

**SELECTIVE DEPOSITION OF SILICON CONTAINING FILMS UTILIZING
ORGANOAMINOPOLYSILOXANES AND ORGANOAMINOPOLYSILAZANES**

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims priority to United States Provisional Patent Application number 63/587,974, filed on October 4, 2023 and United States Provisional Patent Application number 63/687,676, filed on August 27, 2024, the entire contents of which are incorporated by reference.

FIELD

[002] The present application relates to selective formation of passivation layer on a first surface of a substrate relative to a second surface. In addition, further processing can be used to subsequently deposit a different material on the second surface relative to the first.

BACKGROUND

[003] Selective deposition processes are gaining a lot of momentum mostly because of the limitations of contemporary lithographic processes to enable the fabrication of advanced semiconductor devices based on ever diminishing physical dimensions. Traditionally, patterning in the microelectronics industry has been accomplished using various lithography and etch processes. However, since lithography is becoming exponentially more complex and expensive the use of selective deposition to form self-aligned features is becoming much more attractive. The fabrication of self-aligned via structures would benefit significantly from manufacturable selective deposition processes. Another potential application for selective deposition is gap fill. In gap fill, the dielectric "fill" film is grown selectively from the bottom of a trench towards the top. Selective deposition could be used for other applications such as selective sidewall deposition where films are selectively deposited on exposed surfaces of three-dimensional FINFET structures. This would enable the deposition of a sidewall spacer without the need for complex patterning

steps. Selective deposition processes for metal and metal oxide films that are used as gate dielectrics and capacitor dielectrics would also be of great utility in semiconductor device manufacturing.

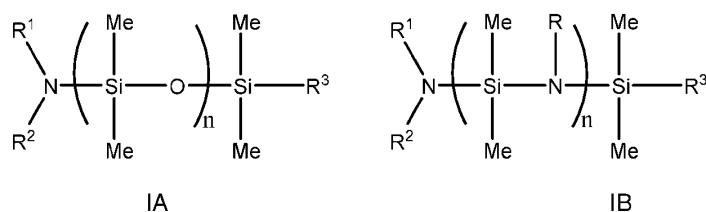
[004] There are previous examples within the technical literature related to the selective formation of surface passivation coatings on wafers with multiple, different chemical surfaces that are exposed. This has been done with the purpose of retarding or preventing the deposition of films through ALD processes on these passivated surfaces, but not preventing deposition on the surfaces where the ALD deposition process is desired to deposit a film. In general, the selectivity of the processes has been less than adequate due to incomplete passivation of the surfaces and / or due to physisorption of ALD precursor molecules and subsequent formation of the ALD film material either within the passivation layer itself or on the surfaces where deposition is not desired.

[005] Selectively passivation of a dielectric over another dielectric to achieve ASD of dielectric on dielectric remains great challenge due to the similarity in their surface chemistry natures, so far relatively few passivation chemistries have been reported that can selectively passivate a dielectric over another dielectric to successfully allow the atomic layer deposition of dielectric films on the other dielectric.

[006] The present disclosure seeks to overcome the limitations of the prior art and provide improved methods for selective deposition of ultra-thin film materials using ALD deposition processes.

SUMMARY

[007] In a first main aspect, a method for passivating a silicon-containing surface of a substrate is provided. The method comprising: (a) providing the substrate in a reaction vessel at temperatures ranging from 20°C to 800°C, the substrate having a first surface comprising a dielectric material with hydroxyl groups and a second surface comprising a different material having fewer hydroxyl groups; (b) forming at least one passivated layer on the first surface by exposing the first surface and the second surface to a passivating composition comprising an organoaminoalkylpolysiloxane or an organoaminoalkylpolysilazane having one of the following formulae:



wherein R^1 and R^2 are each independently selected from a hydrogen, C_1 to C_6 alkyl group with a proviso that R^1 and R^2 cannot be both hydrogen; R^3 and R are each independently selected from hydrogen or methyl; $n=1, 2, 3$; and either R^1 and R^2 are linked to form a cyclic ring structure or R^1 and R^2 are not linked to form a cyclic ring structure; and (c) purging the reactor with inert gas.

[008] In a further aspect of the first main aspect, steps (b) and (c) are repeated to achieve a self-limiting monolayer coverage of the first surface, i.e., the passivating composition reacts all chemically available hydroxyl groups on the first surface.

[009] In a further aspect of the first main aspect, the first surface is selected from the group consisting of silicon oxide, carbon doped silicon oxide, metal oxide, and combinations thereof, and wherein the second surface is selected from the group consisting of silicon nitride or metal nitride.

[0010] In a further aspect of the first main aspect, the second surface comprises a metal or metalloid chosen from the group consisting of ruthenium (Ru), cobalt (Co), copper (Cu), titanium, (Ti), tantalum (Ta), nickel (Ni), tungsten (W), molybdenum (Mo), silicon, and combinations thereof, or wherein the second surface comprises a nitride chosen from the group consisting of silicon nitride, germanium nitride, tantalum nitride (TaN), titanium nitride (TiN), tungsten nitride (WN), tungsten carbonitride (WCN), molybdenum nitride (MoN), copper silicon nitride (CuSiN), and combinations thereof.

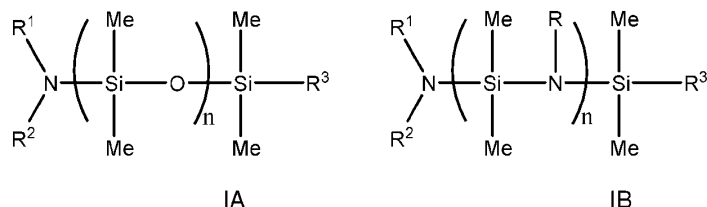
[0011] In a further aspect of the first main aspect, the first surface is selected from the group consisting of metal oxide such as hafnium oxide, zirconium oxide, titanium oxide, and combinations thereof, and wherein the second surface is selected from the group consisting of metal nitride such as titanium nitride, tantalum nitride, tungsten nitride, and combinations thereof.

[0012] In a further aspect of the first main aspect, the passivating composition comprises an organoaminoalkylpolysiloxane chosen from the group consisting of: 1-dimethylamino-1,1,3,3-tetramethyldisiloxane, 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane, 1-dimethylamino-1,1,3,3,5,5-hexamethyltrisiloxane, 1-

dimethylamino-1,1,3,3,5,5,5-heptamethyltrisiloxane, 1-dimethylamino-1,1,3,3,5,5,7,7-octamethyltetrasiloxane, 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane, and combinations thereof.

[0013] In a further aspect of the first main aspect, the passivation composition comprises an organoaminoalkylpolysilazane of Formula IB chosen from the group consisting of: 1-dimethylamino-1,1,3,3,3-pentamethyldisilazane, 1-dimethylamino-1,1,2,3,3,3-hexamethyldisilazane, 1-dimethylamino-1,1,3,3,5,5-hexamethyltrisilazane, 1-dimethylamino-1,1,3,3,5,5,5-heptamethyltrisilazane, 1-dimethylamino-1,1,3,3,5,5,7,7-octamethyltetrasilazane, 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasilazane, and combinations thereof.

[0014] In a second main aspect, a method for selective deposition of a silicon and nitrogen containing film is provided. The method comprising: (a) providing the substrate in a reactor, the substrate having a first surface comprising a dielectric material having hydroxyl groups and a second surface comprising a different dielectric material or metal with fewer or no hydroxyl groups compared to the first surface; (b) forming at least one self-limiting passivated layer on the first surface by exposing the first surface and the second surface to a passivating composition comprising an organoaminoalkylpolysiloxane or an organoaminoalkylpolysilazane having one of the following formulae:



wherein R¹ and R² are independently selected from a hydrogen, C₁ to C₆ alkyl group with a proviso that R¹ and R² cannot be both hydrogen; R³ and R are each independently selected from hydrogen or methyl; n=1, 2, 3; and either R¹ and R² are linked to form a cyclic ring structure or R¹ and R² are not linked to form a cyclic ring structure; (c) purging the reactor with inert gas; (d) introducing a halogenated silicon-containing precursor into the reactor to selectively form a silicon-containing layer on the second surface; (e) purging the reactor using inert gas; (f) introducing a nitrogen source to react with the silicon-containing layer to form a silicon nitride, carbon doped silicon nitride, or silicon oxynitride layer on the second surface; and (g) purging the reactor using inert gas; wherein steps (d) to (g) in this embodiment are repeated to

provide a certain thickness of the silicon nitride or carbon doped silicon nitride or silicon oxynitride layer selectively on the second surface area.

[0015] In a further aspect of the second main aspect, the first surface is selected from the group consisting of silicon oxide and carbon doped silicon oxide, and wherein the second surface comprises silicon nitride.

[0016] In a further aspect of the second main aspect, the first surface is selected from the group consisting of metal oxide such as hafnium oxide, zirconium oxide, titanium oxide, and combinations thereof, and the second surface is selected from the group consisting of metal nitride such as titanium nitride, tantalum nitride, tungsten nitride and combinations thereof.

[0017] In a further aspect of the second main aspect, the second surface comprises a metal chosen from the group consisting of ruthenium (Ru), cobalt (Co), copper (Cu), titanium, (Ti), tantalum (Ta), nickel (Ni), tungsten (W), molybdenum (Mo), and combinations thereof, or wherein the second surface comprises a metal nitride chosen from the group consisting of tantalum nitride (TaN), titanium nitride (TiN), tungsten nitride (WN), tungsten carbonitride (WCN), molybdenum nitride (MoN), copper silicon nitride (CuSiN), and combinations thereof.

[0018] In a further aspect of the second main aspect, step (b) and (c) are repeated to achieve a self-limiting monolayer passivation layer before steps (d) to (g) are conducted.

[0019] In a further aspect of the second main aspect, the self-limiting monolayer passivation layer can range from about 0.2 Å to about 3 Å. In a further aspect of the second main aspect, the self-limiting monolayer passivation layer can range from about 0.2 Å to about 5 Å. In a further aspect of the second main aspect, the self-limiting monolayer passivation layer can range from about 0.2 Å to about 10 Å.

[0020] In a further aspect of the second main aspect, the certain thickness of the silicon nitride or carbon doped silicon nitride or silicon oxynitride film can range from about 1 Å to about 100 Å, or about 5 Å to about 90 Å, or about 5 Å to about 80 Å, or about 5 Å to about 70 Å or about 5 Å to about 60 Å, or about 5 Å to about 50 Å, or about 5 Å to about 40 Å, or about 5 Å to about 30 Å or about 5 Å to about 20 Å.

[0021] In a further aspect of the second main aspect, the organoaminopolysiloxane of Formula IA is selected from the group consisting of 1-dimethylamino-1,1,3,3-tetramethyldisiloxane and 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane.

[0022] In a further aspect of the second main aspect, the organoaminopolysilazane of Formula IB is selected from the group consisting of 1-dimethylamino-1,1,3,3,3-pentamethyldisilazane and 1-dimethylamino-1,1,2,3,3,3-hexamethyldisilazane.

[0023] In a further aspect of the second main aspect, a deposition selectivity of the second surface to the first surface is greater than about 0.3, more preferably greater than about 0.5, and most preferably greater than about 0.6.

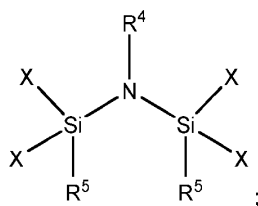
[0024] In a further aspect of the second main aspect, the nitrogen source is selected from the group consisting of for example, ammonia, hydrazine, monoalkylhydrazine, dialkylhydrazine, nitrogen, nitrogen/hydrogen, nitrogen/argon plasma, nitrogen/helium plasma, ammonia plasma, nitrogen plasma, nitrogen/hydrogen plasma, piperazine, organic amines such as tert-butylamine, dimethylamine, diethylamine, isopropylamine, diethylamine plasma, dimethylamine plasma, trimethyl plasma, trimethylamine plasma, ethylenediamine plasma, and an alkoxyamine such as ethanolamine plasma, and mixtures thereof.

[0025] In a further aspect of the second main aspect, the halogenated silicon-containing precursor is selected from the group consisting of: (i) halogenated silanes, (ii) halogenated siloxanes, (iii) halogenated silazanes, and (iv) halogenated carbosilanes.

[0026] In a further aspect of the second main aspect, the halogenated silicon-containing precursor is a halogenated silane of group (i) chosen from the group consisting of: hexachlorodisilane, pentachlorodisilane, tetrachlorodisilane, octachlorotrisilane, dichlorosilane, monochlorosilane, monobromosilane, dibromosilane, tribromosilane, tetrabromosilane, monoiodosilane, diiodosilane, triiodosilane, and tetraiodosilane.

[0027] In a further aspect of the second main aspect, the halogenated silicon-containing precursor is a halogenated siloxane of group (ii) chosen from the group consisting of: hexachlorodisiloxane, pentachlorodisiloxane, tetrachlorodisiloxane, and octachlorotrisiloxane.

[0028] In a further aspect of the second main aspect, the halogenated silicon-containing precursor is a halogenated silazane of group (iii) selected from the group represented by Formula I below:

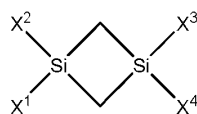


wherein R^4 is selected from the group consisting of hydrogen, a linear or branched C_1 to C_{10} alkyl group, a linear or branched C_3 to C_{10} alkenyl group, a linear or branched C_3 to C_{10} alkynyl group, a C_3 to C_{10} cyclic alkyl group, a C_2 to C_6 dialkylamino group, an electron withdrawing group, and a C_6 to C_{10} aryl group; R^5 is selected from the group consisting of hydrogen, a linear or branched C_1 to C_{10} alkyl group, a linear or branched C_2 to C_6 alkenyl group, a linear or branched C_3 to C_6 alkynyl group, a C_3 to C_{10} cyclic alkyl group, a C_2 to C_6 dialkylamino group, a C_6 to C_{10} aryl group, a linear or branched C_1 to C_6 fluorinated alkyl group, an electron withdrawing group, a C_4 to C_{10} aryl group, and a halide selected from the group consisting of Cl, Br, and I; and X is a halide selected from the group consisting of Cl, Br, and I.

