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(54) Title: ORGANOSILANE PRECURSORS FOR ALD/CVD SILICON-CONTAINING FILM APPLICATIONS

(57) Abstract: Disclosed are Si-containing thin film forming precursors, methods of synthesizing the same, and methods of using the same to deposit silicon- containing films using vapor deposition processes for manufacturing semiconductors, photovoltaics, LCD-TFT, flat panel-type devices, refractory materials, or aeronautics.

ORGANOSILANE PRECURSORS FOR ALD/CVD SILICON-CONTAINING FILM APPLICATIONS

Cross-Reference to Related Applications

This application claims priority to U.S. provisional application No. 61/674,103, filed July 20, 2012, the entire contents of which are incorporated herein by reference.

Technical Field

Disclosed are Si-containing thin film forming precursors, methods of synthesizing the same, and methods of using the same to deposit silicon-containing films using vapor deposition processes for manufacturing semiconductors, photovoltaics, LCD-TFT, flat panel-type devices, refractory materials, or aeronautics.

Background

Si-containing thin films are used widely in the semiconductor, photovoltaic, LCD-TFT, flat panel-type device, refractory material, or aeronautic industries. Si-containing thin films may be used, for example, as dielectric materials having electrical properties which may be insulating (SiO_2, SiN, SiCN, SiCOH, MSiOx, wherein M is Hf, Zr, Ti, Nb, Ta, or Ge and x is greater than zero), Si-containing thin films may be used as conducting films, such as metal silicides or metal silicon nitrides. Due to the strict requirements imposed by downscaling of electrical device architectures towards the nanoscale (especially below 28nm node), increasingly fine-tuned molecular precursors are required which meet the requirements of volatility (for ALD process), lower process temperatures, reactivity with various oxidants and low film contamination, in addition to high deposition rates, conformality and consistency of films produced.

It is well known that silane (SiH_4) can be used for thermal CVD. However this molecule is pyrophoric which makes this room temperature gas a challenge to handle safely. CVD methods employing halosilanes (such as dichlorosilane SiH_2Cl_2) have been used. However, these may require long purge times, cause halogen contamination of the films and particle formation (from ammonium

chloride salts), and even damage certain substrates resulting in undesirable interfacial layer formation. Partially replacing halogen with alkyl groups may yield some improvement, but at a cost of detrimental carbon contamination within the film.

Organoaminosilanes have been used as precursors for CVD of Si-containing films. US 7192626 to Dussarrat et al. reports the use of trisilylamine $N(SiH_3)_3$ for deposition of SiN films. Other reported precursors include diisopropylaminosilane [$SiH_3(NiPr_2)$] and analogous $SiH_3(NR_2)$ compounds (see, e.g., US 7875312 to Thridandam et al.) and phenylmethylaminosilane [$SiH_3(NPhMe)$] and related substituted silylanilines (see, e.g., EP 2392691 to Xiao et al.).

Another related class of Si precursors for CVD of Si-containing films is given by the general formula $(R^1R^2N)_xSiH_{4-x}$ wherein x is between 1 and 4 and the R substituents are independently H, C1-C6 linear, branched, or cyclic carbon chains (see, e.g., WO2006/097525 to Dussarrat et al.).

Hunks et al. disclose a wide range of Si-containing precursors in US2010/0164057, including silicon compounds having the formula $R_{4-x}SiL_x$, wherein x is an integer having a value from 1 to 3; R may be selected from H, branched and unbranched C1-C6 alkyl, C3-C8 cycloalkyl, and C6-C13 aryl groups; and L may be selected from isocyanato, methylethylketoxime, trifluoroacetate, triflate, acyloxy, β-diketiminate, β-di-iminate, amidinate, guanidinate, alkylamino, hydride, alkoxide, or formate ligands. Pinnavaia et al. claim a method for the preparation of a porous synthetic, semi-crystalline hybrid organic-inorganic silicon oxide composition from silicon acetylacetonate and silicon 1,3-diketonate precursors (US6465387).

Silyl esters have been reported as early as 1967 (see, e.g, E.A.V. Ebsworth et al., J. Chem. Soc. A., 1967, 69-72), but do not appear to have been used in vapor deposition methods.

Despite the wide range of choices available for the deposition of Si containing films, additional precursors are continuously sought to provide device engineers the ability to tune manufacturing process requirements and achieve films with desirable electrical and physical properties.

Notation and Nomenclature

Certain abbreviations, symbols, and terms are used throughout the following description and claims, and include:

As used herein, the indefinite article "a" or "an" means one or more.

As used herein, the term "independently" when used in the context of describing R groups should be understood to denote that the subject R group is not only independently selected relative to other R groups bearing the same or different subscripts or superscripts, but is also independently selected relative to any additional species of that same R group. For example in the formula $MR^1_x(NR^2R^3)_{(4-x)}$, where x is 2 or 3, the two or three R^1 groups may, but need not be identical to each other or to R^2 or to R^3. Further, it should be understood that unless specifically stated otherwise, values of R groups are independent of each other when used in different formulas.

As used herein, the term "alkyl group" refers to saturated functional groups containing exclusively carbon and hydrogen atoms. Further, the term "alkyl group" refers to linear, branched, or cyclic alkyl groups. Examples of linear alkyl groups include without limitation, methyl groups, ethyl groups, propyl groups, butyl groups, etc. Examples of branched alkyls groups include without limitation, t-butyl. Examples of cyclic alkyl groups include without limitation, cyclopropyl groups, cyclopentyl groups, cyclohexyl groups, etc.

As used herein, the term "aryl" refers to aromatic ring compounds where one hydrogen atom has been removed from the ring. As used herein, the term "heterocycle" refers to a cyclic compound that has atoms of at least two different elements as members of its ring.

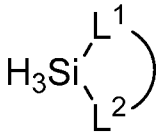
As used herein, the abbreviation "Me" refers to a methyl group; the abbreviation "Et" refers to an ethyl group; the abbreviation "Pr" refers to any propyl group (i.e., n-propyl or isopropyl); the abbreviation "iPr" refers to an isopropyl group; the abbreviation "Bu" refers to any butyl group (n-butyl, iso-butyl, t-butyl, sec-butyl); the abbreviation "tBu" refers to a tert-butyl group; the abbreviation "sBu" refers to a sec-butyl group; the abbreviation "iBu" refers to an iso-butyl group; the abbreviation "Ph" refers to a phenyl group; the abbreviation "Am" refers to any amyl group (iso-amyl, sec-amyl, tert-amyl); and the abbreviation "Cy" refers to a cyclic alkyl group (cyclobutyl, cyclopentyl, cyclohexyl, etc.).

As used herein, the acronym “SRO” stands for a Strontium Ruthenium Oxide film; the acronym “HCDS” stands for hexachlorodisilane; and the acronym “PCDS” stands for pentachlorodisilane.

The standard abbreviations of the elements from the periodic table of elements are used herein. It should be understood that elements may be referred to by these abbreviations (e.g., Si refers to silicon, N refers to nitrogen, O refers to oxygen, C refers to carbon, etc.).

