltrimethoxysilane, pentafluorophenyltriethoxysilane, pentafluorophenyltrichlorosilane, bis(pentaflluorophenyl)dimethoxysilane, 4-bromo-3,3,4,4-tetrafluorobutyltrimethoxysilane,

35 Specific examples of precursor (VI) 3,3,3-trifluoropropyltrimethoxysilane, 4-acetoxyphenylethyltrimethoxysilane, 4-acetoxyphenylethyltriethoxysilane 4--(acetoxyphenylethyl)methyldichlorosilane, 4--(acetoxyphenylethyl)methyldimethoxysilane,

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4-(acetoxyphenylethyl)methyldiethoxysilane, 2-(carbomethoxy)ethyltrimethoxysilane, 2-(carbomethoxy)ethylmethyldimethoxysilane, 2-(carbomethoxy)ethyltrichlorosilane, 2-(carbomethoxy)ethylmethyldichlorosilane, triethoxysilylpropylcarbamate, triethoxysilylpropylmaleamic acid, N-(3-triethoxysilylpropyl)-4-hydroxybutyramide, N-(3-triethoxysilylpropyl)gluconamide, (3-triethoxysilyl)propylsuccinic anhydride, ureidopropyltriethoxysilane, ureidopropyltrimethoxysilane, 3-hydroxy-3,3-bis(trifluoromethyl)propyl triethoxysilane, 4-(methoxymethoxy)trimethoxysilylbenzene and 6-(methoxymethoxy)-2-(trimethoxysilyl)naphthalene.

According to one embodiment, the hydrolysis and polymerization is carried out completely without solvents, or it is carried out in organic solvents, such as in alcohols, esters, ketones and ethers. Specific, suitable solvents are acetone, ethyl methyl ketone, methanol, ethanol, isopropanol, butanol, methyl acetate, ethyl acetate, propyl acetate, butyl acetate and tetrahydrofuran. Particularly suitable solvents are ketones and ethers, particularly where certain stabilizing effect through coordination with the silicon atoms during hydrolysis is present. Such examples are ethyl methyl ketone, methyl tetrahydrofurfuryl ether and ethyl tetrahydrofurfuryl ether.

Controlled hydrolysis of the monomers is obtained by addition of an acid or base solution with molar ratio ranging from 0.0001 M to 1 M. Organic or inorganic acid can be used in the synthesis. Inorganic acids such as nitric acid, sulfuric acid, hydrocholoric acid, hydriodic acid, hydrobromic acid, hydrofluoric acid, boric acid, perchloric acid, carbonic acid and phosphoric acid can be used. Preferably, nitric acid or hydrochloric acid is used due to their low boiling point, which make purification of product simple. In other option, various organic acids can be used instead of inorganic acid. Organic acids are carboxylic acid, sulfonic acid, alcohol, thiol, enol, and phenol groups. Examples are methanesulfonic acid, acetic acid, ethanesulfonic acid, toluenesulfonic acid, formic acid, or oxalic acid. Bases used in the synthesis may similarly be inorganic or organic. Typical inorganic bases and metal hydroxides, carbonates, bicarbonates and other salts that yield an alkaline water solution. Examples of such materials are sodium hydroxide, potassium hydroxide, cesium hydroxide, calcium hydroxide, sodium carbonate, and sodium bicarbonate. Organic bases on the other hand comprise a larger group consisting of metal salts of organic acids (such as sodium acetate, potassium acetate, sodium acrylate, sodium methacrylate, sodium benzoate), linearm branched or cyclic alkylamines (such as diaminoethane, purtescine, cadaverine, triethylamine, butylamine, dibutylamine, tributylamine, piperidine) amidines and guanidines (such as 8-diazabicyclo(5.4.0)undec-7-ene, 1,1,3,3-tetramethylguanidine, 1,5,7-triazabicyclo[4.4.0]-dec-5-ene), phosphazanes

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(such as P_1-t-Bu, P_2-t-Bu, P_4-t-Bu), and quaternary ammonium compounds (such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide).

5 The temperature of the reaction mixture during the hydrolysis and condensation process can be varied between from -30 to 170°C. Those familiar to the art knows that lower reaction temperatures provide improved control of the reaction but at the cost of long reaction times, while excessively high temperatures may make the process too fast for adequate control. Thus, a reaction time of 1-48h at a temperature of 0-100°C is preferred.
10 A reaction time of 2-24h is even more preferred. Using appropriate conditions, the method according to the present invention yields a partially cross-linked, optionally carbon-carbon unsaturated bond containing organosiloxane polymer in an organic solvent system, said polymer having a molecular weight of about 5,000 to 100,000 g/mol, in particular about 1,000 to 50000 g/mol, measured against polystyrene standards.

15

Another embodiment of the invention is that the solvent in which hydrolysis and polymerization is carried out, is after polymerization changed for a solvent that provides the material better coating performance and product storage properties though some form of stabilization. Such stabilizing organic solvent system is formed by an organic ether
20 optionally in mixture with other co-solvent or co-solvents. The organic ether is a linear, branched or cyclic ether comprising generally 4 to 26 carbon atoms and optionally other functional groups, such as hydroxyl groups. Particularly suitable examples are five and six membered cyclic ethers, which optionally bear substituents on the ring, and ethers, such as (C1-20) alkanediol (C1-6) alkyl ethers. Examples of said alkanediol alkyl ethers are
25 propylene glycol monomethyl ether, propylene glycol dimethyl ether, propylene glycol n-butyl ether, dipropylene glycol monomethyl ether, dipropylene glycol. dimethyl ether, dipropyleneglycol n-butyl ether, tripropylene glycol monomethyl ether and mixtures thereof. Particularly preferred examples of the present ethers are methyl tetrahydrofurfuryl ether, tetrahydrofurfuryl alcohol, propylene glycol n-propyl ether, dipropylene glycol
30 dimethyl ether, propylene glycol n-methyl ether, propylene glycol n-ethyl ether and mixtures thereof. The stabilizing solvent system consists of a solvent comprising of the ether of this kind alone, or of a mixture-of such ether with a typical reaction medium of the hydrolyzation or other solvents such as propylene glycol monomethyl ether acetate. The proportion of the ether is, in such a case, about 10 to 90 wt-%, in particular about 20 to 80
35 wt-% of the total amount of the solvent.

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The solid content of the radiation sensitive formulation consisting of selected solvents and the resin material is in the range of 0.1% to no more than 50%. Most preferably in the range of 0.5% to 10%. The solid content (or polymer content) is used to adjust the resultant film thickness during the coating process. To improve the coating performance in terms of coating uniformity, different surfactants such as silicone or fluoro surfactant can be used can be used to lower surface tension of the silanol-containing polyhydrogensilsesquioxane formulation coating. The use of such surfactants may improve coating quality if needed. The amount of surfactant is in a range of 0.001% to no more than 10% by mass compared to silanol-containing polyhydrogensilsesquioxane amount.

It has been found that the introduction of carbon-carbon unsaturated bond moieties (as precursor III) in the polyhydrogensilsesquioxane resin greatly facilitates the pattern forming ability of the coatings compared to HSQ resins. During EUV or similar irradiation method such as e-beam, H* radicals are likely formed from SiH. The formed radicals undergo transformations which lead to the crosslinking of the film. As a result of this, the exposed areas lose their solubility to the aqueous developer. The use of precursors containing unsaturated bonds provide an alternative crosslinking mechanism and this facilitates the crosslinking of the polyhydrogensilsesquioxane resins. The unsaturated bonds may react with the formed radials from SiH.

Figure 4 which shows an embodiment, in which EUV patterning mechanism of the carbon-carbon unsaturated bond containing polyhydrogensilsesquioxane, wherein polymerization of methacrylate-based compound is demonstrated.

Generally speaking, the presence of carbon-carbon unsaturated bonds in the material improves the crosslink of the polymer and thus enhances the sensitivity.

The coatings containing carbon-carbon unsaturated bonds exhibit increased sensitivity as a function of increased amount of the functional groups. As the result, a carbon-carbon unsaturated bond containing polyhydrogensilsesquioxane demonstrates higher sensitivity in EUV lithography compared to those without these carbon-carbon unsaturated bonds in the polymer structures. The effect has been demonstrated in the examples where increased amount of the functional organosilicon precursor containing carbon carbon unsaturated bonds show increased sensitivity, i.e. decreased dose to pattern the resin. Thus, the functional polyhydrogensilsesquioxane resin composition can be adjusted to optimize the outcome of the lithographic patterning process.

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In one embodiment, an amount of 1-30 mol-%, for example 2 to 20 mol-%, of an organosilicon precursor containing carbon-carbon unsaturated bonds in the resin composition is employed. Such an addition will increase the sensitivity.

5

The effect of the functional organosilicon precursor containing carbon-carbon unsaturated bonds was demonstrated by E-beam lithography and the scanning electron microscope (SEM) images of the patterns are presented in Figure 5.

10 Examples 1–2 and Comparative Example 1 outline resin compositions with a 1.3% solid content which was used to cast a coating, irradiated with EUV and finally developed with 2.38% TMAH to obtain patterned image.

As seen in Figure 5, high resolution SEM images of half pitches of 22 nm have been
15 obtained. Required dose to obtain pattern decreased by 33% and 42% when 2.5% and 5% MAPTMOS monomer was used in the syntheses, respectively. By choice of different functional organosilicon precursor containing carbon-carbon unsaturated bonds the sensitivity could be further enhanced and 9% less dose was required when an acrylate based precursor was used instead of a methacrylate based precursor (Figure 8). Similar
20 results were also found by the used of functional organosilicon precursors containing a norborene moiety (Examples 6 and 7). This was further confirmed using EUV (Figure 9).

Other organosilicon precursors containing carbon-carbon unsaturated bonds can be used in embodiments according to the present invention.

25

It has also been found out that the use of functional organosilicon precursor containing halogen atoms in a polyhydrogensilsesquioxane resin composition can yield a similar effect where the coated resin exhibits higher sensitivity to irradiation which leads to decreased doses applied in the exposure step in lithographic patterning of the coated
30 resin (Example 4).

Further, it has been found that the combined use of functional organosilicon precursors containing carbon-carbon unsaturated bonds together with monomers in combination with functional organosilicon precursors containing halogen atoms contribute to an increased
35 sensitivity to irradiation which leads to decreased dose requirements, as discussed in Example 3. Referene is also made to Figures 6 and 7.

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Non-functional polyhydrogensilsesquioxane resin or traditional HSQ resins may exhibit scumming or residues between patterned lines or other shapes. In case of over exposure these residues develop to bridging of lines, i.e. the desired patterned lines are connected though an unwanted 'bridge'. Thus, methods to decrease bridging is needed, preferably
5 so that the dose range is as wide as possible to permit a large process window.

Scumming, or residues between the lines, can be reduced by adding another functional organosilicon precursor to the polyhydrogensilsesquioxane resin composition. Such functional organosilicon precursors enhance the solubility of the resin into the developer.
10 This has been demonstrated by example 10 and 11 (Figure 11).

It is a surprising finding that a functional organosilicon precursor to the polyhydrogensilsesquioxane resin composition not only decreased the residues in the formed patterns, but also increased the process window for the resin.