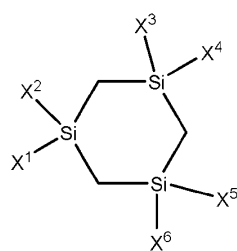
[0029] In a further aspect of the second main aspect, the halogenated silazane is chosen from group (iii) and is chosen from the group consisting of: 1,1,1,3,3,3-hexachloro-disilazane, 1,1,1,3,3-pentachloro-disilazane, 1,1,1,3,3,3-hexachloro-2-methyldisilazane, 1,1,1,3,3,3-hexachloro-2-ethyldisilazane, 1,1,1,3,3,3-hexachloro-2-n-propyldisilazane, 1,1,1,3,3,3-hexachloro-2-iso-propyldisilazane, 1,1,1,3,3,3-hexachloro-2-n-butyldisilazane, 1,1,1,3,3,3-hexachloro-2-iso-butyldisilazane, 1,1,1,3,3,3-hexachloro-2-sec-butyldisilazane, 1,1,1,3,3,3-hexachloro-2-tert-butyldisilazane, 1,1,1,3,3,3-hexabromo-2-methyldisilazane, 1,1,1,3,3,3-bromo-2-ethyldisilazane, 1,1,1,3,3,3-bromo-2-n-propyldisilazane, 1,1,1,3,3,3-bromo-2-iso-propyldisilazane, 1,1,1,3,3,3-bromo-2-n-butyldisilazane, 1,1,1,3,3,3-bromo-2-iso-butyldisilazane, 1,1,1,3,3,3-bromo-2-sec-butyldisilazane, 1,1,1,3,3,3-bromo-2-tert-butyldisilazane, 1,1,1,3,3,3-hexaiodo-2-methyldisilazane, 1,1,1,3,3,3-iodo-2-ethyldisilazane, 1,1,1,3,3,3-iodo-2-n-propyldisilazane, 1,1,1,3,3,3-iodo-2-iso-propyldisilazane, 1,1,1,3,3,3-iodo-2-n-butyldisilazane, 1,1,1,3,3,3-iodo-2-iso-butyldisilazane, 1,1,1,3,3,3-iodo-2-sec-butyl-disilazane, 1,1,1,3,3,3-iodo-2-tert-butyl-disilazane, 1,1,1,3,3-pentachloro-2-methyldisilazane, 1,1,1,3,3-pentachloro-2-ethyldisilazane, 1,1,1,3,3-pentachloro-2-n-propyldisilazane, 1,1,1,3,3-pentachloro-2-iso-propyldisilazane, 1,1,1,3,3-pentachloro-2-methyl-3-methyl-disilazane, 1,1,1,3,3-pentachloro-2-ethyl-3-methyldisilazane, 1,1,1,3,3-pentachloro-2-n-propyl-3-

methyldisilazane, 1,1,1,3,3-pentachloro-2-iso-propyl-3-methyldisilazane, 1,1,3,3-tetrachloro-2-methyldisilazane, 1,1,3,3-tetrachloro-2-ethyldisilazane, 1,1,3,3-tetrachloro-2-n-propyldisilazane, 1,1,3,3-tetrachloro-2-iso-propyldisilazane, 1,1,3,3-tetrachloro-2-n-butyldisilazane, 1,1,3,3-tetrachloro-2-iso-butyldisilazane, 1,1,3,3-tetrachloro-2-sec-butyldisilazane, 1,1,3,3-tetrachloro-2-tert-butyldisilazane, 1,1,3,3-tetrabromo-2-methyldisilazane, 1,1,3,3-tetrabromo-2-ethyldisilazane, 1,1,3,3-tetrabromo-2-n-propyldisilazane, 1,1,3,3-tetrabromo-2-iso-propyldisilazane, 1,1,3,3-tetrabromo-2-n-butyldisilazane, 1,1,3,3-tetrabromo-2-iso-butyldisilazane, 1,1,3,3-tetrabromo-2-sec-butyldisilazane, 1,1,3,3-tetrachloro-2-tert-butyldisilazane, 1,1,3,3-tetraiodo-2-methyldisilazane, 1,1,3,3-tetraiodo-2-ethyldisilazane, 1,1,3,3-tetraiodo-2-n-propyldisilazane, 1,1,3,3-tetraiodo-2-iso-propyldisilazane, 1,1,3,3-tetraiodo-2-n-butyldisilazane, 1,1,3,3-tetraiodo-2-iso-butyldisilazane, 1,1,3,3-tetraiodo-2-sec-butyldisilazane, 1,1,3,3-tetraiodo-2-tert-butyldisilazane, 1,1,3,3-tetrachloro-2-cyclopentyldisilazane, 1,1,3,3-tetrachloro-2-cyclohexyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-cyclopentyl-2-cyclopentyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-cyclohexyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-methyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-tetrachloro-2-ethyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-n-propyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-iso-propyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-n-butyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-iso-butyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-sec-butyldisilazane, and 1,1,3,3-tetrachloro-1,3-dimethyl-2-tert-butyldisilazane.

[0030] In a further aspect of the second main aspect, the halogenated silicon-containing precursor is a halogenated carbosilane of group (iv) selected from the group consisting of: silicon compounds having one or two Si-C-Si linkages. Preferred carbosilanes of group iv include those represented by Formulae II, and III:



II



III

wherein X^1 , X^2 , X^3 , X^4 , X^5 , and X^6 are each independently chosen from a H atom; a halide atom selected from F, Cl, Br, and I; isocyanate; an amino group having the

formula NR^5R^6 wherein R^5 and R^6 are independently selected from the group consisting of hydrogen, a C_{1-10} linear alkyl group; a C_{3-10} branched alkyl group; a C_{3-10} cyclic alkyl group; a C_{3-10} alkenyl group; a C_{4-10} aryl group; and a C_{4-10} heterocyclic group; In some embodiments of Formula I, II, or both I and II, and one or more of substituents X^1 , X^2 , X^3 , X^4 , X^5 , and X^6 is linked to form a substituted or unsubstituted, saturated or unsaturated, cyclic group. In one particular embodiment of Formula II, III, or both II and III, any one or more of substituents X^1 , X^2 , X^3 , X^4 , X^5 , and X^6 is either halide or amino group described above. For II, X^1 , X^2 , X^3 , X^4 , X^5 , and X^6 cannot be all amino groups. In certain embodiments of Formula II or III, R^5 and R^6 in the amino group having the formula NR^5R^6 are linked together to form a ring. In one particular embodiment, R^5 and R^6 are selected from a linear or a branched C_3 to C_6 alkyl group and are linked to form a cyclic ring. In alternative embodiments of Formula II or III, R^5 and R^6 are not linked together to form a ring. In other embodiments, R^5 and R^6 are different.

[0031] In a further aspect of the second main aspect, the halogenated silicon-containing precursor is a halogenated carbosilane chosen from the group consisting of: 1,1,1,3,3,3-hexachloro-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-methyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2,2-dimethyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-ethyl-1,3-disilapropane, 1,1,1,3,3,5,5-octachloro-1,3,5-trisilapentane, 1,1,3,3,5,5-hexachloro-1,5-dimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane, 1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane, and 1,1,5,5-tetrachloro-1,3,5-trisilapentane, 1-chloro-1,3-disilacyclobutane, 1-bromo-1,3-disilacyclobutane, 1-iodo-1,3-disilacyclobutane, 1,3-dichloro-1,3-disilacyclobutane, 1,3-dibromo-1,3-disilacyclobutane, 1,3-diiodo-1,3-disilacyclobutane, 1,1-dichloro-1,3-disilacyclobutane, 1,1-dibromo-1,3-disilacyclobutane, 1,1-diiodo-1,3-disilacyclobutane, 1,1,3-trichloro-1,3-disilacyclobutane, 1,1,3-tribromo-1,3-disilacyclobutane, 1,1,3-triiodo-1,3-disilacyclobutane, 1,1,3,3-tetrachloro-1,3-disilacyclobutane, 1,1,3,3-tetrabromo-1,3-disilacyclobutane, 1,1,3,3-tetraiodo-1,3-disilacyclohexane, 1,1,3,3-tetra(dimethylamino)-1,3-disilacyclobutane, 1,3-bis(dimethylamino)-1,3-dichloro-1,3-disilacyclobutane, 1-(dimethylamino)-1,3,3-trichloro-1,3-disilacyclobutane, 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, 1,3-bis(dimethylamino)-1,3-dimethyl-1,3-disilacyclobutane, 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane, 1,1,3,3-tetrachloro-1,3,5-trisilacyclohexane, 1,3,5-trichloro-1,3,5-trisilacyclohexane, and combinations thereof.

[0032] The embodiments of the disclosure can be used alone or in combination with each other.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033] The accompanying drawings, which are included to provide a further understanding of the disclosed subject matter and are incorporated in and constitute a part of this specification, illustrate embodiments of the disclosed subject matter and together with the description serve to explain the principles of the disclosed subject matter. In the drawings:

[0034] FIG. 1 illustrates an exemplary process comprising: a surface pre-clean, oxide passivation, and selective deposition wherein a dielectric film is selectively deposited on a nitride film, while the first surface (comprising oxide) is passivated;

[0035] FIG. 2 illustrates an exemplary process comprising: a surface pre-clean, silicon oxide passivation, and selective deposition wherein a dielectric film is selectively deposited on a silicon nitride film, while the first surface (silicon oxide) is passivated; and

[0036] FIG. 3 illustrates an exemplary process comprising: a surface pre-clean, zirconium oxide passivation, and selective deposition wherein a dielectric film is selectively deposited on a titanium nitride film, while the first surface (zirconium oxide) is passivated.

DETAILED DESCRIPTION

[0037] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0038] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the disclosure (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (i.e., meaning "including, but not limited to,") unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All

methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the disclosure and does not pose a limitation on the scope of the claims unless otherwise stated explicitly. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the subject matter of this disclosure.

[0039] Preferred embodiments of this disclosure are described herein, including the best mode known to the inventors for carrying out the claimed subject matter. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventor expects skilled artisans to employ such variations as appropriate, and the inventor intends for the claimed subject matter to be practiced otherwise than as specifically described herein. Accordingly, this disclosure includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the claimed subject matter unless otherwise indicated herein or otherwise clearly contradicted by context.

[0040] There are a variety of methods that could be used for selective depositions. Embodiments of the disclosure are directed to methods that employ surface deactivation by taking advantage of the surface chemistry of two different surfaces. Since two different surfaces will have different reactive handles, the differences can be taken advantage of by utilizing molecules that will react with one surface (to deactivate that surface) and not react with the other surface.

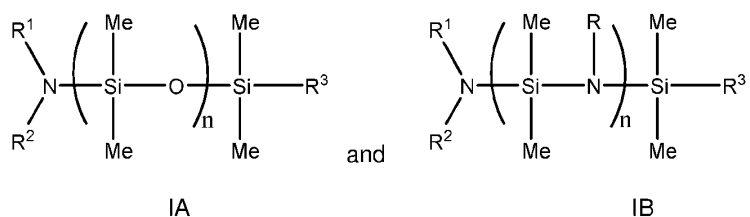
[0041] In this disclosure, it has been conceived and demonstrated that a dielectric such as silicon dioxide can be selectively passivated using an organoaminopolysiloxane or an organoaminopolysilazane, therefore allowing great inhibition of dielectric growth on passivated silicon oxide surface, but highly selective growth of dielectric film such as silicon-containing dielectric film on dielectric surface such as silicon nitride at relative higher temperatures.

[0042] Various aspects of the disclosure will now be described with reference to the drawings and tables disclosed herein, if applicable, with like reference numbers referring to like elements, unless specified otherwise.

[0043] Selective deposition processes are gaining a lot of momentum mostly because of the limitations of contemporary lithographic processes to enable the fabrication of advanced semiconductor devices based on ever diminishing physical dimensions. Traditionally, patterning in the microelectronics industry has been accomplished using various lithography and etch processes. However, since lithography is becoming exponentially more complex and expensive the use of selective deposition to form self-aligned features is becoming much more attractive. The fabrication of self-aligned via structures would benefit significantly from manufacturable selective deposition processes. Another potential application for selective deposition is gap fill. In gap fill, the dielectric "fill" film is grown selectively from the bottom of a trench towards the top. Selective deposition could be used for other applications such as selective sidewall deposition where films are selectively deposited on exposed surfaces of three-dimensional FIN-FET structures. This would enable the deposition of a sidewall spacer without the need for complex patterning steps. Selective deposition processes for metal and metal oxide films that are used as gate dielectrics and capacitor dielectrics would also be of great utility in semiconductor device manufacturing.

[0044] There are previous examples within the technical literature related to the selective formation of surface passivation coatings on wafers with multiple, different chemical surfaces that are exposed. This has been done with the purpose of retarding or preventing the deposition of films through ALD processes on these passivated surfaces, but not preventing deposition on the surfaces where the ALD deposition process is desired to deposit a film. In general, the selectivity of the processes has been less than adequate due to incomplete passivation of the surfaces and / or due to physisorption of ALD precursor molecules and subsequent formation of the ALD film material either within the passivation layer itself or on the surfaces where deposition is not desired.

[0045] In a first aspect, a method is provided for passivating surface comprising predominantly hydroxyl groups. The method comprises: (a) providing the substrate in a reaction vessel at temperatures ranging from 20°C to 800°C, the substrate having a first surface comprising a dielectric material with hydroxyl groups and a second surface comprising a material having less amount of hydroxyl groups; (b) forming at least one passivated layer on the first surface by exposing the first surface and the second surface to a passivating composition comprising an organoaminoalkylpolysiloxane or organoaminoalkylpolysilazane having one of the following formulae:



wherein R¹ and R² are each independently selected from a hydrogen, C₁ to C₆ alkyl group with a proviso that R¹ and R² cannot be both hydrogen; R³ and R are each independently selected from hydrogen or methyl with a proviso that R¹ and R² cannot be both hydrogen; n=1, 2, 3; and either R¹ and R² are linked to form a cyclic ring structure or R¹ and R² are not linked to form a cyclic ring structure; (c) purging the reactor with inert gas; Steps (b) and (c) can be repeated to achieve self-limiting monolayer coverage of the first surface.

[0046] In an illustrated embodiment, organoaminopolysiloxanes and organoaminopolysilazanes are used to selectively passivate the oxide surface versus a nitride surface. This process is depicted in FIG. 1. The process results in the selectivity to grow thicker dielectric film on the nitride surface.

Processes:

[0047] An illustrative process 100 is shown in FIG. 1. Step 1 comprises a pre-cleaning of the first surface 102 (comprising an oxide, preferably SiO₂) and the second surface 104 (comprising a nitride, preferably silicon nitride). The pre-cleaning is preferably done with an acid, H₂, high temperature, or a combination thereof. Following the pre-clean, preferably, the first surface 102 and the second surface 104 are co-planar, as a result of a chemical mechanical planarization (CMP) as shown in FIG. 1 prior to the pre-cleaning step.

[0048] Step 2 comprises passivation of the oxide surface 102 by exposing the dielectric to form a passivating/blocking organic layer 106 employing a passivating composition preferably comprising an organoaminopolysiloxane such as 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane. Following passivation of the first surface 102, Step 3 includes depositing a dielectric layer 108 is formed on the nitride surface 104, preferably by ALD of a silicon precursor and a nitrogen precursor.

[0049] Preferably, the first surface is an oxide, which can be a silicon-containing or metal-containing dielectric material comprising predominantly hydroxyl groups is selected from the group consisting of silicon oxide, carbon doped silicon oxide, and

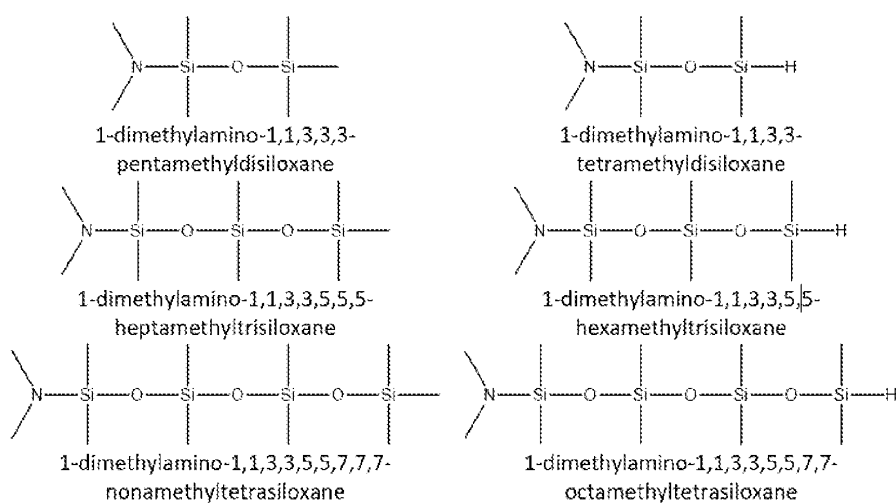
metal oxide, while the second surface comprising a dielectric material is selected from the group consisting of silicon nitride, amorphous silicon.