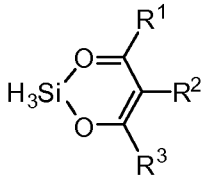
Summary

Disclosed are molecules having the following formula:



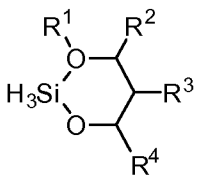
wherein each L^1 and L^2 is an oxygen atom; L^1 and L^2 being joined together via a carbon bridge having one to three carbon atoms; L^1, L^2 and the carbon bridge forming a monoanionic ligand bonded to silicon. The disclosed molecules may have one or more of the following aspects:

- the molecule having the following formula:



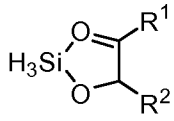
wherein R^1, R^2, and R^3 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle;

- R^1 and R^2 and/or R^2 and R^3 joined to form cyclic chains;
- the molecule being H_3Si(-O=C(tBu)-CH=C(tBu)-O-) or H_3Si(O=C(Me)-CH=C(Me)-O-);
- the molecule having the following formula:



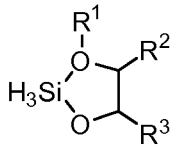
wherein R^1, R^2, R^3, and R^4 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle;

- R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 joined to form cyclic chains;
- the molecule being $H_3Si(-O(iPr)-C_3H_6-O-)$ or $H_3Si(-O(tBu)-C_3H_6-O-)$;
- the molecule having the following formula:



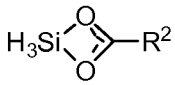
wherein R^1 and R^2 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle;

- R^1 and R^2 joined to form a cyclic chain;
- the molecule being $H_3Si(-O=C(tBu)-CH_2-O-)$;
- the molecule having the following formula:



wherein R^1, R^2, and R^3 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle;

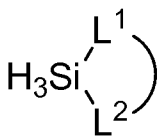
- R^1 and R^2 and/or R^2 and R^3 joined to form cyclic chains;
- the molecule being $H_3Si(-O(iPr)-C_2H_4-O-)$ or $H_3Si(-O(tBu-C_2H_4-O-)$;
- the molecule having the following formula:



wherein R^1 may be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle; and

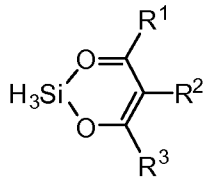
- the molecule being $H_3Si(-O-C(Et)-O-)$ or $H_3Si(-O-C(nBu)-O-)$.

Also disclosed are Si-containing thin film forming precursors having the following formula:



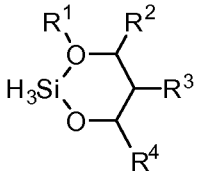
wherein each L^1 and L^2 is an oxygen atom; L^1 and L^2 being joined together via a carbon bridge having one to three carbon atoms; L^1, L^2 and the carbon bridge forming a monoanionic ligand bonded to silicon. The disclosed molecules may have one or more of the following aspects:

- the Si-containing thin film forming precursor having the following formula:



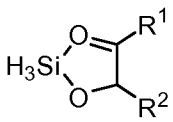
wherein R^1, R^2, and R^3 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle;

- R^1 and R^2 and/or R^2 and R^3 joined to form cyclic chains;
- the Si-containing thin film forming precursor being H_3Si(-O=C(tBu)-CH=C(tBu)-O-) or H_3Si(O=C(Me)-CH=C(Me)-O-);
- the Si-containing thin film forming precursor having the following formula:



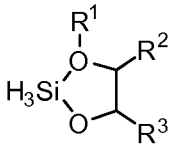
wherein R^1, R^2, R^3, and R^4 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle;

- R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 joined to form cyclic chains;
- the Si-containing thin film forming precursor being H_3Si(-O(iPr)-C_3H_6-O-) or H_3Si(-O(tBu)-C_3H_6-O-);
- the Si-containing thin film forming precursor having the following formula:



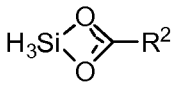
wherein R^1 and R^2 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle;

- R^1 and R^2 joined to form a cyclic chain;
- the Si-containing thin film forming precursor being H_3Si(-O=C(tBu)-CH_2-O-);
- the Si-containing thin film forming precursor having the following formula:



wherein R^1, R^2, and R^3 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle;

- R^1 and R^2 and/or R^2 and R^3 joined to form cyclic chains;
- the Si-containing thin film forming precursor being H_3Si(-O(iPr)-C_2H_4-O-) or H_3Si(-O(tBu-C_2H_4-O-);
- the Si-containing thin film forming precursor having the following formula:



wherein R^1 may be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle; and

- the Si-containing thin film forming precursor being H_3Si(-O-C(Et)-O-) or H_3Si(-O-C(nBu)-O-).

Also disclosed are methods of depositing a Si-containing layer on a substrate.

At least one organosilane precursor disclosed above is introduced into a reactor having at least one substrate disposed therein. At least part of the organosilane precursor is deposited onto the at least one substrate to form a Si-containing layer using a vapor deposition method. The disclosed methods may have one or more of the following aspects:

- introducing into the reactor a vapor comprising at least one second precursor;
- an element of the at least one second precursor being selected from the group consisting of group 2, group 13, group 14, transition metal, lanthanides, and combinations thereof;
- the element of the at least one second precursor being selected from Mg, Ca, Sr, Ba, Zr, Hf, Ti, Nb, Ta, Al, Si, Ge, Y, or lanthanides;
- introducing into the reactor at least one co-reactant;

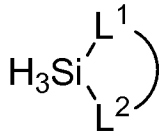
- the co-reactant being selected from the group consisting of O_2, O_3, H_2O, H_2O_2, NO, NO_2, a carboxylic acid, radicals thereof, and combinations thereof;
- the co-reactant being plasma treated oxygen;
- the co-reactant being ozone;
- the Si-containing layer being a silicon oxide layer;
- the co-reactant being selected from the group consisting of H_2, NH_3, $(SiH_3)_3N$, hydridosilanes (such as SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10}, Si_5H_{10}, Si_6H_{12}), chlorosilanes and chloropolysilanes (such as $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, Si_2Cl_6, Si_2HCl_5, Si_3Cl_8), alkysilanes (such as Me_2SiH_2, Et_2SiH_2, $MeSiH_3$, $EtSiH_3$), hydrazines (such as N_2H_4, $MeHNNH_2$, MeHNNHMe), organic amines (such as $NMeH_2$, $NEtH_2$, NMe_2H, NEt_2H, NMe_3, NEt_3, $(SiMe_3)_2NH$), pyrazoline, pyridine, B-containing molecules (such as B_2H_6,9-borabicylo[3,3,1]none, trimethylboron, triethylboron, borazine), alkyl metals (such as trimethylaluminum, triethylaluminum, dimethylzinc, diethylzinc), radical species thereof, and mixtures thereof.
- the co-reactant being selected from the group consisting of H_2, NH_3, SiH_4, Si_2H_6, Si_3H_8, SiH_2Me_2, SiH_2Et_2, $N(SiH_3)_3$, hydrogen radicals thereof, and mixtures thereof;
- the co-reactant being plasma-treated;
- the co-reactant being remote plasma-treated;
- the co-reactant not being plasma-treated;
- the co-reactant being H_2;
- the co-reactant being NH_3;
- the co-reactant being HCDS;
- the co-reactant being PCDS;
- the co-reactant being tetrachlorosilane;
- the co-reactant being trichlorosilane;
- the co-reactant being hexachlorocyclohexasilane;
- the vapor deposition process being a chemical vapor deposition process;
- the vapor deposition process being an atomic layer deposition (ALD) process;

