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62/190,404 9 July 2015 (09.07.2015) US(71) Applicant: **L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE** [FR/FR]; 75 Quai d'Orsay, F-75007 Paris (FR).(71) Applicant (for US only): **AMERICAN AIR LIQUIDE, INC.** [US/US]; 46409 Landing Parkway, Fremont, California 94538 (US).

(72) Inventors; and

(71) Applicants (for US only): **FAFARD, Claudia** [US/US]; 2 Bisbee Road, Newark, Delaware 19711 (US). **KUCHENBEISER, Glenn** [US/US]; 24 Newbrook Road, Newark, Delaware 19711 (US). **PALLEM, Venkateswara R.** [IN/US]; 277 Chippenham Lane, Hockessin, Delaware19707 (US). **GIRARD, Jean-Marc** [FR/FR]; 16 rue Montbauron, F-78000 Versailles (FR). **NODA, Naoto** [JP/JP]; #205, 851-1 Kurakake, Tsukuba-shi, Ibaraki 305-0024 (JP).(74) Agents: **MCQUEENEY, Patricia E.** et al.; 9811 Katy Freeway, Suite 100, Houston, Texas 77024 (US).

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(54) Title: ALKYLAMINO-SUBSTITUTED HALOCARBOSILANE PRECURSORS

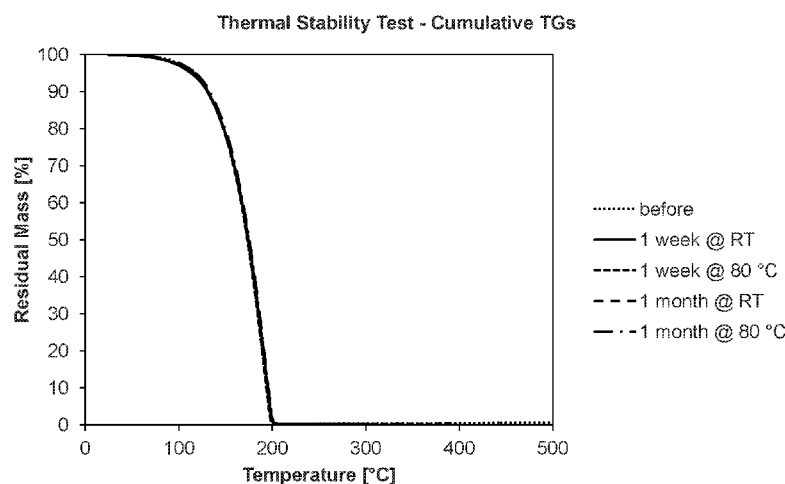


FIG 6

(57) Abstract: Disclosed are Si-containing film forming compositions comprising alkylamino-substituted halocarbosilane precursors, methods of synthesizing the same, and their use for vapor deposition processes.



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ALKYLAMINO-SUBSTITUTED HALOCARBOSILANE PRECURSORS

Cross Reference to Related Applications

The present application claims the benefit of U.S. Provisional Application Serial No. 62/190,404 filed July 9, 2015, herein incorporated by reference in its entirety for all purposes.

Technical Field

Disclosed are Si-containing film forming compositions comprising alkylamino-substituted halocarbosilane precursors, methods of synthesizing the same, and their use for vapor deposition processes.

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 , SiC , SiCN , SiCOH , MSiO_x , 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 vapor deposition processes), suitable temperature process window, reactivity with various oxidants and low film contamination, in addition to high deposition rates, conformality and consistency of films produced.

Fukazawa et al. (US2013/0224964) disclose a method of forming a dielectric film having Si-C bonds on a semiconductor substrate by atomic layer deposition (ALD). The precursor has a Si-C-Si bond in its molecule, and the reactant gas is oxygen-free and halogen-free and is constituted by at least a rare gas.

Vrtis et al. (EP2048700) disclose forming antireflective coatings using, amongst many others, $\text{R}^1_n(\text{OR}^2)_p(\text{NR}^4_z)_{3-n-p}\text{Si}-\text{R}^7-\text{Si}-\text{R}^3_m(\text{NR}^5_z)_q(\text{OR}^6)_{3-m-q}$, wherein R^1 and R^3 are independently H or C_1 to C_4 linear or branched, saturated, singly or

multiply unsaturated, cyclic, partially or fully fluorinated hydrocarbon; R^2 , R^6 , and R^7 are independently C_1 to C_6 linear or branched, saturated, singly or multiply unsaturated, cyclic, aromatic, partially or fully fluorine hydrocarbon, alternatively, R^7 is an amine or an organoamine group; R^4 and R^5 are independently H, C_1 to C_6 linear or branched, saturated, singly or multiply unsaturated, cyclic, aromatic, partially or fully fluorinated hydrocarbon, z is 1 or 2; n is 0 to 3; m is 0 to 3; q is 0 to 3; and p is 0 to 3, provided that $n+p \leq 3$ and $m+q \leq 3$.

Ohhashi et al. (US2013/0206039) disclose monosilane or bisilane compounds having dimethylamino groups used in the hydrophobization treatment of surface substrates. The bisilane compounds have the formula $R^2_b[N(CH_3)_2]_3-bSi-R^4-SiR^3_c[N(CH_3)_2]_3-c$, wherein R^2 and R^3 are each independently a hydrogen atom or a straight chain or branched chain alkyl group with 1 to 4 carbon atoms, R^4 is a straight chain or branched chain alkylene group with 1 to 16 carbon atoms, and b and c are each independently an integer of 0 to 2.