[0050] The first surface may include a metal oxide such as hafnium oxide, zirconium oxide, titanium oxide, or combinations thereof.

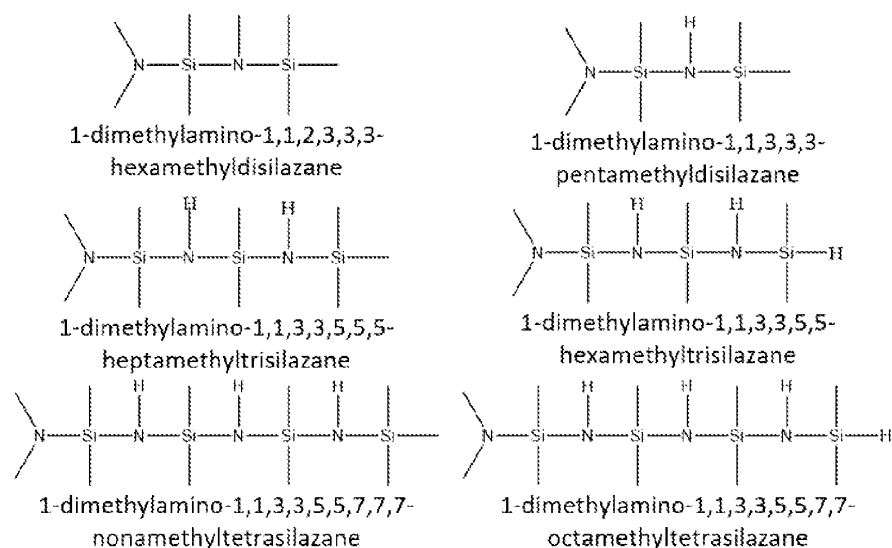
[0051] The second surface may comprise a metal, including but are not limited to, ruthenium (Ru), cobalt (Co), copper (Cu), titanium, (Ti), tantalum (Ta), nickel (Ni), tungsten (W), molybdenum (Mo), etc., and combinations thereof. Examples of metal nitride films include, but are not limited to, tantalum nitride (TaN), titanium nitride (TiN), tungsten nitride (WN), tungsten carbonitride (WCN), molybdenum nitride (MoN), copper silicon nitride (CuSiN), etc., and combinations thereof.

[0052] The second surface may include a metal nitride such as titanium nitride, tantalum nitride, tungsten nitride, or combinations thereof.

[0053] The examples of preferred organoaminoalkylpolysiloxanes IA wherein R¹ and R² are both methyl, R³ is hydrogen or methyl, include, but are not limited to, the following compounds:

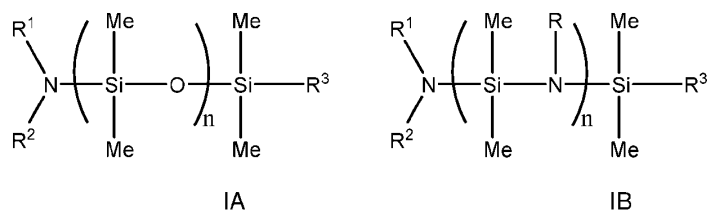


[0054] The examples of preferred organoaminoalkylpolysilazanes organoaminoalkylpolysiloxanes IB wherein R¹ and R² are both methyl, R and R³ are hydrogen or methyl, include, but are not limited to, the following compounds:



[0055] In a second aspect, a method is provided for selective deposition of silicon nitride, carbon doped silicon nitride, or silicon oxynitride. The method comprises:

- (a) providing the substrate in a reaction vessel at temperature at 500 °C or higher, the substrate having a first surface comprising a dielectric material with hydroxyl groups and a second surface comprising a different material having fewer hydroxyl groups, wherein the second surface preferably comprises silicon nitride;
- (b) forming at least one passivated layer on the first surface by exposing the first surface and the second surface to a passivating composition comprising an organoaminoalkylpolysiloxane or organoaminoalkylpolysilazane having one of the following formulae:



wherein R¹ and R² are each independently selected from a hydrogen, C₁ to C₆ alkyl group with a proviso that R¹ and R² cannot be both hydrogen; R³ and R are each

independently selected from hydrogen or methyl with a proviso that R^1 and R^2 cannot be both hydrogen; $n=1, 2, 3$; and either R^1 and R^2 are linked to form a cyclic ring structure or R^1 and R^2 are not linked to form a cyclic ring structure;

- (c) purging the reactor with inert gas;
- (d) introducing a halogenated silicon-containing precursor into the reactor to react with the silicon nitride or carbon doped silicon nitride film to form a silicon-containing layer;
- (e) purging the reactor using inert gas;
- (f) introducing a nitrogen source to react with the silicon-containing layer to form a silicon nitride or carbon doped silicon nitride layer;
- (g) purging the reactor using inert gas

[0056] Steps (d) to (g) in this embodiment may be repeated to provide a certain thickness of silicon nitride or carbon doped silicon nitride or silicon oxynitride. In some embodiments, step (b) and (c) can be repeated to achieve a self-limiting monolayer passivation layer (i.e. saturation passivation layer) before Steps (d) to (g) are conducted.

[0057] The nitrogen source is selected from the group consisting of for example, ammonia, hydrazine, monoalkylhydrazine, dialkylhydrazine, nitrogen, nitrogen/hydrogen, nitrogen/argon plasma, nitrogen/helium plasma, ammonia plasma, nitrogen plasma, nitrogen/hydrogen plasma, organic amines such as tert-butylamine, dimethylamine, diethylamine, isopropylamine, diethylamine plasma, dimethylamine plasma, trimethyl plasma, trimethylamine plasma, ethylenediamine plasma, and an alkoxyamine such as ethanolamine plasma, and mixtures thereof. In yet other embodiments, the nitrogen-containing source comprises an ammonia plasma, a plasma comprising nitrogen and argon, a plasma comprising nitrogen and helium or a plasma comprising hydrogen and nitrogen source gas.

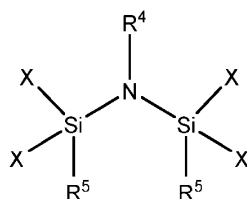
[0058] Preferably, the halogenated silicon-containing compounds can be selected from the group consisting of: (i) halogenated silanes, (ii) halogenated siloxanes, (iii) halogenated silazanes, and (iv) halogenated carbosilanes.

[0059] The halogenated silanes of group (i) include but are not limited to, hexachlorodisilane, pentachlorodisilane, tetrachlorodisilane, octachlorotrisilane,

dichlorosilane, monochlorosilane, monobromosilane, dibromosilane, tribromosilane, tetrabromosilane, monoiodosilane, diiodosilane, triiodosilane, tetraiodosilane.

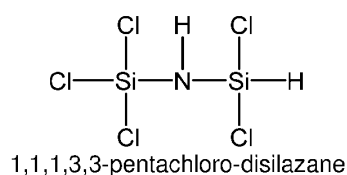
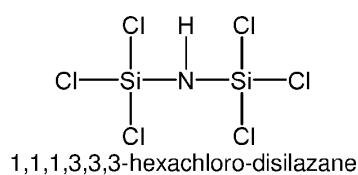
[0060] The halogenated siloxanes of group (ii) include, but are not limited to, hexachlorodisiloxane, pentachlorodisiloxane, tetrachlorodisiloxane, octachlorotrisiloxane.

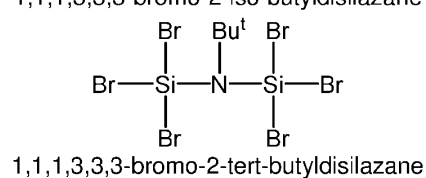
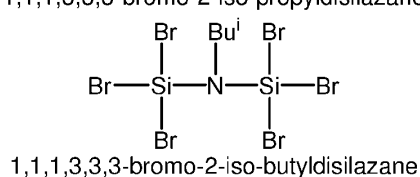
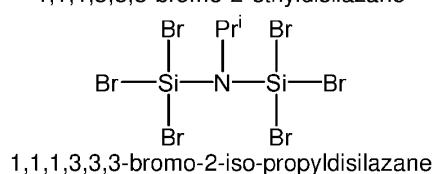
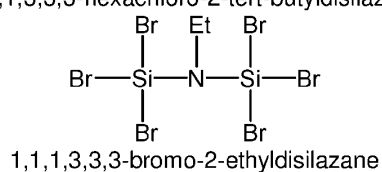
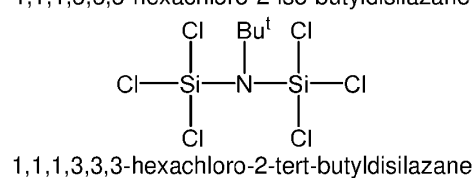
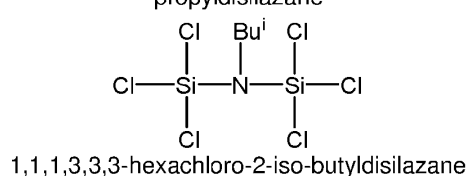
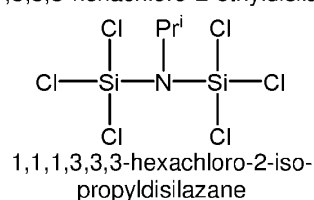
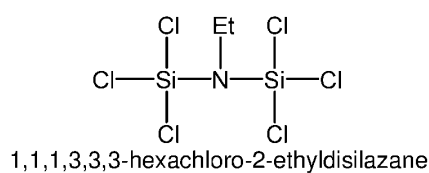
[0061] The halogenated silazanes of group (iii) are selected from the groups represented by the following Formula I below:

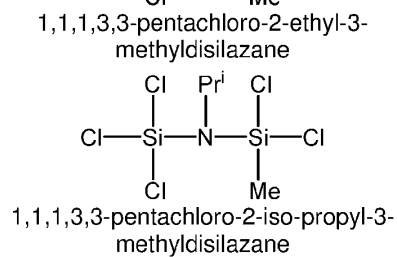
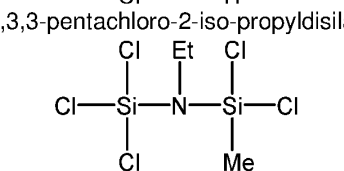
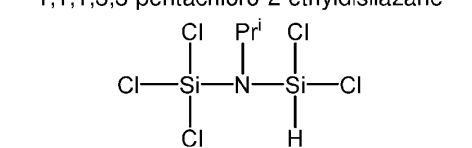
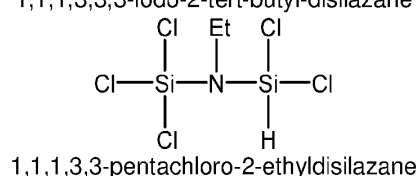
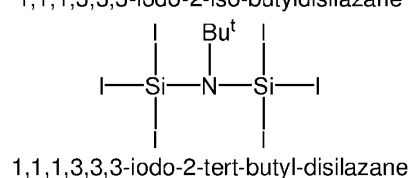
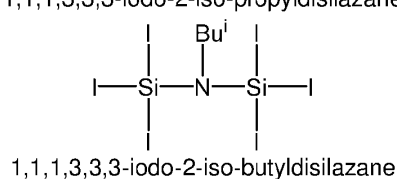
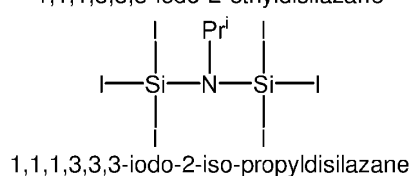
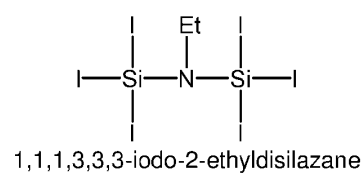
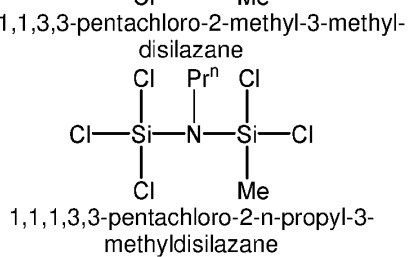
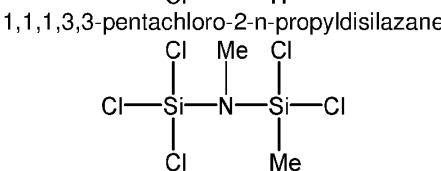
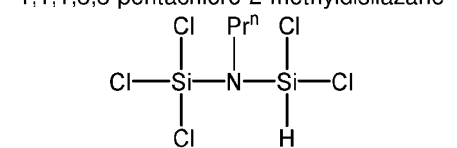
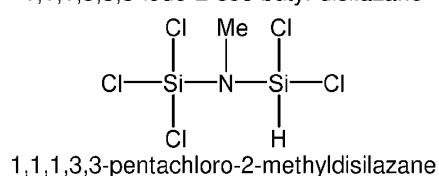
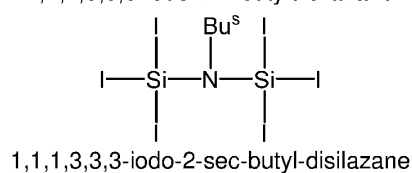
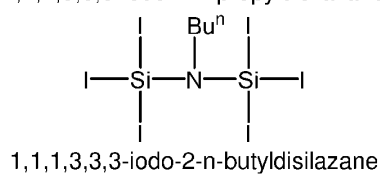
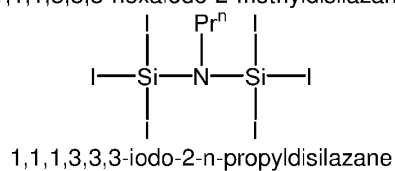
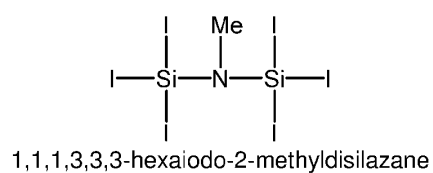


