

SILICON-CONTAINING FILMS HAVING SURFACES MODIFIED FROM HALOGENATED SILICON-CONTAINING COMPOUNDS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to United States Provisional Patent Application number 63/588,994, filed on October 9, 2023, the entire contents of which are herein incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention is directed to compositions and methods for the fabrication of an electronic device. More specifically, the invention is directed to compounds, compositions and methods for the deposition of a high quality silicon-containing film such as, without limitation, a silicon nitride, a carbon-doped silicon nitride film, a silicon oxynitride, and a carbon-doped silicon oxynitride film.

BACKGROUND OF THE INVENTION

[0003] Silicon nitride films are used in semiconductors for a variety of applications. For example, a silicon nitride film is commonly used as a final passivation and mechanical protective layer for integrated circuits, a mask layer for selective oxidation of silicon, as one of the dielectric materials in a stacked oxide-nitride-oxide (O-N-O) layer in a DRAM capacitor or in 3D NAND flash memory chips, or as a CMP stop layer in a shallow trench isolation application.

[0004] There is a need to form a conformal and continuous thin layer < 200 Å or less, < 150 Å or less, < 100 Å or less, < 50 Å or less, < 30 Å or less, < 20 Å or less, < 15 Å or less, < 10 Å or less of high quality silicon-containing films such as silicon nitride, carbon doped silicon oxide, silicon oxynitride or carbon doped silicon oxynitride on an oxide surface such as silicon oxide or other metal oxide. Chlorosilanes or chlorodisilanes, such as dichlorosilane and, hexachlorodisilane, and

ammonia-based process are commonly used to deposit high quality silicon nitride. However, chloro- ligands have relatively high activation energy to react with the oxide surface, resulting in so-called island growth. The silicon-containing films needs to be a certain critical thickness for chlorosilane based films to achieve smooth and continuous films.

[0005] Furthermore, pitch width shrinks with every generation of semiconductor devices, which in turn cause the films to shrink. In some applications, a thin silicon nitride layer is deposited on top of a silicon oxide or other type of metal oxide using atomic layer deposition (ALD) processes including chlorosilanes/chlorodisilanes and ammonia. At the beginning of the deposition process the films have island growth which is not uniform and continuous. After reaching certain critical thickness, the island growth becomes a smooth and continuous layer of Si nitride. Therefore, there is a need to develop a process for forming smooth and continuous high quality silicon-containing such as silicon nitride or carbon-doped silicon nitride using a chemical vapor deposition (CVD) or an atomic layer deposition (ALD) process or an ALD-like process, such as without limitation a cyclic CVD process.

[0006] Olsen, "Analysis of LPCVD Process Conditions for the Deposition of Low Stress Silicon Nitride", 5 Materials Science in Semiconductor Process 51 (2002) describes a wide range of process conditions that are used to optimize the deposition of low stress silicon nitride films by low-pressure chemical vapor deposition. The results show that an increase in the index of refraction beyond 2.3 by means of increasing the gas flow did not reduce the residual stress appreciably but had a significant detrimental effect on the thickness uniformity and deposition rate.

[0007] M. Tanaka et al., "Film Properties of Low-k Silicon Nitride Films Formed by Hexachlorodisilane and Ammonia", 147 J. Electrochem. Soc. 2284 (2000) describes a low-temperature process with good step coverage of silicon nitride (SiN) formed by low-pressure chemical vapor deposition (LPCVD) using hexachlorodisilane (HCDS).

[0008] JP2000100812 describes a method for depositing a film using SiCl_4 and NH_3 as source gases. The substrate surface may be nitrified using NH_3 prior to deposition. An extremely thin film having an improved insulator property is formed. The silicon

nitride film is useful as a capacitor insulator film of a semiconductor integrated circuit.

[0009] US Pat. No. 6,355,582 describes a method for forming a silicon nitride film wherein the substrate to be subjected to the film formation is heated, and silicon tetrachloride and ammonia gases are supplied to the substrate heated to a predetermined temperature.

[0010] US Pat. No. 10,049,882 describes an atomic layer deposition (ALD) method for fabricating a semiconductor device including the step of forming a dielectric layer on a structure having a height difference. The method includes forming a structure with a height difference on a substrate and forming a dielectric layer structure on the structure. Forming the dielectric layer structure includes forming a first dielectric layer including silicon nitride on the structure with the height difference. Forming the first dielectric layer includes feeding a first gas including pentachlorodisilane (PCDS) or diisopropylamine pentachlorodisilane (DPDC) as a silicon precursor, and a second gas including nitrogen components into a chamber including the substrate such that the first dielectric layer is formed in situ on the structure having the height difference.

[0011] US Pub. No. 2022119947 A discloses a class of chlorodisilazanes, silicon-heteroatom compounds synthesized therefrom, devices containing the silicon-heteroatom compounds, methods of making the chlorodisilazanes, the silicon-heteroatom compounds, and the devices; and uses of the chlorodisilazanes, silicon-heteroatom compounds, and devices.

[0012] US Pat. No. 11,142,462 discloses a composition that includes trichlorodisilane as a silicon precursor for use in film forming. The composition includes the silicon precursor compound and at least one of an inert gas, molecular hydrogen, a carbon precursor, a nitrogen precursor, and an oxygen precursor. The publication also discloses a method of forming a silicon-containing film on a substrate using the silicon precursor compound and the silicon-containing film formed thereby.

