The term about" when used in reference to numerical values includes a range of ±10% of the recited numerical value, unless otherwise specified.

The term "alkyl", as used herein, refers to saturated substituents containing exclusively carbon and hydrogen atoms. Alkyls include linear, branched and cyclic groups. Examples of linear alkyl groups include without limitation, methyl groups, ethyl groups, *n*-propyl groups, *n*-butyl groups, etc. Examples of branched alkyls groups include without limitation, isopropyl, isobutyl, *sec*-butyl, and *t*-butyl. Examples of cycloalkyls include without limitation, cyclopropyl groups, cyclopentyl groups, cyclohexyl groups, etc.

The term "alkylamino", as used herein, refers to NR_2 group, wherein at least one R is an alkyl, and each R is independently selected from H and an alkyl. Examples of alkylamino substituents include dimethylamino and diethylamino substituents.

The term "independently selected", when referring to R substituent selection in a molecule containing multiple R groups, means that the selection of R substituents at different atoms of a molecule is independent and that the selection of R substituents at one atom having multiple R substituents is also independent. In molecules containing multiple R groups, R groups may be same or different.

Silicon-containing films with controlled thicknesses can be deposited on semiconductor substrates by sequentially exposing the substrate to a silicon-containing precursor and to a reactant, where the reactant reacts with the silicon-containing precursor and forms a film of desired composition. The reactions are typically limited by the amount of a silicon-containing precursor and/or reactant residing on the surface of the substrate, and are typically repeated as many times as necessary for depositing a film with desired thickness. For example, silicon oxide films can be deposited by sequentially exposing the substrate to a silicon-containing precursor and an oxygen-containing reactant, such as O_2, O_3, H_2O, H_2O_2, and N_2O, where the reactant may be optionally activated in a plasma. However, when deposition occurs at relatively low temperature (e.g., at less than about 500 °C), the deposited silicon oxide often has low quality. This stems largely from the low thermal energy of the system, which in turn leads to such problems as low film density, lowered reactivity of Si-containing precursor on the surface, and increased atomic impurities as a consequence of more challenging byproduct removal. In order to deposit high quality silicon oxide, deposition often needs to be performed at temperatures of at least about 500

In some embodiments suitable compounds having N-Si-N motif are adducts containing 2,2-bipyridine (bipy), 1,10-phenantroline (phen) or N,N,N'N'-tetramethylethylenediamine (TMEDA). Examples of such compounds include SiX_4bipy, and SiX_4TMEDA where each X is independently selected from a group consisting of a halogen (e.g., Cl or Br), H, and an alkyl (e.g., methyl or ethyl). Specific examples include SiH_2Cl_2(bipy), $SiHCl_3$(bipy), $SiCl_3Me$(bipy), $SiCl_2Me$(bipy), $SiCl_3H$(TMEDA), and $SiCl_2H_2$(TMEDA). These compounds can be synthesized by reacting a silicon-containing starting material (e.g., H_2SiCl_2, $HSiCl_3$, $MeSiCl_3$) with a desired ligand (e.g., bipy, phen, or TMEDA).

In some embodiments the silicon-containing precursor is a silylene (a divalent, dicoordinate silicon species). Examples of silylenes are compounds 7 and 8 shown in Figure 2. Stability of silylenes is typically enhanced by presence of bulky groups. In some embodiments R^1 in compound 7 is a sterically bulky group such as *t*-butyl. A specific example of such silylene is *N*,*N'*-di-tert-butyl-1,3-diaza-2-silacyclopent-4-en-2-ylidene. These compounds can be obtained by a reaction of silicon (IV) halide (e.g., $SiCl_4$) with a lithiated N,N'-di-tert-butyl-1,4-diazabutadiene, followed by a reduction by alkali metal or potassium graphite to produce the silicon (II) compound 7.

Precursors containing O-Si-O motif

In another aspect, a silicon-containing precursor that is suitable for high temperature deposition is a compound that contains at least one silicon atom that forms bonds with at least two oxygen atoms, wherein at least two oxygen atoms are linked to form a cyclic ring. The cyclic ring includes the silicon atom and both oxygen atoms, and may be, for example, 4-membered, 5-membered, or 6 membered. In some embodiments, the precursor includes more than one of such rings. For example, silicon compounds with β-diketonate ligands (e.g., with acetylacetonate) may be used. In one embodiment, the compound has a formula $Si(A)_3X$, where A is a substituted or unsubstituted acetylacetonate, and X is a halogen (e.g., chloride). In another embodiment, the compound has a formula $Si(A)_2RX$, where A is a β-diketonate (e.g., substituted or unsubstituted acetylacetonate), X is a halogen (e.g., chloride), and R is an alkyl (e.g., methyl). Acetylacetonate silicon compounds can be prepared, for example, via a reaction of silicon halide (e.g., $SiCl_4$) with acetylacetone or acetylacetonate. In another embodiment the compound is $Si(A)R_3$, where A is a β-diketonate (e.g.,

acetylacetonate or dibenzoylmethane), and each R is independently selected from the group consisting of an alkyl, and haloalkyl (e.g., CF_3)