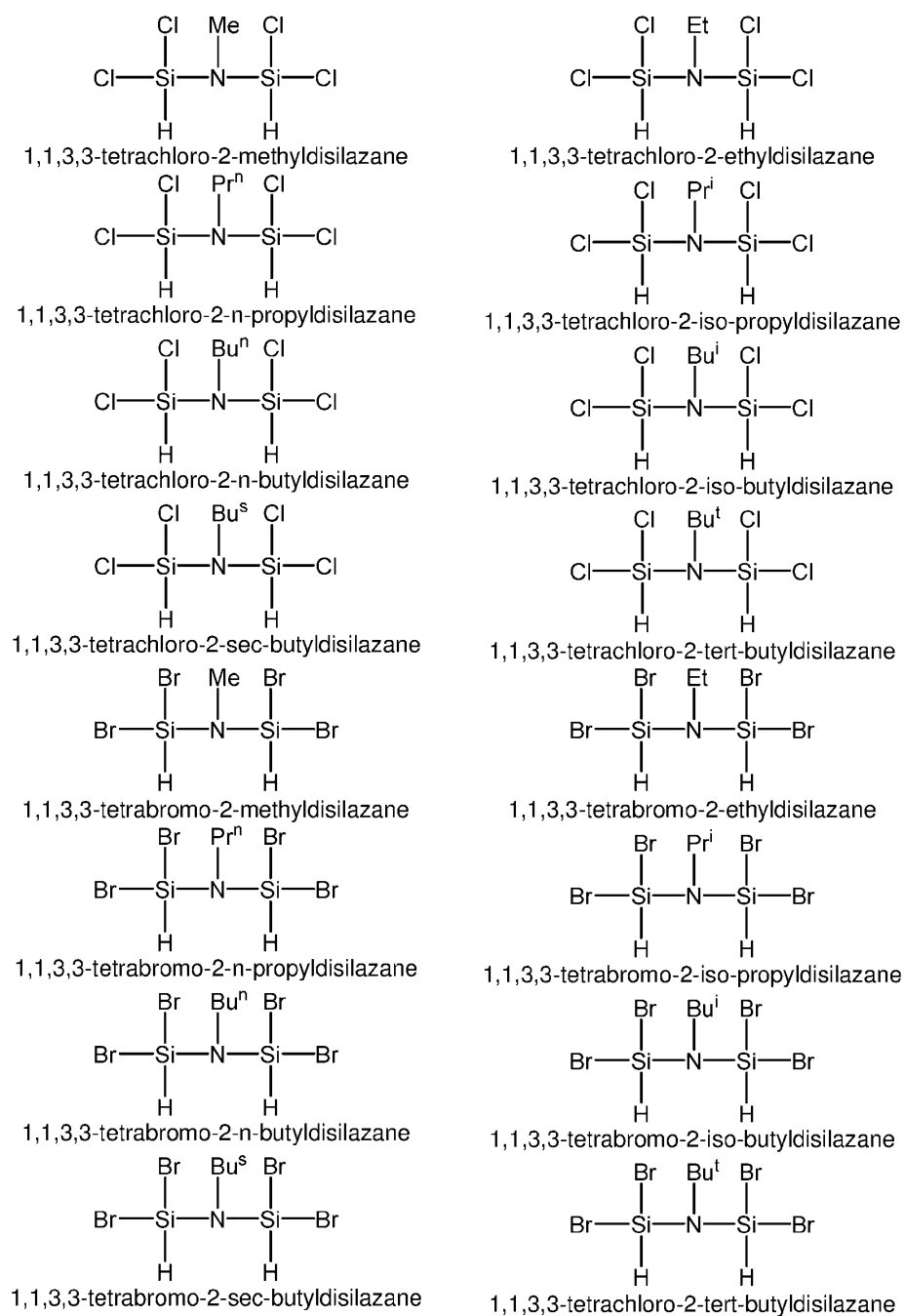
wherein R^4 is selected from the group consisting of hydrogen, a linear or branched C_1 to C_{10} alkyl group, a linear or branched C_3 to C_{10} alkenyl group, a linear or branched C_3 to C_{10} alkynyl group, a C_3 to C_{10} cyclic alkyl group, a C_2 to C_6 dialkylamino group, an electron withdrawing group, and a C_6 to C_{10} aryl group; R^5 is selected from the group consisting of hydrogen, a linear or branched C_1 to C_{10} alkyl group, a linear or branched C_2 to C_6 alkenyl group, a linear or branched C_3 to C_6 alkynyl group, a C_3 to C_{10} cyclic alkyl group, a C_2 to C_6 dialkylamino group, a C_6 to C_{10} aryl group, a linear or branched C_1 to C_6 fluorinated alkyl group, an electron withdrawing group, a C_4 to C_{10} aryl group, and a halide selected from the group consisting of Cl, Br, and I; and X is a halide selected from the group consisting of Cl, Br, and I.

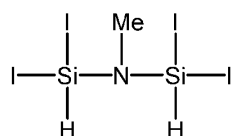
[0062] Examples of group (iii) of halogenated silazanes may be represented in structures below:



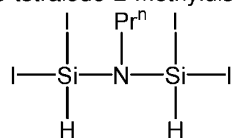




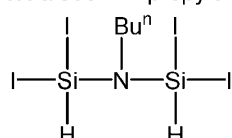




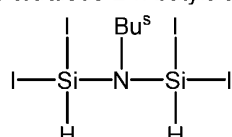
1,1,3,3-tetraiodo-2-methyldisilazane



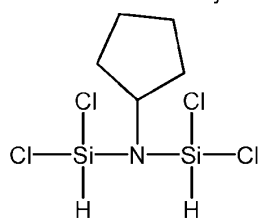
1,1,3,3-tetraiodo-2-n-propyldisilazane



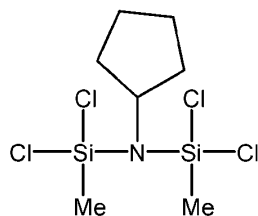
1,1,3,3-tetraiodo-2-n-butyldisilazane



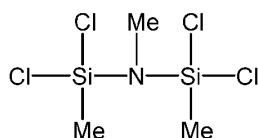
1,1,3,3-tetraiodo-2-sec-butyldisilazane



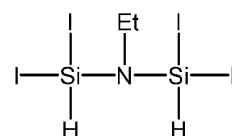
1,1,3,3-tetrachloro-2-cyclopentyldisilazane



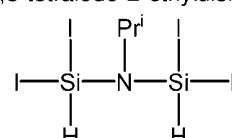
1,1,3,3-tetrachloro-1,3-dimethyl-2-cyclopentyl-2-cyclopentyldisilazane



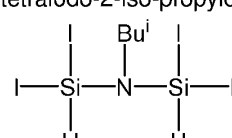
1,1,3,3-tetrachloro-1,3-dimethyl-2-methyldisilazane



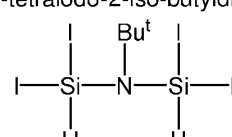
1,1,3,3-tetraiodo-2-ethyldisilazane



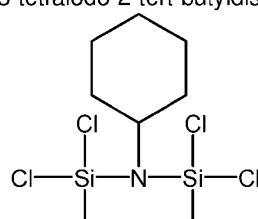
1,1,3,3-tetraiodo-2-iso-propyldisilazane



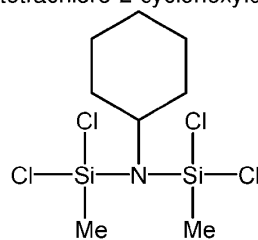
1,1,3,3-tetraiodo-2-iso-butyldisilazane



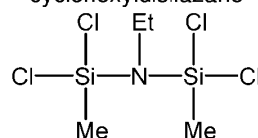
1,1,3,3-tetraiodo-2-tert-butyldisilazane



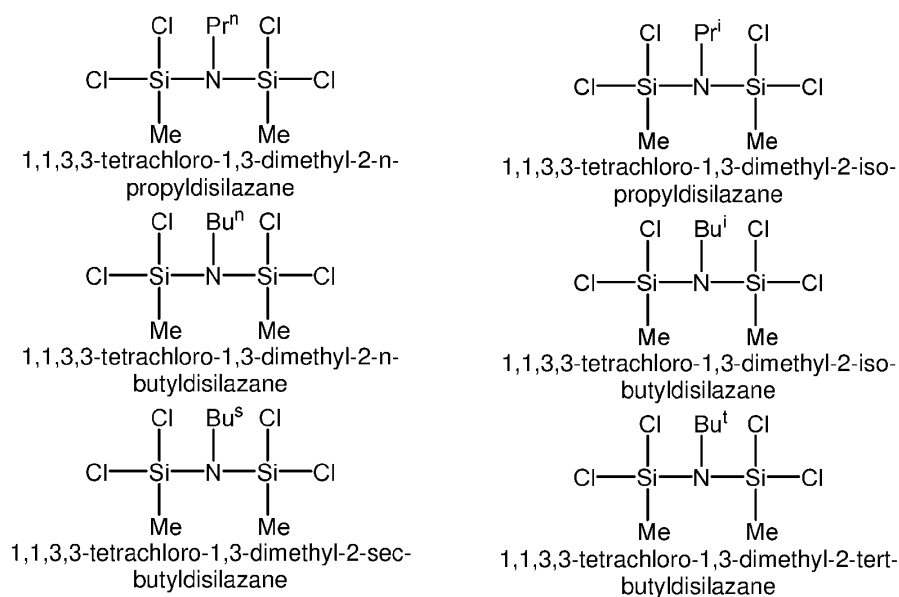
1,1,3,3-tetrachloro-2-cyclohexyldisilazane



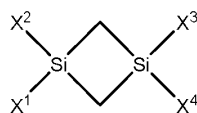
1,1,3,3-tetrachloro-1,3-dimethyl-2-cyclohexyldisilazane



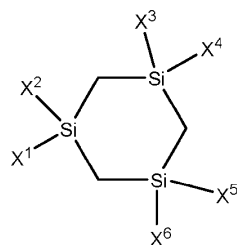
1,1,3,3-tetrachloro-1,3-dimethyl-tetrachloro-2-ethyldisilazane



[0063] The halogenated carbosilanes of group (iv) are selected from the group consisting of silicon compounds having one or two Si-C-Si linkages. Exemplary carbosilanes of group iv include those represented by Formulae II, and III:



II

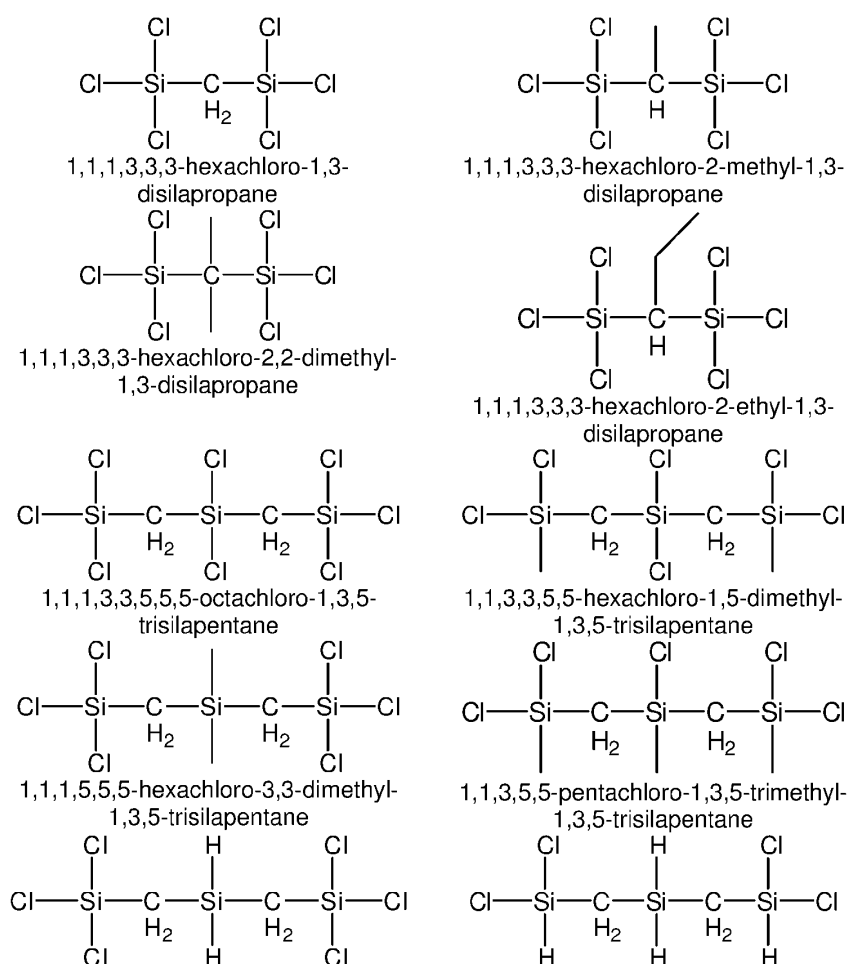


III

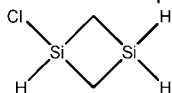
wherein X^1 , X^2 , X^3 , X^4 , X^5 , and X^6 are each independently chosen from a H atom; a halide atom selected from F, Cl, Br, and I; isocyanate; an amino group having the formula NR^5R^6 wherein R^5 and R^6 are independently selected from the group consisting of hydrogen, a C_{1-10} linear alkyl group; a C_{3-10} branched alkyl group; a C_{3-10} cyclic alkyl group; a C_{3-10} alkenyl group; a C_{4-10} aryl group; and a C_{4-10} heterocyclic group; In some embodiments of Formula I, II, or both I and II, and one or more of substituents X^1 , X^2 , X^3 , X^4 , X^5 , and X^6 is linked to form a substituted or unsubstituted,

saturated or unsaturated, cyclic group. In one particular embodiment of Formula II, III, or both II and III, any one or more of substituents X^1 , X^2 , X^3 , X^4 , X^5 , and X^6 is either halide or amino group described above. For II, X^1 , X^2 , X^3 , X^4 , X^5 , and X^6 cannot be all amino groups. In certain embodiments of Formula II or III, R^5 and R^6 in the amino group having the formula NR^5R^6 are linked together to form a ring. In one particular embodiment, R^5 and R^6 are selected from a linear or a branched C_3 to C_6 alkyl group and are linked to form a cyclic ring. In alternative embodiments of Formula II or III, R^5 and R^6 are not linked together to form a ring. In other embodiments, R^5 and R^6 are different.

[0064] Examples of group (iv) halogenated carbosilanes may be represented by the structures below:

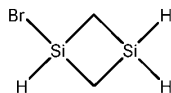


1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane

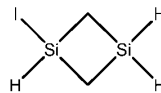


1-chloro-1,3-disilacyclobutane

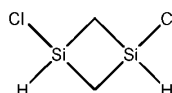
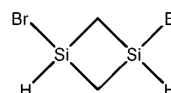
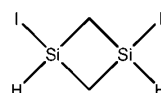
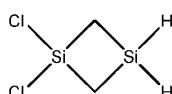
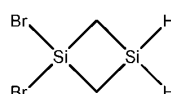
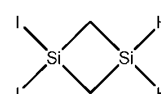
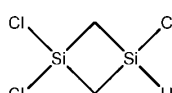
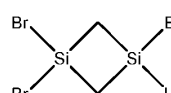
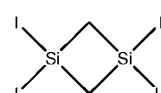
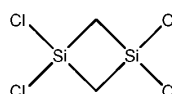
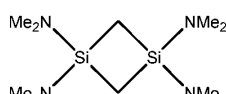
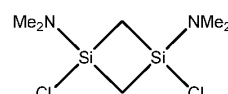
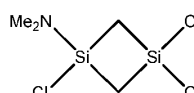
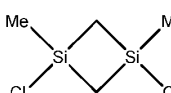
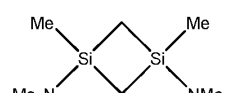
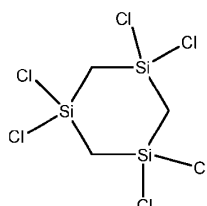
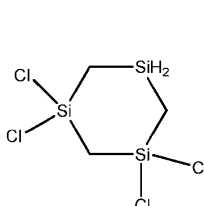
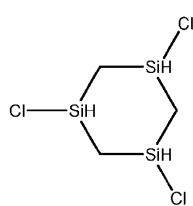
1,1,5,5-tetrachloro-1,3,5-trisilapentane



1-bromo-1,3-disilacyclobutane



1-iodo-1,3-disilacyclobutane

1,3-dichloro-
1,3-disilacyclobutane1,3-dibromo-
1,3-disilacyclobutane1,3-diiodo-
1,3-disilacyclobutane1,1-dichloro-
1,3-disilacyclobutane1,1-dibromo-
1,3-disilacyclobutane1,1-diiodo-
1,3-disilacyclobutane1,1,3-trichloro-
1,3-disilacyclobutane1,1,3-tribromo-
1,3-disilacyclobutane1,1,3-triiodo-
1,3-disilacyclobutane1,1,3,3-tetrachloro-
1,3-disilacyclobutane1,1,3,3-tetra(dimethylamino)-1,3-
disilacyclobutane1,3-bis(dimethylamino)-1,3-dichloro-
1,3-disilacyclobutane1-(dimethylamino)-1,3,3-trichloro-
1,3-disilacyclobutane1,3-dichloro-1,3-dimethyl-
1,3-disilacyclobutane1,3-bis(dimethylamino)-1,3-dimethyl-
1,3-disilacyclobutane1,1,3,3,5,5-hexachloro-
1,3,5-trisilacyclohexane1,1,3,3-tetrachloro-
1,3,5-trisilacyclohexane1,3,5-trichloro-
1,3,5-trisilacyclohexane

[0065] As described above, a need exists in the art to deposit dielectric materials, such as silicon nitride or carbon doped silicon nitride, selectively on top of a dielectric surface relative to a different dielectric surface in a semiconductor manufacturing process using a thermal process without using a plasma at temperatures ranging from 500 °C to 800 °C with high selectivity. The selectivity is defined as $(\text{the thickness of silicon-containing film on the second surface} - \text{the thickness of silicon-containing film on the first surface}) / (\text{the thickness of silicon-containing film on the first surface} + \text{the thickness of silicon-containing film on the second surface})$. The selectivity is preferred to be 30% or greater, or 40% or greater, or 50% or greater, 60% or greater.