[0013] US Pat. No. 9,984,868 discloses cyclical methods of depositing a silicon nitride film on a substrate. In one embodiment such a method includes supplying a

halogen silane as a silicon precursor into a reactor; supplying a purge gas to the reactor; and providing an ionized nitrogen precursor into the reactor to react with the substrate and form the silicon nitride film.

[0014] US Pub. No. 2009/0155606 discloses cyclical methods of depositing a silicon nitride film on a substrate. In one embodiment a method includes supplying a chlorosilane to a reactor in which a substrate is processed; supplying a purge gas to the reactor; and providing ammonia plasma to the reactor. The method allows a silicon nitride film to be formed at a low process temperature and a high deposition rate. The resulting silicon nitride film has relatively few impurities and a relatively high quality. In addition, a silicon nitride film having good step coverage over features having high aspect ratios and a thin and uniform thickness can be formed.

[0015] The disclosures of the previously identified patents, patent applications and publications are hereby incorporated by reference.

BRIEF SUMMARY OF THE INVENTION

[0016] The above-described needs are met in one respect by providing a novel deposition method comprising an ALD thinner seed layer followed ALD thicker layer to achieve a conformal and continuous high quality silicon-containing films such as silicon nitride to meet the requirements for future semi-conductor devices.

[0017] The above needs and others are met by a method for deposition of a high quality smooth and continuous silicon-containing film that includes a) providing at least one substrate in a reactor, b) heating the reactor to at least one temperature ranging from ambient temperature to about 750°C and optionally maintaining the reactor at a pressure of about 100 torr or less, c) introducing into the reactor at least one first silicon precursor comprising at least one organoamino group and at least one halido group having a formula:



wherein $m = 0, 1, 2$; $n = 1, 2, 3$, and $m + n \leq 3$; X is selected from the group consisting of Cl, Br, and I; R^1 and R^2 are each independently selected from the group

consisting of 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, to form a first silicon-containing layer, d) purging any unreacted precursor from the reactor using inert gas, e) introducing a nitrogen source to react with the first silicon-containing layer to form a seed layer comprising at least one selected from the group consisting of silicon nitride and carbon doped silicon nitride, f) purging the reactor using inert gas, g) introducing at least one second silicon precursor comprising a halogenated silicon-containing compound into the reactor to react with the seed layer and form a second silicon-containing layer comprising at least one selected from the group consisting of silicon nitride, carbon doped silicon nitride, silicon oxynitride and carbon doped silicon oxynitride, h) purging the reactor using inert gas, i) introducing a nitrogen source to react with the second silicon-containing layer to form a silicon nitride or carbon doped silicon nitride, and j) purging the reactor using inert gas.

BRIEF DESCRIPTION OF THE DRAWING

[0018] Figure 1 shows GPC for silicon nitride deposition on silicon oxide with or without silicon nitride seed layer according to Working Example 1 in the following.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Throughout the description, the term “ALD or ALD-like” refers to a process including, but not limited to, the following processes: a) each reactant including silicon precursor and reactive gas is introduced sequentially into a reactor such as a single wafer ALD reactor, semi-batch ALD reactor, or batch furnace ALD reactor; b) each reactant including silicon precursor and reactive gas is exposed to a substrate by moving or rotating the substrate to different sections of the reactor and each section is separated by inert gas curtain, i.e. spatial ALD reactor or roll to roll ALD reactor.

[0020] Throughout the description, the term “plasma including/comprising ammonia” refers to a reactive gas or gas mixture generated in situ or remotely via a

plasma generator. The gas or gas mixture is selected from the group consisting of ammonia, a mixture of ammonia and helium, a mixture of ammonia and neon, a mixture of ammonia and argon, a mixture of ammonia and nitrogen, a mixture of ammonia and hydrogen, and combinations thereof.

[0021] Throughout the description, the term “plasma including/comprising hydrogen or deuterium” refers to a reactive gas or gas mixture generated in situ or remotely via a plasma generator. The gas or gas mixture is selected from the group consisting of hydrogen or deuterium, a mixture of hydrogen or deuterium and helium, a mixture of hydrogen or deuterium and neon, a mixture of hydrogen and argon, a mixture of hydrogen or deuterium and nitrogen and combinations thereof. Throughout the description, the term “alkyl” refers a linear or branched C₁ to C₂₀ hydrocarbon, cyclic C₆ to C₂₀ hydrocarbon. Exemplary hydrocarbons include, but are not limited to, methyl, ethyl, iso-propyl, n-propyl, sec-butyl, iso-butyl, n-butyl, tert-butyl.

[0022] In one embodiment, the method described according to an exemplary embodiment comprises:

- a) providing at least one substrate in a reactor,
- b) heating the reactor to at least one temperature ranging from ambient temperature to about 750°C and optionally maintaining the reactor at a pressure of about 100 torr or less;
- c) introducing into the reactor at least one first silicon precursor comprising at least one organoamino group and at least one halido group having a formula $\text{SiH}_m\text{X}_n(\text{NR}^1\text{R}^2)_{4-m-n}$ wherein $m = 0, 1, 2$; $n = 1, 2, 3$ and $m + n \leq 3$; X is selected from the group consisting of Cl, Br, and I; R¹ and R² are each independently selected from the group consisting of 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 that forms a silicon-containing layer;
- d) purging any unreacted precursor from the reactor using inert gas;
- e) introducing a nitrogen source to react with the silicon-containing layer to form a silicon nitride or carbon doped silicon nitride seed layer;

- f) purging the reactor using inert gas;
- g) introducing a second silicon precursor comprising halogenated silicon compounds into the reactor to react with the silicon nitride or carbon doped silicon nitride film to form a silicon nitride or carbon doped silicon nitride or silicon oxynitride or carbon doped silicon oxynitride;
- h) purging the reactor using inert gas;
- i) introducing a nitrogen source to react with the silicon-containing layer to form a silicon nitride or carbon doped silicon nitride seed layer, and;
- j) purging the reactor using inert gas.