15

Given that the cure mechanism predominately proceeds through a radical reaction mechanism, the scumming or bridging may also be addressed by addition of radical scavengers in the functional polyhydrogensilsesquioxane resin formulation. By addition of commonly known radical inhibitors, we found that the residues could be reduced (example
20 8 and 9, Figure 12).

The present invention contains one more finding related to stabilization of hydrolyzed solutions of organosilicon precursors. Hydrolysis of multifunctional organosilicon precursors, in the presence of acid or base catalysts, initiates a hydrolysis and
25 condensation process that ultimately leads to crosslinked polymer network. Generally, this process is described as sol-gel materials. When an organosilicon precursor solution as such or as a part of a mixture with organic solvents is introduced to water in the presence of a catalyst, a hydrolysis and subsequent condensation process is initiated. Initially, the precursors hydrolyze and condense forming a 'sol', i.e. a material soluble in solvents or
30 solvent combinations. As the condensation reactions proceed, a multifunctional precursor will yield a crosslinked network, which no longer is soluble. Such state is often referred as a 'gel' when a diluent in the form of a solvent is present.

Given that the plurality of compounds most preferable to use in this invention are
35 multifunctional organosilicon precursors, it is of significant interest to provide means to reduce the rate of condensation reactions when the material is stored in its 'sol' state. It has been found that addition of organic acids surprisingly will lead to stabilizing effect.

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This stabilizing effect can be monitored by GPC. Addition of organic acids or diacids to a polyhydrogensilsesquioxane resin solutions have to our surprise significantly improved the stability of these (example 12 and 13).

5 In certain embodiments, the present invention relates to the use of compositions described herein in the formation of patterns on a semiconductor substrate, as illustrated in Figures 1 and 2.

Thus, in a process of the present kind, typically a substrate surface 10 is coated with an
10 organic underlayer 12, followed by coating and curing of an inorganic middle layer 14, which typically consist of a high silicon containing material. On top of this, a photoresist 16 is coated. After irradiation 18 using 193nm wavelengths a pattern is formed and developed. Such a combination of layers is frequently described in the literature as a 'tri-layer' stack, referring to the number of layers.

15

Subsequent pattern transfer etch processes can be applied to transfer the pattern formed on the photoresist to the substrate (Figure 1). It is worth noting that the stack of various layers used in lithography can be higher than 3.

20 Another combination of layers is a four-layer stack wherein an organic underlayer 12 is first applied, followed by coating and curing of an inorganic middle layer 14, which typically consist of a high silicon containing material. On top of this, an organic bottom anti-reflective 18 layer is applied prior to a photoresist 16 which completes the four-layer stack (Figure 2).

25

In photoresist patterning of the present kind, all described underlayers may not only be coated and cured but also be applied by gas phase deposition processes such as chemical vapor deposition (CVD), atomic layer deposition (ALD) and similar methods.

30 The same procedure can be applied to EUVL at 13.5nm. However, due to absorption challenges, stochastic distribution of both photo acid and the photon irradiation, a commonly use CAR used in the process faces serious challenges, in particular related to the LER and LWR. Therefore, significant amount of interest has been directed to the use of inorganic photoresists which promise the stack simplification where both number of
35 layers are reduced and the LER and LWR challenges are reduced. In most cases the inorganic resist consists of metal oxides of one or more compounds in the form of readily hydrolysable or hydrolyzed metal oxide precursors, and hydrogensilsesquioxanes. The

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benefits of these have been: metal oxide resist yield an unprecendented EUVL dose sensitivity while hydrogensilsesquioxane polymers give excellent resolution with low LER/LWR with very poor EUVL sensitivity. Thus, both methods have attributes which render them challenging to use in EUVL patterning processes. The present invention uses 5 carbon-carbon unsaturated bonds and/or halogen containing siloxanes as the preferred method to achieve both stack simplification and the reduction of metals used in the patterning process.

Reference is made to the embodiment shown in Figure 3. In that embodiment, a substrate 10 20 is coated with a predominately organic coating 22 in the form of a spin on carbon or an amorphous carbon layer in EUV. The thin, patternable film according to the present invention 22 is based on carbon-carbon unsaturated bond and/or halogen and/or solubility enhancer containing polyhydrogensilsesquioxane resin 24. This coating is readily patternable by EUVL with high sensitivity compared to HSQ resins in the literature and 15 significantly lower LER/LWR compared to CAR and inorganic resins described in the literature. In particular, the present invention provides a mean to high resolution patterning with a bilayer structure in the absence of metals which may be a significant advantage in producing fully functional transistor dies without significant yield losses.

20 Silicon containing materials have relatively low absorption to EUV. On the other hand, halogen containing resist may improve the EUV absorption to EUV and thus improve patterning result.

Desirable carbon-carbon unsaturated bond and solubility enhancer containing 25 polyhydrogensilsesquioxane solutions, generally in non-aqueous solvent provide high resolution patterning in which the solutions have a high degree of stability for the formation of radiation patternable coatings with good radiation sensitivity. Desirable features of coatings formed with the carbon-carbon unsaturated bond and solubility enhancer containing polyhydrogensilsesquioxane solutions provide for superior direct 30 patterning for the formation of a patterned silicon oxide coating. In embodiments of interest, exposure to radiation converts the irradiated coating material into a material that is resistant to removal with a developer composition such that it can be selectively removed. Thus, the coating can be negatively patterned. Selective removal of at least a portion of the coating material can leave a pattern where regions of coating have been 35 removed to expose the underlying substrate. After development of the coating following irradiation, the patterned silicon oxide materials can be used for facilitating processing in device formation with excellent pattern resolution. The coating materials can be designed

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to be sensitive to selected radiation, such as extreme ultraviolet light, ultraviolet light and/or electron beams.

Furthermore, the precursor solutions can be formulated to be stable with an appropriate
5 shelf life for commercial distribution.

The radiation sensitive coating material can be used as negative radiation patterning coating. In the negative patterning, exposure to radiation converts the irradiated coating material into a material that is more resistant to removal with a developer composition
10 relative to the non-irradiated coating material. Selectively removal of at least a portion of the coating material leaves a pattern where regions have been removed to expose the underlying substrate.

The formation of integrated electronic devices and the like generally involves the
15 patterning of the materials to form individual elements or components within the structures. This patterning can involve different compositions covering selected portions of stacked layers that interface with each other vertically and/or horizontally to induce desired functionality.

20 The various materials can comprise semiconductors, which can have selected dopants, dielectrics, electrical conductors and/or other types of materials.

To form high resolution patterns, radiation sensitive organic compositions can be used to introduce patterns, and the compositions can be referred to as resists since portions of the
25 composition are processed to be resistant to development/etching such that selective material removal can be used to introduce a selected pattern.

Radiation with the selected pattern or the negative of the pattern can be used to expose the resist and to form a pattern or latent image with developer resistant regions and
30 developer dissolvable regions. The radiation sensitive metal and silanol containing polyhydrogensilsesquioxane compositions described herein can be used for the direct formation of desired inorganic material structures within the device and/or as a radiation patternable inorganic resist that is a replacement for an organic resist. In either case, significant processing improvements can be exploited, and the structure of the patterned
35 material can be also improved.

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Based on the examples presented in this invention, it is evident that the presence of solubility enhancer containing compound facilitates the dissolution of non-exposed areas or prevent reactions on non-exposed areas and thus improves the resolution and LER/LWR. Similarly, radical inhibitor or antioxidant additives prevent radicals formed in the exposed areas to unwantedly migrate to the non-exposed areas. Thus, lower LER/LWR can be achieved.

Certain embodiments comprise deposition of a carbon rich underlayer 22 on a surface 20 used in manufacturing of integrated circuits. The underlayer is deposited by gas phase processes such as CVD or by spin coat and cure. Then a composition as described herein is applied 24 yielding a predominately silicon and metal rich oxide coating which can be directly patterned by novel patterning techniques such as EUVL.

After application by spin coating or other suitable deposition methods for liquids, a prebake step is applied to remove the solvents and volatile compounds which are included in the coating material. This is necessary to avoid contamination in the manufacturing equipment. Prebake can be done at different temperatures and times depending on the boiling temperature of the solvents and volatile components. Usually, prebake can be done at 60 °C to 120 °C for a period of 30 seconds to no more than 30 minutes.

After the drying or prebake step, exposure of the coating to EUV light, electron beam or similar exposure method (26) through an optionally used mask is used to generate the patterns on the substrate. The dose needed to generate patterns is at minimum 10 mJ/cm^2 and at maximum 200 mJ/cm^2.

As noted previously, in embodiments of the present technology, a lower dose is preferred due to various reasons among which include a reasonable throughput in industrial application and addressing the RLS trade off.

A post exposure bake is optionally carried out after EUV exposure. This step can improve the crosslinking of the exposed regions which would lead to higher contrast of the resist. Post exposure bake can be done in a temperature of 80 °C to no more than 150 °C for a time ranging from 30 seconds to no more than 30 minutes.

Development is carried out to remove the unexposed region, thus obtaining designed pattern. During the development step, non-exposed regions of the resist 24 dissolves in the developer.

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Aqueous base developer commonly used in the industry based on bases such as tetramethylammonium hydroxide, potassium hydroxide, sodium hydroxide with different mass ratio of 0.1% to 25% can be effectively used. The development is carried out
5 commonly known methods using a spray or puddle of the developer solution method to apply the developer. Alternatively, the substrate can be immersed in bath consisting of the developer.

A curing step to densify the exposed and developed pattern may be optionally carried out
10 to obtain a further crosslinked material or to alter the shape of the resist pattern through process where the material exhibits some reflow. This step may result in higher etch resistance material compared to that of material prepared without the curing step. Curing can be done at 120 °C to 400 °C for 2 minutes to no more than 30 minutes. Curing can be done by heating the coating placed on a hot plate or in an oven.

15

Embodiments are represented by the following

A functional polyhydrogensilsesquioxane resist composition in particular for extreme ultraviolet or electron beam lithography comprising at least of 50 mol-% of first siloxy
20 repeating units containing a Si-H and up to 30 mol-% of third siloxy repeating units having an unsaturated hydrocarbyl radical, wherein the first siloxy repeating units are derived from trialkoxysilane monomers and the third siloxy repeating units are derived from 3-(alk)acryloxyalkyltrialkokxysilane monomers, the molar ratio of the first to the third units being 99:1 to 85:15.

25

A functional polyhydrogensilsesquioxane resist composition in particular for extreme ultraviolet or electron beam lithography comprising at least of 50 mol-% of first siloxy repeating units containing a Si-H and up to 30 mol-% of third siloxy repeating units having an unsaturated hydrocarbyl radical, wherein the first siloxy repeating units are derived
30 from trialkoxysilane monomers and the third siloxy repeating units are derived from norbornene trialkoxysilane monomers, the molar ratio of the first to the third units being 99:1 to 85:15.

In the above embodiments, the alkoxy and alkyl groups are preferably derived from lower ,
35 linear or branched alkoxy and alkyl groups, containing 1 to 6, in particular 1 to 4 carbon atoms.

The following non-limiting examples illustrate embodiments.

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EXAMPLES

Methods

5 Gel permeation chromatography data was collected on an Agilent 1260 Infinity LC equipped with Shodex KF columns (KF-G; KF-803L; KF-802; KF-801) connected in series. The detector and column temperature was held at 40 °C. Flow rate of THF eluent was 1.0 ml/min.