Machida et al. (JP2002158223) disclose the formation of insulator films using Si-type materials with the formula: $\{R_3(R_4)N\}_3Si-\{C(R_1)R_2\}_n-Si\{N(R_5)R_6\}_3$, where R_1 , R_2 = H, hydrocarbon groups C_1 -3, or X(halogen atom)-substituted hydrocarbon groups (R_1 and R_2 can be same), n = 1-5 integer, R_3 , R_4 , R_5 and R_6 = H, hydrocarbon groups C_1 -3 or X(halogen atom)-substituted hydrocarbon groups (R_3 , R_4 , R_5 and R_6 can be same). The insulator films may be formed on substrates by CVD.

Jansen et al. (Z.Naturforsch. B. 52, 1997, 707-710) disclose the synthesis of bis[tris(methylamino)silyl]methane and bis[tris(phenylamino)silyl]methane as potential precursors of porous oxygen-free solids.

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 terms “approximately” or “about” or “ca.” mean $\pm 10\%$ of the value stated.

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 “halocarbosilane” refers to a linear or branched molecule with a backbone having alternate Si and C atoms and at least one Si-C-Si unit and at least one halide bonded to the Si.

As used herein, the term “hydrocarbyl group” refers to a functional group containing carbon and hydrogen; the term “alkyl group” refers to saturated functional groups containing exclusively carbon and hydrogen atoms. The hydrocarbyl group may be saturated or unsaturated. Either term refers to linear, branched, or 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, 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); the abbreviation "Cy" refers to a cyclic alkyl group (cyclobutyl, cyclopentyl, cyclohexyl, etc.); and the abbreviation "R_{amd}" refers to an R-N-C(Me)-N-R amidinate ligand, with R being an alkyl group (e.g., ⁱPr_{amd} is iPr-N-C(Me)-N-iPr).

5 As used herein, 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.). Similarly, a halide refers to a negative element from column 17 of the Periodic Table, namely F⁻, Cl⁻, Br⁻, I⁻, or At⁻.

Any and all ranges recited herein are inclusive of their endpoints (i.e., x=1 to 4 or x ranges from 1 to 4 includes x=1, x=4, and x=any number in between), irrespective of whether the term "inclusively" is used.

15 Please note that the films or layers deposited, such as silicon oxide or silicon nitride, may be listed throughout the specification and claims without reference to their proper stoichiometry (i.e., SiO₂, SiO₃, Si₃N₄). The layers may include pure (Si) layers, carbide (Si_oC_p) layers, nitride (Si_kN_l) layers, oxide (Si_nO_m) layers, or mixtures thereof, wherein k, l, m, n, o, and p inclusively range from 1 to 6. For instance, silicon oxide is Si_nO_m, wherein n ranges from 0.5 to 1.5 and m ranges from 1.5 to 3.5. More preferably, the silicon oxide layer is SiO₂ or SiO₃. These films may also contain Hydrogen, typically from 0 at% to 15 at%. However, since not routinely measured, film compositions are given while ignoring their H content, unless explicitly stated otherwise.

Brief Description of the Drawings

For a further understanding of the nature and objects of the present invention, reference should be made to the following detailed description, taken in conjunction with the accompanying drawings, in which like elements are given the same or analogous reference numbers and wherein:

30 **FIG. 1** is a side view of one embodiment of the Si-containing film forming composition delivery device 1;

FIG. 2 is a side view of a second embodiment of the Si-containing film forming composition delivery device 1;

FIG 3 is a 400 MHz proton Nuclear Magnetic Resonance (NMR) spectrum of $(\text{Me}_2\text{N})_2\text{ClSi-CH}_2\text{-SiCl(NMe}_2)_2$ taken in deuterated benzene solvent;

FIG 4 is a ThermoGravimetric Analysis (TGA) graph demonstrating the percentage of weight loss with increasing temperature of $(\text{Me}_2\text{N})_2\text{ClSi-CH}_2\text{-SiCl(NMe}_2)_2$;

FIG 5 is a TGA graph demonstrating the percentage of weight loss with increasing temperature of $(\text{Me}_2\text{N})\text{Cl}_2\text{Si-CH}_2\text{-SiCl}_2(\text{NMe}_2)$;

FIG 6 is a TGA graph demonstrating the percentage of weight loss with increasing temperature of $(\text{Me}_2\text{N})\text{Cl}_2\text{Si-CH}_2\text{-SiCl}_2(\text{NMe}_2)$ after 1 week or 1 month at room temperature or 80°C;

FIG 7 is a a schematic diagram of the vapor deposition apparatus used for the testing in Example 4; and

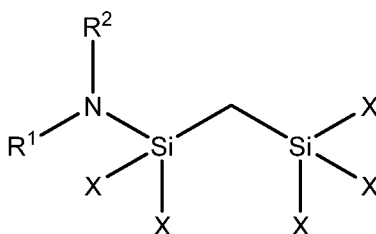
FIG 8 is a X-ray Photoelectron Spectroscopy (XPS) graph showing the film composition of a SiOC film deposited by ALD using $(\text{Me}_2\text{N})\text{Cl}_2\text{Si-CH}_2\text{-SiCl}_2(\text{NMe}_2)$ as a Si source, water (H_2O) as an oxygen source, and pyridine as a catalyst