[0023] In some embodiments, steps g to j are repeated to provide a certain thickness of smooth and continuous silicon nitride or carbon doped silicon nitride or silicon oxynitride or carbon doped silicon oxynitride after step f. In other embodiments of this invention, steps c to f are repeated to achieve a desired thickness of silicon nitride or silicon carbonitride seed layer ranging from about 0.2 Å to about 1 Å or less, 0.2 Å to about 2 Å or less, or about 0.2 Å to about 3 Å or less, or about 0.2 Å to about 5 Å or less, or about 0.2 Å to about 8 Å or less, or about 0.2 Å to about 10 Å or less, followed repeating steps g to j to provide a desired thickness of smooth and continuous silicon nitride or carbon doped silicon nitride or silicon oxynitride or carbon doped silicon oxynitride ranging from about 5 Å to about 2000 Å or more, or about 5 Å to about 1000 Å or more, or about 5 Å to about 800 Å or more, or about 5 Å to about 500 Å or more, or about 5 Å to about 400 Å or more, or about 5 Å to about 100 Å or more, or about 5 Å to about 50 Å or more, or about 5 Å to about 20 Å or more.

[0024] According to an exemplary embodiment, steps c to f are conducted in one reactor chamber while steps g to j are performed at a same or different substrate temperature in the same reactor chamber or another reactor chamber.

[0025] 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.

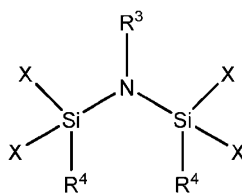
[0026] Some exemplary first silicon precursors are selected from the group consisting of (di-iso-propylamino)chlorosilane, (di-iso-propylamino)dichlorosilane, (di-iso-propylamino)trichlorosilane, (di-sec-butylamino)chlorosilane, (di-sec-butylamino)dichlorosilane, (di-sec-butylamino)trichlorosilane, (di-iso-propylamino)bromosilane, (di-iso-propylamino)dibromosilane, (di-iso-propylamino)tribromosilane, (di-sec-butylamino)bromosilane, (di-sec-butylamino)dibromosilane, (di-sec-butylamino)tribromosilane, (di-iso-propylamino)iodosilane, and (di-iso-propylamino)diiodosilane. It is believed that the organoamino group reacts with hydroxyl group on the substrate surface to provide a conformal silicon halido-containing monolayer which would react with ammonia to result in smooth and continuous silicon nitride seed layer.

[0027] Exemplary halogenated silicon compounds can be selected from the group consisting of i) halogenated silanes, ii) halogenated siloxanes, iii) halogenated silazanes, and iv) halogenated carbosilanes.

[0028] The halogenated silanes of group i include but are not limited to, monochlorosilane, dichlorosilane, trichlorosilane, tetrachlorosilane, hexachlorodisilane, pentachlorodisilane, tetrachlorodisilane, octachlorotrisilane, dichlorosilane, monochlorosilane, monobromosilane, dibromosilane, tribromosilane, tetrabromosilane, monoiodosilane, diiodosilane, triiodosilane, tetraiodosilane.

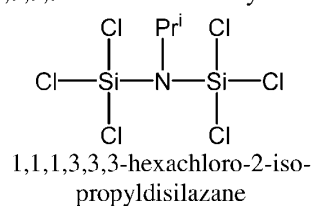
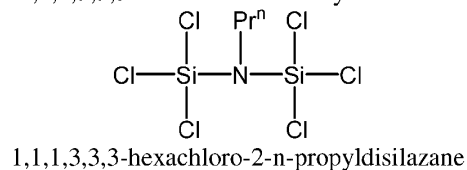
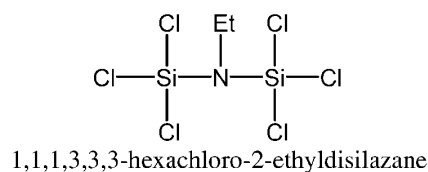
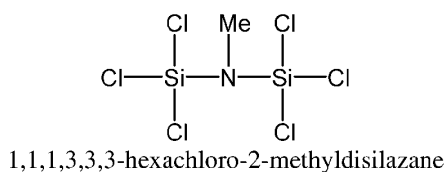
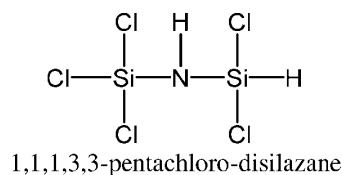
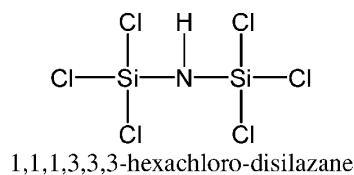
[0029] The halogenated siloxanes of group ii include, but are not limited to, hexachlorodisiloxane, pentachlorodisiloxane, tetrachlorodisiloxane, octachlorotrisiloxane.