10 E-beam lithography was carried out on a Vistec tool. The formulations are 1.3% solid content. The formulations were spin coated on silicon wafers via a spin coater with a spinning speed of 1500 rpm for 30 seconds. Soft bake was then carried out on a hot plate at temperature of 80 °C for 1 minute. The e-beam doses were varied from 100 to 900 µC/cm2 at 100 kV and current of 1 nA. The development step was carried out by 15 immersing the film in 2.38% TMAH solution for 1 minute. The film was then washed repeatedly three times with deionized water and finally dried with nitrogen gas.
EUV lithography: The polymer formulation of 1.3% solid content was spin coated on silicon wafers via a spin coater with a spinning speed of 1500 rpm for 30 seconds. Soft bake was then carried out on a hot plate at temperature of 80 °C for 1 minute. The film 20 samples after soft bake were irradiated with a XIL-II EUV tool at Paul Scherrer Institute, Villigen, Switzerland. The doses were varied from 2 to 150 mJ/cm^2. The development step was carried out by immersing the film in 2.38% TMAH solution for 1 minute. The film was then washed repeatedly three times with deionized water and finally dried with nitrogen gas.

25

Example 1

Preparation of polymer solution with HTEOS : MAPTMOS = 97.5 : 2.5 molar ratio

In one flask a mixture of 100 grams of triethoxysilane (HTEOS) and 3.88 grams of 3- 30 methacryloxypropyltrimethoxysilane (MAPTMOS) monomers, was dissolved in 193.02 grams of methyl tetrahydrofurfurylether (MeOTHF). The HTEOS:MAPTMOS molar ratio is 97.5:2.5. A mixture of 48.26 grams of MeOTHF, 21.55 grams of deionized water (DIW) and 9.88 grams of 0.01 mole nitric acid was mixed and added to the above monomers' solution into three equal portions in 1.5 hours. After the completion of addition, the 35 reaction was continued to mix for another 17 hours. Evaporation was carried out to obtain 15-25% of solid content. Methyl ethyl ketone (MEK) was added four times to the polymer

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weight. The obtained polymer solution was filtered with 0.2-micron filter. Gel permeation chromatography data shows Mw of 3945, Mn of 2047, and polydispersity of 1.93.

Example 2

5 Preparation of polymer solution with HTEOS : MAPTMOS = 95 : 5 molar ratio

In one flask a mixture of 100 grams of triethoxysilane (HTEOS) and 7.96 grams of 3-methacryloxypropyltrimethoxysilane (MAPTMOS) monomers, was dissolved in 193.02 grams of methyl tetrahydrofurfurylether (MeOTHF). The HTEOS:MAPTMOS molar ratio is 10 95:5. A mixture of 48.28 grams of MeOTHF, 22.12 grams of deionized water (DIW) and 10.14 grams of 0.01 mole nitric acid was mixed and added to the above monomers' solution into three equal portions in 1.5 hours. After the completion of addition, the reaction was continued to mix for another 17 hours. Evaporation was carried out to obtain 15-25% of solid content. Methyl ethyl ketone (MEK) was added four times to the polymer 15 weight. The obtained polymer solution was filtered with 0.2-micron filter. Gel permeation chromatography data shows Mw of 3052, Mn of 1690, and polydispersity of 1.81.

Comparative Example 1

Preparation of polymer solution with 100% triethoxysilane (HTEOS) -based polymer as 20 reference

In one flask a mixture of 100 grams of triethoxysilane (HTEOS) was dissolved in 193.02 grams of methyl tetrahydrofurfurylether (MeOTHF). A mixture of 48.26 grams of MeOTHF, 21.04 grams of deionized water (DIW) and 9.63 grams of 0.01 mole nitric acid was mixed 25 and added to the above monomers' solution into three equal portions in 1.5 hours. After the completion of addition, the reaction was continued to mix for another 17 hours. Evaporation was carried out to obtain 15-25% of solid content. Methyl ethyl ketone (MEK) was added four times to the polymer weight. The obtained polymer solution was filtered with 0.2-micron filter. Gel permeation chromatography data shows Mw of 3311, Mn of 30 1669, and polydispersity of 1.98.

Testing of polymers

The film samples were prepared from 1.3% solid polymer solutions by spin coating with a 35 spinning speed of 1500 rpm for 30 seconds. Soft bake was carried out with temperature of 80 °C for 1 minute. The 2.38% TMAH solution was used as developer in e-beam lithography.

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Evaluation of results. Scanning electron microscope images in Examples 1 and 2 demonstrate high resolution patterning using e-beam lithography (Fig. 5). Examples 1 and 2 showed clear improvements in sensitivity compared with material prepared in Comparative Example 1.

Example 3

Preparation of polymer solution with HTEOS:MAPTMOS:Cl-TEOS = 90:5:5 molar ratio

In one flask a mixture of 100 grams of triethoxysilane (HTEOS), 8.40 grams of 3-methacryloxypropyltrimethoxysilane (MAPTMOS), and 8.14 gram of 3-chloropropyltriethoxysilane (Cl-TEOS) monomers, HTEOS:MAPTMOS:Cl-TEOS molar ratio of 90:5:5, was dissolved in 214.47 grams of methyl tetrahydrofurfurylether (MeOTHF). A mixture of 53.60 grams of MeOTHF, 23.35 grams of deionized water (DIW) and 10.73 grams of 0.01 mole nitric acid was mixed and added to the above monomers' solution into three equal portions in 1.5 hours. After the completion of addition, the reaction was continued to mix for another 17 hours. Evaporation was carried out to obtain 15-25% of solid content. Methyl ethyl ketone (MEK) was added four times to the polymer weight. The obtained polymer solution was filtered with 0.2-micron filter. Gel permeation chromatography data shows Mw of 2630, Mn of 1500, and polydispersity of 1.75.

Testing of polymers

The film samples was prepared from 1.3% solid polymer solutions by spin coating with a spinning speed of 1500 rpm for 30 seconds. Soft bake was carried out with temperature of 80 °C for 1 minute. The 2.38% TMAH solution was used as developer in e-beam lithography.

Evaluation of results. Scanning electron microscope images in Example 3 demonstrate high resolution patterning using e-beam lithography (Fig. 6). Resist prepared in Example 3 showed improved sensitivity compared with Examples 1-2 and Reference sample in Comparative Example 1 showed clear improvements in sensitivity compared with material prepared in Comparative Example 1.

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Example 4

Preparation of polymer solution with HTEOS:Cl-TEOS = 95 : 5 molar ratio

In one flask a mixture of 50 grams of triethoxysilane (HTEOS) and 3.86 gram of 3-chloropropyltriethoxysilane (Cl-TEOS) monomers, HTEOS:Cl-TEOS molar ratio of 95:5, was dissolved in 101.59 grams of methyl tetrahydrofurfurylether (MeOTHF). A mixture of 25.39 grams of MeOTHF, 11.06 grams of deionized water (DIW) and 5.07 grams of 0.01 mole nitric acid was mixed and added to the above monomers' solution into three equal portions in 1.5 hours. After the completion of addition, the reaction was continued to mix for another 17 hours. Evaporation was carried out to obtain 15-25% of solid content. Methyl ethyl ketone (MEK) was added four times to the polymer weight. The obtained polymer solution was filtered with 0.2-micron filter. Gel permeation chromatography data shows Mw of 2130, Mn of 1224, and polydispersity of 1.74.

Testing of polymers

The film samples were prepared from 1.3% solid polymer solutions by spin coating with a spinning speed of 1500 rpm for 30 seconds. Soft bake was carried out with temperature of 80 °C for 1 minute. The 2.38% TMAH solution was used as developer in e-beam lithography.

Evaluation of results. Scanning electron microscope images in Example 3 demonstrate high resolution patterning using e-beam lithography (Fig. 7). Resist prepared in Example 3 showed improved sensitivity compared with Examples 1-2 and Reference sample in Comparative Example 1 showed clear improvements in sensitivity compared with material prepared in Comparative Example 1.

Example 5

Preparation of polymer solution with HTEOS: APTMOS = 90 : 10 molar ratio

In one flask a mixture of 25 grams of triethoxysilane (HTEOS) and 3.96 gram of 3-acryloxypropyltrimethoxysilane (APTMOS) monomers, HTEOS: APTMOS molar ratio of 90:10, was dissolved in 60.08 grams of methyl tetrahydrofurfurylether (MeOTHF). A mixture of 15.02 grams of MeOTHF, 5.84 grams of deionized water (DIW) and 2.67 grams of 0.01 mole nitric acid was mixed and added to the above monomers' solution into three equal portions in 1.5 hours. After the completion of addition, the reaction was continued to mix for another 17 hours. Evaporation was carried out to obtain 15-25% of solid content.

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Methyl ethyl ketone (MEK) was added four times to the polymer weight. The obtained polymer solution was filtered with 0.2-micron filter. Gel permeation chromatography data shows Mw of 2302, Mn of 1409, and polydispersity of 1.63.

5 **Comparative Example 2**

Preparation of polymer solution with HTEOS : MAPTMOS = 90 : 10 molar ratio
In one flask a mixture of 25 grams of triethoxysilane (HTEOS) and 4.2 grams of 3-methacryloxypropyltrimethoxysilane (MAPTMOS) monomers, was dissolved in 60.08
10 grams of methyl tetrahydrofurfurylether (MeOTHF). The HTEOS:MAPTMOS molar ratio is 90:10. A mixture of 15.02 grams of MeOTHF, 5.84 grams of deionized water (DIW) and 2.67 grams of 0.01 mole nitric acid was mixed and added to the above monomers' solution into three equal portions in 1.5 hours. After the completion of addition, the reaction was continued to mix for another 17 hours. Evaporation was carried out to obtain
15 15-25% of solid content. Methyl ethyl ketone (MEK) was added four times to the polymer weight. The obtained polymer solution was filtered with 0.2-micron filter. Gel permeation chromatography data shows Mw of 2281, Mn of 1396, and polydispersity of 1.63.

Polymer testing

20

Film samples were prepared by spin coating the polymer solutions, 1.3%, with a spinning speed of 1500 rpm for 30 seconds. Soft bake was then carried out with temperature of 80 ℃ for 1 minute. The 2.38% TMAH solution was used as developer in e-beam lithography.

25 **Evaluation of results**. Example 5 and Comparative Example 2 show that the acrylate functionality gives higher sensitivity compared to that of methacrylate-functionalized polymer resist. (SEM images of e-beam result in Fig. 8). The higher sensitivity can be explained by less steric hindrance of the acrylate group and thus higher activation energy compared to that of methacrylate group.

30

Example 6

Preparation of polymer solution with HTEOS: NorTEOS = 95 : 5 molar ratio

In one flask a mixture of 30 grams of triethoxysilane (HTEOS) and 2.46 gram of
35 norbornene triethoxysilane (NorTEOS) monomers, HTEOS: NorTEOS molar ratio of 95:5, was dissolved in 60.95 grams of methyl tetrahydrofurfurylether (MeOTHF). A mixture of 15.24 grams of MeOTHF, 6.64 grams of deionized water (DIW) and 3.04 grams of 0.01

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mole nitric acid was mixed and added to the above monomers' solution into three equal portions in 1.5 hours. After the completion of addition, the reaction was continued to mix for another 17 hours. Evaporation was carried out to obtain 15-25% of solid content. Methyl ethyl ketone (MEK) was added four times to the polymer weight. The obtained
5 polymer solution was filtered with 0.2-micron filter. Gel permeation chromatography data shows Mw of 2960, Mn of 1424, and polydispersity of 2.08.