Summary

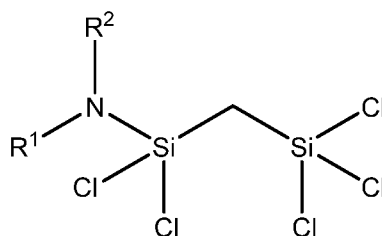
Disclosed are Si-containing film forming compositions comprising alkylamino substituted halocarbosilane precursors having the formula $\text{R}_3\text{Si-CH}_2\text{-SiR}_3$, wherein each R is independently H, a halide, a hydrocarbyl group, or an alkylamino group, provided that at least one R is a halide and at least one R is an alkylamino group having the formula NR^1R^2 , wherein R^1 and R^2 is each independently H, a C1-C6 alkyl group, a C1-C6 alkenyl group, or a C3-C10 aryl or heterocycle group. The disclosed precursors may include one or more of the following aspects:

- At least one R being F;
- At least one R being Cl;
- At least one R being I;
- At least one R being Br;
- At least one R being H;
- At least one R being a hydrocarbyl group;
- At least one R being an alkyl group;
- At least one R being Me;

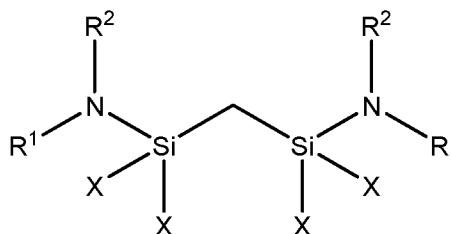
- At least one R being Et;
- At least one R being Pr;
- At least one R being Bu;
- Each R being selected from H, a halide, or the alkylamino group;
- 5 • Each R being selected from a halide or the alkylamino group;
- R¹ and R² each independently being selected from H, Me, Et, nPr, iPr, Bu, or Am;
- R¹ and R² each independently being selected from H, Me, Et, nPr, or iPr;
- R¹ being H;
- 10 • R¹ being Me;
- R¹ being Et;
- R¹ being nPr;
- R¹ being iPr;
- R¹ being Bu;
- 15 • R¹ being Am;
- R² being H;
- R² being Me;
- R² being Et;
- R² being nPr;
- 20 • R² being iPr;
- R² being Bu;
- R² being Am;
- R¹ and R² being joined to form a cyclic chain on one N atom or on adjacent N atoms;
- 25 • R¹ and R² forming pyridine, pyrrole, pyrrolidine, morpholine, or imidazole ring structures on one N atom;
- R¹ and R² forming amidinate or diketimine ligands on adjacent N atoms;
- The alkylamino-substituted halocarbosilane precursor having the formula:



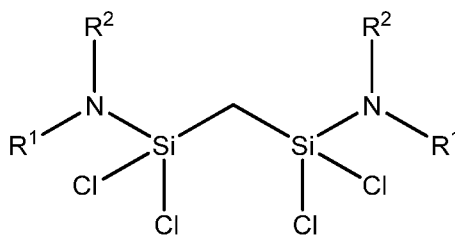
- The alkylamino-substituted halocarbosilane precursor having the formula:



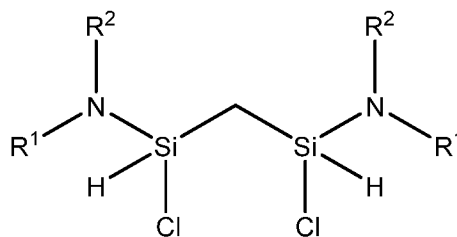
- alkylamino-substituted halocarbosilane precursor having the formula:



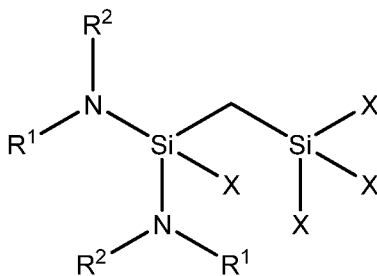
- 5
- alkylamino-substituted halocarbosilane precursor having the formula:



- alkylamino-substituted halocarbosilane precursor having the formula:

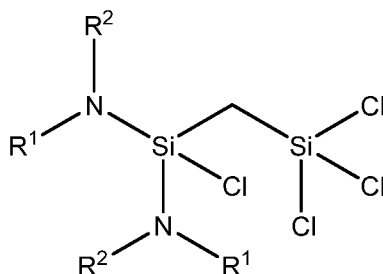


- alkylamino-substituted halocarbosilane precursor having the formula:

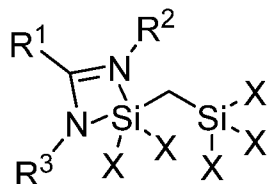


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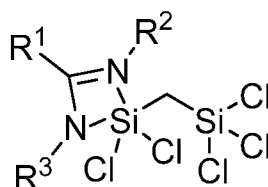
- alkylamino-substituted halocarbosilane precursor having the formula:



- alkylamidinate-substituted halocarbo-silane precursor having the formula:

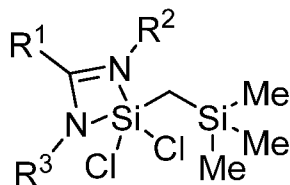


- alkylamidinate-substituted halocarbo-silane precursor having the formula:

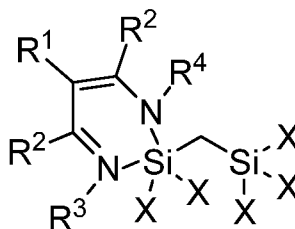


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- alkylamidinate-substituted halocarbo-silane precursor having the formula:

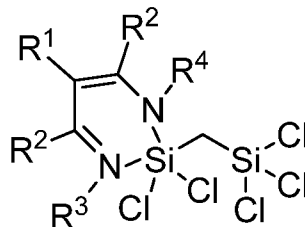


- diketiminate-substituted halocarbo-silane precursor having the formula:

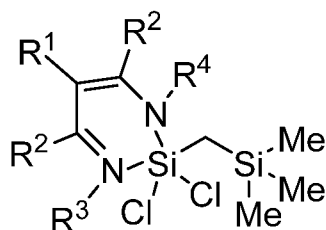


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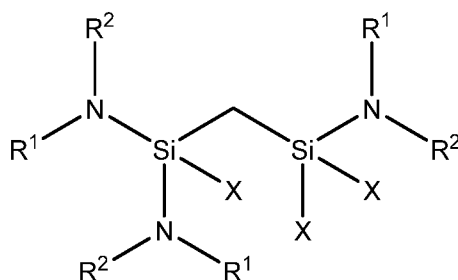
- diketiminate-substituted halocarbo-silane precursor having the formula:



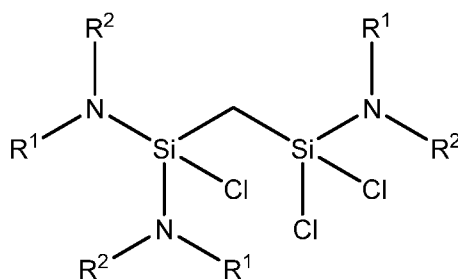
- diketiminate-substituted halocarbo-silane precursor having the formula:



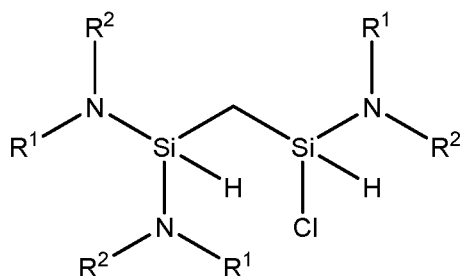
- R³ being H, a C1 to C6 alkyl group, or a C3-C10 aryl or heterocycle group;
- R³ being H, Me, Et, nPr, iPr, Bu, or Am;
- R³ being H, Me, Et, nPr, or iPr;
- R³ being H;
- R³ being Me;
- R³ being Et;
- R³ being nPr;
- R³ being iPr;
- R³ being Bu;
- R³ being Am;
- alkylamino-substituted halocarbosilane precursor having the formula:



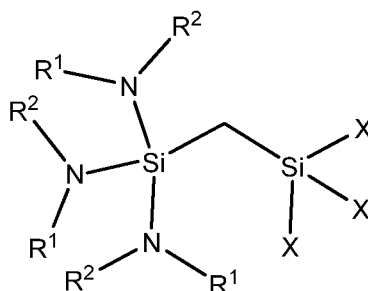
- alkylamino-substituted halocarbosilane precursor having the formula:



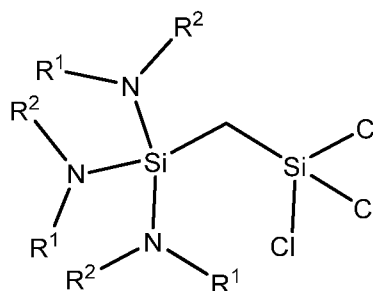
- alkylamino-substituted halocarbosilane precursor having the formula:



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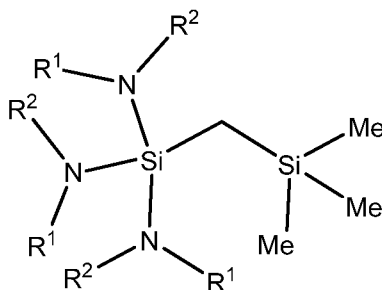


- alkylamino-substituted halocarbosilane precursor having the formula:

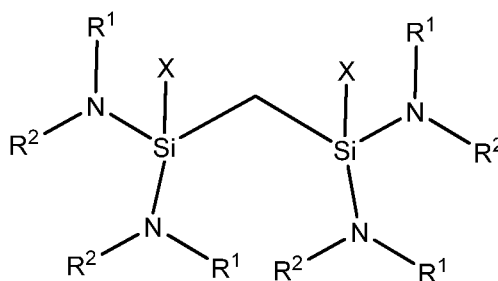


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- alkylamino-substituted halocarbosilane precursor having the formula:

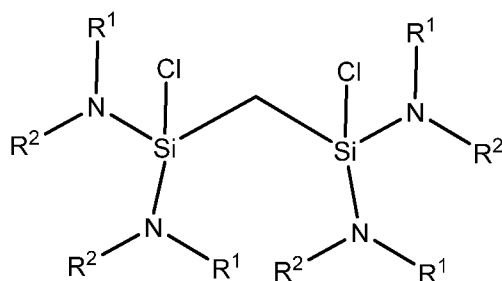


- alkylamino-substituted halocarbosilane precursor having the formula:

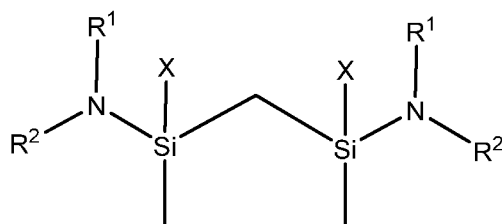


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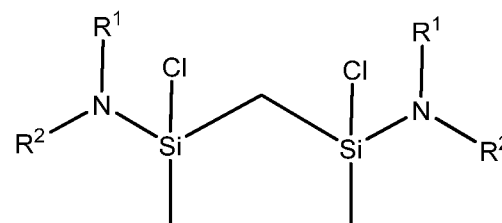
- alkylamino-substituted halocarbosilane precursor having the formula:



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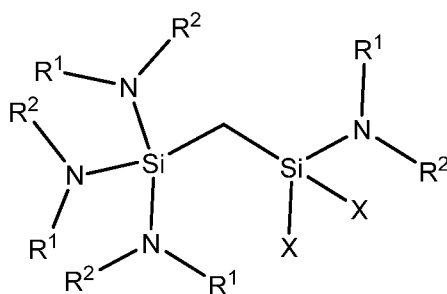


- alkylamino-substituted halocarbosilane precursor having the formula:

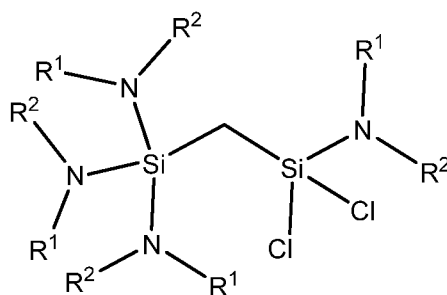


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- alkylamino-substituted halocarbosilane precursor having the formula:

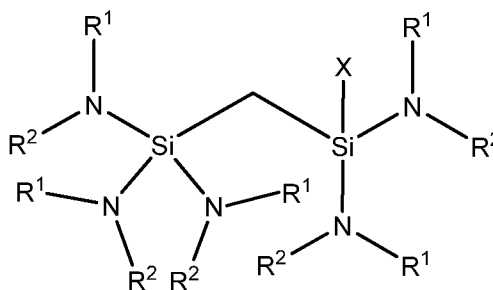


- alkylamino-substituted halocarbosilane precursor having the formula:

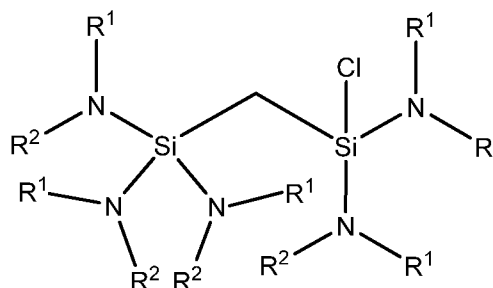


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- alkylamino-substituted halocarbosilane precursor having the formula:



- alkylamino-substituted halocarbo-silane precursor having the formula:



- the Si-containing film forming composition comprising between approximately 0.1 molar % and approximately 50 molar % of the alkylamino-substituted halocarbo-silane precursor;
- the Si-containing film forming composition comprising between approximately 93% w/w to approximately 100% w/w of the alkylamino-substituted halocarbo-silane precursor;
- the Si-containing film forming composition comprising between approximately 99% w/w to approximately 100% w/w of the alkylamino-substituted halocarbo-silane precursor;
- the Si-containing film forming composition comprising between approximately 0 % w/w and 5 % w/w of hexane, substituted hexane, pentane, substituted pentane, dimethyl ether, or anisole;
- further comprising a solvent;
- the solvent being selected from the group consisting of C1-C16 hydrocarbons, THF, DMO, ether, pyridine, and combinations thereof;
- the solvent being a C1-C16 hydrocarbons;
- the solvent being tetrahydrofuran (THF);
- the solvent being dimethyl oxalate (DMO);
- the solvent being ether;
- the solvent being pyridine;
- the solvent being ethanol; or

- the solvent being isopropanol.

Also disclosed are Si-containing film forming composition delivery devices comprising a canister having an inlet conduit and an outlet conduit and containing any of the Si-containing film forming compositions disclosed above. The disclosed device may include one or more of the following aspects:

- the Si-containing film forming composition having a total concentration of metal contaminants of less than 10 ppmw;
- an end of the inlet conduit end located above a surface of the Si-containing film forming composition and an end of the outlet conduit located below the surface of the Si-containing film forming composition;
- an end of the inlet conduit end located below a surface of the Si-containing film forming composition and an end of the outlet conduit located above the surface of the Si-containing film forming composition;
- further comprising a diaphragm valve on the inlet and the outlet;
- the Si-containing film forming composition being $(\text{Me}_2\text{N})_2\text{ClSi-CH}_2\text{-SiCl(NMe}_2)_2$; and
- the Si-containing film forming composition being $(\text{Me}_2\text{N})\text{Cl}_2\text{Si-CH}_2\text{-SiCl}_2(\text{NMe}_2)$.

Also disclosed are processes for the deposition of a Silicon-containing film on a substrate. The vapor of any of the alkylamino-substituted halocarbosilane precursors disclosed above is introduced into a reactor having a substrate disposed therein. At least part of the alkylamino-substituted halocarbosilane precursor is deposited onto the substrate to form the Silicon-containing film. The disclosed processes include one or more of the following aspects:

- introducing a reactant into the reactor;
- the reactant being plasma-treated;
- the reactant being remote plasma-treated;
- the reactant not being plasma-treated;
- the reactant being selected from the group consisting of H_2 , NH_3 , $(\text{SiH}_3)_3\text{N}$, 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 Me_2SiH_2 , Et_2SiH_2 , MeSiH_3 , EtSiH_3), hydrazines (such as N_2H_4 , MeHNNH_2 , MeHNNHMe), organic