[0066] As described above, there is also a need in the art to deposit silicon-containing dielectric materials, such as silicon carbonitride, carbon doped silicon oxide, carbon doped silicon oxynitride selectively on top of a second surface relative to a first surface of different dielectric in a semiconductor manufacturing process using a thermal process without using a plasma at temperatures ranging from 100 °C to 800 °C with high selectivity. The selectivity is defined as $(\text{the thickness of silicon-containing film on the second surface} - \text{the thickness of silicon-containing film on the first surface}) / (\text{the thickness of silicon-containing film on the first surface} + \text{the thickness of silicon-containing film on the second surface})$. The selectivity is preferred to be 30% or greater, or 40% or greater, or 50% or greater, 60% or greater.

[0067] Accordingly, disclosed herein in a first aspect of the invention, is a novel, and non-obvious, selective thermal atomic layer deposition (ALD) process, that selectively deposits dielectric materials on top of a dielectric material, in an ALD reactor.

[0068] In a preferred embodiment of this method, the dielectric material may be selected from the group consisting of silicon oxide, carbon doped silicon oxide, silicon oxynitride, carbon doped oxynitride, silicon nitride, and metal oxide such as zirconium oxide, hafnium oxide, silicon doped zirconium oxide, silicon doped hafnium oxide, or any other high k materials. The metal in a preferred embodiment may be selected from the group consisting of cobalt, aluminum, copper, tantalum, ruthenium, molybdenum, tungsten, platinum, iridium, nickel, titanium, silver, gold, or a combination thereof.

[0069] As used in this specification and the appended claims, the term “substrate” and “wafer” are used interchangeably, both referring to a surface, or portion of a surface, upon which a process acts. It will also be understood by those skilled in the

art that reference to a substrate can also refer to only a portion of the substrate, unless the context clearly indicates otherwise. Additionally, reference to depositing on a substrate can mean both a bare substrate and a substrate with one or more films or features deposited or formed thereon.

[0070] A “substrate” as used herein, refers to any substrate or material surface formed on a substrate upon which film processing is performed during a fabrication process. For example, a substrate surface on which processing can be performed include materials such as silicon, silicon oxide, strained silicon, silicon on insulator (SOI), carbon doped silicon oxides, silicon nitride, doped silicon, germanium, gallium arsenide, glass, sapphire, and any other materials such as metals, metal nitrides, metal alloys, and other conductive materials, depending on the application. Substrates include, without limitation, semiconductor wafers. Substrates may be exposed to a pretreatment process to polish, etch, reduce, oxidize, hydroxylate, anneal and/or bake the substrate surface. In addition to film processing directly on the surface of the substrate itself, in the present disclosure, any of the film processing steps disclosed may also be performed on an underlayer formed on the substrate as disclosed in more detail below, and the term “substrate surface” is intended to include such underlayer as the context indicates. For example, where a film/layer or partial film/layer has been deposited onto a substrate surface, the exposed surface of the newly deposited film/layer becomes the substrate surface. What a given substrate surface comprises will depend on what films are to be deposited, as well as the particular chemistry used. In one or more embodiments, the first substrate surface will comprise a metal, and the second substrate surface will comprise a dielectric, or vice versa. In some embodiments, a substrate surface may comprise certain functionality (e.g., -OH, -NH, etc.).

[0071] Likewise, the films that can be used in the methods described herein are quite varied. In some embodiments, the films may comprise, or consist essentially of a metal or metal nitride. Examples of metal films include, but are not limited to, ruthenium (Ru), cobalt (Co), copper (Cu), titanium, (Ti), tantalum (Ta), nickel (Ni), tungsten (W), molybdenum (Mo), etc., and combinations thereof. Examples of metal nitride films include, but are not limited to, tantalum nitride (TaN), titanium nitride (TiN), tungsten nitride (WN), tungsten carbonitride (WCN), molybdenum nitride (MoN), copper silicon nitride (CuSiN), etc., and combinations thereof. In some embodiments, the film comprises a dielectric. Examples include, silicon oxide, carbon doped silicon oxide, silicon nitride, hafnium oxide, zirconium oxide etc.

[0072] In embodiments of the present disclosure, the substrate has at least two discrete surfaces wherein each discrete surface is characterized by a different chemistry. For example, in an embodiment, the surface of the substrate comprises at least a first surface comprising a dielectric such as silicon dioxide and at least a second surface comprising a further dielectric material such as silicon nitride.

[0073] In some embodiments, the disclosure provides methods of selectively depositing a film such as, for example, a silicon nitride, onto one surface of a substrate over a second surface on the same substrate wherein the two surfaces are co-planar created by chemical mechanical planarization. In other embodiments, the disclosure provides methods of selectively depositing a film such as, for example, a silicon nitride, onto one surface of a substrate over a second surface on the same substrate wherein the two surfaces are not co-planar. As used in this specification and the appended claims, the term “selectively depositing a film on one surface over another surface,” and the like, means that one of the first or second surface is passivated to substantially prevent deposition on the passivated layer and a film is deposited on the second (non-passivated) surface. The term “over” used in this regard does not imply a physical orientation of one surface on top of another surface, rather a relationship of the thermodynamic or kinetic properties of the chemical reaction with one surface relative to the other surface. For example, selectively depositing a cobalt film onto a copper surface over a dielectric surface means that the cobalt film deposits on the copper surface and less or no cobalt film deposits on the dielectric surface; or that the formation of the cobalt film on the copper surface is thermodynamically or kinetically favorable relative to the formation of a cobalt film on the dielectric surface.

[0074] The method of the present disclosure includes the optional step of contacting the surface of the substrate with a wet chemical composition to obtain a treated substrate. Exemplary wet chemical treatments include known chemical treatments such as, for example, RCA clean chemicals SC-1 and SC-2, aqueous HF, peroxide, H_2SO_4 / H_2O_2 , NH_4OH , buffered HF solutions, and mixtures thereof.

[0075] In preferred embodiments, the wet chemical composition comprises at least one selected from the group consisting of a composition comprising H_2O_2 (28 % aq.), NH_4OH (28-30 %), and H_2O ; HF (0.01 % - 10% (aq.)); peroxide; RCA clean chemicals SC-1 and SC-2; and a mixture of H_2SO_4 / H_2O_2 .

[0076] As is known in the art, “RCA clean chemicals” refers to compositions comprising an ammonium hydroxide and hydrogen peroxide mixture wherein the basic

cleaning procedure developed by the Radio Corporation of America in the 1960s. The RCA Standard-Clean-1 (SC-1) procedure uses an ammonium hydroxide and hydrogen peroxide solution and water heated to a temperature of about 70 °C. The SC-1 procedure dissolves films and removes Group I and II metals. The Group I and II metals are removed through complexing with the reagents in the SC-1 solution. The RCA Standard-Clean-2 (SC-2) procedure utilizes a mixture of hydrogen peroxide, hydrochloric acid, and water heated to a temperature of about 70 °C. The SC-2 procedure removes the metals that are not removed by the SC-1 procedure.

[0077] Contacting with the wet chemical composition can occur by any method known to those skilled in the art such as, for example, dipping or spraying. The contacting step can be one discrete step or more than one step.

[0078] In some embodiments, the temperature of the wet chemical composition during the contacting step can be, for example, from about ambient temperature to about 100 °C. In other embodiments, the temperature of the wet chemical composition during the contacting step can be, for example, from about 55 °C to about 95 °C. In other embodiments, the temperature of the wet chemical composition during the contacting step can be, for example, from about 60 °C to about 90 °C.

[0079] Embodiments also include the step of rinsing the surface of the substrate with deionized water after the step of contacting the surface of the substrate with the wet chemical composition. The rinsing step is typically carried out by any suitable means, for example, rinsing the surface of the substrate with de-ionized water by immersion or spray techniques.

[0080] Embodiments also include the step of drying at least the surface of the substrate after the rinsing step. The drying step is typically carried out by any suitable means, for example, the application of heat, isopropyl alcohol (IPA) vapor drying, or by centripetal force.

[0081] Embodiments also optionally include the step of treating the surface with hydrogen plasma, argon plasma, or ammonia plasma. Suitable processes include plasma processes (hydrogen plasma, NH_3 / NF_3 plasmas, HF, ClF_3 , water plasmas, and the like). The optional plasma step functions to remove undesired deposits on the surface and activate the surface for subsequent deposition of passivation reagents. Such plasma treatments may be most preferably applied after some deposition on the surface has been performed in order to remove non-selectively deposited material from

the previously passivated surface and to remove residual passivation reagents after the desired deposition thickness has been achieved.

[0082] As employed throughout the description, the term “alkyl” means a saturated hydrocarbon group which is straight-chained or branched. In some embodiments, the alkyl group has from 1 to 20 carbon atoms, from 2 to 20 carbon atoms, from 1 to 10 carbon atoms, from 2 to 10 carbon atoms, from 1 to 8 carbon atoms, from 2 to 8 carbon atoms, from 1 to 6 carbon atoms, from 2 to 6 carbon atoms, from 1 to 4 carbon atoms, from 2 to 4 carbon atoms, from 1 to 3 carbon atoms, or 2 or 3 carbon atoms. Examples of alkyl groups include, but are not limited to, methyl (Me), ethyl (Et), propyl (e.g., n-propyl and iso-propyl), butyl (e.g., n-butyl, t-butyl, iso-butyl), pentyl (e.g., n-pentyl, iso-pentyl, neo-pentyl), hexyl, iso-hexyl, heptyl, octyl, nonyl, 4,4dimethylpentyl, 2,2,4-trimethylpentyl, decyl, undecyl, dodecyl, 2-methyl-1-propyl, 2-methyl-2-propyl, 2-methyl-1-butyl, 3-methyl-1-butyl, 2-methyl-3-butyl, 2-methyl-1-pentyl, 2,2-dimethyl-1-propyl, 3-methyl-1-pentyl, 4-methyl-1-pentyl, 2-methyl-2-pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, 2,2-dimethyl-1-butyl, 3,3-dimethyl-1-butyl, 2-ethyl-1-butyl, and the like.

[0083] As employed throughout the description, the term “cyclic alkyl” denotes a cyclic functional group having from 3 to 10 or from 4 to 10 carbon atoms. Exemplary cyclic alkyl groups include, but are not limited to, cyclobutyl, cyclopentyl, cyclohexyl, and cyclooctyl groups.

[0084] As used herein, the term “aryl” means a monocyclic, bicyclic, or polycyclic (e.g., having 2, 3 or 4 fused rings) aromatic hydrocarbon. In some embodiments, the aryl group has from 6 to 20 carbon atoms or from 6 to 10 carbon atoms. Examples of aryl groups include, but are not limited to, phenyl, naphthyl, anthracenyl, phenanthrenyl, indanyl, indenyl, and tetrahydronaphthyl, and the like.

[0085] As employed throughout the description, the term “alkenyl group” denotes a group which has one or more carbon-carbon double bonds and has from 2 to 18 or from 2 to 10 carbon atoms. Exemplary alkenyl groups include, but are not limited to, vinyl or allyl groups.

[0086] As used herein, the term “alkynyl” means a straight or branched alkyl group having 2 to 20 carbon atoms and one or more triple carbon-carbon bonds. In some embodiments, the alkynyl group has from 2 to 10 carbon atoms, from 2 to 8 carbon atoms, from 2 to 6 carbon atoms, or from 2 to 4 carbon atoms. Examples of alkynyl

groups include, but are not limited to, acetylene, 1-propylene, 2-propylene, and the like.

[0087] As used herein, the phrase “optionally substituted” means that a substitution is optional and, therefore, includes both unsubstituted and substituted atoms and moieties. A “substituted” atom or moiety indicates that any hydrogen atom on the designated compound or moiety can be replaced with a selection from the indicated substituent groups, provided that the normal valency of the designated compound or moiety is not exceeded, and that the substitution results in a stable compound. For example, if a methyl group is optionally substituted, then 1, 2, or 3 hydrogen atoms on the carbon atom within the methyl group can be replaced with 1, 2, or 3 of the recited substituent groups.

[0088] As used herein, the term “phenyl” means $-C_6H_5$. A phenyl group can be unsubstituted or substituted with one, two, or three suitable substituents.

[0089] As used herein, the term “halo” means halogen groups and includes, but is not limited to, fluoro, chloro, bromo, and iodo.

[0090] As used herein, the term “dielectric material” refers a silicon-containing or metal-containing film. Examples of dielectric material include, but are not limited to, silicon oxide, carbon doped silicon oxide, metal oxide such as hafnium oxide, zirconium oxide, titanium oxide, tantalum oxide, niobium oxide, tungsten oxide, and combinations thereof.

[0091] Vapor phase or gas phase reactions include the exposure of the heated substrate to the precursor molecule(s) and / or co-reactants in a suitable chamber that must be capable of providing the necessary pressure control and that can also supply heat to the substrate and / or chamber walls; the chamber should also provide suitable purity for the reactions that will take place, generally through high leak integrity and the use of ultra-high purity carrier and reactive gases.

[0092] As used in this specification and the appended claims, the terms “reactive gas”, “precursor”, “reactant”, and the like, are used interchangeably to mean a gas that includes a species which is reactive with a substrate surface. For example, a first “reactive gas” may simply adsorb onto the surface of a substrate and be available for further chemical reaction with a second reactive gas. They may be used in conjunction with ultra-high purity carrier gases (as defined previously) and in any desired mixtures with one another (i.e., more than one type of precursor can be used either together or

in discrete, independent steps to form the desired passivation layer with whatever order of precursor introduction is desired).

[0093] The precursor(s) and / or co-reactants may be delivered to the reactor using mass flow controllers (perhaps with heated lines), liquid injection vaporizers (perhaps with heated lines) or with no metering device (i.e., neat introduction of the vapor and or gas from a vessel that is isolated from the reactor using a simple valve). Any of the foregoing may also be used in combination with one another. Any means of providing the gas and / or vapor(s) to the reaction chamber that provides sufficient purity and repeatability may be used.

[0094] The precursor(s) and / or co-reactants may be introduced independently to the reactor, mixed prior to introduction to the reactor, mixed in the reactor or in any combination of the preceding in multiple, independent steps that might include differences in how the precursors are introduced between steps.