Precursors containing Si-N-Si motif

In another aspect, a silicon-containing precursor that is suitable for high temperature deposition is a compound that contains at least one nitrogen atom that forms bonds with at least two silicon atoms. In some embodiments the precursor is compound 10 shown in Figure 3A, where each R is the same or different and is independently selected from the group consisting of H, and alkyl, and wherein each R^1 is independently selected from the group consisting of H, alkyl, and $Si(R^2)_3$, where each R^2 is independently selected from the group consisting of H, and an alkyl. In some embodiments alkyls are C1-C4 alkyls, such as C1-C3 alkyls. Specific examples of compounds 10 include tris(trimethylsilyl)amine, trisilylamine, isopropyl(disilyl)amine, ethyl-bis(trimethylsilyl)amine, disilylhydrazine. In some implementations precursors of formula 10 have structure 11 as shown in Figure 3A. Precursors of this class can be prepared, for example, from a haloalkylsilane and the corresponding base under acidic conditions. For example, isopropylamine can be stirred in the presence of excess HCl with chlorotrimethylsilane to form isopropylamino-trimethyl-silane.

Cyclic precursors

In another aspect, a silicon-containing precursor that is suitable for high temperature deposition is a compound that contains at least one silicon atom that is part of a cyclic ring. Examples of rings include 4-membered, 5-membered, 6-membered, and 7-membered rings. In some embodiments at least one silicon atom forms bonds with two carbon atoms, where the two carbon atoms are linked to form a cyclic ring. In some embodiments, the at least one silicon atom further forms bonds with one or two nitrogen atoms. An example of such precursor is precursor 12 shown in Figure 3B, where R^1 and R^2 are same or different and are independently selected from the group consisting of an alkyl (e.g., C1-C4 alkyl), and H.

In some embodiments at least one silicon atom forms bonds with a carbon atom and a nitrogen atom, where the carbon atom and the nitrogen atom are linked to form a cyclic ring. An example of such precursor is precursor 13 shown in Figure 3B, where R^1 and R^2

CLAIMS

1. A method of forming a silicon-containing layer on a semiconductor substrate, the method comprising:

(a) exposing the semiconductor substrate to a silicon-containing precursor in a process chamber, wherein the silicon-containing precursor is a compound that has:

at least two Si-Si bond;

at least one Si-X bond, wherein X is selected from the group consisting of a halogen, triflate, tosylate, CN, N_3, and NR_1R_2, wherein R_1 and R_2 are independently selected from the group consisting of H, and an alkyl, wherein R_1 and R_2 are either linked to form a cyclic ring structure or not linked; and

at least one Si-R bond, wherein R is selected from the group consisting of H, and an alkyl;

(b) exposing the semiconductor substrate to a reactant in the process chamber; and

(c) reacting the silicon-containing precursor with the reactant on a surface of the semiconductor substrate to form at least a portion of the silicon-containing layer, wherein operations (a) – (c) are performed at a temperature of at least about 500 °C

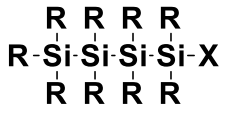
2. The method of claim 1, wherein the reactant is an oxygen-containing reactant and wherein (c) comprises reacting the silicon-containing precursor with the oxygen-containing reactant in an absence of plasma to form a silicon oxide layer.

3. The method of claim 1, further comprising purging the process chamber between exposures of the semiconductor substrate to the silicon-containing precursor and the reactant.

4. The method of claim 1, wherein operations (a) – (c) are performed at a temperature of at least about 550 °C.

5. The method of claim 1, wherein the silicon-containing precursor is selected from the group consisting of:


, and


, wherein each R is the same or different and is independently selected from the group consisting of H, and C1-C3 alkyl.

6. The method of claim 1, wherein the silicon-containing precursor is selected from the group consisting of: 1-diethylaminotrisilane, and 1-bromotetrasilane.

7. The method of claim 1, wherein R is an alkyl, and wherein the silicon-containing precursor does not include Si-H bonds.

8. The method of claim 1, further comprising repeating operations (a)-(c) until the silicon-containing layer reaches a target thickness.

9. The method of claim 1, wherein the method comprises depositing a first portion of the silicon-containing layer in an absence of plasma and a second portion of the silicon-containing layer using a plasma-assisted reaction while using the same silicon-containing precursor for both thermal and plasma-assisted deposition.

10. The method as in claim 1, wherein the silicon-containing layer is selected from the group consisting of silicon nitride, silicon oxynitride, silicon carbide, and silicon oxycarbide.

11. The method of claim 1, wherein the silicon-containing precursor is $Si_nR_{(2n+1)}X$, wherein n is selected from 2 to 10, and wherein each R is the same or different and is independently selected from the group consisting of H, an alkyl, an alkenyl, and an alkynyl.

12. The method of claim 1, wherein the silicon-containing precursor comprises at least one silicon atom that is part of a cycle.

13. The method as in claim 1, further comprising:

applying photoresist to a semiconductor substrate;

exposing the photoresist to light;

patterning the photoresist;

transferring the pattern to the semiconductor substrate; and

selectively removing the photoresist from the semiconductor substrate.

14. An apparatus for depositing a silicon-containing layer on a semiconductor substrate, the apparatus comprising:

a process chamber configured for housing the semiconductor substrate, wherein the process chamber includes an inlet for introduction of a silicon-containing precursor; and a controller comprising program instructions for causing deposition of the silicon-containing layer on the semiconductor substrate in accordance with the method of claim 1.