- amines (such as NMeH₂, NEtH₂, NMe₂H, NEt₂H, NMe₃, NEt₃, (SiMe₃)₂NH), diamines (such as ethylene diamine, dimethylethylene diamine, tetramethylethylene diamine), aminoalcohols (such as ethanolamine [HO-CH₂-CH₂-NH₂], bis ethanolamine [HN(C₂H₅OH)₂] or tris ethanolamine[N(C₂H₅OH)₃]), pyrazoline, pyridine, B-containing molecules (such as B₂H₆, 9-borabicyclo[3,3,1]nonane, trimethylboron, triethylboron, borazine, substituted borazine, dialkylaminoboranes), alkyl metals (such as trimethylaluminum, triethylaluminum, dimethylzinc, diethylzinc), radical species thereof, and mixtures thereof;
- 5
- 10
- the reactant being selected from the group consisting of H₂, H₂CO, N₂H₄, NH₃, SiH₄, Si₂H₆, Si₃H₈, SiH₂Me₂, SiH₂Et₂, N(SiH₃)₃, hydrogen radicals thereof, and mixtures thereof;
 - the reactant being selected from SiH₄, Si₂H₆, Si₃H₈, Si₄H₁₀, Si₅H₁₀, Si₆H₁₂, radical species thereof, and mixtures thereof;
- 15
- the reactant being selected from Me₂SiH₂, Et₂SiH₂, MeSiH₃, EtSiH₃, radical species thereof, and mixtures thereof;
 - the reactant being selected from NMeH₂, NEtH₂, NMe₂H, NEt₂H, NMe₃, NEt₃, (SiMe₃)₂NH, radical species thereof, and mixtures thereof;
 - the reactant being selected from ethylene diamine, dimethylethylene diamine, tetramethylethylene diamine, radical species thereof, and mixtures thereof;
- 20
- the reactant being selected from ethanolamine [HO-CH₂-CH₂-NH₂], bis ethanolamine [HN(C₂H₅OH)₂], tris ethanolamine[N(C₂H₅OH)₃], radical species thereof, and mixtures thereof;
- 25
- the reactant being selected from trimethylaluminum, triethylaluminum, dimethylzinc, diethylzinc, radical species thereof, and mixtures thereof;
 - the reactant being H₂;
 - the reactant being NH₃;
 - the reactant being selected from the group consisting of: O₂, O₃, H₂O, H₂O₂, NO, N₂O, NO₂, a diol (such as ethylene glycol or hydrated hexafluoroacetone), oxygen radicals thereof, and mixtures thereof;
- 30
- the reactant being H₂O;
 - the reactant being plasma treated O₂;

- the reactant being O₃;
- the Si-containing film forming composition and the reactant being introduced into the reactor simultaneously;
- the reactor being configured for chemical vapor deposition;
- 5 • the Si-containing film forming composition and the reactant being introduced into the chamber sequentially;
- the reactor being configured for atomic layer deposition;
- the deposition being plasma enhanced.

10 **Detailed Description of Preferred Embodiments**

Disclosed are Si-containing film forming compositions comprising alkylamino-substituted halocarbosilane precursors, methods of synthesizing the same, and methods of using the same to deposit silicon-containing films for manufacturing semiconductors.

15 The disclosed alkylamino-substituted halocarbosilane precursors have the formula R₃Si-CH₂-SiR₃, wherein each R is independently H, a halide X, a hydrocarbyl group, or an alkylamino group, provided that at least one R is a halide X and at least one R is an alkylamino group having the formula NR₁R₂, wherein each R' is independently H, a C1-C6 alkyl group, a C1-C6 alkenyl group, or a C3-
20 C10 aryl or heterocycle group. Preferably, R¹ and R² is each independently H, Me, Et, nPr, iPr, Bu, or Am. R¹ and R² may be joined to form a cyclic chain on one N atom or on adjacent N atoms. For example, R¹ and R² may form pyridine, pyrrole, pyrrolidine, morpholine, or imidazole ring structures on one N atom or amidinate or diketimine ligands on adjacent N atoms.

25 Preferably, at least one R is a halide, and more particularly a Cl, particularly for ALD. Halides are known for their high reactivity. Applicants believe that at least one halide on the disclosed alkylamino-substituted halocarbosilane precursor will improve the deposition rate as compared to alkylamino-substituted halocarbosilane precursors having no halide ligand. The halide may also improve
30 volatility.

Preferably at least one R is H because the hydrogen bonded to the Si atom may help increase the volatility of the precursor. Additionally, in ALD processes, the Si-H bonds of the disclosed precursors may help to provide a larger growth

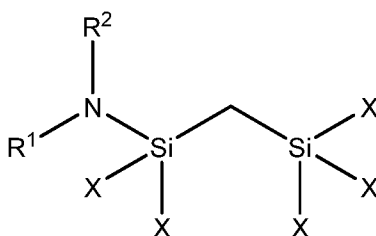
rate per cycle when compared to the analogous halocarbosilane precursors because the H atoms occupy less surface area, resulting in more molecules on the substrate surface.

Preferably, at least R^1 or R^2 is H because the hydrogen bonded to the N atom may help increase the volatility of the precursor. Additionally, in ALD processes, the N-H bonds of the disclosed precursors may help to provide a larger growth rate per cycle when compared to the analogous halocarbosilane precursors because the H atoms occupy less surface area, resulting in more molecules on the substrate surface. NH also provides improved reactivity when compared to NR molecules.

Even more preferably, at least one R is H and R^1 or R^2 is H for the same reasons described above.

One of ordinary skill in the art will recognize that at least one R may include an alkyl group, such as Me, Et, Pr, or Bu, when deposited films having some carbon are desired. However, the alkyl group may be detrimental to volatility of the precursor.

Exemplary alkylamino-substituted halocarbosilane precursors having one alkylamino group include:



wherein R^1 and R^2 is each independently H, a C1-C6 alkyl group, a C1-C6 alkenyl group, or a C3-C10 aryl or heterocycle group. Preferably, R_1 and R_2 is each independently H, Me, Et, nPr, iPr, Bu, or Am. R_1 and R_2 may be joined to form a cyclic chain on the N atom. For example, NR_1R_2 may form pyridine, pyrrole, pyrrolidine, morpholine, or imidazole ring structures.