- the vapor deposition process being a spatial ALD process;
- the silicon-containing layer being Si;
- the silicon-containing layer being SiO_2;
- the silicon-containing layer being SiN;
- the silicon-containing layer being SiON;
- the silicon-containing layer being SiCN; and
- the silicon-containing layer being SiCOH.

Description of Preferred Embodiments

Disclosed are Si-containing thin film forming precursors, methods of synthesizing the same, and methods of using the same to deposit silicon-containing films using vapor deposition processes for manufacturing semiconductors.

The disclosed organosilane precursors have the following formula:

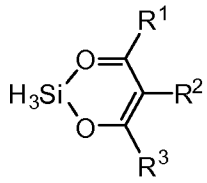


wherein L^1 and L^2 is an oxygen atom, L^1 and L^2 being joined together via a carbon bridge having one to three carbon atoms; L^1, L^2, and the carbon bridge form a monoanionic ligand bonded to silicon. As illustrated in the formula, the L^1 and L^2 oxygen atoms are bonded to the silicon atom, resulting in a pentacoordinate Si(IV) center. The carbon atoms in the carbon bridge may be sp^2 hybridized, resulting in a delocalized charge across the monoanionic ligand. Alternatively, the carbon atoms in the carbon bridge may be either sp^3 hybridized or some combination of sp^2 and sp^3 hybridized, resulting in a negative charge on one of L^1 or L^2 and resulting in a neutral charge on the other of L^1 or L^2. Each of the oxygen and carbon atoms may independently be substituted by H, C1-C6 alkyl groups, aryl groups, or heterocycle groups.

The disclosed organosilane precursors may be more reactive than other $R_{4-x}SiL_x$ precursors due to hypercoordination at the silicon atom. In other words, although the silicon atom is +IV, the three hydrogen bonds and the monoanionic chelating ligand results in a total of 5 bonds to the silicon atom.

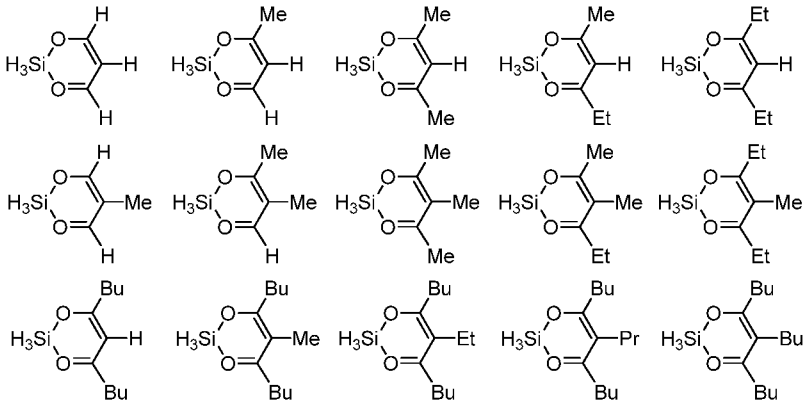
Due to the increased oxygen content resulting from the two oxygen atoms on the –O-(C(R))$_n$-O- ligand, with n being 1-3, these molecules may be used to produce silicon-containing films that also contain oxygen, such as SiO_2, SiOC, or SiON, or to tune the amount of oxygen in a SiO_2, SiOC, or SiON containing film.

When the carbon bridge of the disclosed organosilane precursors includes three (3) carbon atoms (i.e., -O-(C(R))$_3$-O-), the resulting precursors may be diketonate compounds. Exemplary diketonate organosilane precursors may have the following formula:



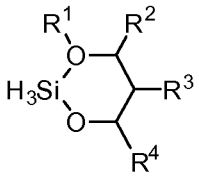
wherein R^1, R^2, and R^3 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle. R^1 and R^2 and/or R^2 and R^3 may be joined to form cyclic chains. The three carbon atoms are sp^2 hybridized. If R^1 and R^3 are the same (i.e., both Me), the resulting nuclear magnetic transform Fourier-Transform Infra Red (FTIR) spectra for these molecules will produce one peak for both of the O atoms due to the delocalization of the electrons across the ligand.

Exemplary precursors with the above formula include:



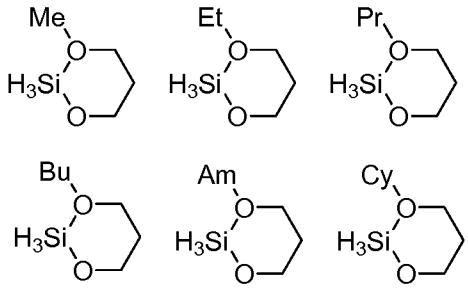
Preferably, the diketonate precursor is H_3Si(-O-C(tBu)=CH-C(tBu)=O-) or H_3Si(O-C(Me)=CH-C(Me)=O-).

Alternatively, when the carbon bridge of the disclosed organosilane precursors includes three (3) carbon atoms (i.e., -O-(C(R))$_3$-O-),, the resulting precursors may be silylalkoxyether compounds. Exemplary silylalkoxyether organosilane precursors may have the following formula:



wherein R^1, R^2, R^3, and R^4 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle. One of ordinary skill in the art will recognize the implied H on the carbons in the structure above, which have been left off due to space constraints. R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 may be joined to form cyclic chains. The three carbon atoms may be sp2 or sp3 hybrizidized. An anionic charge may be localized at one of the oxygen atoms. The other oxygen atom may form a dative bond to the Si atom. Due to the unsymmetrical nature of the ligand, the three carbon atoms will produce different peaks in nuclear magnetic resonance (NMR) spectra.

Exemplary silylalkoxyether precursors with the above formula include:



Preferably, the silylalkoxyether precursor is H_3Si(-O(iPr)-C_3H_6-O-) or H_3Si(-O(tBu)-C_3H_6-O-).

The $H_3Si[O(CR)_3O]$ and $H_3Si[RO(CR)_3O]$ precursors may be synthesized by combining a hydrocarbon solution of $SiXH_3$, wherein X is Cl, Br, I, or triflate ($SO_3CF_3^-$), with a neat or hydrocarbon solution of the ligand compound, such as $Li[O(CR)_3O]$ or $Li[RO(CR)_3O]$ under atmosphere of nitrogen, the outlet of the mixing flask being connected to an oil bubbler to inhibit backflow of air and moisture.