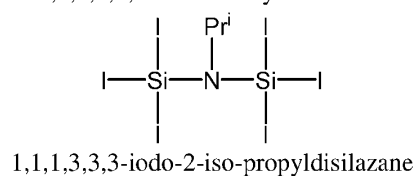
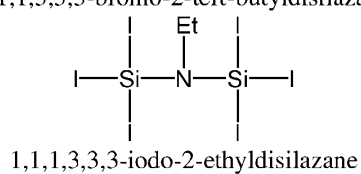
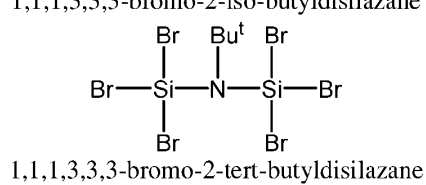
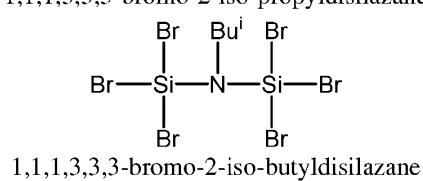
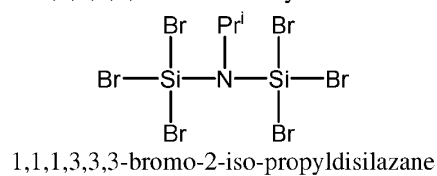
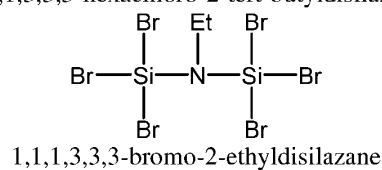
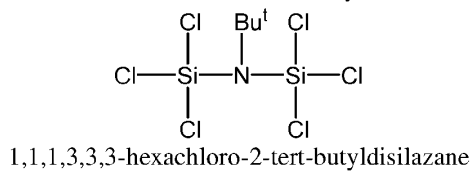
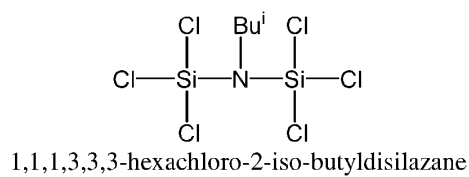
[0030] The halogenated silazanes of group iii are selected from the groups represented by the following Formula I below:

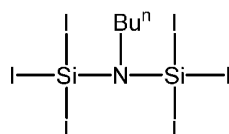


wherein R^3 is selected from the group consisting of hydrogen, a linear or branched C_1 to C_{10} alkyl group, a linear or branched C_3 to C_{10} alkenyl group, a linear or branched C_3 to C_{10} alkynyl group, a C_3 to C_{10} cyclic alkyl group, a C_2 to C_6 dialkylamino group, an electron withdrawing group, and a C_6 to C_{10} aryl group; R^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_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.

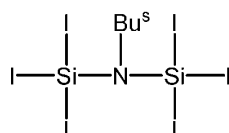
[0031] Examples of group iii of halogenated silazanes may be represented in structures below:



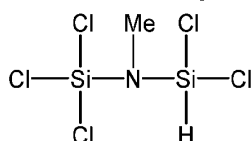




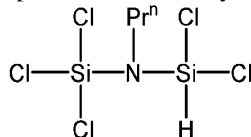
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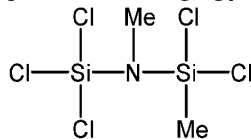
1,1,1,3,3,3-iodo-2-sec-butyl-disilazane



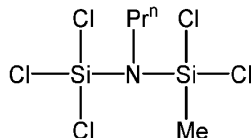
1,1,1,3,3-pentachloro-2-methyldisilazane



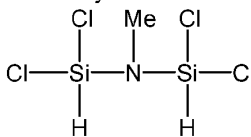
1,1,1,3,3-pentachloro-2-n-propyldisilazane



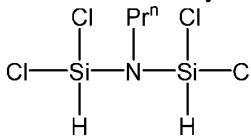
1,1,1,3,3-pentachloro-2-methyl-3-methyl-disilazane



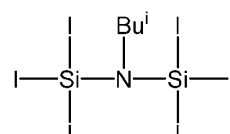
1,1,1,3,3-pentachloro-2-n-propyl-3-methyldisilazane



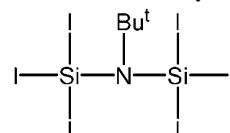
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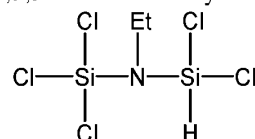
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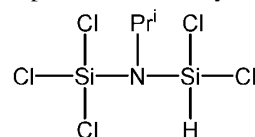
1,1,1,3,3,3-iodo-2-iso-butyldisilazane



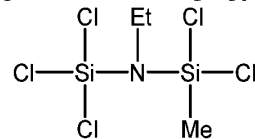
1,1,1,3,3,3-iodo-2-tert-butyl-disilazane



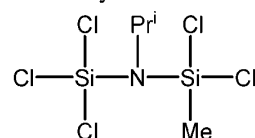
1,1,1,3,3-pentachloro-2-ethyldisilazane



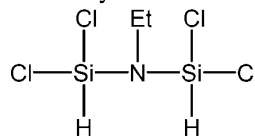
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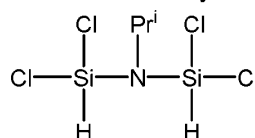
1,1,1,3,3-pentachloro-2-ethyl-3-methyldisilazane