Example 7

Preparation of polymer solution with HTEOS: NorTEOS = 90 : 10 molar ratio

10

In one flask a mixture of 10 grams of triethoxysilane (HTEOS) and 1.73 gram of norbornene triethoxysilane (NorTEOS) monomers, HTEOS: NorTEOS molar ratio of 90:10, was dissolved in 24.03 grams of methyl tetrahydrofurfurylether (MeOTHF). A mixture of 6.01 grams of MeOTHF, 2.34 grams of deionized water (DIW) and 1.07 grams
15 of 0.01 mole nitric acid was mixed and added to the above monomers' solution into three equal portions in 1.5 hours. After the completion of addition, the reaction was continued to mix for another 17 hours. Evaporation was carried out to obtain 15-25% of solid content. Methyl ethyl ketone (MEK) was added four times to the polymer weight. The obtained polymer solution was filtered with 0.2-micron filter. Gel permeation chromatography data
20 shows Mw of 3332, Mn of 1475, and polydispersity of 2.26.

Polymer testing

Film samples were prepared by spin coating the polymer solutions, 1.3%, with a spinning
25 speed of 1500 rpm for 30 seconds. Soft bake was then carried out with temperature of 80 °C for 1 minute. The 2.38% TMAH solution was used as developer in the EUV lithography. **Evaluation of EUV results**. Examples 6-7 and Comparative Example 1 demonstrate the beneficial effect of incorporated norbornene functionality in the polymer resist. Addition of only few weight percentages can clearly eliminate the scumming issue and improve the
30 LER (SEM images in Figure 9).

Example 8

Preparation of polymer solution with 1% MA

35 Polymer solution prepared in Example 1 was added with 1% by weight (wt%) maleic acid. The obtained mixture can be further diluted with propylene glycol monomethyl ether

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acetate (PGMEA) solvent to obtain desired thickness formulation. The final formulation was filtered with 0.2-micron filter.

Example 9

5 Preparation of polymer solution with 2% MA

Polymer solution prepared in Example 1 was added with 2% by weight (wt%) maleic acid. The obtained mixture can be further diluted with propylene glycol monomethyl ether acetate (PGMEA) solvent to obtain desired thickness formulation. The final formulation
10 was filtered with 0.2-micron filter.

Polymer testing

Film samples were prepared by spin coating the polymer solutions, 1.3%, with a spinning
15 speed of 1500 rpm for 30 seconds. Soft bake was then carried out with temperature of 80 ℃ for 1 minute. The 2.38% TMAH solution was used as developer in e-beam lithography. **Evaluation of results**. Examples 8-9 and Comparative Example 1 demonstrate the beneficial effect of added maleic acid in the polymer resist. E-beam result in Figure 10 shows the stabilization of polymers with 1% and 2% MA.

20

Example 10

Preparation of polymer solution with HTEOS: HFIPTEOS = 99:1 molar ratio

In one flask a mixture of 40 grams of triethoxysilane (HTEOS) and 0.92 gram of
25 hexafluoroisopropyltriethoxysilane (HFIPTEOS) monomers, HTEOS:HFIPTEOS molar ratio of 99:1, was dissolved in 77.99 grams of methyl tetrahydrofurfurylether (MeOTHF). A mixture of 19.50 grams of MeOTHF, 8.50 grams of deionized water (DIW) and 3.89 grams of 0.01 mole nitric acid was mixed and added to the above monomers' solution into three equal portions in 1.5 hours. After the completion of addition, the reaction was continued to
30 mix for another 17 hours. Evaporation was carried out to obtain 15-25% of solid content. Methyl ethyl ketone (MEK) was added four times to the polymer weight. The obtained polymer solution was filtered with 0.2-micron filter. Gel permeation chromatography data shows Mw of 4612, Mn of 1558, and polydispersity of 2.96.

35

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Example 11

Preparation of polymer solution with HTEOS: HFIPTEOS = 98:2 molar ratio

In one flask a mixture of 40 grams of triethoxysilane (HTEOS) and 1.85 gram of
5 hexafluoroisopropyltriethoxysilane (HFIPTEOS) monomers, HTEOS:HFIPTEOS molar ratio of 99:1, was dissolved in 78.78 grams of methyl tetrahydrofurfurylether (MeOTHF). A mixture of 19.70 grams of MeOTHF, 8.59 grams of deionized water (DIW) and 3.93 grams of 0.01 mole nitric acid was mixed and added to the above monomers' solution into three equal portions in 1.5 hours. After the completion of addition, the reaction was continued to
10 mix for another 17 hours. Evaporation was carried out to obtain 15-25% of solid content. Methyl ethyl ketone (MEK) was added four times to the polymer weight. The obtained polymer solution was filtered with 0.2-micron filter. Gel permeation chromatography data shows Mw of 3762, Mn of 1247, and polydispersity of 3.02.

15 **Testing of polymers**

The film samples were prepared from 1.3% solid polymer solutions by spin coating with a spinning speed of 1500 rpm for 30 seconds. Soft bake was carried out with temperature of 80 °C for 1 minute. The 2.38% TMAH solution was used as developer in EUV lithography.

20

Evaluation of results. Resist prepared in Examples 11 shows much less scumming issue in compared with that of polymer sample prepared in Comparative Example 1 (SEM images in Fig. 4).

25 **Example 12**

Polymer solution prepared in Comparative Example 1 was added with 1% by weight (wt%) maleic acid and 0.75wt% pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (I1010) inhibitor. The obtained mixture can be further diluted
30 with propylene glycol monomethyl ether acetate (PGMEA) solvent to obtain desired thickness formulation. The final formulation was filtered with 0.2-micron filter.

Example 13

35 Polymer solution prepared in Example 15 was added with 1% by weight (wt%) maleic acid and 1.25wt% pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (I1010) inhibitor. The obtained mixture can be further diluted with propylene glycol

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monomethyl ether acetate (PGMEA) solvent to obtain desired thickness formulation. The final formulation was filtered with 0.2-micron filter.

Testing of polymers

5

The film samples of polymers in Example 27-28 and Comparative Example 1 were prepared from 1.3% solid polymer solutions by spin coating with a spinning speed of 1500 rpm for 30 seconds. Soft bake was carried out with temperature of 80 ℃ for 1 minute. The 2.38% TMAH solution was used as developer in EUV lithography.

10

Evaluation of results. EUV result shows that the addition of small amount of I1010 improve scumming issue and thus better LER compared with Comparative Example 1 (Figure 12).

15

INDUSTRIAL APPLICABILITY

Generally, the present technology can be used in the semiconductor industry. For example, the present technology can be used for achieving complex circuitry in
20 microelectronic devices in particular using lithographic processes, such as photolithographic processes. Embodiments comprising polyhydrogensilsesquioxane resins containing carbon-carbon unsaturated bond, halogen, and solubility-enhancer content. Adjustment of the carbon-carbon unsaturated bond, halogen, and solubility-enhancer content will make it possible to obtain a highly sensitive coating for application in
25 extreme ultraviolet lithography.

ABBREVIATIONS

CAR	chemically amplified resist
EBL	electron beam lithography
EUV	extreme ultraviolet (wavelength)
EUVL	extreme ultraviolet lithography
GPC	gel permeation chromatography
HSQ	hydrogen silsesquioxane
LER	line-edge roughness
LWR	line width roughness
NIL	nanoimprint lithography

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PBL	photon beam lithography
SEM	scanning electron microscope
TEOS	tetraethoxysilane
TMAH	tetramethylammonium hydroxide

5

LIST OF REFERENCES

Non-Patent Literature

10 1. Okoroanyanwu, U. Molecular Theory of Lithography. (SPIE Press, 2015).
2. Gangnaik, A. S., Georgiev, Y. M. & Holmes, J. D. New Generation Electron Beam Resists: A Review. Chem. Mater. 29, 1898–1917 (2017).
3. Simone, D. De et al. Progresses and Challenges of EUV Lithography Materials. J. Photopolym. Sci. Technol. 27, 601–610 (2014).
15 4. Higgins, C. D. et al. Resolution, line-edge roughness, sensitivity tradeoff, and quantum yield of high photo acid generator resists for extreme ultraviolet lithography. Jpn. J. Appl. Phys. 50, 1–8 (2011).
5. De Simone, D., Vesters, Y. & Vandenberghe, G. Photoresists in extreme ultraviolet lithography (EUVL). Adv. Opt. Technol. 6, 163–172 (2017).
20 6. Takeo Watanabe. Current status and prospect for EUV lithography. 2017 7th Int. Conf. Integr. Circuit, Des. Verif. 3–8 (2017).
7. Grigorescu, A. E. & Hagen, C. W. Resists for sub-20-nm electron beam lithography with a focus on HSQ: State of the art. Nanotechnology 20, 292001 (2009).
25 8. Yang, J. K. W. et al. Understanding of hydrogen silsesquioxane electron resist for sub-5-nm-half-pitch lithography. J. Vac. Sci. Technol. B Microelectron. Nanom. Struct. 27, 2622 (2009).

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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.

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, comprising an acid or a latent acid or a base or a latent base, and optionally a latent catalyst.

5. 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.

6. 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 precursors a functional polyhydrogensilsesquioxane.

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

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

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

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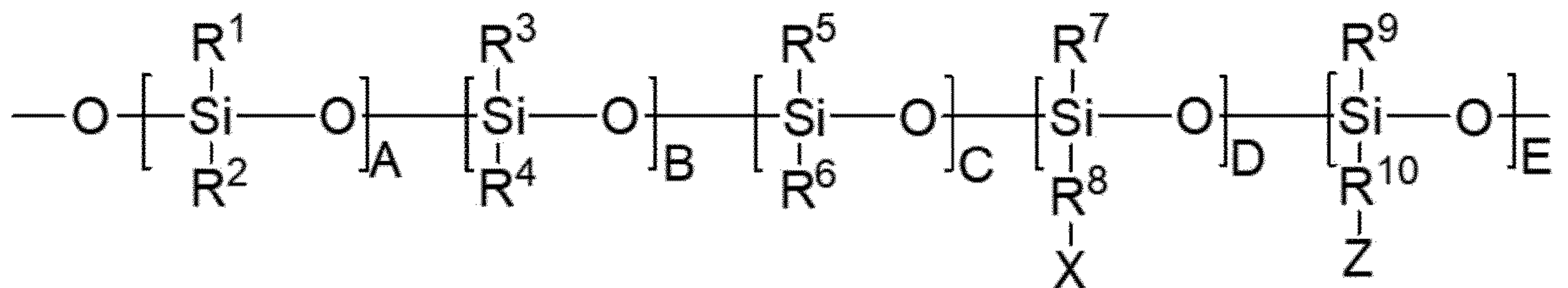
hydrocarbyl radical, and an intermediate siloxy (SiO) portion that can be independently selected from non-functional and halogen containing hydrrocarbyl radicals wherein the polymer has a molecular weight of from 500 to 50,000 g/mol, and the composition preferably further comprising an acid and/or base catalyst and a solvent.