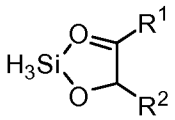
A second synthetic route to the disclosed $H_3Si[O(CR)_3O]$ and $H_3Si[RO(CR)_3O]$ precursors is by reaction of the protonated ligand ($HO(CR)_3O$ or $RO(CR)_3OH$) with either a neat or a hydrocarbon solution of a dialkylaminosilane [$SiH_3(NR_2)$] performed under an inert atmosphere.

Alternatively, the disclosed $H_3Si[O(CR)_3O]$ and $H_3Si[RO(CR)_3O]$ precursors may be synthesized by reaction of SiH_nCl_{4-n} with a single equivalent of the ligand

compound (i.e., $Li[O(CR)_3O]$ or $Li[RO(CR)_3O]$) and subsequent reduction using a selected metal hydride such as LAH (lithium aluminum hydride).

In all three synthesis routes, the resulting solution may be stirred at room temperature overnight. Exemplary hydrocarbon solutions suitable for these synthesis methods include diethyl ether, pentane, hexane, or toluene. The resulting suspension is filtered and the resulting solution distilled to remove solvent. Purification of the resulting liquid or solid is carried out by distillation or sublimation, respectively. Except for the ligand compounds $Li[O(CR)_3O]$ or $Li[RO(CR)_3O]$ all of the starting materials are commercially available. The ligand compound may be synthesized by combining a hydrocarbon solution of metalorganic salt (i.e., alkyl lithium) to a hydrocarbon solution of the appropriate hydroxy ketone or hydroxy ether (i.e., $R^1O\text{-}CR^2\text{-}CR^3\text{-}CR^4\text{-}OH$, $O{=}CR^1\text{-}CR^2\text{-}CR^3\text{-}OH$, and $O{=}CR^1\text{-}CR^2{=}CR^3\text{-}OH$). One of ordinary skill in the art would recognize that proper selection of the ligand will result in the saturated silylalkoxyether or unsaturated diketonate precursor.

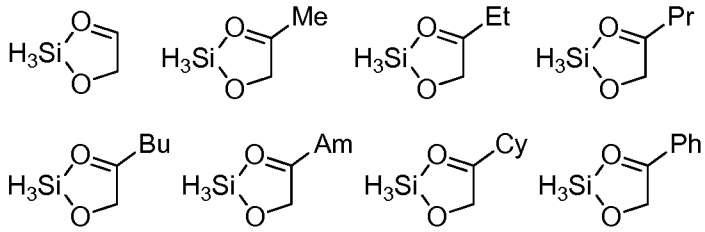
When the carbon bridge of the disclosed organosilane precursors includes two (2) carbon atoms (i.e., $-O\text{-}(C(R))_2\text{-}O-$), the resulting precursors may be silyldioxalane compounds. Exemplary silyldioxalane organosilane precursors may have the following formula:



wherein R^1 and R^2 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle. One of ordinary skill in the art will recognize the implied H on the carbon in the structure above, which has been left off due to space constraints. R^1 and R^2 may be joined to form cyclic chains. The two carbon atoms may be sp^2 or sp^3 hybridized. The formula above illustrates an anionic charge localized at the "bottom" oxygen atom. The oxygen atom having the double bond to $C(R^1)$ forms a dative bond to the silicon atom. However, one of ordinary skill in the art will recognize that the double bond may also be delocalized across the ring when the carbon atoms are sp^2 hybridized. If R^1 and R^2 are the same (i.e., both Me), the resulting Fourier-transform Infra Red (FTIR) spectra for

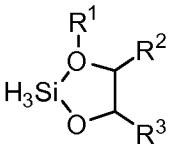
the delocalized molecules will produce one peak for both of the O atoms due to the delocalization of the electrons across the ligand.

Exemplary silyldioxalane precursors with the above formula include:



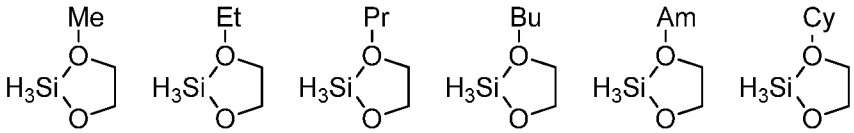
Preferably, the silyldioxalane precursor is $H_3Si(-O=C(tBu)-CH_2-O-)$.

Alternatively, when the carbon bridge of the disclosed organosilane precursors includes two (2) carbon atoms (i.e., $-O-(C(R))_2-O-$),, the resulting precursors may be alkoxysilylether compounds. Exemplary alkoxysilylether organosilane precursors may have the following formula:



wherein R^1, R^2, and R^3 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle. One of ordinary skill in the art will recognize the implied H on the carbons in the structure above, which have been left off due to space constraints. R^1 and R^2 and/or R^2 and R^3 may be joined to form cyclic chains. The two carbon atoms may be sp2 or sp3 hybridized. An anionic charge may be localized at one of the oxygen atoms. The other oxygen atom may form a dative bond to the Si atom. Due to the unsymmetrical nature of the ligand, the two carbon atoms will produce different peaks in nuclear magnetic resonance (NMR) spectra.

Exemplary alkoxysilylether precursors with the above formula include:



Preferably, the alkoxysilylether precursor is $H_3Si(-O(iPr)-C_2H_4-O-)$ or $H_3Si(-O(tBu-C_2H_4-O-)$.

The $H_3Si[O(CR)_2O]$ and $H_3Si[RO(CR)_2O]$ precursors may be synthesized by combining a hydrocarbon solution of $SiXH_3$, wherein X is Cl, Br, I, or triflate ($SO_3CF_3^-$), with a neat or hydrocarbon solution of the ligand compound, such as

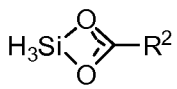
$Li[O(CR)_2O]$ or $Li[RO(CR)_2O]$ under atmosphere of nitrogen, the outlet of the mixing flask being connected to an oil bubbler to inhibit backflow of air and moisture.

A second synthetic route to the disclosed $H_3Si[O(CR)_2O]$ and $H_3Si[RO(CR)_2O]$ precursors is by reaction of the protonated ligand ($HO(CR)_2O$ or $RO(CR)_2OH$) with either a neat or a hydrocarbon solution of a dialkylaminosilane $[SiH_3(NR_2)]$ performed under an inert atmosphere.

Alternatively, the disclosed $H_3Si[O(CR)_2O]$ and $H_3Si[RO(CR)_2O]$ precursors may be synthesized by reaction of SiH_nCl_{4-n} with a single equivalent of the ligand compound (i.e., $Li[O(CR)_2O]$ or $Li[RO(CR)_2O]$) and subsequent reduction using a selected metal hydride, such as LAH (lithium aluminum hydride).