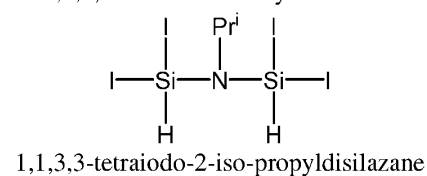
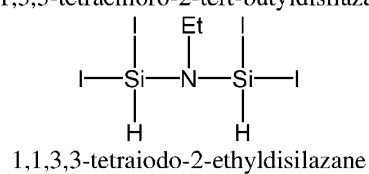
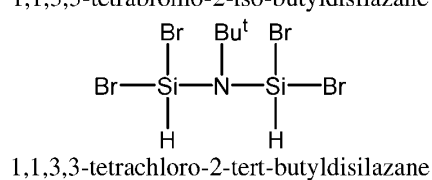
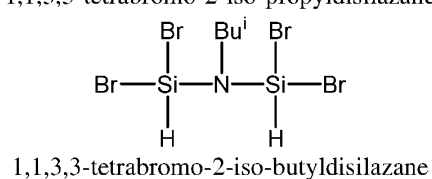
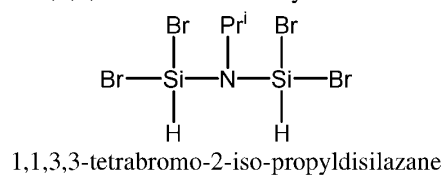
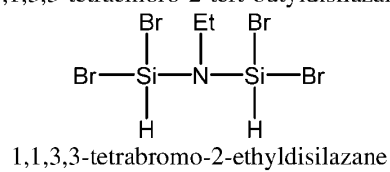
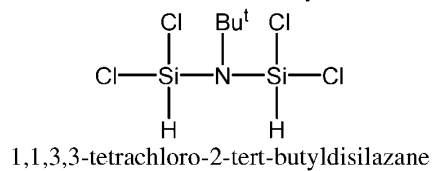
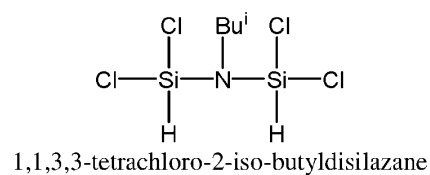
1,1,1,3,3-pentachloro-2-iso-propyl-3-methyldisilazane

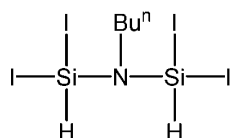


1,1,3,3-tetrachloro-2-ethyldisilazane

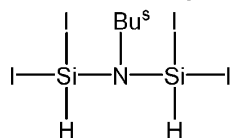


1,1,3,3-tetrachloro-2-iso-propyldisilazane

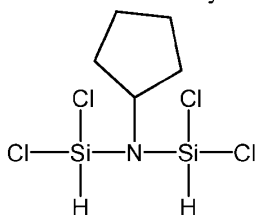




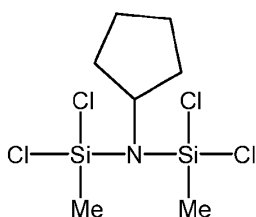
1,1,3,3-tetraiodo-2-n-butylidisilazane



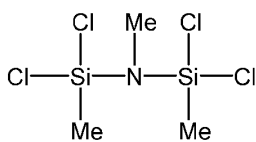
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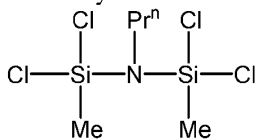
1,1,3,3-tetrachloro-2-cyclopentylidisilazane



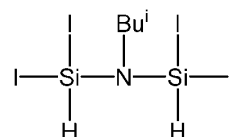
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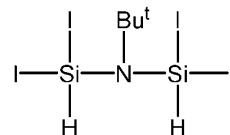
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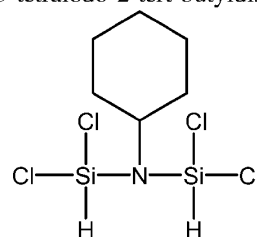
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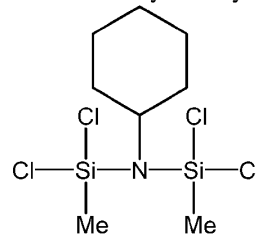
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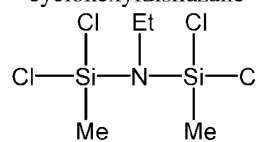
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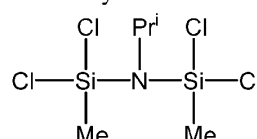
1,1,3,3-tetrachloro-2-cyclohexylidisilazane



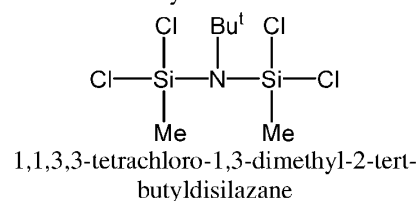
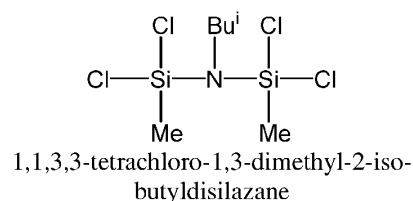
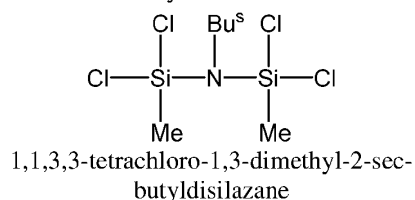
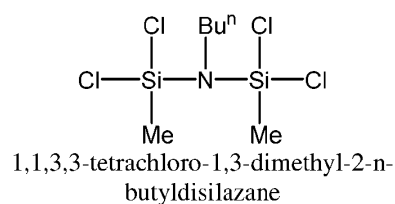
1,1,3,3-tetrachloro-1,3-dimethyl-2-cyclohexylidisilazane