Exemplary mono-alkylamino substituted precursors include $(NMe_2)Cl_2Si-CH_2-SiCl_3$, $(NMe_2)Br_2Si-CH_2-SiBr_3$, $(NMe_2)I_2Si-CH_2-SiI_3$, $(NMe_2)F_2Si-CH_2-SiF_3$, $(NEt_2)Cl_2Si-CH_2-SiCl_3$, $(NEt_2)Br_2Si-CH_2-SiBr_3$, $(NEt_2)I_2Si-CH_2-SiI_3$, $(NEt_2)F_2Si-CH_2-SiF_3$, $(NMeEt)Cl_2Si-CH_2-SiCl_3$, $(NMeEt)Br_2Si-CH_2-SiBr_3$, $(NMeEt)I_2Si-CH_2-SiI_3$, $(NMeEt)F_2Si-CH_2-SiF_3$, $(NEtH)Cl_2Si-CH_2-SiCl_3$, $(NEtH)Br_2Si-CH_2-SiBr_3$,

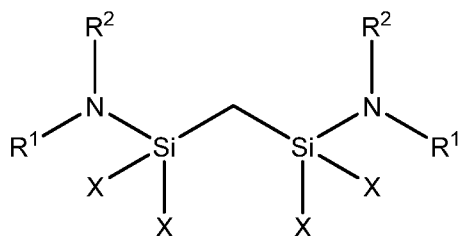
(NEtH)₂Si-CH₂-SiI₃, (NEtH)F₂Si-CH₂-SiF₃, (NiPrH)Cl₂Si-CH₂-SiCl₃, (NiPrH)Br₂Si-CH₂-SiBr₃, (NiPrH)I₂Si-CH₂-SiI₃, or (NiPrH)F₂Si-CH₂-SiF₃.

The monoalkylamino-1,1,3,3,3-pentachloro-1,3-disilapropane may be synthesized at approximately -78 °C to approximately room temperature (approx. 25°C) by mixing or dissolving excess amine and a nonpolar solvent. 1,1,1,3,3,3-hexachloro-1,3-disilapropane is slowly added to the mixture to form the desired compound. The reactants are commercially available or may be synthesized according to J. Organomet. Chem. 92, 1975 163-168.

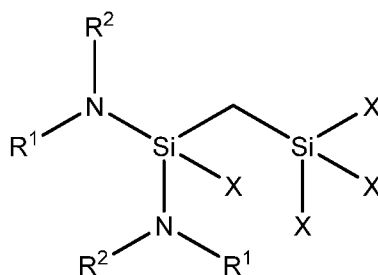
The 2-ethylamino-2,4-disilapentane (H₃C-(NH₂Et)HSi-CH₂-SiH₂-CH₃) and the 2,4-bis(ethylamino)-2,4-disilapentane (H₃C-(NH₂Et)HSi-CH₂-SiH-(NH₂Et)-CH₃) may be synthesized in similar conditions using respectively H₃C-ClHSi-CH₂-SiH₂-CH₃ and H₃C-ClHSi-CH₂-SiHCl-CH₃ as starting materials.

Alternatively, alkyl lithium is combined with a primary or secondary amine (NH₂R or NHR₂) in a solvent, such as ether or any other polar solvents, at approximately -78°C to approximately room temperature (approx. 25°C) to form lithium amide. The lithium amide may be isolated and reacted with 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired compound. Alternatively, the lithium amide solution may be added to 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired compound.

Exemplary alkylamino-substituted halocarbosilane precursors having two alkylamino groups include symmetric molecules having the formula:



or asymmetric molecules having the formula:



wherein R^1 and R^2 is each independently H, a C1-C6 alkyl group, a C1-C6 alkenyl group, or a C3-C10 aryl or heterocycle group. Preferably, R_1 and R_2 is each independently H, Me, Et, nPr, iPr, Bu, or Am. R_1 and R_2 may be joined to form a cyclic chain on one N atom or, on the unsymmetric compound, on adjacent N atoms. For example, NR_1R_2 may form pyridine, pyrrole, pyrrolidine, morpholine, or imidazole ring structures or, on the unsymmetric compound, $R_1-N-Si-N-R_2$ may form an amidinate or diketiminate structure.

Exemplary asymmetric di-alkylamino substituted precursors include $(NMe_2)_2ClSi-CH_2-SiCl_3$, $(NMe_2)_2BrSi-CH_2-SiBr_3$, $(NMe_2)_2ISi-CH_2-SiI_3$, $(NMe_2)_2FSi-CH_2-SiF_3$, $(NEt_2)_2ClSi-CH_2-SiCl_3$, $(NEt_2)_2BrSi-CH_2-SiBr_3$, $(NEt_2)_2ISi-CH_2-SiI_3$, $(NEt_2)_2FSi-CH_2-SiF_3$, $(NMeEt)_2ClSi-CH_2-SiCl_3$, $(NMeEt)_2BrSi-CH_2-SiBr_3$, $(NMeEt)_2ISi-CH_2-SiI_3$, $(NMeEt)_2FSi-CH_2-SiF_3$, $(NEtH)_2ClSi-CH_2-SiCl_3$, $(NEtH)_2BrSi-CH_2-SiBr_3$, $(NEtH)_2ISi-CH_2-SiI_3$, $(NEtH)_2FSi-CH_2-SiF_3$, $(NiPrH)_2ClSi-CH_2-SiCl_3$, $(NiPrH)_2BrSi-CH_2-SiBr_3$, $(NiPrH)_2ISi-CH_2-SiI_3$, or $(NiPrH)_2FSi-CH_2-SiF_3$.