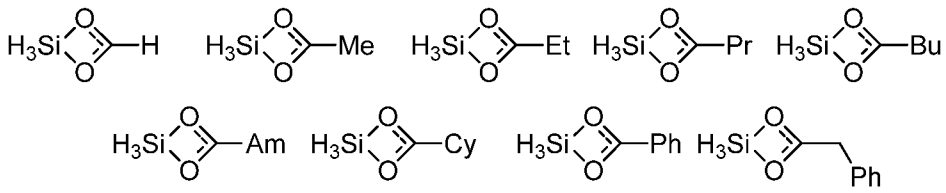
In all three synthesis routes, the resulting solution may be stirred at room temperature overnight. Exemplary hydrocarbon solutions suitable for these synthesis methods include diethyl ether, pentane, hexane, or toluene. The resulting suspension is filtered and the resulting solution distilled to remove solvent. Purification of the resulting liquid or solid is carried out by distillation or sublimation, respectively. Except for the ligand compounds $Li[O(CR)_2O]$ or $Li[RO(CR)_2O]$ all of the starting materials are commercially available. The ligand compound may be synthesized by combining a hydrocarbon solution of metalorganic salt (i.e., alkyl lithium) to a hydrocarbon solution of the appropriate hydroxy ketone or hydroxy ether (i.e., $R^1O\text{-}CR^2\text{-}CR^3\text{-}OH$ or $O{=}CR^1\text{-}CR^2\text{-}OH$). One of ordinary skill in the art would recognize that proper selection of the ligand will result in the saturated alkoxysilylether or unsaturated silyldioxalane precursor.

When the carbon bridge of the disclosed organosilane precursors includes one (1) carbon atom (i.e., -O-C(R)-O-),, the resulting precursors are silyl carboxylate compounds. Exemplary silyl carboxylate organosilane precursors may have the following formula:

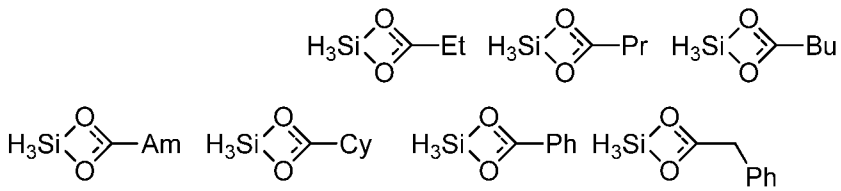


wherein R^2 may be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle. The carbon atom is sp^2 hybridized allowing delocalization of charge across the ligand.

Exemplary precursors with the above formula include:



Preferably, the silyl carboxylate precursor is selected from:



More preferably, the silyl carboxylate is H_3Si(-O-C(Et)-O-) or H_3Si(-O-C(nBu)-O-).

The $H_3Si[OC(R^2)O]$ precursors may be synthesized by combining a hydrocarbon solution of $SiXH_3$, wherein X is Cl, Br, I, or triflate ($SO_3CF_3^-$), with a neat or hydrocarbon solution of the ligand compound, such as $Li[OC(R^2)O]$, under atmosphere of nitrogen, the outlet of the mixing flask being connected to an oil bubbler to inhibit backflow of air and moisture.

A second synthetic route to the disclosed $H_3Si[OC(R^2)O]$ precursors is by reaction of the protonated ligand ($HOC(R^2)=O$) with either a neat or a hydrocarbon solution of a dialkylaminosilane [$SiH_3(NR_2)$] performed under an inert atmosphere.

Alternatively, the disclosed $H_3Si[OC(R^2)O]$ precursors may be synthesized by reaction of SiH_nCl_{4-n} with a single equivalent of the ligand compound (i.e., $Li[OC(R^2)O]$) and subsequent reduction using a selected metal hydride, such as LAH (lithium aluminum hydride).

In all three synthesis routes, the resulting solution may be stirred at room temperature overnight. Exemplary hydrocarbon solutions suitable for these synthesis methods include diethyl ether, pentane, hexane, or toluene. The resulting suspension is filtered and the resulting solution distilled to remove solvent. Purification of the resulting liquid or solid is carried out by distillation or sublimation, respectively. Except for the ligand compounds $Li[OC(R^2)O]$ all of the starting materials are commercially available. The ligand compound may be synthesized by bubbling carbon dioxide (i.e., O=C=O) into a hydrocarbon solution of metalorganic salt (i.e., alkyl lithium).

Also disclosed are methods of using the disclosed organosilane precursors for vapor deposition methods. The disclosed methods provide for the use of the organosilane precursors for deposition of silicon-containing films. The disclosed methods may be useful in the manufacture of semiconductor, photovoltaic, LCD-TFT, or flat panel type devices. The method includes: providing a substrate; providing a vapor including at least one of the disclosed organosilane precursors: and contacting the vapor with the substrate (and typically directing the vapor to the substrate) to form a silicon-containing layer on at least one surface of the substrate.

The disclosed methods also provide for forming a bimetal-containing layer on a substrate using a vapor deposition process and, more particularly, for deposition of $SiMO_x$ films, wherein x may be 0-4 and M is Ta, Hf, Nb, Mg, Al, Sr, Y, Ba, Ca, As, Sb, Bi, Sn, Pb, Co, lanthanides (such as Er), or combinations thereof. The disclosed methods may be useful in the manufacture of semiconductor, photovoltaic, LCD-TFT, or flat panel type devices. The method includes: providing a substrate; providing a vapor including at least one of the disclosed organosilane precursors and contacting the vapor with the substrate (and typically directing the vapor to the substrate) to form a bi metal-containing layer on at least one surface of the substrate. An oxygen source, such as O_3, O_2, H_2O, NO, H_2O_2, acetic acid, formalin, para-formaldehyde, oxygen radicals thereof, and combinations thereof, but preferably O_3 or plasma treated O_2 may also be provided with the vapor.

The disclosed organosilane precursors may be used to deposit silicon-containing films using any deposition methods known to those of skill in the art. Examples of suitable deposition methods include without limitation, conventional chemical vapor deposition (CVD), low pressure chemical vapor deposition (LPCVD), atomic layer deposition (ALD), pulsed chemical vapor deposition (P-CVD), thermal ALD, thermal CVD, plasma enhanced atomic layer deposition (PE-ALD), plasma enhanced chemical vapor deposition (PE-CVD), spatial ALD, or combinations thereof. Preferably, the deposition method is ALD, spatial ALD, or PE-ALD.

The vapor of the organosilane precursor is introduced into a reaction chamber containing at least one substrate. The temperature and the pressure

within the reaction chamber and the temperature of the substrate are held at conditions suitable for vapor deposition of at least part of the organosilane precursor onto the substrate. In other words, after introduction of the vaporized precursor into the chamber, conditions within the chamber are such that at least part of the vaporized precursor is deposited onto the substrate to form the silicon-containing film. A co-reactant may also be used to help in formation of the Si-containing layer.