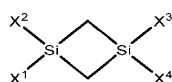
1,1,3,3-tetrachloro-1,3-dimethyl-2-ethylidisilazane



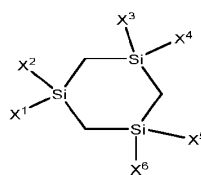
1,1,3,3-tetrachloro-1,3-dimethyl-2-iso-propylidisilazane



[0032] 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

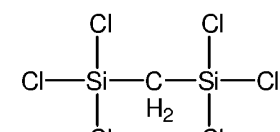


III

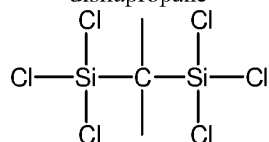
wherein X^1 , X^2 , X^3 , X^4 , X^5 , and X^6 are each independently chosen from a H atom; a halide atom selected from F, Cl, Br, and I; isocyanate; an amino group having the formula NR^5R^6 wherein R^5 and R^6 are independently selected from the group consisting of hydrogen, a C_{1-10} linear alkyl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

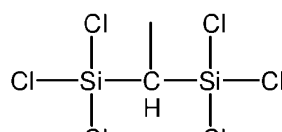
[0033] Examples of group iv halogenated carbosilanes may be represented by the structures below:



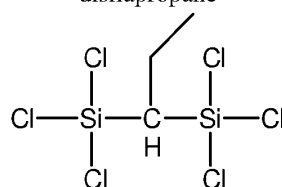
1,1,1,3,3,3-hexachloro-1,3-disilapropane



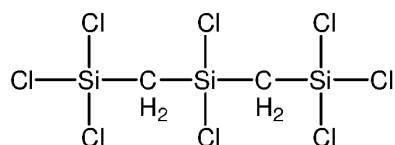
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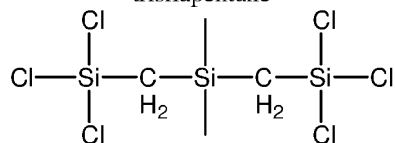
1,1,1,3,3,3-hexachloro-2-methyl-1,3-disilapropane



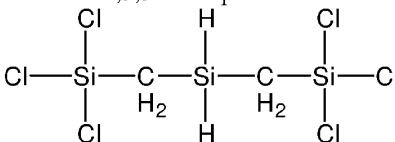
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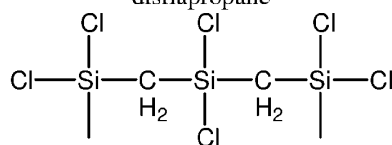
1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane



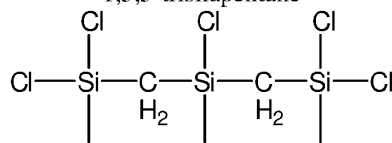
1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane



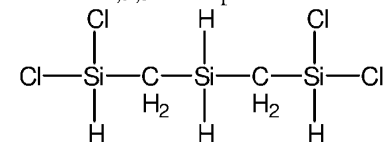
1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane



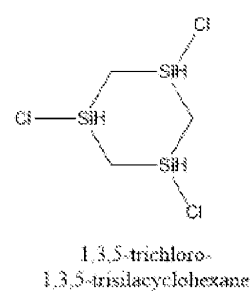
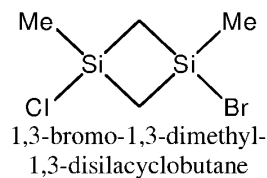
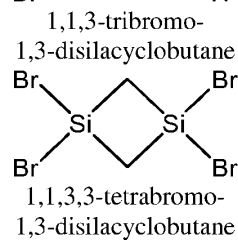
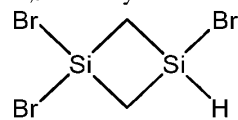
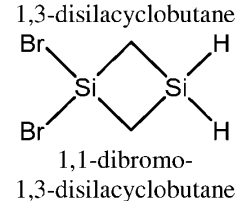
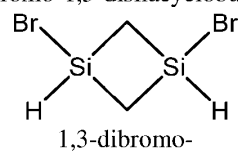
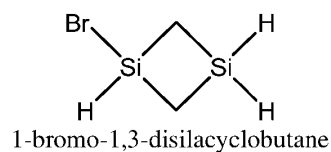
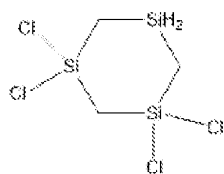
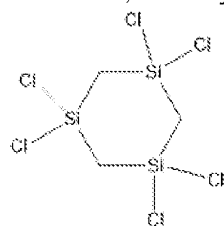
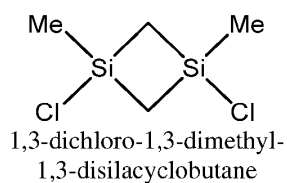
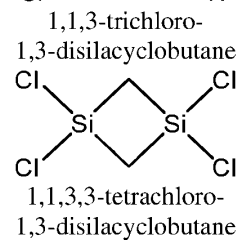
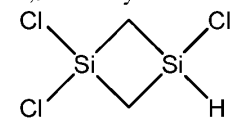
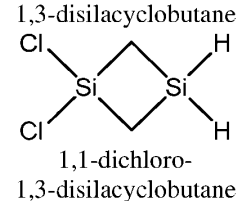
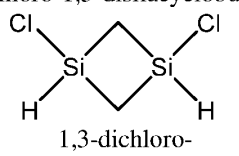
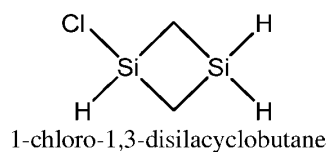
1,1,3,3,5,5-hexachloro-1,5-dimethyl-1,3,5-trisilapentane