5

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



10 (I)

wherein

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

X stands for a halogen atom;

15 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 and R^4 to R^{10} independently stands for hydrogen or hydrocarbyl radical, in particular hydrocarbyl radical.

20

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 directly or using a mask.

25

12. Method of producing a functional polyhydrogensilsesquioxane composition according to preceding claims, containing at least an SiH moieties and unsaturated hydrocarbyl radicals covalently bound to Si, and optionally hydrocarbon radicals containing halogen, solubility-enhancing moieties.

30

13. The method according to claim 12, comprising

- hydrolyzing a first monomeric hydrogen containing silicon compound having at least two or three hydrolysable groups attached to the silicon with

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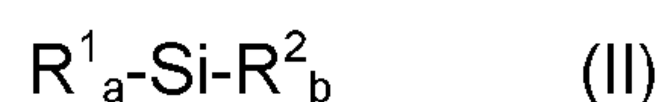
- a second monomeric silicon compound having at least zero, one, two or three hydrocarbyl radicals, and at least one hydrolyzable group attached to the silicon atom of the compound, optionally together with at least one of
- a third monomeric silicon compound having at least one functional group and 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
- 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
- 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 stable composition in a solvent system.

14. The method according to claim 12 or 13, wherein 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. The method according to any of claims 12 to 14, comprising hydrolyzing a first silicon compound having the general formula II



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

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 can independently be selected from hydroxyl, alkoxy, acyloxy and halogen.

16. 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 second compound having the general formula III

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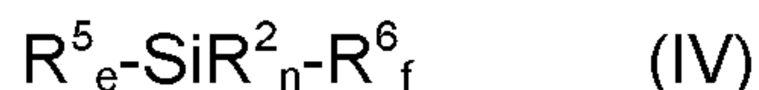
$$R^3_c\text{-}SiR^2_n\text{-}R^4_d \qquad (III)$$

wherein

5

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
10 group, a hydroxy group, a cyclic amino group, or a cyano group, or a combination of them,
R^2 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,
15 wherein the total value of c + n + d may not exceed 4.

17. 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
20 in formula II, with a second compound having the general formula IV



$$R^5_e\text{-}SiR^2_n\text{-}R^6_f \qquad (IV)$$

wherein
25 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
30 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^2 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
35 less.

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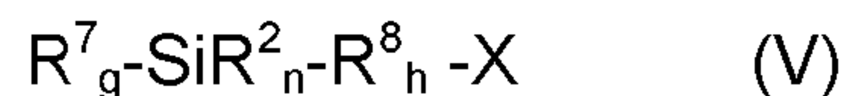
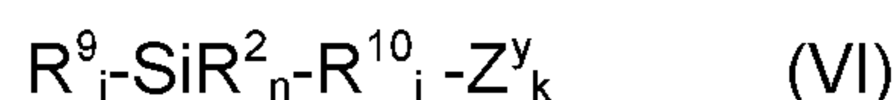
18. The method according to any of claims 12 to 17, comprising producing a composition comprising a copoly(organosiloxane) by hydrolyzing a first silicon compound having the general formula II, wherein the symbols a, b, R^1 and R^2 have the same meaning as above in formula II, with a second compound having the general formula 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 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^2 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, and
h is an integer of 0 to 1, and
wherein the total value of g + n + h is 4 or less.

19. 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 second compound having the general formula 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

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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
5 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^2 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

10 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. The method according to any of claims 12 to 19, comprising using HTEOS
15 ($HSi(OC_2H_5)_3$) 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 controlled hydrolytic/condensation reaction, for making partially condensed polyhydrogensilsesquioxane resins.

20

21. The method according to any of the preceding claims, the obtained polyhydrogensilsesquioxane resins or the coating solutions are added with radical inhibitors or antioxidants.

25 22. The method according to the claim 21, wherein the radical inhibitors or antioxidants.

23. The method according to any of the preceding claims, the obtained polyhydrogensilsesquioxane resins or the coating solutions are added with stabilizers which prevent the aging of the polyhydrogensilsesquioxane resins.

30

24. The method according to the claim 23, wherein the stabilizers are typically selected from dicarboxylic acids, typically maleic acid, malonic acid, and succinic acid.

25. Method of patterning a carbon-carbon unsaturated bond containing, and halogen
35 containing, and solubility-enhancer containing polyhydrogensilsesquioxane coated substrate with radiation of light at a specific wavelength, the method comprising the steps of

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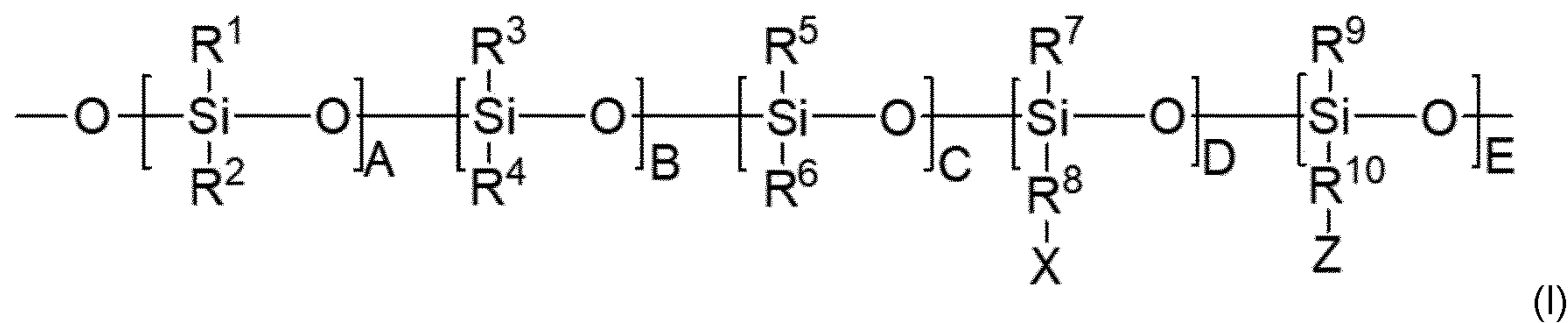
- irradiating a coated substrate along a selected pattern to form an irradiated structure with a region of irradiated coating and a region with un-irradiated coating; and
- selectively developing the irradiated structure to remove a substantial portion of
5 the un-irradiated coating to form a patterned substrate.

26. The method according to claim 25, 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
10 wavelength between 1 and 200nm.

27. The method according to claim 26, wherein a carbon-carbon unsaturated bond containing, and halogen containing, and solubility-enhancer containing containing polyhydrogensilsesquioxane coated substrate is irradiated with radiation of light at a
15 wavelength of 13.5 nm.

28. The method according to any of claims 25 to 27, wherein the coating comprises a siloxane polymer containing SiO moieties, a plurality of reactive sites distributed along the polymer, a plurality of reactive sites distributed along the polymer, and a first SiH
20 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
25 molecular weight of from 500 to 50000 g/mol.

29. The method according to any of claims 25 to 28, wherein the coating comprises a polyhydrogensilsesquioxane resin having the general formula (I)



30 (I)

wherein

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

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X stands for a halogen atom;

Z stands for functional group enhancing solubility to alkaline developers;

R^1 stands for hydrogen

R^3 stands for hydrocarbyl radicals containing unsaturated moieties

5 R^2 and R^4 to R^{10} independently stand for hydrogen or hydrocarbyl radicals, in particular R^2 and R^4 to R^{10} independently stand for hydrocarbyl radicals.

30. The method according to any of claims 25 to 29, comprising patterning a substrate, comprising:

10
- 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;

15
- 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.

20 31. The method of any of claims 25 to 30, 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.

25 32. The method of any of claims 25 to 1 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.

30

33. A method of forming of a resist film by application of a composition according to any of claims 1 to 9 for forming a resist underlayer film onto a semiconductor substrate and baking the composition.

35 34. A method for producing a semiconductor device, comprising:

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- 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.

35. 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.

36. 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 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.

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37. 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 9 for forming a resist film onto the organic underlayer film and baking the composition to form a resist
5 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
10 patterned; and
- fabricating the semiconductor substrate using the organic underlayer film thus patterned.

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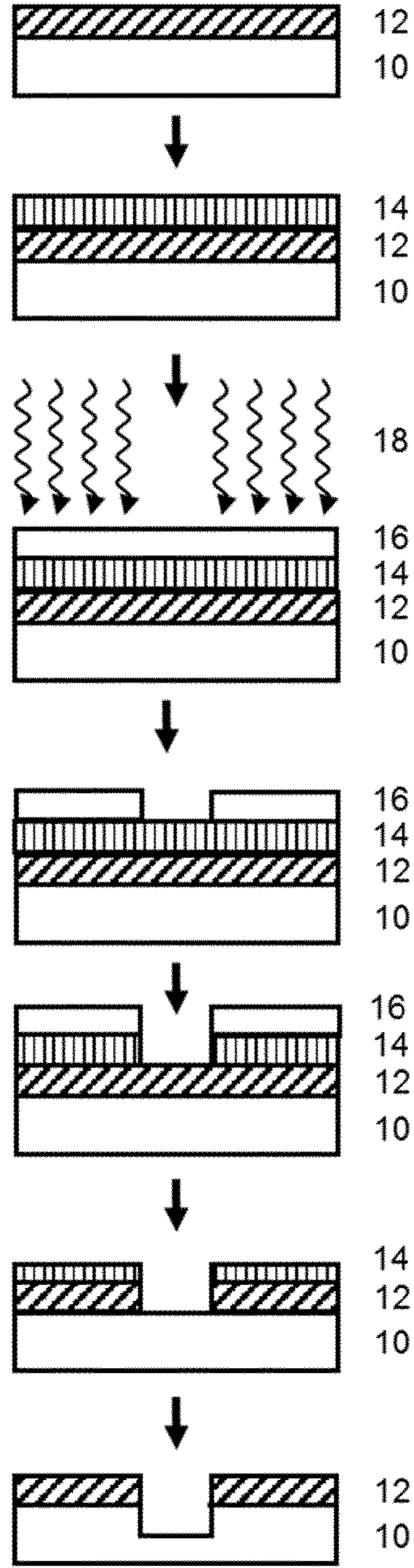