The reaction chamber may be any enclosure or chamber of a device in which deposition methods take place, such as, without limitation, a parallel-plate type reactor, a cold-wall type reactor, a hot-wall type reactor, a single-wafer reactor, a multi-wafer reactor, or other such types of deposition systems. All of these exemplary reaction chambers are capable of serving as an ALD reaction chamber. The reaction chamber may be maintained at a pressure ranging from about 0.5 mTorr to about 20 Torr. In addition, the temperature within the reaction chamber may range from about 20°C to about 600°C. One of ordinary skill in the art will recognize that the temperature may be optimized through mere experimentation to achieve the desired result.

The temperature of the reactor may be controlled by either controlling the temperature of the substrate holder or controlling the temperature of the reactor wall. Devices used to heat the substrate are known in the art. The reactor wall is heated to a sufficient temperature to obtain the desired film at a sufficient growth rate and with desired physical state and composition. A non-limiting exemplary temperature range to which the reactor wall may be heated includes from approximately 20°C to approximately 600°C. When a plasma deposition process is utilized, the deposition temperature may range from approximately 20°C to approximately 550°C. Alternatively, when a thermal process is performed, the deposition temperature may range from approximately 300°C to approximately 600°C.

Alternatively, the substrate may be heated to a sufficient temperature to obtain the desired silicon-containing film at a sufficient growth rate and with desired physical state and composition. A non-limiting exemplary temperature range to which the substrate may be heated includes from 150°C to 600°C. Preferably, the temperature of the substrate remains less than or equal to 500°C.

The type of substrate upon which the silicon-containing film will be deposited will vary depending on the final use intended. In some embodiments, the substrate may be a patterned photoresist film made of hydrogenated carbon, for example CH_x, wherein x is greater than zero. In some embodiments, the substrate may be chosen from oxides which are used as dielectric materials in MIM, DRAM, or FeRam technologies (for example, ZrO_2 based materials, HfO_2 based materials, TiO_2 based materials, rare earth oxide based materials, ternary oxide based materials, etc.) or from nitride-based films (for example, TaN) that are used as an oxygen barrier between copper and the low-k layer. Other substrates may be used in the manufacture of semiconductors, photovoltaics, LCD-TFT, or flat panel devices. Examples of such substrates include, but are not limited to, solid substrates such as metal nitride containing substrates (for example, TaN, TiN, WN, TaCN, TiCN, TaSiN, and TiSiN); insulators (for example, SiO_2, Si_3N_4, SiON, HfO_2, Ta_2O_5, ZrO_2, TiO_2, Al_2O_3, and barium strontium titanate); or other substrates that include any number of combinations of these materials. The actual substrate utilized may also depend upon the specific precursor embodiment utilized. In many instances though, the preferred substrate utilized will be selected from hydrogenated carbon, TiN, SRO, Ru, and Si type substrates, such as polysilicon or crystalline silicone substrates.

The disclosed organosilane precursors may be supplied either in neat form or in a blend with a suitable solvent, such as toluene, ethyl benzene, xylene, mesitylene, decane, dodecane, octane, hexane, pentane, tertiary amines, acetone, tetrahydrofuran, ethanol, ethylmethylketone, 1,4-dioxane, or others. The disclosed precursors may be present in varying concentrations in the solvent. For example, the resulting concentration may range from approximately 0.05 M to approximately 2 M.

The neat or blended organosilane precursors are introduced into a reactor in vapor form by conventional means, such as tubing and/or flow meters. The precursor in vapor form may be produced by vaporizing the neat or blended precursor solution through a conventional vaporization step such as direct vaporization, distillation, by bubbling, or by using a sublimator such as the one disclosed in PCT Publication WO2009/087609 to Xu et al. The neat or blended precursor may be fed in liquid state to a vaporizer where it is vaporized before it is

introduced into the reactor. Alternatively, the neat or blended precursor may be vaporized by passing a carrier gas into a container containing the precursor or by bubbling the carrier gas into the precursor. The carrier gas may include, but is not limited to, Ar, He, or N_2, and mixtures thereof. Bubbling with a carrier gas may also remove any dissolved oxygen present in the neat or blended precursor solution. The carrier gas and precursor are then introduced into the reactor as a vapor.

If necessary, the container may be heated to a temperature that permits the organosilane precursor to be in its liquid phase and to have a sufficient vapor pressure. The container may be maintained at temperatures in the range of, for example, 0-150°C. Those skilled in the art recognize that the temperature of the container may be adjusted in a known manner to control the amount of organosilane precursor vaporized.

In addition to the disclosed precursor, a reaction gas may also be introduced into the reactor. The reaction gas may be an oxidizing agent such as one of O_2; O_3; H_2O; H_2O_2; oxygen containing radicals such as $O^{\cdot}$ or $OH^{\cdot}$; NO; NO_2; carboxylic acids such as formic acid, acetic acid, propionic acid; radical species of NO, NO_2, or the carboxylic acids; para-formaldehyde; and mixtures thereof. Preferably, the oxidizing agent is selected from the group consisting of O_2, O_3, H_2O, H_2O_2, oxygen containing radicals thereof such as $O^{\cdot}$ or $OH^{\cdot}$, and mixtures thereof. Preferably, when an ALD process is performed, the co-reactant is plasma treated oxygen, ozone, or combinations thereof. When an oxidizing gas is used, the resulting silicon containing film will also contain oxygen.

Alternatively, the reaction gas may be a reducing agent such as one of H_2, NH_3, $(SiH_3)_3N$, hydridosilanes (such as SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10}, Si_5H_{10}, Si_6H_{12}), chlorosilanes and chloropolysilanes (such as $SiHCl_3$, SiH_2Cl_2, SIH_3Cl, Si_2Cl_6, Si_2HCl_5, Si_3Cl_8), alkylsilanes (such as $(CH_3)_2SiH_2$, $(C_2H_5)_2SiH_2$, $(CH_3)SiH_3$, $(C_2H_5)SiH_3$), hydrazines (such as N_2H_4, $MeHNNH_2$, MeHNNHMe), organic amines (such as $N(CH_3)H_2$, $N(C_2H_5)H_2$, $N(CH_3)_2H$, $N(C_2H_5)_2H$, $N(CH_3)_3$, $N(C_2H_5)_3$, $(SiMe_3)_2NH$), pyrazoline, pyridine, B-containing molecules (such as B_2H_6, 9-borabicyclo[3,3,1]none, trimethylboron, triethylboron, borazine), alkyl metals (such as trimethylaluminum, triethylaluminum, dimethylzinc, diethylzinc), radical species thereof, and mixtures thereof. Preferably, the reducing agent is H_2, NH_3, SiH_4,

Si_2H_6, Si_3H_8, SiH_2Me_2, SiH_2Et_2, $N(SiH_3)_3$, hydrogen radicals thereof, or mixtures thereof. When a reducing agent is used, the resulting silicon containing film may be pure Si.