1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane



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



Working Example 1. Use of (di-iso-propylamino)dichlorosilane for silicon nitride seed layer

[0034] (Di-iso-propylamino)dichlorosilane was used to form nitride seed layer on silicon native oxide surface. The subsequent silicon nitride was growth with monochlorosilane and ammonia. The deposition process was performed using a Picosun screening ALD tool equipped with a J.A.Woollam in-situ ellipsometer.

[0035] The silicon nitride seed layer was achieved by exposing (di-iso-propylamino)dichlorosilane on the wafer surface and confirmed with the use of the J.A.Woollam in-situ ellipsometer.

[0036] The process steps for deposition silicon nitride were as follows:

- a. Introduce Si wafer with native oxide into the reactor
- b. Heat up the reactor to 300 °C
- c. Introduce (di-iso-propylamino)dichlorosilane into the reactor for 40 s
- d. Purge reaction byproducts from the reactor using 500 sccm Ar for 10 s
- e. Introduce NH₃ plasma for 10 s
 - NH₃ flow = 30 sccm
 - Ar flow = 150 sccm
 - Plasma power = 2500 W; Plasma frequency = 2 GHz
- f. Purge reaction byproducts from the reactor using 500 sccm Ar for 10 s
- g. Introduce monochlorosilane (MCS) into reactor for 1s
 - MCS flow = 80 sccm.
- h. Purge reaction byproducts from the reactor using 500 sccm Ar for 10 s
- i. Introduce NH₃* for 10 s
 - NH₃ flow = 30 sccm
 - Ar flow = 150 sccm
 - Plasma power = 2500 W; Plasma frequency = 2 GHz

- j. Purge reaction byproducts from the reactor using 500 sccm Ar for 10 s

Steps g-j were repeated 100 times to get desired thickness of silicon nitride. The sample was removed from the reactor.

For comparison, monochlorosilane and NH_3 plasma was used to grow silicon nitride on silicon native oxide surface without seed layer. The process utilized steps below:

- a. Introduce Si wafer with native oxide into the reactor
- b. Heat up the reactor to 300 °C
- c. Introduce NH_3 plasma for 10 s
 - NH_3 flow = 30 sccm
 - Ar flow = 150 sccm
 - Plasma power = 2500 W; Plasma frequency = 2 GHz
- d. Purge reaction byproducts from the reactor using 500 sccm Ar for 10 s
- e. Introduce monochlorosilane (MCS) into reactor for 1s
 - MCS flow = 80 sccm.
- f. Purge reaction byproducts from the reactor using 500 sccm Ar for 10 s
- g. Introduce NH_3 plasma for 10 s
 - NH_3 flow = 30 sccm
 - Ar flow = 150 sccm
 - Plasma power = 2500 W; Plasma frequency = 2 GHz
- h. Purge reaction byproducts from the reactor using 500 sccm Ar for 10 s

Steps e to h were repeated 100 times to get desired thickness of silicon nitride. The sample was removed from the reactor.

[0037] In-situ the ellipsometer was used to determine film thickness and calculate film growth. Figure 1 shows growth per cycle (GPC) of as-deposited silicon nitride using monochlorosilane and NH_3 plasma on silicon oxide surface at 600 °C. Error bar represents 5 repeated runs (circle) for deposition without seed layer on silicon oxide

surface; (cross) for deposition on silicon oxide surface with seed layer using (di-iso-propylamino)dichlorosilane with steps c to f being conducted once.

[0038] Films deposited on treated surface have GPC (~0.4 Å/cycle) starting from the 1st deposition cycle. The GPC was consistent over the deposition process of 10 cycles. On the other hand, the films deposited on non-treated surface have larger variations. In addition, the film deposited with a seed layer has better smoothness than the one deposited without a seed layer. Both smoother films and lower GPC variation on film growth on the surface with silicon nitride seed layer on silicon oxide surface suggested more consistent, higher quality film deposition.

[0039] Atomic Force Microscopy (AFM) was used to measure film roughness. Table 1 shows surface roughness of deposited films, indicating the treated surface provides a much smoother silicon nitride film, i.e. 0.12 nm vs 0.15nm.

Table 1. Roughness of deposited films

	Roughness (nm)
Non-treated surface	0.149 ± 0.008
Seed layer using (di-iso-propylamino)dichlorosilane silane	0.120 ± 0.005

[0040] Although illustrated and described above with reference to certain specific embodiments and working examples, the present invention is nevertheless not intended to be limited to the details shown. Rather, various modifications may be made in the details within the scope and range of equivalents of the claims and without departing from the spirit of the invention. It is expressly intended, for example, that all ranges broadly recited in this document include within their scope all narrower ranges which fall within the broader ranges.