Fig. 1

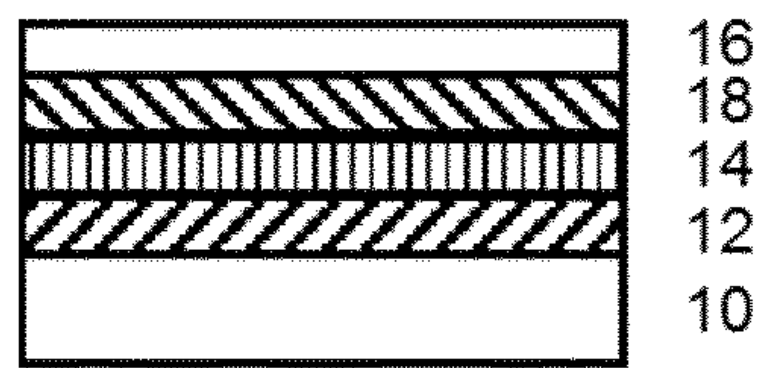

Fig. 2

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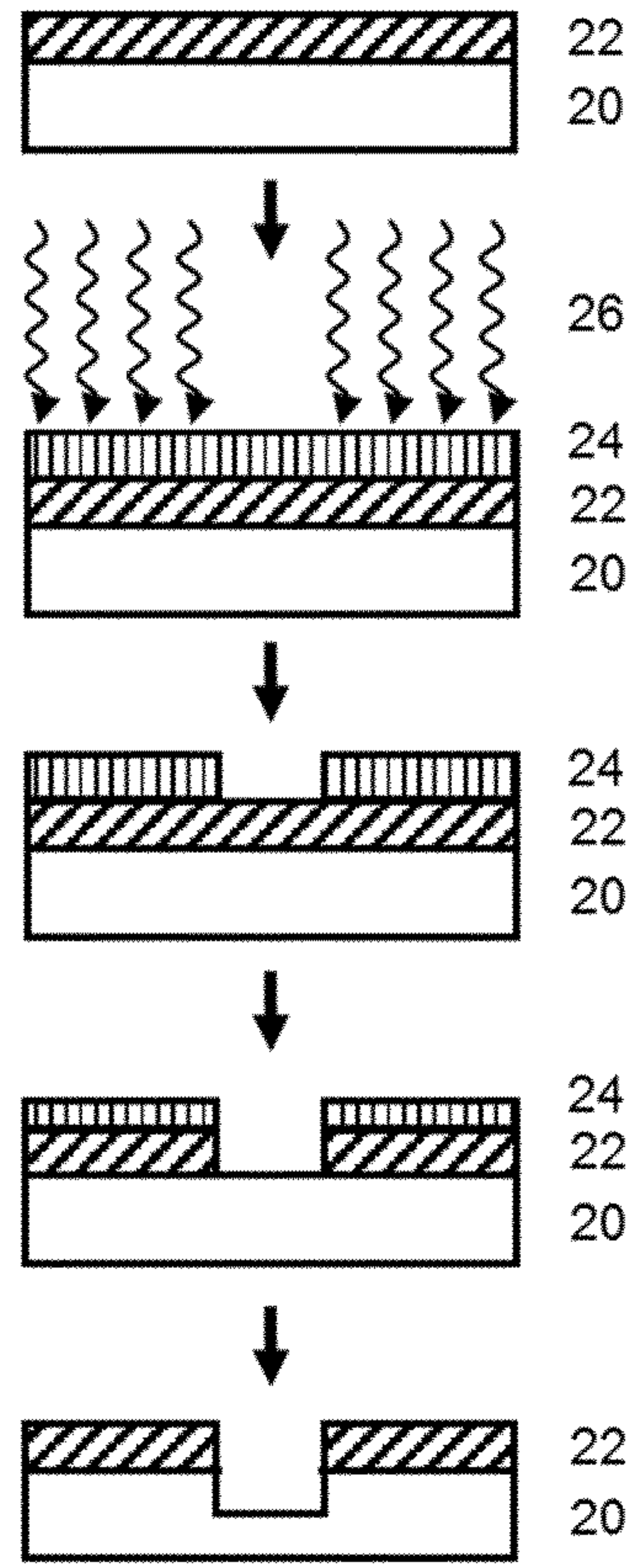

Fig. 3

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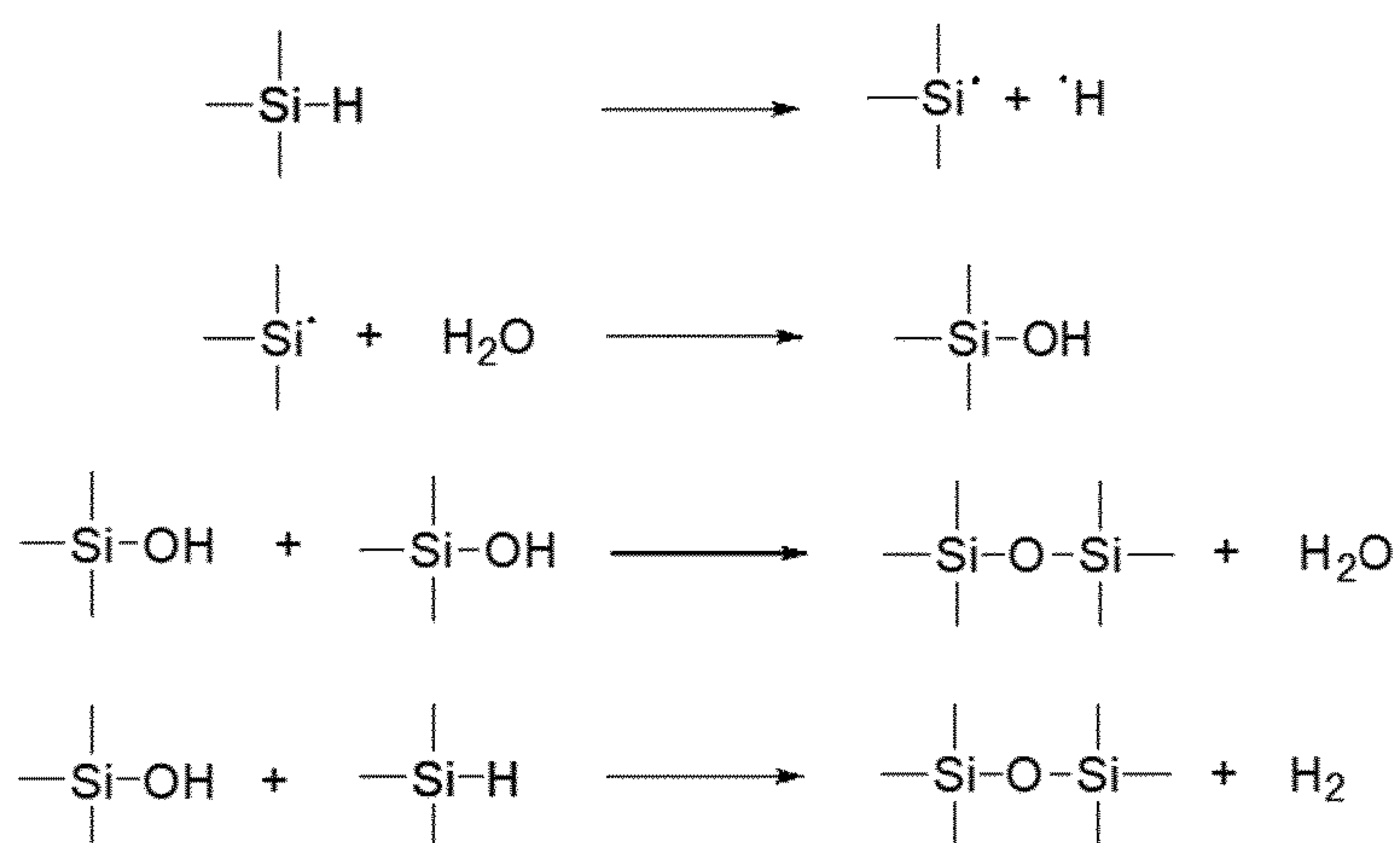
1) condensation



2) Double bond polymerization: methacrylate polymerization

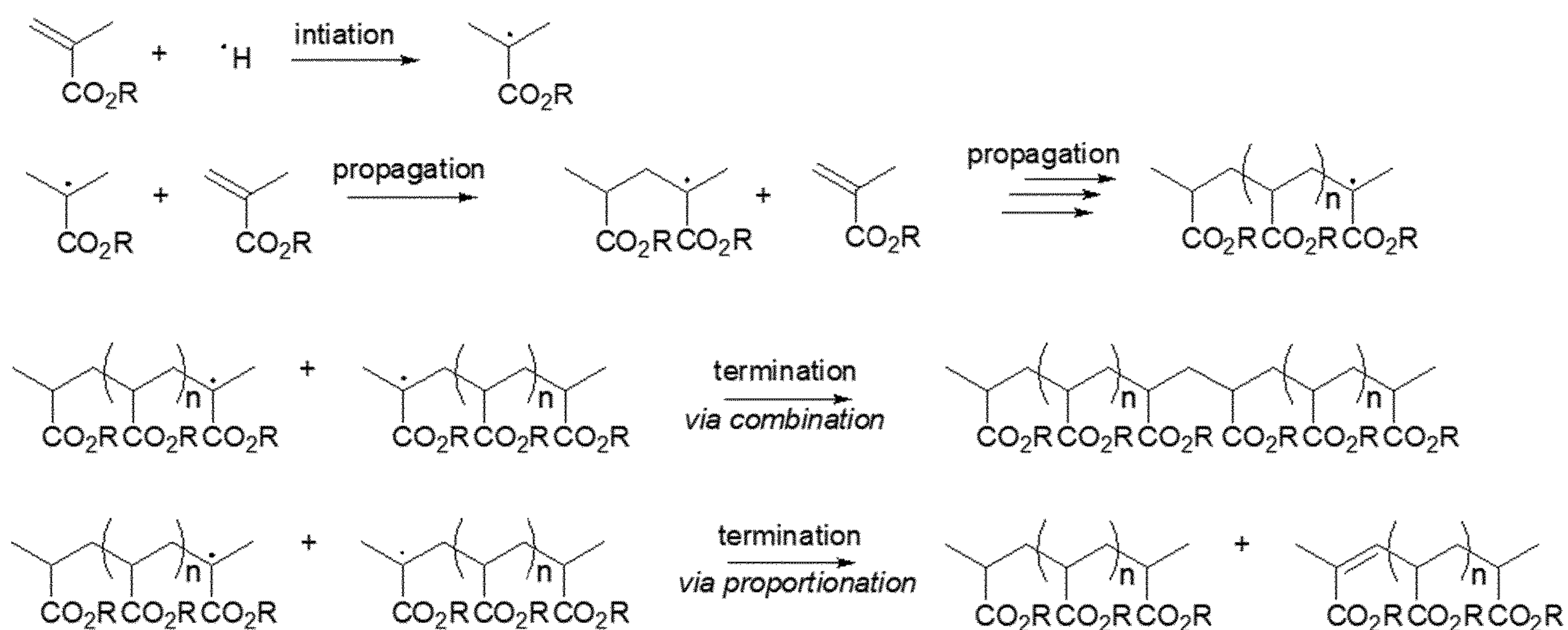


Fig. 4

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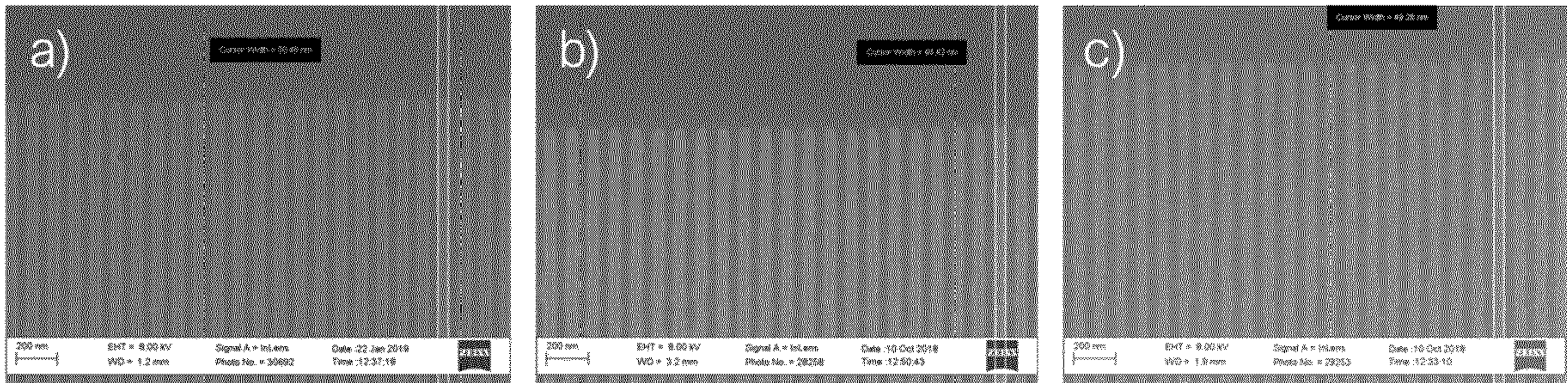

Figure 5 E-beam result of a) Comparative Example 1, b) Example 1, and c) Example 2. Required dose to obtain pattern decreased by b) 33% and c) 42%.