The reaction gas may be treated by a plasma, in order to decompose the reaction gas into its radical form. N_2 may also be utilized as a reducing agent when treated with plasma. For instance, the plasma may be generated with a power ranging from about 50 W to about 500 W, preferably from about 100 W to about 200 W. The plasma may be generated or present within the reactor itself. Alternatively, the plasma may generally be at a location removed from the reactor, for instance, in a remotely located plasma system. One of skill in the art will recognize methods and apparatus suitable for such plasma treatment.

The disclosed organosilane precursors may also be used with a halosilane or polyhalodisilane, such as hexachlorodisilane, pentachlorodisilane, or tetrachlorodisilane, and one or more co-reactant gases to form SiN or SiCN films, as disclosed in PCT Publication Number WO2011/123792, the entire contents of which are incorporated herein in their entireties.

When the desired silicon-containing film also contains another element, such as, for example and without limitation, Ta, Hf, Nb, Mg, Al, Sr, Y, Ba, Ca, As, Sb, Bi, Sn, Pb, Co, lanthanides (such as Er), or combinations thereof, the co-reactants may include a metal-containing precursor which is selected from, but not limited to, metal alkyls, such as $Ln(RCp)_3$ or $Co(RCp)_2$, metal amines, such as $Nb(Cp)(NtBu)(NMe_2)_3$ and any combination thereof.

The organosilane precursor and one or more co-reactants may be introduced into the reaction chamber simultaneously (chemical vapor deposition), sequentially (atomic layer deposition), or in other combinations. For example, the organosilane precursor may be introduced in one pulse and two additional metal sources may be introduced together in a separate pulse [modified atomic layer deposition]. Alternatively, the reaction chamber may already contain the co-reactant prior to introduction of the organosilane precursor. The co-reactant may be passed through a plasma system localized or remotely from the reaction chamber, and decomposed to radicals. Alternatively, the organosilane precursor may be introduced to the reaction chamber continuously while other metal sources are introduced by pulse (pulsed-chemical vapor deposition). In each

example, a pulse may be followed by a purge or evacuation step to remove excess amounts of the component introduced. In each example, the pulse may last for a time period ranging from about 0.01 s to about 10 s, alternatively from about 0.3 s to about 3 s, alternatively from about 0.5 s to about 2 s. In another alternative, the organosilane precursor and one or more co-reactants may be simultaneously sprayed from a shower head under which a susceptor holding several wafers is spun (spatial ALD).

In one non-limiting exemplary atomic layer deposition type process, the vapor phase of an organosilane precursor is introduced into the reaction chamber, where it is contacted with a suitable substrate. Excess organosilane precursor may then be removed from the reaction chamber by purging and/or evacuating the reaction chamber. An oxygen source is introduced into the reaction chamber where it reacts with the absorbed organosilane precursor in a self-limiting manner. Any excess oxygen source is removed from the reaction chamber by purging and/or evacuating the reaction chamber. If the desired film is a silicon oxide film, this two-step process may provide the desired film thickness or may be repeated until a film having the necessary thickness has been obtained.

Alternatively, if the desired film is a silicon metal oxide film (i.e., $SiMO_x$, wherein x may be 0-4 and M is Ta, Hf, Nb, Mg, Al, Sr, Y, Ba, Ca, As, Sb, Bi, Sn, Pb, Co, lanthanides (such as Er), or combinations thereof), the two-step process above may be followed by introduction of a second vapor of a metal-containing precursor into the reaction chamber. The metal-containing precursor will be selected based on the nature of the silicon metal oxide film being deposited. After introduction into the reaction chamber, the metal-containing precursor is contacted with the substrate. Any excess metal-containing precursor is removed from the reaction chamber by purging and/or evacuating the reaction chamber. Once again, an oxygen source may be introduced into the reaction chamber to react with the metal-containing precursor. Excess oxygen source is removed from the reaction chamber by purging and/or evacuating the reaction chamber. If a desired film thickness has been achieved, the process may be terminated. However, if a thicker film is desired, the entire four-step process may be repeated. By alternating the provision of the organosilane precursor, metal-containing precursor, and oxygen source, a film of desired composition and thickness can be deposited.

Additionally, by varying the number of pulses, films having a desired stoichiometric M:Si ratio may be obtained. For example, a $SiMO_2$ film may be obtained by having one pulse of the organosilane precursor and one pulses of the metal-containing precursor, with each pulse being followed by pulses of the oxygen source. However, one of ordinary skill in the art will recognize that the number of pulses required to obtain the desired film may not be identical to the stoichiometric ratio of the resulting film.

In another alternative, Si or SiCOH films may be deposited via an ALD or modified ALD process using the disclosed compounds and a halosilane compound having the formula $Si_aH_{2a+2-b}X_b$, wherein X is F, Cl, Br, or I; a=1 through 6; and b=1 through (2a+2); or a cyclic halosilane compound having the formula $–Si_cH_{2c-d}X_d-$, wherein X is F, Cl, Br, or I; c=3-8; and d=1 through 2c. Preferably the halosilane compound is trichlorosilane, hexachlorodisilane (HCDS), pentachlorodisilane (PCDS), tetrachlorodisilane, or hexachlorocyclohexasilane. One of ordinary skill in the art will recognize that the Cl in these compounds may be substituted by Br or I when lower deposition temperatures are necessary, due to the lower bond energy in the Si-X bond (i.e., Si-Cl = 456 kJ/mol; Si-Br = 343 kJ/mol; Si-I = 339 kJ/mol). If necessary, the deposition may further utilize an O-containing co-reactant, such as ozone or oxygen. Vapors of the disclosed precursors and the halosilane compounds may be introduced sequentially or simultaneously into the reactor, depending on the desired concentration of the final film. The selected sequence of precursor injection will be determined based upon the desired film composition targeted. The precursor introduction steps may be repeated until the deposited layer achieves a suitable thickness. One of ordinary skill in the art will recognize that the introductory pulses may be simultaneous when using a spatial ALD device. The order of the introduction of the precursors may be varied and the deposition may be performed with or without the O-containing co-reactant in order to tune the amounts of carbon and nitrogen in the SiCOH film.

The silicon-containing films resulting from the processes discussed above may include SiO_2, SiN, SiON, SiCN, SiCOH, or $MSiO_x$, whererin M is an element such as Hf, Zr, Ti, Nb, Ta, or Ge, and x may be 4, depending of course on the oxidation state of M. One of ordinary skill in the art will recognize that by judicial

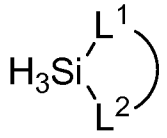
selection of the appropriate organosilane precursor and co-reactants, the desired film composition may be obtained.

Upon obtaining a desired film thickness, the film may be subject to further processing, such as thermal annealing, furnace-annealing, rapid thermal annealing, UV or e-beam curing, and/or plasma gas exposure. Those skilled in the art recognize the systems and methods utilized to perform these additional processing steps. For example, the silicon-containing film may be exposed to a temperature ranging from approximately 200°C and approximately 1000°C for a time ranging from approximately 0.1 second to approximately 7200 seconds under an inert atmosphere, a H-containing atmosphere, a N-containing atmosphere, an O-containing atmosphere, or combinations thereof. Most preferably, the temperature is 600°C for less than 3600 seconds under a H-containing atmosphere. The resulting film may contain fewer impurities and therefore may have improved performance characteristics. The annealing step may be performed in the same reaction chamber in which the deposition process is performed. Alternatively, the substrate may be removed from the reaction chamber, with the annealing/flash annealing process being performed in a separate apparatus. Any of the above post-treatment methods, but especially thermal annealing, has been found effective to reduce carbon and nitrogen contamination of the silicon-containing film.