[0095] The temperature range of substrate in the reactors may be between room temperature and 800° C. In some cases, the temperature range of substrate in the reactors may be between room temperature and 650 °C. In yet other cases, the temperature range of substrate in the reactors may be between room temperature and 100° C. The pressure may range from 10-10 Torr to 3000 Torr and may be maintained under dynamic flow conditions (i.e., with a valve and a butterfly valve type arrangement) or may be maintained under static conditions (i.e., an evacuated chamber is exposed to the desired precursor(s) and / or co-reactant(s) until a total desired pressure is achieved and then the chamber is isolated from both the precursor(s) and / or co-reactant(s) source(s) and the vacuum pump). The reactor can be evacuated fully and re-exposed to fresh precursor(s) and / or co-reactants as many times as necessary. Precursor(s) and / or co-reactants may be introduced using any mixtures and / or concentrations desired.

[0096] The exposure of the surface can be conducted for 0.1-60 minutes, preferably in 1-5 minutes and most preferably for 1 minute. The partial pressure of the organic halide in the reaction chamber can vary from about 1% of its saturated vapor pressure at the substrate temperature up to almost 100% of its saturation vapor pressure. Most preferably, it will be between 20 and 50% of its saturation vapor pressure. The chamber pressure can be the same as the partial pressure of the organic halide vapors but can be higher with the balance of the atmosphere comprising a carrier gas. Preferred carrier gases include N₂, He, and Ar, but also other gases such as H₂ may

be used. The exposure vapors can be static (not flowing) for all or part of the exposure period. The preferred embodiment is to flow the vapors of the organic halide along with the optional carrier gas through the exposure chamber so that fresh vapors are exposed to the surface of the substrate for at least a portion of the exposure period.

[0097] The exposure chamber can be kept at near ambient temperature or can optionally be heated. Heat can be supplied to the outer walls of the chamber (hot wall) or only to the substrate (cold-wall reactor). Substrate heating in a cold wall reactor can be achieved by use of incident radiation through a transparent window (lamp heating), by resistive heating of the substrate itself or from resistive heating elements in the platform that the substrate is contacting, through induction or by other means known in the art. The temperature of the treatment is preferably between about 20 °C to about 400 °C, preferably between 20°C to about 200 °C, and most preferably between 20 °C to about 100 °C. The temperature can be constant during the exposure period or can vary within the specified temperature range.

[0098] Unreacted vapor of the at least one organic halide can then optionally be removed by evacuation or purging of the chamber with suitable inert gas before removing the substrate from the chamber or before chemical vapor or atomic-layer deposition processing. Optionally, the exposure chamber might also be used for subsequent processing steps to improve process efficiency so that the process may be repeated from step c), if necessary, to strip the protective film and any non-selective ALD deposit and then re-form a protective film.

[0099] The choice of the at least one organoaminopolysiloxane or organoaminopolysilazane and the exposing conditions used in this method should be optimized by standard experimentation to optimize selectivity of the protection afforded the silicon nitride surface against potential non-selective passivation, processing time, reagent cost, etc. depending on the requirements imposed by subsequent processing steps. For example, selectivity can be adjusted/optimized by varying the nature of the R¹ or R² group of the at least one organoaminopolysiloxane or organoaminopolysilazane having the structure represented by Formula IA or IB. Typically, since reactivity and selectivity are often inversely related, if the two surfaces are similar in chemistry, experimenting with the R¹ or R² group may be required to optimize the process.

Disclosed and Claimed Passivating Compositions

[00100] Given the forgoing, in one embodiment the disclosed and claimed subject relates to passivating composition or passivating agent that include, consist essentially of and/or consist of an organoaminopolysiloxanes or organoaminopolysilazanes. The passivating composition is particularly well-suited for performing enhanced passivation of metallic substrates. In one aspect of this embodiment, the organoaminopolysiloxanes or organoaminopolysilazanes, consists essentially of or consists of one or more organoaminopolysiloxanes or organoaminopolysilazanes.

[00101] In one embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB is substantially free of impurities that may react with metallic surface during a passivation process. In one embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB is substantially free of impurities that react with precursors during a deposition process.

[00102] In one embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB is substantially free of impurities that passivate non-metallic surface and suppress growth on non-metallic surface.

[00103] In one embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB is substantially free of halogen-containing impurities. In one aspect of this embodiment, the halogen-containing impurities are one or more of a fluorohydrocarbon, a chlorohydrocarbon, a bromohydrocarbon and an iodohydrocarbon. In one aspect of this embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB has a residual concentration of halogen-containing impurities of less than about 1000 ppm. In one aspect of this embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB has a residual concentration of halogen-containing impurities of less than about 500 ppm. In one aspect of this embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB has a residual concentration of halogen-containing impurities of less than about 100 ppm. In one aspect of this embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB has a residual concentration of halogen-containing impurities of less than about 50 ppm. In one aspect of this embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB has a residual concentration of halogen-containing impurities of less than about 25 ppm. In one aspect of this embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB has a residual concentration of

halogen-containing impurities of less than about 10 ppm. In one aspect of this embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB is free of halogen-containing impurities. In the forgoing aspects, the residual concentration of halogen-containing impurities is detected by one or more of the following: Gas Chromatography (GC) and its associated hyphenated techniques comprising but not limited to GC-FID, GC-ECD, GC-MS; Liquid Chromatography (as defined as to encompass LC, HPLC, or UPLC variations) and its associated hyphenated techniques comprising but not limited to LC-DAD and LC-MS; Ion Chromatography (IC) and its associated forms; Spectroscopic techniques comprising but not limited to infrared (IR), Ultraviolet/Visible (UV/Vis), Near infrared (NIR), Raman and Nuclear Magnetic Resonance (NMR) spectroscopies; Inductively Coupled Plasma spectroscopy or spectrometry (ICP) and their associated hyphenated techniques comprising but not limited to ICP-MS, ICP-OES, GC-ICP-MS, and GC-ICP-OES; Elemental analyses such as X-ray fluorescence spectroscopy (XRF) and its associated forms (example WD-XRF) or Atomic Absorbance spectroscopy (AA) and its forms; and finally wet chemical techniques comprising but not limited to Titration (example halogen titration by with silver nitrate) and electrochemical detection (examples, cyclic voltammetry, ion selective electrodes, etc.). In one embodiment of the forgoing aspects, the residual concentration of halogen-containing impurities is detected by one or more of GC-MS, GC-ICP-MS, GC-ICP-OES, GC-FID, GC-ECD, HPLC and UV/Vis.

[00104] In one embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB is purified by exposure to molecular sieves. In one embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB is purified by exposure to silica gel. In one embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB is purified by exposure to one or more adsorbent materials.

[00105] In one embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB is purified by treatment with one or more group 1 metal followed by a distillation process. In one aspect of this embodiment, the organoaminopolysiloxane or organoaminopolysilazane is treated with metallic sodium. In another aspect embodiment, the metal and the organoaminopolysiloxane or organoaminopolysilazane are separated by filtration and the organoaminopolysiloxane or organoaminopolysilazane is distilled to remove non-volatile products of the reaction of impurities with metals.

[00106] In one embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB is purified by treatment with one or more group (II) metal followed by a distillation process. In one aspect of this embodiment, the organoaminopolysiloxane or organoaminopolysilazane is treated with metallic magnesium. In another aspect embodiment, the metal and the organoaminopolysiloxane or organoaminopolysilazane are separated by filtration and the organoaminopolysiloxane or organoaminopolysilazane is distilled to remove non-volatile products of the reaction of impurities with metals.

[00107] In one embodiment, the organoaminopolysiloxane or organoaminopolysilazane having formula IA or IB is purified by exposure to activated carbon. In one aspect of this embodiment the organoaminopolysiloxane or organoaminopolysilazane is separated by filtration and is distilled to remove non-volatile products after treatment with activated carbon.

EXAMPLE 1: Growth of a silicon and nitrogen containing film on silicon oxide surface passivated using 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane.

[00108] A silicon-containing film comprising silicon and nitrogen (i.e. silicon carbonitride) was deposited on silicon oxide surface in a screening ALD reactor. Both passivation layer and film growth were evaluated in real-time using an in-situ ellipsometer. The film was deposited using 1,1,3,3-tetrachloro-1,3-disilacyclobutane and NH₃ thermally. The passivation layer was formed using 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane as passivating agent. A passivation layer using dimethylaminotrimethylsilane was also used as comparison. The substrate temperature was 300 °C.

[00109] The silicon oxide surface was prepared by exposing the silicon coupon to 180 s of oxygen plasma. The plasma consisted of 200 sccm of O₂ and 100 sccm of Ar. The plasma power used was 3000W at 2 GHz.

[00110] Detailed process steps are as follows:

Table 1. Deposition of silicon-containing film comprising silicon and nitrogen on passivated silicon oxide surface

Step	Process	Notes
1	Introduce silicon with native oxide coupons into reactor and heat to 300°C	
2	Prepare surface for deposition	O ₂ flow = 200 sccm

		Ar flow = 100 sccm Plasma = 3000 W, 2 GHz
3	Purge system to remove oxygen plasma byproducts and unreacted species	
4	Introduce passivating agent and confirm thickness saturation using in-situ ellipsometer	Flow = 2 s for 50 times Total time = 100 s
5	Purge passivating agent and reaction byproducts out from the reactor	
6	Introduce 1,1,3,3- tetrachloro-1,3-disilacyclobutane to the reactor	Flow = 2 s Soak = 60s
7	Purge reaction byproducts and unreacted species from the reactor	
8	Flow nitrogen source to react with the surface	NH ₃ = 500 sccm for 15 s Soak = 20 s
9	Purge reaction byproducts and unreacted species from the reactor	
10	Remove Si coupons from the reactor	

[00111] Steps 6 to 9 were repeated multiple times in order to achieve a desired thickness.

[00112] A saturated passivation layer from 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane was saturated at $4 \pm 0.5 \text{ \AA}$ while a saturated passivation layer employing dimethylaminotrimethylsilane was only saturated at $2.5 \pm 0.5 \text{ \AA}$, demonstrating 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane is a better passivation agent than dimethylaminotrimethylsilane.

Table 2. Comparison of film growth after 100 cycles on passivated and non-passivated silicon oxide surfaces.

Passivation agent	Film thickness (Å)
None (control)	28 Å
dimethylaminotrimethylsilane	18 Å
1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane	12 Å

[00113] A saturated passivation layer from 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane provides better passivation protection than well-known dimethylaminotrimethylsilane, i.e. less film growth as shown in above table.

EXAMPLE 2: Growth of silicon-containing film comprising silicon and nitrogen on silicon oxide surface passivated using using 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane

[00114] A silicon-containing film comprising silicon and nitrogen (i.e. silicon carbonitride) was deposited on silicon oxide surface with in a screening ALD reactor. We evaluated both passivation layer and film growth in real-time using an in-situ ellipsometer. The film was deposited using 1,1,3,3-tetrachloro-1,3-disilacyclobutane and NH_3 thermally. . The passivation layer was formed using 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane. A passivation layer using dimethylaminotrimethylsilane was also used as comparison. The substrate temperature was 300 °C.

[00115] The silicon oxide surface was prepared by exposing the silicon coupon to 180 s of oxygen plasma. The plasma consisted of 200 sccm of O_2 and 100 sccm of Ar. The plasma power used was 3000W at 2 GHz.

[00116] Deposition process followed the steps listed in Table 1. Step 6 to 9 were repeated multiple times in order to get desired thickness.

[00117] A saturated passivation layer from 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane was saturated at 5.5 ± 0.5 Å while a saturated passivation layer employing dimethylaminotrimethylsilane was only saturated at 2.5 ± 0.5 Å.

Table 3. Comparison of film growth after 100 cycles on passivated and non-passivated silicon oxide surface.

Passivation agent	Film thickness (Å)
None (control)	28 Å
Dimethylaminotrimethylsilane	18 Å
1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane	9 Å

[00118] Above table shows that there is much less film growth on silicon oxide surface having passivation layer from 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane than that of (dimethylamino)trimethylsilane, demonstrating 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane is a better passivation agent than dimethylaminotrimethylsilane .

EXAMPLE 3: Growth of silicon-containing film comprising silicon and nitrogen on silicon oxide surface passivation using 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane.

[00119] A silicon-containing film comprising silicon and nitrogen (e.g. silicon nitride) was deposited on silicon oxide surface with a passivation layer in a screening ALD reactor. We evaluated both passivation layer and film growth in real-time using an in-situ ellipsometer. The film was deposited using 1,1,1,3,3,3-hexachlorodisilazane and ammonia. The passivation layer was formed using 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane while a passivation layer using dimethylaminotrimethylsilane was also used as comparison. The substrate temperature was 400 °C.

[00120] The silicon oxide surface was prepared by exposing the silicon coupon to 180 s of oxygen plasma. The plasma consisted of 200 sccm of O₂ and 100 sccm of Ar. The plasma power used was 3000W at 2 GHz. The detailed process steps are listed below.

Table 4. Deposition of silicon-containing film comprising silicon and nitrogen on passivated silicon oxide surface.

Step	Process	Notes
1	Introduce silicon with native oxide coupons into reactor and heat to 400°C	
2	Prepare surface for deposition	O ₂ flow = 200 sccm Ar flow = 100 sccm Plasma = 3000 W, 2 GHz
3	Purge system to remove oxygen plasma byproducts and unreacted species	
4	Introduce passivation agent and confirm thickness saturation using in-situ ellipsometer	Flow = 2 s for 50 times Total time = 100 s
5	Purge passivating agent and reaction byproducts out from the reactor	
6	Introduce 1,1,1,3,3,3-hexachlorodisilazane to the reactor	Flow = 2 s Soak = 17s
7	Purge reaction byproducts and unreacted species from the reactor	
8	Flow nitrogen source to react with the surface	NH ₃ = 500 sccm for 60 s
9	Purge reaction byproducts and unreacted species from the reactor	
10	Remove Si coupons from the reactor	

[00121] Steps 6 to 9 were repeated multiple times in order to get desired thickness.

[00122] A saturated passivation layer from 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane was saturated at 4 ± 0.5 Å while a saturated passivation layer employing dimethylaminotrimethylsilane was only saturated at 2.5 ± 0.5 Å.

Table 5. Comparison of film growth after 50 cycles on passivated and non-passivated silicon oxide layer.

Passivation agent	Film thickness (Å)
None (control)	32 Å
Dimethylaminotrimethylsilane	20 Å
1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane	10 Å

[00123] Thicker passivation layer from 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane provides better passivation, i.e. less film growth, compared to a surface passivated with dimethyl-aminotrimethylsilane.

EXAMPLE 4: Silicon and nitrogen containing film growth on silicon oxide surface passivation using 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane.

[00124] A silicon and nitrogen containing film (e.g. silicon nitride) was deposited on silicon oxide surface with a single layer of inhibitor in a screening ALD reactor. We evaluated both passivation layer and film growth in real-time using an in-situ ellipsometer. The film was deposited using 1,1,1,3,3,3-hexachlorodisilazane and NH_3 thermally. The passivation layer selected was 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane. Dimethylaminotrimethylsilane passivation was also used as comparison. Process temperature was 400 °C

[00125] For silicon oxide surface was prepared the Si coupon was exposed to 180 s of oxygen plasma. The plasma consisted of 200 sccm of O_2 and 100 sccm of Ar. The plasma power used was 3000W at 2 GHz.

[00126] Deposition followed the steps listed in Table 1. Step 6 to 9 were repeated multiple times in order to get desired thickness.