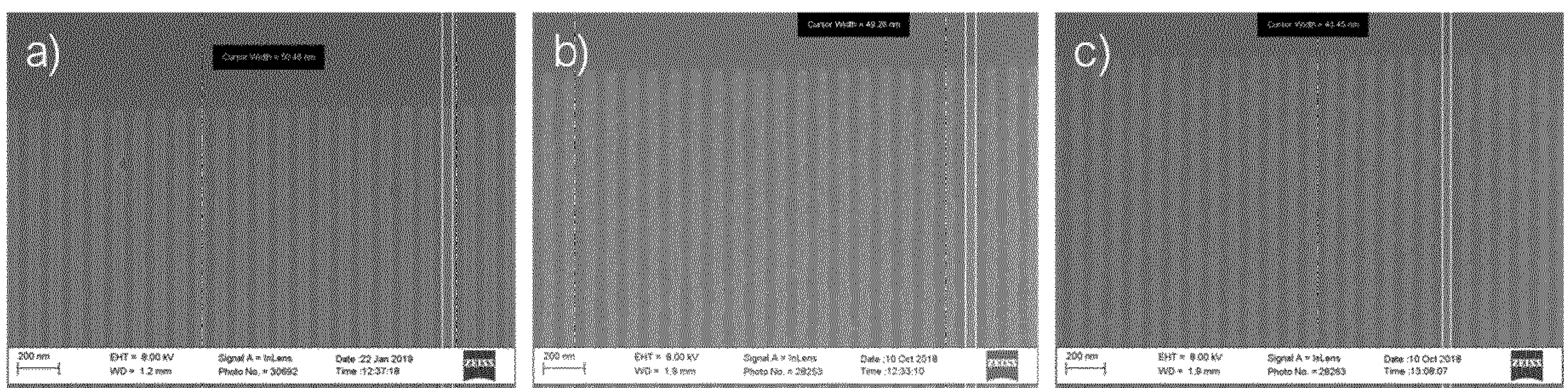

Figure 6 E-beam result of a) Comparative Example 1, b) Example 2, and c) Example 3. Required dose to obtain pattern decreased by b) 42% and c) 70%.

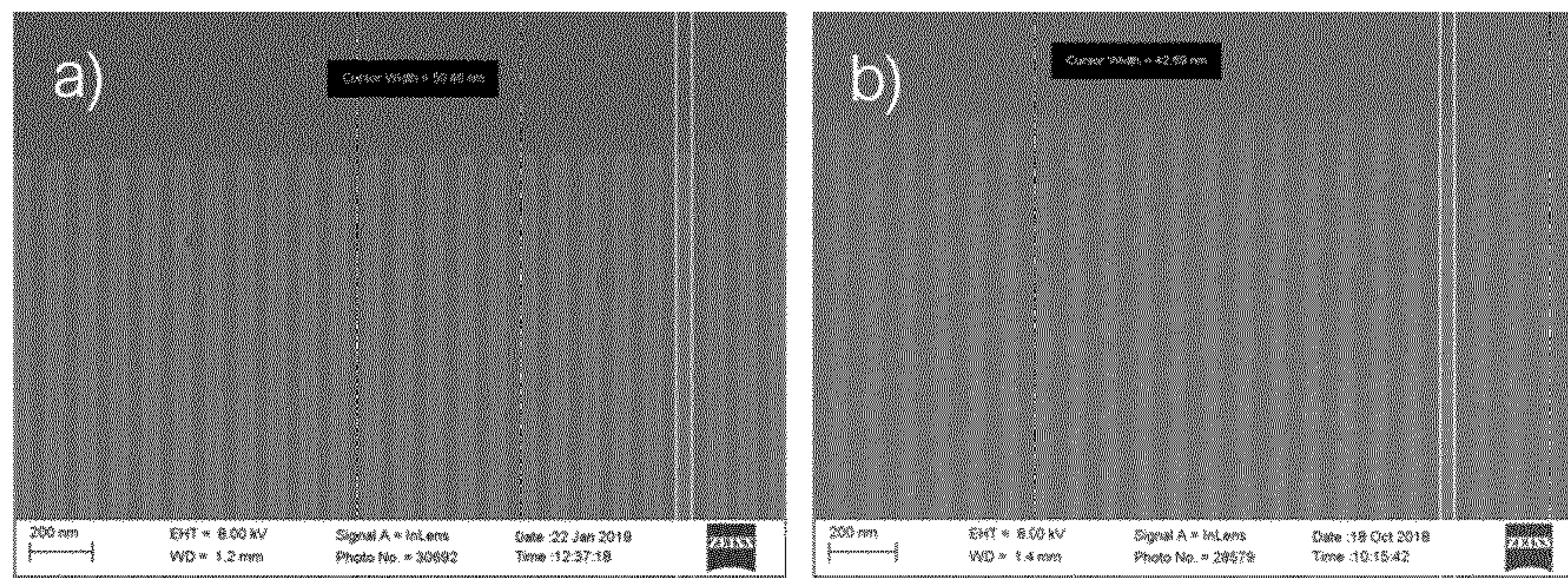

Figure 7 E-beam result of a) Comparative Example 1, b) Example 4. Required dose to obtain pattern decreased by b) 70%.

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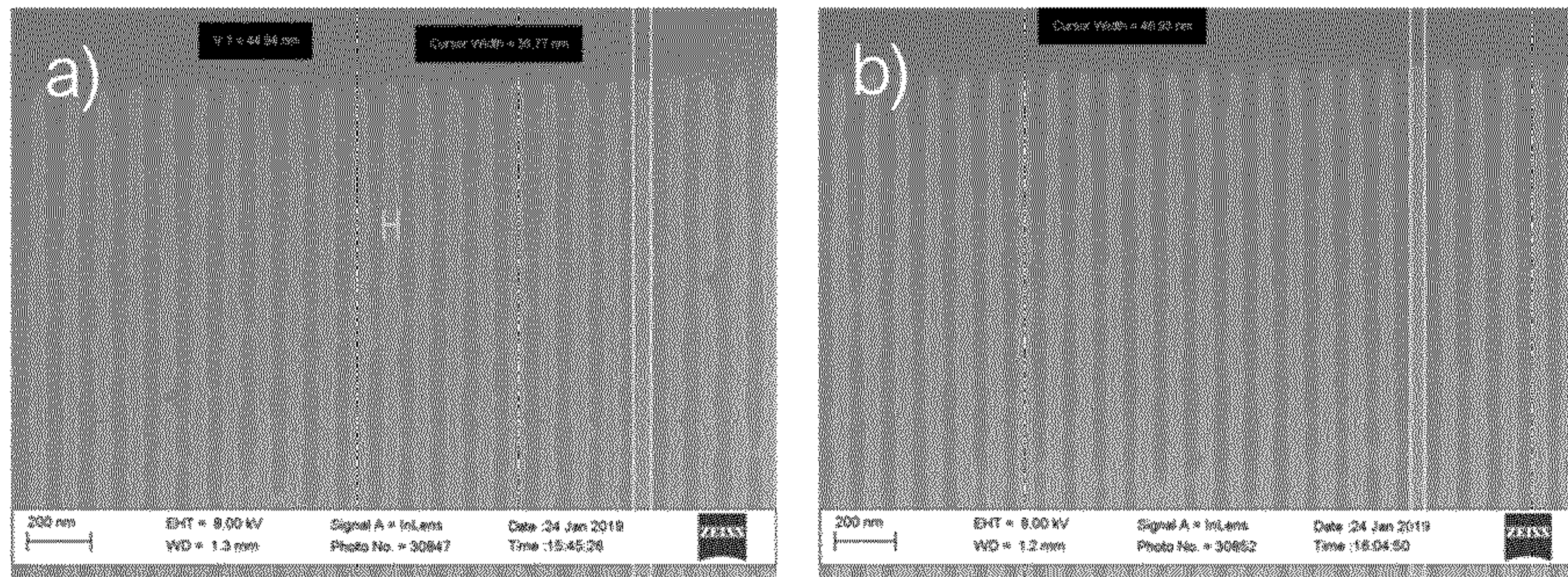

Figure 8 E-beam result of a) Example 5, b) Comparative Example 2. Required dose to obtain pattern decreased by b) 9%.

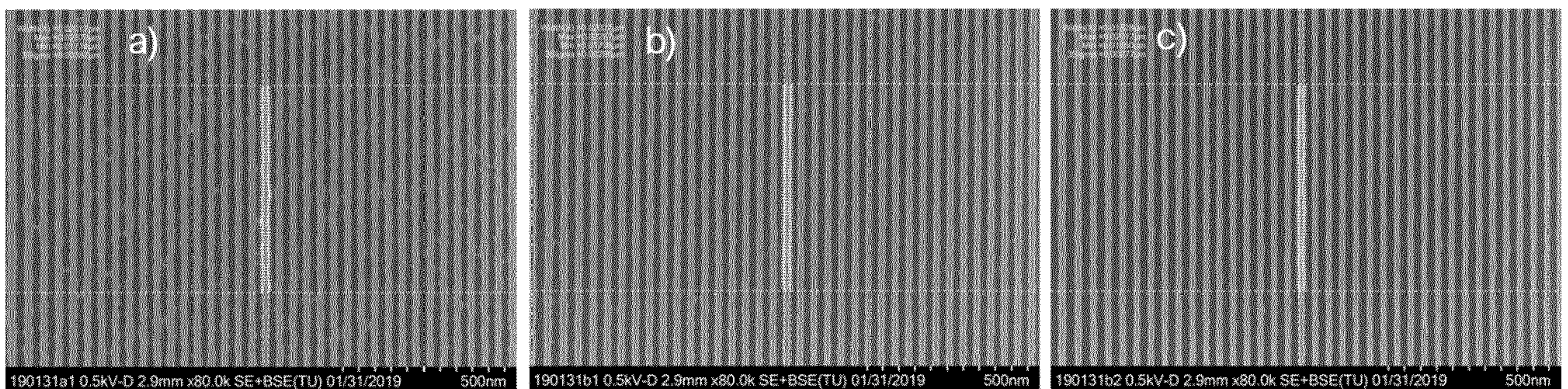

Figure 9 SEM image showing 22nm half pitch patterned lines obtained by EUVL using materials in a) Comparative Example 1 exhibiting LER = 3.87nm, b) Example 6 exhibiting LER = 2.86nm, and c) Example 7 exhibiting LER = 2.77nm; where applied EUV doses are 77.5 mJ/cm^2, 97.5 mJ/cm^2, and 82.5 mJ/cm^2, corresponding to a, b, and c, respectively.