THE FOLLOWING IS CLAIMED

1) A method for deposition of high quality smooth and continuous silicon-containing film, comprising:

a) providing at least one substrate in a reactor,

b) heating the reactor to at least one temperature ranging from ambient temperature to about 750°C and optionally maintaining the reactor at a pressure of about 100 torr or less;

c) introducing into the reactor at least one first silicon precursor comprising at least one organoamino group and at least one halido group having a formula:



wherein $m = 0, 1, 2$; $n = 1, 2, 3$, and $m + n \leq 3$; X is selected from the group consisting of Cl, Br, and I; R^1 and R^2 are each independently selected from the group consisting of 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, to form a first silicon-containing layer;

d) purging any unreacted precursor from the reactor using inert gas;

e) introducing a nitrogen source to react with the first silicon-containing layer to form a seed layer comprising at least one selected from the group consisting of silicon nitride and carbon doped silicon nitride;

f) purging the reactor using inert gas

g) introducing at least one second silicon precursor comprising a halogenated silicon-containing compound into the reactor to react with the seed layer and form a second silicon-containing layer comprising at least one selected from the group consisting of silicon nitride, carbon doped silicon nitride, silicon oxynitride and carbon doped silicon oxynitride;

h) purging the reactor using inert gas;

i) introducing a nitrogen source to react with the second silicon-containing layer to form a silicon nitride or carbon doped silicon nitride; and

j) purging the reactor using inert gas.

2) The method of claim 1 wherein steps c to f are repeated to provide a certain thickness of the seed layer, and steps g to j are repeated to achieve a smooth and continuous second silicon-containing layer.

3) The method of claim 2 wherein steps c to f are repeated to achieve a thickness of the seed layer ranging from about 0.2 Å to about 20 Å, preferably 0.2 Å to about 10 Å, most preferably 0.2 Å to about 5 Å

4) The method of claim 2 wherein steps g to j are repeated to achieve a thickness of the second silicon-containing layer ranging from about 5 Å to about 2000 Å.

5) The method of claim 1, wherein steps c to f are conducted in one reactor chamber while steps g to j are performed at the same or different substrate temperature in the same reactor chamber or another reactor chamber.

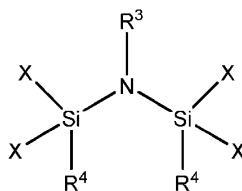
6) The method of claim 1, wherein the at least one first silicon precursor is one or more selected from the group consisting of (di-iso-propylamino)chlorosilane, (di-iso-propylamino)dichlorosilane, (di-iso-propylamino)trichlorosilane, (di-sec-butylamino)chlorosilane, (di-sec-butylamino)dichlorosilane, (di-sec-butylamino)trichlorosilane, (di-iso-propylamino)bromosilane, and (di-iso-propylamino)dibromosilane, (di-iso-propylamino)iodosilane, and (di-iso-propylamino)diiodosilane.

7) The method of claim 1 wherein the at least one second silicon precursor is at least one selected from the group consisting of i) halogenated silanes, ii) halogenated siloxanes, iii) halogenated silazanes, and iv) halogenated carbosilanes.

8) The method of claim 7 wherein the halogenated silane is selected from the group consisting of monochlorosilane, dichlorosilane, trichlorosilane, tetrachlorosilane, hexachlorodisilane, pentachlorodisilane, tetrachlorodisilane, octachlorotrisilane, dichlorosilane, monochlorosilane, monobromosilane, dibromosilane, tribromosilane, tetrabromosilane, monoiodosilane, diiodosilane, triiodosilane, and tetraiodosilane.

9) The method of claim 7 wherein the halogenated siloxane is selected from the group consisting of hexachlorodisiloxane, pentachlorodisiloxane, tetrachlorodisiloxane, and octachlorotrisiloxane.

10) The method of claim 7 wherein the halogenated silazane has a structure according to Formula I:

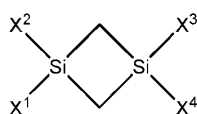


Formula I

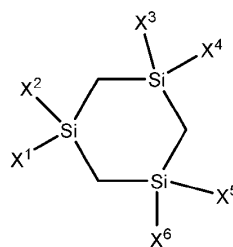
wherein R^3 is selected from the group consisting of hydrogen, a linear or branched C_1 to C_{10} alkyl group, a linear or branched C_3 to C_{10} alkenyl group, a linear or branched C_3 to C_{10} alkynyl group, a C_3 to C_{10} cyclic alkyl group, a C_2 to C_6 dialkylamino group, an electron withdrawing group, and a C_6 to C_{10} aryl group; R^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_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 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.

11) The method of claim 7 wherein the halogenated carbosilane has a structure according to Formulae II or III:



Formula II



Formula III

wherein X¹, X², X³, X⁴, X⁵, and X⁶ are each independently chosen from hydrogen, a halide atom selected from F, Cl, Br, and I, isocyanate, an amino group having the formula NR⁵R⁶ wherein R⁵ and R⁶ are independently selected from the group consisting of hydrogen, a C₁₋₁₀ linear alkyl group; a C₃₋₁₀ branched alkyl group, a C₃₋₁₀ cyclic alkyl group, a C₃₋₁₀ alkenyl group, a C₄₋₁₀ aryl group, and a C₄₋₁₀ heterocyclic group, and optionally are linked together to form a ring,

and wherein for either Formula II or Formula III one or more of substituents X¹, X², X³, X⁴, X⁵, and X⁶ is optionally linked to form a substituted or unsubstituted, saturated or unsaturated, cyclic group, or optionally are either halide or amino group as described above with the proviso that X¹, X², X³, X⁴, X⁵, and X⁶ cannot be all amino groups, and optionally in Formula II or III, R⁵ and R⁶ in the amino group having the formula NR⁵R⁶ are linked together to form a ring.