[00127] A passivation layer from 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane was saturated at $5.3 \text{ Å} \pm 0.5 \text{ Å}$ while a passivation layer using dimethylaminotrimethylsilane was saturated at $2.5 \text{ Å} \pm 0.5 \text{ Å}$.

Table 6. Comparison film growth after 50 cycles on passivated and non-passivated silicon oxide layer.

Passivation agent	Film thickness (Å)
None (control)	32 Å
Dimethylaminotrimethylsilane	20 Å
1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane	6 Å

[00128] Thicker passivation layer from 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane provides better passivation, i.e. less film growth, compared to a surface passivated with dimethylaminotrimethylsilane.

EXAMPLE 5: Silicon and nitrogen containing film growth on silicon oxide surface passivation using 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane.

[00129] A silicon and nitrogen (e.g. silicon nitride) containing film was deposited on silicon oxide surface with a single layer of inhibitor in a screening ALD reactor. We evaluated both passivation layer and film growth in real-time using an in-situ ellipsometer. The film was deposited using 1,1,1,3,3,3-hexchloromethylidisilazane and NH₃ thermally. The passivation layer selected was 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane.

[00130] The silicon oxide surface was prepared by exposing the silicon coupon to 180 s of oxygen plasma. The plasma consisted of 200 sccm of O₂ and 100 sccm of Ar. The plasma power used was 3000 W at 2 GHz. Process temperature was 600 °C.

[00131] The detailed deposition steps are as follows:

Table 7. Deposition of silicon and nitrogen containing films on passivated silicon oxide surface

Step	Process	Notes
1	Introduce silicon with native oxide coupons into reactor and heat to 600 °C	
2	Prepare surface for deposition	O ₂ flow = 200 sccm Ar flow = 100 sccm Plasma = 3000 W, 2 GHz
3	Purge system to remove oxygen plasma byproducts and unreacted species	
4	Introduce passivating agent and confirm thickness saturation using in-situ ellipsometer	Flow = 2 s for 50 times Total time = 100 s
5	Purge passivating agent and reaction byproducts out from the reactor	
6	Introduce 1,1,1,3,3,3-hexachloromethylsilazane to the reactor	Flow = 2 s Soak = 17s
7	Purge reaction byproducts and unreacted species from the reactor	
8	Flow nitrogen source to react with the surface	NH ₃ = 500 sccm for 60 s
9	Purge reaction byproducts and unreacted species from the reactor	
10	Remove Si coupons from the reactor	

[00132] Steps 6 to 9 were repeated multiple times in order to get desired thickness.

[00133] A passivation layer from 1-(dimethylamino)-1,1,3,3,3-pentamethyldisiloxane was saturated at $3.2\text{Å} \pm 0.5\text{Å}$.

Table 8. Comparison of film growth after 50 cycles on passivated and non-passivated silicon oxide layer.

Passivation agent	Film thickness (Å)
None (control)	23 Å
1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane	16 Å

[00134] Film growth on the surface passivated with 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane is thinner than the one without passivation layer.

EXAMPLE 6: Silicon and nitrogen containing film growth on silicon oxide surface passivation using 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane.

[00135] A silicon and nitrogen containing film (e.g. silicon nitride) was deposited on silicon oxide surface with a single layer of inhibitor in a screening ALD reactor. We evaluated both passivation layer and film growth in real-time using an in-situ ellipsometer. The inhibitor layer selected was 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane. Process temperature was 600 °C

[00136] The silicon oxide surface was prepared by exposing the silicon coupon to 180 s of oxygen plasma. The plasma consisted of 200 sccm of O₂ and 100 sccm of Ar. The plasma power used was 3000 W at 2 GHz.

[00137] Deposition followed the steps listed in Table 3. Step 6 to 9 were repeated multiple times in order to get desired thickness.

[00138] An inhibitor layer from 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane at $4.3\text{Å} \pm 0.5\text{Å}$.

Table 9. Comparison of film growth after 50 cycles on passivated and non-passivated silicon oxide layer.

Passivation agent	Film thickness (Å)
None (control)	23 Å
1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane	13 Å

[00139] Film growth on the surface passivated with 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane is thinner than the one without passivation layer.

EXAMPLE 7. Selective deposition on silicon nitride (growth surface) over silicon oxide (non-growth surface) using 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane.

[00140] In this example, we demonstrated selective deposition on growth surface (e.g. silicon nitride) and non-growth surface (e.g. silicon oxide). Both growth and non-growth surfaces were prepared in-situ without breaking vacuum prior to film deposition. Growth surface was prepared by depositing ~100 Å silicon nitride using chlorosilane and ammonia plasma at 400 °C. The passivation layer was introduced by exposing Si coupon to 100 s of 1-dimethylamino-1,1,3,3,3 pentamethyldisiloxane. The non-growth surface was prepared by exposing silicon coupon with native oxide to oxygen plasma for 180 s. Film was deposited using 1,1,1,3,3,3-hexachlorodisilazane and ammonia thermally. Process temperature was 400 °C.

[00141] Details of both surface preparation and film deposition are listed on Table 4.

[00142] Saturation of the passivation layer using 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane on the non-growth surface (silicon oxide), was confirmed after exposure via in-situ ellipsometry with a total thickness of $4.2 \text{ Å} \pm 0.5 \text{ Å}$ as measured by in-situ ellipsometer. Thickness of the passivation layer on the growth surface was 1.0 Å after the same exposure time.

Table 10. Deposition of films on growth or non-growth surface with passivation layer.

Step	Process	Notes
1	Introduce silicon with native oxide coupons into reactor and heat to 400°C	
2	Prepare surface for deposition Non-growth surface: 3000W 200 sccm O ₂ plasma for 180 total seconds. Growth surface: chlorosilane and 2000W NH ₃ plasma for 100 Å	
3	Purge system to remove oxygen plasma byproducts and unreacted species	
4	Introduce passivating agent and confirm thickness saturation using in-situ ellipsometer	Flow = 2 s for 50 times Total time = 100 s
5	Purge passivating agent and reaction byproducts out from the reactor	
6	Introduce 1,1,1,3,3,3-hexchlorodisilazane to the reactor	Flow = 2 s Soak = 17s
7	Purge reaction byproducts and unreacted species from the reactor	
8	Flow nitrogen source to react with the surface	NH ₃ = 500 sccm for 60 s
9	Purge reaction byproducts and unreacted species from the reactor	
10	Remove Si coupons from the reactor	

[00143] Steps 6 through 9 were repeated until reaching desired thickness.

Table 11. Comparison of film growth after 50 cycles on passivated and non-passivated silicon oxide layer.

Surface	Film thickness (Å)
Silicon Nitride (growth surface)	32 Å
Silicon Oxide (non-growth surface)	10 Å

[00144] Table 11 demonstrates silicon nitride film (growth surface) has thickness of 32 Å compared to 10 Å on the silicon oxide (non-growth) surface. This confirms 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane passivation layer enables selective film growth on different surfaces.

EXAMPLE 8. Selective deposition on silicon nitride (growth surface) over silicon oxide (non-growth surface) using 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane.

[00145] In this example, we demonstrated selective deposition on growth surface (e.g. silicon nitride) and non-growth surface (e.g. silicon oxide). Both growth and non-growth surfaces were prepared in-situ without breaking vacuum prior to film deposition. Growth surface was prepared by depositing ~100 Å silicon nitride using chlorosilane and ammonia plasma at 500 °C. The passivation layer was introduced by exposing Si coupon to 100 s of 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane. The non-growth surface was prepared by exposing silicon coupon with native oxide to oxygen plasma for 180 s. Film was deposited using 1,1,1,3,3,3-hexachlorodisilazane and ammonia thermally. Process temperature was 500 °C.

[00146] Details of both surface preparation and film deposition are listed on Table 12. A monolayer of 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane on the non-growth surface (silicon oxide) passivated at $5.3 \text{ Å} \pm 0.5 \text{ Å}$. Thickness of the passivator on the growth surface (silicon nitride) was $2.0 \text{ Å} \pm 0.5 \text{ Å}$ after the same exposure time.

Table 12. Deposition of films on growth or non-growth surface with passivation layer.

Step	Process	Notes
1	Introduce silicon with native oxide coupons into reactor and heat to 500°C	
2	Prepare surface for deposition Non-growth surface: 3000W 200 sccm O ₂ plasma for 180 total seconds. Growth surface: chlorosilane and 2000W NH ₃ plasma for 100 Å	
3	Purge system to remove oxygen plasma byproducts and unreacted species	
4	Introduce passivating agent and confirm thickness saturation using in-situ ellipsometer	Flow = 2 s for 50 times Total time = 100 s
5	Purge passivating agent and reaction byproducts out from the reactor	
6	Introduce 1,1,1,3,3,3-hexchloromethylsilazane to the reactor	Flow = 2 s Soak = 17s
7	Purge reaction byproducts and unreacted species from the reactor	
8	Flow nitrogen source to react with the surface	NH ₃ = 500 sccm for 60 s
9	Purge reaction byproducts and unreacted species from the reactor	
10	Remove Si coupons from the reactor	

[00147] Steps 6 through 9 were repeated until reaching desired thickness.

Table 13. Comparison of film growth after 50 cycles on passivated and non-passivated silicon oxide layer.

Surface	Film thickness (Å)
Silicon Nitride (growth surface)	14 Å
Silicon Oxide (non-growth surface)	2 Å

[00148] Table 13 confirms that silicon nitride film (growth surface) has thickness of 14 Å of silicon nitride film compared to 2 Å on the silicon oxide (non-growth) surface. This confirms 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane passivation layer enables selective film growth on different surfaces.

[00149] An illustrative process 300 is shown in FIG. 3. Step 1 comprises a pre-cleaning of the first surface 302 (comprising zirconium oxide) and the second surface 304 (comprising titanium nitride), preferably with an acid, H₂, high temperature, or a combination thereof. Following the pre-clean, preferably, the first surface 302 and the second surface 304 are co-planar, as a result of a chemical mechanical planarization (CMP) as shown in FIG. 3 prior to the pre-cleaning step.

[00150] Step 2 comprises passivation of the ZrO₂ surface 302 by exposing the dielectric to form a passivating/blocking organic layer 306 employing a passivating composition preferably comprising an organoaminopolysiloxane such as 1-dimethylamino-1,1,3,3,3,3-pentamethyldisiloxane. Following passivation of the first surface 302, Step 3 includes depositing a SiN containing dielectric layer 308 on the second surface 304 (TiN), preferably by ALD of a silicon precursor and a nitrogen precursor.

[00151] It is anticipated that the disclosed and claimed methods could be used in conjunction with deposition tools commonly found at semiconductor manufacturing sites to produce molybdenum-containing layers for logic applications and other potential functions.

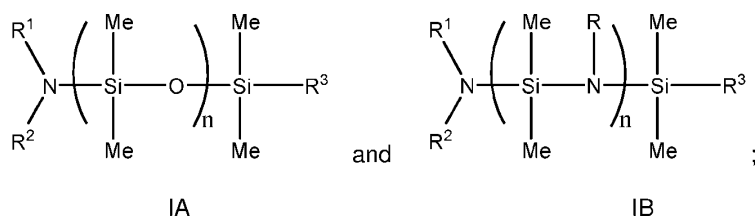
[00152] The foregoing description is intended primarily for purposes of illustration. Although the disclosed and claimed subject matter has been shown and described with respect to an exemplary embodiment thereof, it should be understood by those skilled in the art that the foregoing and various other changes, omissions, and additions in the form and detail thereof may be made therein without departing from the spirit and scope of the disclosed and claimed subject matter.

[00153] While the principles of the disclosure have been described above in connection with preferred embodiments, it is to be clearly understood that this description is made only by way of example and not as a limitation of the scope of the claimed subject matter.

CLAIMS

What is claimed is:

1. A method for passivating a silicon-containing or metal-containing surface of a substrate comprising:
 - (a) providing the substrate in a reaction vessel at temperatures ranging from 20°C to 800°C, the substrate having a first surface comprising a dielectric material with hydroxyl groups and a second surface comprising a different material having fewer hydroxyl groups than the first surface;
 - (b) forming at least one passivated layer on the first surface by exposing the first surface and the second surface to a passivating composition comprising an organoaminoalkylpolysiloxane or an organoaminoalkylpolysilazane having one of the following formulae:



wherein R¹ and R² are each independently selected from a hydrogen, C₁ to C₆ alkyl group with a proviso that R¹ and R² cannot be both hydrogen; R³ and R are each independently selected from hydrogen or methyl; n=1, 2, 3; and either R¹ and R² are linked to form a cyclic ring structure or R¹ and R² are not linked to form a cyclic ring structure; and

- (c) purging the reactor with inert gas.
2. The method of claim 1, wherein steps (b) and (c) are repeated to achieve a self-limiting monolayer coverage of the first surface.
3. The method of claim 1, wherein the first surface is selected from the group consisting of silicon oxide, carbon doped silicon oxide, metal oxide, and combinations thereof, and wherein the second surface is selected from the group consisting of silicon nitride or metal nitride.

4. The method of claim 1, wherein the second surface comprises a metal or metalloid chosen from the group consisting of ruthenium (Ru), cobalt (Co), copper (Cu), titanium (Ti), tantalum (Ta), nickel (Ni), tungsten (W), molybdenum (Mo), silicon, and combinations thereof, or wherein the second surface comprises a nitride chosen from the group consisting of silicon nitride, germanium nitride, tantalum nitride (TaN), titanium nitride (TiN), tungsten nitride (WN), tungsten carbonitride (WCN), molybdenum nitride (MoN), copper silicon nitride (CuSiN), and combinations thereof.

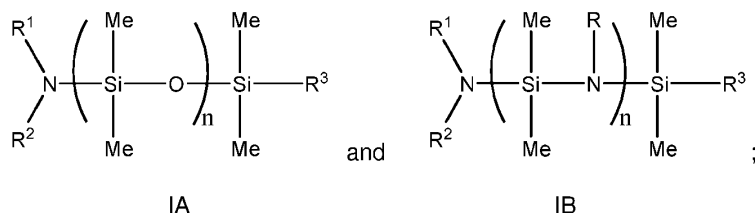
5. The method of claim 1, wherein the passivating composition comprises an organoaminoalkylpolysiloxane IA chosen from the group consisting of: 1-dimethylamino-1,1,3,3-tetramethyldisiloxane, 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane, 1-dimethylamino-1,1,3,3,5,5-hexamethyltrisiloxane, 1-dimethylamino-1,1,3,3,5,5,5-heptamethyltrisiloxane, 1-dimethylamino-1,1,3,3,5,5,7,7-octamethyltetrasiloxane, 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane, and combinations thereof.

6. The method of claim 1, wherein the passivation composition comprises an organoaminoalkylpolysilazane IB chosen from the group consisting of: 1-dimethylamino-1,1,3,3,3-pentamethyldisilazane, 1-dimethylamino-1,1,2,3,3,3-hexamethyldisilazane, 1-dimethylamino-1,1,3,3,5,5-hexamethyltrisilazane, 1-dimethylamino-1,1,3,3,5,5,5-heptamethyltrisilazane, 1-dimethylamino-1,1,3,3,5,5,7,7-octamethyltetrasilazane, 1-dimethylamino-1,1,3,3,5,5,7,7,7-nonamethyltetrasilazane, and combinations thereof.