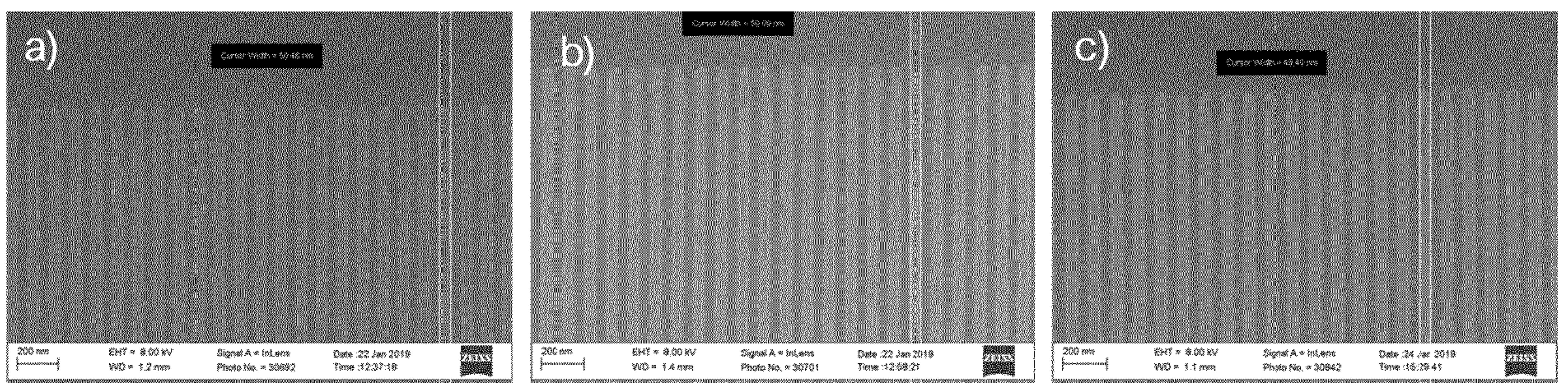

Figure 10 E-beam result of a) Comparative Example 1, b) Example 8, and c) Example 9 showing similar performance with same dose.

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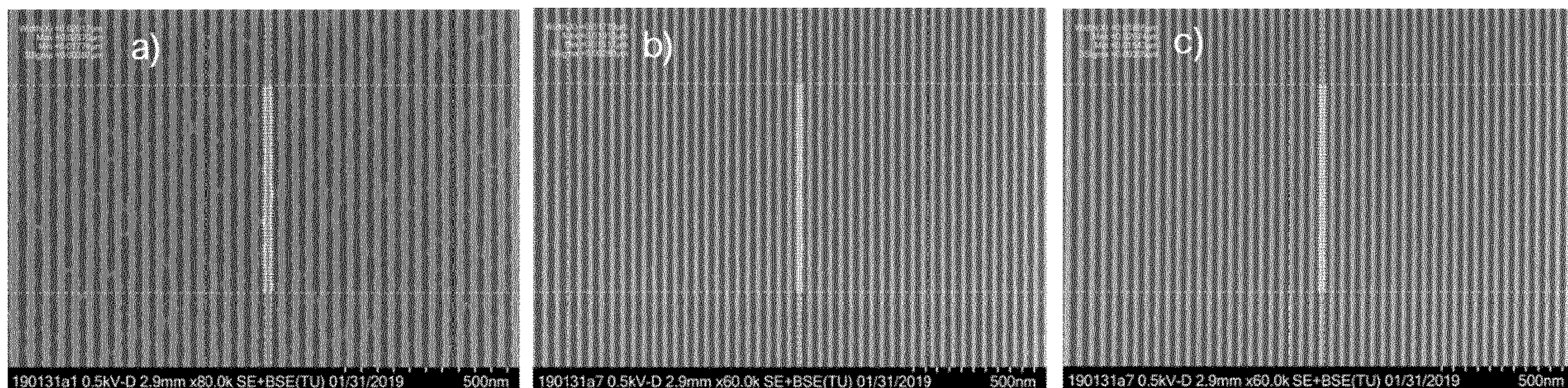

Figure 11 SEM image showing 22nm half pitch patterned lines obtained by EUVL using materials in a) Comparative Example 1 exhibiting LER = 3.87nm, b) Example 10 exhibiting LER = 2.80nm, and c) Example 11 exhibiting LER = 3.05nm; where applied EUV doses are 77.5 mJ/cm^2, 87.5 mJ/cm^2, and 107.5 mJ/cm^2, corresponding to a, b, and c, respectively.

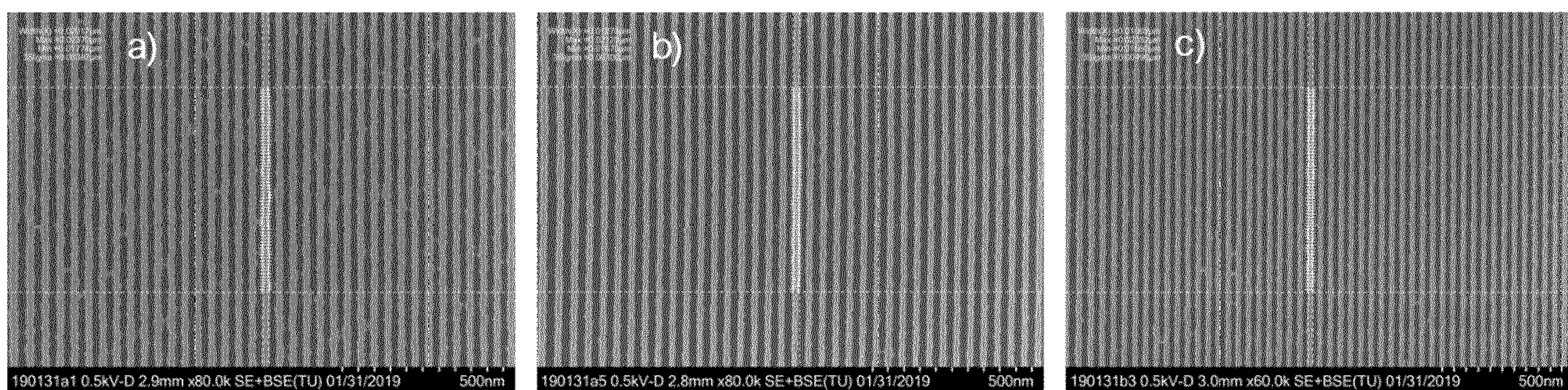

Figure 12 SEM image showing 22nm half pitch patterned lines obtained by EUVL using materials in a) Comparative Example 1 exhibiting LER = 3.87nm, b) Example 10 exhibiting LER = 4.96nm, and c) Example 11 exhibiting LER = 3.00nm; where applied EUV doses are 77.5 mJ/cm^2, 87.5 mJ/cm^2, and 90 mJ/cm^2, corresponding to a, b, and c, respectively.

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FINNISH PATENT AND REGISTRATION OFFICE **SEARCH REPORT**

Finnish Patent and Registration Office
FI-00091 PRH

PATENT APPLICATION No.	CLASSIFICATION	
20195142	IPC	CPC
	C08G 77/24 (2006.01)	**C08G 77/24**
	H01L 21/02 (2006.01)	**C08L 83/06**
	C08L 83/06 (2006.01)	**H01L 21/02**
	G03F 7/075 (2006.01)	**G03F 7/075**
	G03F 1/22 (2012.01)	G03F 1/22
	B32B 25/20 (2006.01)	B32B 25/20
	C08G 77/00 (2006.01)	C08G 77/70

PATENT CLASSES SEARCHED (classification systems and classes)

IPC: C08G, C08L, H01L, G03F, B32B

DATABASES CONSULTED DURING THE SEARCH

EPODOC, WPIAP, EPO-Internal full-text databases, Full-text translation databases from Asian languages, XP3GPP, XPAIP, XPCPVO, XPESP, XPETSI, XPI3E, XPIEE, XPIETF, XPIOP, XPIPCOM, XPJPEG, XPMISC, XPOAC, XPRD, XPTK, BIOSIS, COMPDX, EMBASE, INSPEC, MEDLINE, TDB, NPL

DOCUMENTS CONSIDERED TO BE RELEVANT

Category*)	Bibliographic data on the document and relevant passages	Relevant to claims
X	WO 03044078 A1 (HONEYWELL INT INC [US]) 30 May 2003 (30.05.2003) page 5, last paragraph; page 28, catalyst; examples: 1; 6, page 63, lines 8-18; 10, page 83; 46, page 117; figure 3; claim 48	1-37
X	WO 2011011140 A2 (DOW CORNING [US]) 27 January 2011 (27.01.2011) paragraphs [0007], [0025], [0027], [0029], [0048]; example 2	1-6, 8, 9, 11-27, 30-37

Continued on the next sheet ☒

*) X Document indicating that the invention is not novel or does not involve an inventive step with respect to the state of the art.
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This document has been electronically signed. **Further information given in the annex** ☐

Date	**Patent Examiner**
12.07.2019	Arja Lipponen
	Telephone 029 509 5000

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PATENT APPLICATION No.
20195142

DOCUMENTS CONSIDERED TO BE RELEVANT, CONTINUED		
Category*)	**Bibliographic data on the document and relevant passages**	**Relevant to claims**
X	JP 2019001961 A (TOAGOSEI CO LTD) 10 January 2019 (10.01.2019) page 20, table & abstract [online] EPOQUENET EPODOC & WPI & machine translation into English by the TXPMTJEA [online] [retrieved 10.7.2019] paragraphs [0055], [0057], [0061]; example, paragraphs [0092], [0098], [0099]	1-3, 5, 6, 8, 9, 11-17, 20-24, 33
X	JP 2006143835 A (HITACHI CHEMICAL CO LTD) 08 June 2006 (08.06.2006) page 11, table & abstract [online] EPOQUENET EPODOC & WPI & machine translation into English by the TXPJPEA [online] [retrieved 10.7.2019] paragraphs [0004], [0013], [0017], [0024], examples, paragraphs [0030]-[0035]	1-37
X	US 5973095 A (HACKER NIGEL P [US] et al.) 26 October 1999 (26.10.1999) example 25, claims 1, 11-13	1-3, 5-7, 9, 11-20, 23
X	JP 2006169391 A (HITACHI CHEMICAL CO LTD) 29 June 2006 (29.06.2006) claims, page 2 & abstract [online] EPOQUENET EPODOC & WPI & machine translation into English by the TXPMTJEA [online] [retrieved 10.7.2019] paragraphs [0032], [0046], [0058]; examples, claims 1-5	1-37
X	EP 0725106 A2 (DOW CORNING ASIA LTD [JP]) 07 August 1996 (07.08.1996) column 4, lines 32; see column 7, lines 5-9; column 8, lines 16-30; reference examples 3, 4, 11, 13; examples 1 and 10; claim 1	1-37