It will be understood that many additional changes in the details, materials, steps, and arrangement of parts, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims. Thus, the present invention is not intended to be limited to the specific embodiments in the examples given above and/or the attached drawings.

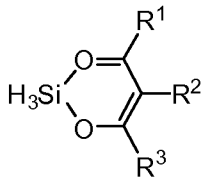
What is claimed is:

1. A Si-containing thin film forming precursor having the following formula:



wherein each L^1 and L^2 is an oxygen atom; L^1 and L^2 being joined together via a carbon bridge having one to three carbon atoms; L^1, L^2 and the carbon bridge forming a monoanionic ligand bonded to silicon.

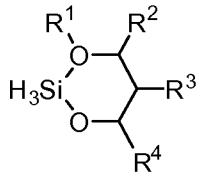
2. The Si-containing thin film forming precursor of claim 1, having the following formula:



wherein R^1, R^2, and R^3 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle.

3. The Si-containing thin film forming precursor of claim 2, wherein the Si-containing thin film forming precursor is H_3Si(-O=C(tBu)-CH=C(tBu)-O-) or H_3Si(O=C(Me)-CH=C(Me)-O-).

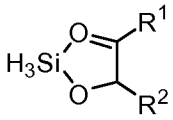
4. The Si-containing thin film forming precursor of claim 1, having the following formula:



wherein R^1, R^2, R^3, and R^4 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle.

5. The Si-containing thin film forming precursor of claim 4, wherein the Si-containing thin film forming precursor is $H_3Si(-O(iPr)-C_3H_6-O-)$ or $H_3Si(-O(tBu)-C_3H_6-O-)$.

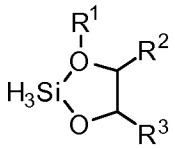
6. The Si-containing thin film forming precursor of claim 1, having the following formula:



wherein R^1 and R^2 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle.

7. The Si-containing thin film forming precursor of claim 6, wherein the Si-containing thin film forming precursor is $H_3Si(-O=C(tBu)-CH_2-O-)$.

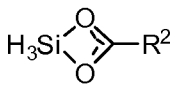
8. The Si-containing thin film forming precursor of claim 1, having the following formula:



wherein R^1, R^2, and R^3 may each independently be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle.

9. The Si-containing thin film forming precursor of claim 8, wherein the Si-containing thin film forming precursor is $H_3Si(-O(iPr)-C_2H_4-O-)$ or $H_3Si(-O(tBu-C_2H_4-O-)$.

10. The Si-containing thin film forming precursor of claim 1, having the following formula:



wherein R^1 may be H, a C1 to C6 alkyl group, or a C3-C20 aryl or heterocycle.

11. The Si-containing thin film forming precursor of claim 10, wherein the Si-containing thin film forming precursor is $H_3Si(-O-C(Et)-O-)$ or $H_3Si(-O-C(nBu)-O-)$.

12. A method of depositing a Si-containing layer on a substrate, the method comprising:

introducing at least one Si-containing thin film forming precursor of any one of claims 1 to 11 into a reactor having at least one substrate disposed therein;

depositing at least part of the Si-containing thin film forming precursor onto the at least one substrate to form a Si-containing layer using a vapor deposition method.

13. The method of claim 12, further comprising introducing into the reactor at least one co-reactant.

14. The method of claim 13, wherein the co-reactant is selected from the group consisting of O_2, O_3, H_2O, H_2O_2, NO, NO_2, a carboxylic acid, radicals thereof, and combinations thereof, preferably plasma treated oxygen or ozone.

15. The method of claim 13, wherein the co-reactant is selected from the group consisting of H_2, NH_3, $(SiH_3)_3N$, hydridosilanes (such as SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10}, Si_5H_{10}, Si_6H_{12}), chlorosilanes and chloropolysilanes (such as $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, Si_2Cl_6, Si_2HCl_5, $Si_2H_2Cl_4$, Si_3Cl_8), alkysilanes (such as Me_2SiH_2, Et_2SiH_2, $MeSiH_3$, $EtSiH_3$), hydrazines (such as N_2H_4, $MeHNNH_2$, MeHNNHMe), organic amines (such as $NMeH_2$, $NEtH_2$, NMe_2H, NEt_2H, NMe_3, NEt_3, $(SiMe_3)_2NH$), pyrazoline, pyridine, B-containing molecules (such as B_2H_6, 9-borabicylo[3,3,1]none, trimethylboron, triethylboron, borazine), alkyl metals (such as trimethylaluminum, triethylaluminum, dimethylzinc, diethylzinc), radical species thereof, and mixtures thereof.

16. The method of claim 15, wherein the co-reactant is selected from the group consisting of H_2, NH_3, SiH_4, Si_2H_6, Si_3H_8, SiH_2Me_2, SiH_2Et_2, $N(SiH_3)_3$, hydrogen radicals thereof, and mixtures thereof.

17. The method of claim 15, wherein the co-reactant is selected from the group consisting of $SiHCl_3$, Si_2Cl_6, Si_2HCl_5, $Si_2H_2Cl_4$., and cyclo-$Si_6H_6Cl_6$.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/051255

A. CLASSIFICATION OF SUBJECT MATTER

C07F 7/07(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07F 7/07; C07F 7/00; C01B 21/068; C23C 8/00; C07F 19/00; C01B 33/113; C23C 16/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: silicon(IV) , precurrsor, diketonato, acac, hydrogen, pentacoordinate , thin film

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Gerardo Gonzalez-Garcia et al., 'Pentacoordinate mono(β-diketonato)- and hexacoordinate bis-(β-diketonato)-silicon(IV) complexes obtained from (thiocyanato-N)hydridosilanes', Polyhedron 41 (2012) 127-133 (Available online 7 May 2012) See scheme 2.	1-17
A	EP 1310500 A1 (SHIPLEY CO. L.L.C.) 14 May 2003 See page 3.	1-17
A	WO 01-79578 A1 (ADVANCED TECHNOLOGY MATERIALS, INC.) 25 October 2001 See page 6.	1-17
A	KR 10-2011-0009739 A (UMT CO., LTD.) 31 January 2011 See [0033]-[0038]	1-17

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 November 2013 (22.11.2013)	**25 November 2013 (25.11.2013)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/051255

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1310500 A1	14/05/2003	US 2003-118725 A1	26/06/2003
WO 01-79578 A1	25/10/2001	AU 2001-51457 A1 US 6736993 B1	30/10/2001 18/05/2004
KR 10-2011-0009739 A	31/01/2011	None	