7. A method for selective deposition of a silicon and nitrogen containing film comprising:

- (a) providing the substrate in a reaction vessel, the substrate having a first surface comprising a dielectric material having hydroxyl groups and a second surface comprising a different material having fewer or no hydroxyl groups compared to the first surface;

- (b) forming at least one self-limiting passivated layer on the first surface by exposing the first surface and the second surface to a passivating composition comprising an organoaminoalkylpolysiloxane or an organoaminoalkylpolysilazane having one of the following formulae:



wherein R¹ and R² are independently selected from a hydrogen, C₁ to C₆ alkyl group with a proviso that R¹ and R² cannot be both hydrogen; R³ and R are each independently selected from hydrogen or methyl; n=1, 2, 3; and either R¹ and R² are linked to form a cyclic ring structure or R¹ and R² are not linked to form a cyclic ring structure;

- (c) purging the reactor with inert gas;
- (d) introducing a halogenated silicon-containing precursor into the reactor to selectively form a silicon-containing layer on the second surface;
- (e) purging the reactor using inert gas;
- (f) introducing a nitrogen source to react with the silicon-containing layer to form a silicon nitride, carbon doped silicon nitride, or silicon oxynitride layer on the second surface; and
- (g) purging the reactor using inert gas;

wherein steps (d) to (g) in this embodiment are repeated to provide a certain thickness of the silicon nitride or carbon doped silicon nitride or silicon oxynitride layer selectively on the second surface area.

8. The method of claim 7, wherein the first surface is selected from the group consisting of silicon oxide, carbon doped silicon oxide, a metal oxide, and combinations thereof, and wherein the second surface comprises silicon nitride or a metal nitride.

9. The method of claim 7, wherein the second surface comprises a metal or metalloid chosen from the group consisting of ruthenium (Ru), cobalt (Co), copper (Cu), titanium, (Ti), tantalum (Ta), nickel (Ni), tungsten (W), molybdenum (Mo), and combinations thereof, or wherein the second surface comprises a metal nitride chosen from the group consisting of tantalum nitride (TaN), titanium nitride (TiN), tungsten nitride (WN), tungsten carbonitride (WCN), molybdenum nitride (MoN), copper silicon nitride (CuSiN), silicon, germanium, and combinations thereof.
10. The method of claim 7, wherein step (b) and (c) are repeated to achieve a self-limiting monolayer passivation layer before steps (d) to (g) are conducted.
11. The method of claim 10, wherein the self-limiting monolayer passivation layer can range preferably from about 0.2 Å to about 10 Å, more preferably from about 0.2 Å to about 5 Å, and most preferably from about 0.2 Å to about 3 Å.
12. The method of claim 7, wherein the certain thickness of the silicon nitride or carbon doped silicon nitride or silicon oxynitride film can range from about 1 Å to about 100 Å, or about 5 Å to about 90 Å, or about 5 Å to about 80 Å, or about 5 Å to about 70 Å or about 5 Å to about 60 Å, or about 5 Å to about 50 Å, or about 5 Å to about 40 Å, or about 5 Å to about 30 Å or about 5 Å to about 20 Å.
13. The method of claim 7, wherein the organoaminopolysiloxane of Formula IA is selected from the group consisting of 1-dimethylamino-1,1,3,3-tetramethyldisiloxane and 1-dimethylamino-1,1,3,3,3-pentamethyldisiloxane.
14. The method of claim 7, wherein the organoaminopolysilazane of Formula IB is selected from the group consisting of 1-dimethylamino-1,1,3,3,3-pentamethyldisilazane and 1-dimethylamino-1,1,2,3,3,3-hexamethyldisilazane.
15. The method of claim 7, wherein a deposition selectivity of the second surface to the first surface is greater than about 0.3, more preferably greater than about 0.5, and most preferably greater than about 0.6.

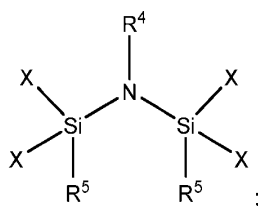
16. The method of claim 7, wherein the nitrogen source is selected from the group consisting of for example, ammonia, hydrazine, monoalkylhydrazine, dialkylhydrazine, nitrogen, nitrogen/hydrogen, nitrogen/argon plasma, nitrogen/helium plasma, ammonia plasma, nitrogen plasma, nitrogen/hydrogen plasma, piperazine, organic amines such as tert-butylamine, dimethylamine, diethylamine, isopropylamine, diethylamine plasma, dimethylamine plasma, trimethyl plasma, trimethylamine plasma, ethylenediamine plasma, and an alkoxyamine such as ethanolamine plasma, and mixtures thereof.

17. The method of claim 7, wherein the halogenated silicon-containing precursor is selected from the group consisting of: (i) halogenated silanes, (ii) halogenated siloxanes, (iii) halogenated silazanes, and (iv) halogenated carbosilanes.

18. The method of claim 17, wherein the halogenated silicon-containing precursor is a halogenated silane of group (i) chosen from the group consisting of: hexachlorodisilane, pentachlorodisilane, tetrachlorodisilane, octachlorotrisilane, dichlorosilane, monochlorosilane, monobromosilane, dibromosilane, tribromosilane, tetrabromosilane, monoiodosilane, diiodosilane, triiodosilane, and tetraiodosilane.

19. The method of claim 17, wherein the halogenated silicon-containing precursor is a halogenated siloxane of group (ii) chosen from the group consisting of: hexachlorodisiloxane, pentachlorodisiloxane, tetrachlorodisiloxane, and octachlorotrisiloxane.

20. The method of claim 17, wherein the halogenated silicon-containing precursor is a halogenated silazane of group (iii) selected from the group represented by Formula I below:

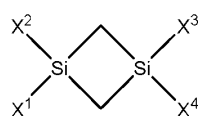


wherein R⁴ is selected from the group consisting of hydrogen, a linear or branched C₁ to C₁₀ alkyl group, a linear or branched C₃ to C₁₀ alkenyl group, a linear or branched C₃ to C₁₀ alkynyl group, a C₃ to C₁₀ cyclic alkyl group, a C₂ to C₆ dialkylamino group, an electron withdrawing group, and a C₆ to C₁₀ aryl group; R⁵ is selected from the group consisting of hydrogen, a linear or branched C₁ to C₁₀ alkyl group, a linear or branched C₂ to C₆ alkenyl group, a linear or branched C₃ to C₆ alkynyl group, a C₃ to C₁₀ cyclic alkyl group, a C₂ to C₆ dialkylamino group, a C₆ to C₁₀ aryl group, a linear or branched C₁ to C₆ fluorinated alkyl group, an electron withdrawing group, a C₄ to C₁₀ aryl group, and a halide selected from the group consisting of Cl, Br, and I; and X is a halide selected from the group consisting of Cl, Br, and I.

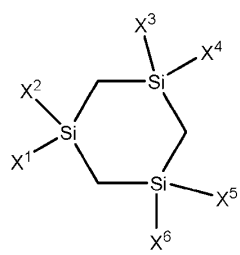
21. The method of claim 20, wherein the halogenated silazane is chosen from group (iii) and is chosen from the group consisting of: 1,1,1,3,3,3-hexachloro-disilazane, 1,1,1,3,3,3-pentachloro-disilazane, 1,1,1,3,3,3-hexachloro-2-methyldisilazane, 1,1,1,3,3,3-hexachloro-2-ethyldisilazane, 1,1,1,3,3,3-hexachloro-2-n-propyldisilazane, 1,1,1,3,3,3-hexachloro-2-iso-propyldisilazane, 1,1,1,3,3,3-hexachloro-2-n-butyldisilazane, 1,1,1,3,3,3-hexachloro-2-iso-butyldisilazane, 1,1,1,3,3,3-hexachloro-2-sec-butyldisilazane, 1,1,1,3,3,3-hexachloro-2-tert-butyldisilazane, 1,1,1,3,3,3-hexabromo-2-methyldisilazane, 1,1,1,3,3,3-bromo-2-ethyldisilazane, 1,1,1,3,3,3-bromo-2-n-propyldisilazane, 1,1,1,3,3,3-bromo-2-iso-propyldisilazane, 1,1,1,3,3,3-bromo-2-n-butyldisilazane, 1,1,1,3,3,3-bromo-2-iso-butyldisilazane, 1,1,1,3,3,3-bromo-2-sec-butyldisilazane, 1,1,1,3,3,3-bromo-2-tert-butyldisilazane, 1,1,1,3,3,3-hexaiodo-2-methyldisilazane, 1,1,1,3,3,3-iodo-2-ethyldisilazane, 1,1,1,3,3,3-iodo-2-n-propyldisilazane, 1,1,1,3,3,3-iodo-2-iso-propyldisilazane, 1,1,1,3,3,3-iodo-2-n-butyldisilazane, 1,1,1,3,3,3-iodo-2-iso-butyldisilazane, 1,1,1,3,3,3-iodo-2-sec-butyl-disilazane, 1,1,1,3,3,3-iodo-2-tert-butyl-disilazane, 1,1,1,3,3,3-pentachloro-2-methyldisilazane, 1,1,1,3,3,3-pentachloro-2-ethyldisilazane, 1,1,1,3,3,3-pentachloro-2-n-propyldisilazane, 1,1,1,3,3,3-pentachloro-2-iso-propyldisilazane, 1,1,1,3,3,3-pentachloro-2-methyl-3-methyl-disilazane, 1,1,1,3,3,3-pentachloro-2-ethyl-3-methyldisilazane, 1,1,1,3,3,3-pentachloro-2-n-propyl-3-methyldisilazane, 1,1,1,3,3,3-pentachloro-2-iso-propyl-3-methyldisilazane, 1,1,3,3,3-tetrachloro-2-methyldisilazane, 1,1,3,3,3-tetrachloro-2-ethyldisilazane, 1,1,3,3,3-tetrachloro-2-n-propyldisilazane, 1,1,3,3,3-tetrachloro-2-iso-propyldisilazane, 1,1,3,3,3-tetrachloro-2-n-butyldisilazane, 1,1,3,3,3-tetrachloro-2-iso-butyldisilazane, 1,1,3,3,3-tetrachloro-2-sec-butyldisilazane, 1,1,3,3,3-tetrachloro-2-tert-butyldisilazane, 1,1,3,3,3-

tetrabromo-2-methyldisilazane, 1,1,3,3-tetrabromo-2-ethyldisilazane, 1,1,3,3-tetrabromo-2-n-propyldisilazane, 1,1,3,3-tetrabromo-2-iso-propyldisilazane, 1,1,3,3-tetrabromo-2-n-butyldisilazane, 1,1,3,3-tetrabromo-2-iso-butyldisilazane, 1,1,3,3-tetrabromo-2-sec-butyldisilazane, 1,1,3,3-tetrachloro-2-tert-butyldisilazane, 1,1,3,3-tetraiodo-2-methyldisilazane, 1,1,3,3-tetraiodo-2-ethyldisilazane, 1,1,3,3-tetraiodo-2-n-propyldisilazane, 1,1,3,3-tetraiodo-2-iso-propyldisilazane, 1,1,3,3-tetraiodo-2-n-butyldisilazane, 1,1,3,3-tetraiodo-2-iso-butyldisilazane, 1,1,3,3-tetraiodo-2-sec-butyldisilazane, 1,1,3,3-tetraiodo-2-tert-butyldisilazane, 1,1,3,3-tetrachloro-2-cyclopentyldisilazane, 1,1,3,3-tetrachloro-2-cyclohexyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-cyclopentyl-2-cyclopentyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-cyclohexyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-methyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-tetrachloro-2-ethyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-n-propyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-iso-propyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-n-butyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-iso-butyldisilazane, 1,1,3,3-tetrachloro-1,3-dimethyl-2-sec-butyldisilazane, and 1,1,3,3-tetrachloro-1,3-dimethyl-2-tert-butyldisilazane, and combinations thereof.

22. The method of claim 17, wherein the halogenated silicon-containing precursor is a halogenated carbosilane of group (iv) selected from the group consisting of: silicon compounds having one or two Si-C-Si linkages. Preferred carbosilanes of group iv include those represented by Formulae II, and III:



II



III

wherein X^1 , X^2 , X^3 , X^4 , X^5 , and X^6 are each independently chosen from a H atom; a halide atom selected from F, Cl, Br, and I; isocyanate; an amino group having the formula NR^5R^6 wherein R^5 and R^6 are independently selected from the group consisting of hydrogen, a C_{1-10} linear alkyl group; a C_{3-10} branched alkyl group; a C_{3-10}

cyclic alkyl group; a C₃₋₁₀ alkenyl group; a C₄₋₁₀ aryl group; and a C₄₋₁₀ heterocyclic group; In some embodiments of Formula I, II, or both I and II, and one or more of substituents X¹, X², X³, X⁴, X⁵, and X⁶ is linked to form a substituted or unsubstituted, saturated or unsaturated, cyclic group. In one particular embodiment of Formula II, III, or both II and III, any one or more of substituents X¹, X², X³, X⁴, X⁵, and X⁶ is either halide or amino group described above. For II, X¹, X², X³, X⁴, X⁵, and X⁶ cannot be all amino groups. In certain embodiments of Formula II or III, R⁵ and R⁶ in the amino group having the formula NR⁵R⁶ are linked together to form a ring. In one particular embodiment, R⁵ and R² are selected from a linear or a branched C₃ to C₆ alkyl group and are linked to form a cyclic ring. In alternative embodiments of Formula II or III, R⁵ and R⁶ are not linked together to form a ring. In other embodiments, R⁵ and R⁶ are different.

23. The method of claim 17, wherein the halogenated silicon-containing precursor is a halogenated carbosilane chosen from the group consisting of: 1,1,1,3,3,3-hexachloro-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-methyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2,2-dimethyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-ethyl-1,3-disilapropane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,3,3,5,5-hexachloro-1,5-dimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane, 1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane, and 1,1,5,5-tetrachloro-1,3,5-trisilapentane, 1-chloro-1,3-disilacyclobutane, 1-bromo-1,3-disilacyclobutane, 1-iodo-1,3-disilacyclobutane, 1,3-dichloro-1,3-disilacyclobutane, 1,3-dibromo-1,3-disilacyclobutane, 1,3-diiodo-1,3-disilacyclobutane, 1,1-dichloro-1,3-disilacyclobutane, 1,1-dibromo-1,3-disilacyclobutane, 1,1-diiodo-1,3-disilacyclobutane, 1,1,3-trichloro-1,3-disilacyclobutane, 1,1,3-tribromo-1,3-disilacyclobutane, 1,1,3-triiodo-1,3-disilacyclobutane, 1,1,3,3-tetrachloro-1,3-disilacyclobutane, 1,1,3,3-tetrabromo-1,3-disilacyclobutane, 1,1,3,3-tetraiodo-1,3-disilacyclohexane, 1,1,3,3-tetra(dimethylamino)-1,3-disilacyclobutane, 1,3-bis(dimethylamino)-1,3-dichloro-1,3-disilacyclobutane, 1-(dimethylamino)-1,3,3-trichloro-1,3-disilacyclobutane, 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, 1,3-bis(dimethylamino)-1,3-dimethyl-1,3-disilacyclobutane, 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane, 1,1,3,3-tetrachloro-1,3,5-trisilacyclohexane, 1,3,5-trichloro-1,3,5-trisilacyclohexane, and combinations thereof.

24. The method of claim 1, wherein a pre-clean step is conducted prior to step (a), the pre-clean step comprising exposing the surfaces to alcohol, a plasma comprising hydrogen, or a composition comprising fluorine.

25. The method of claim 1, wherein R^1 and R^2 are both methyl groups or wherein R^1 is hydrogen and R^2 is a methyl group.