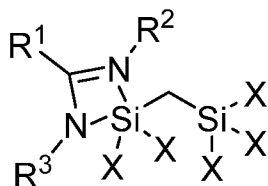
Exemplary symmetric di-alkylamino substituted precursors include $(NMe_2)_2Cl_2Si-CH_2-SiCl_2(NMe_2)$, $(NMe_2)_2Br_2Si-CH_2-SiBr_2(NMe_2)$, $(NMe_2)_2I_2Si-CH_2-SiI_2(NMe_2)$, $(NMe_2)_2F_2Si-CH_2-SiF_2(NMe_2)$, $(NEt_2)_2Cl_2Si-CH_2-SiCl_2(NEt_2)$, $(NEt_2)_2Br_2Si-CH_2-SiBr_2(NEt_2)$, $(NEt_2)_2I_2Si-CH_2-SiI_2(NEt_2)$, $(NEt_2)_2F_2Si-CH_2-SiF_2(NEt_2)$, $(NMeEt)_2Cl_2Si-CH_2-SiCl_2(NMeEt)$, $(NMeEt)_2Br_2Si-CH_2-SiBr_2(NMeEt)$, $(NMeEt)_2I_2Si-CH_2-SiI_2(NMeEt)$, $(NMeEt)_2F_2Si-CH_2-SiF_2(NMeEt)$, $(NEtH)_2Cl_2Si-CH_2-SiCl_2(NEtH)$, $(NEtH)_2Br_2Si-CH_2-SiBr_2(NEtH)$, $(NEtH)_2I_2Si-CH_2-SiI_2(NEtH)$, $(NEtH)_2F_2Si-CH_2-SiF_2(NEtH)$, $(NiPrH)_2Cl_2Si-CH_2-SiCl_2(NiPrH)$, $(NiPrH)_2Br_2Si-CH_2-SiBr_2(NiPrH)$, $(NiPrH)_2I_2Si-CH_2-SiI_2(NiPrH)$, or $(NiPrH)_2F_2Si-CH_2-SiF_2(NiPrH)$.

At approximately -78 °C to approximately room temperature (approx. 25°C), 2 equivalents of amine are mixed with or dissolved in a nonpolar solvent. 1,1,1,3,3,3-hexachloro-1,3-disilapropane is slowly added to form the desired compound. The reactants are commercially available or may be synthesized according to J. Organomet. Chem. 92, 1975 163-168.

Alternatively, at approximately -78°C to approximately room temperature (approx. 25°C), alkyl lithium is combined with a primary or secondary amine (NH_2R or NHR_2) in a solvent, such as ether or any other polar solvents, to form lithium amide. The lithium amide may be isolated and one equivalent reacted with 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired compound.

Alternatively, one equivalent of the lithium amide solution may be added to 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired compound.

Exemplary amidinate-substituted halocarbosilane precursors having 2 alkylamino groups with the adjacent NR atoms joined by an unsaturated alkyl chain to form an amidinate ligand include:

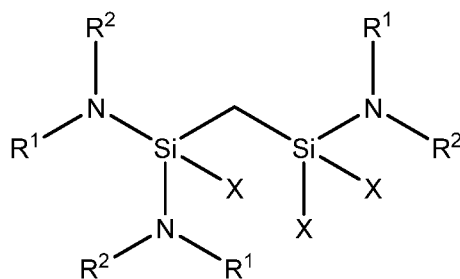


wherein R^1 , R^2 , R^3 may each independently be H, a C1 to C6 alkyl group, or a C3-C10 aryl or heterocycle group. R^1 and R^2 and/or R^1 and R^3 may also be joined to form cyclic chains.

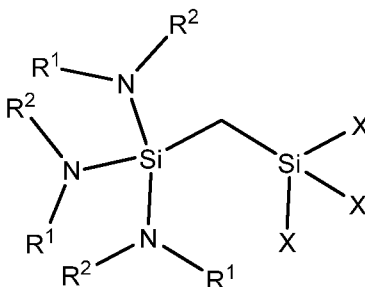
Exemplary amidinate substituted halocarbosilane precursors include (^{Me}amd)SiCl₂-CH₂-SiCl₃, (^{Et}amd)SiCl₂-CH₂-SiCl₃, (^{iPr}amd)SiCl₂-CH₂-SiCl₃, (^{tBu}amd)SiCl₂-CH₂-SiCl₃, (^{Me}amd)SiBr₂-CH₂-SiBr₃, (^{Et}amd)SiBr₂-CH₂-SiBr₃, (^{iPr}amd)SiBr₂-CH₂-SiBr₃, (^{tBu}amd)SiBr₂-CH₂-SiBr₃, (^{Me}amd)SiF₂-CH₂-SiF₃, (^{Et}amd)SiF₂-CH₂-SiF₃, (^{iPr}amd)SiF₂-CH₂-SiF₃, (^{tBu}amd)SiF₂-CH₂-SiF₃, (^{Me}amd)SiI₂-CH₂-SiI₃, (^{Et}amd)SiI₂-CH₂-SiI₃, (^{iPr}amd)SiI₂-CH₂-SiI₃, or (^{tBu}amd)SiI₂-CH₂-SiI₃.

At approximately 0°C to approximately room temperature (approx. 25°), alkyl lithium is combined with carbodiimide in a solvent, such as ether or any other organic solvents, to form lithium amidinate. The reaction is exothermic. The lithium amidinate may be isolated and one equivalent reacted with one equivalent 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired compound. Alternatively, one equivalent of the lithium amidinate solution may be added to one equivalent of the 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired compound.

Exemplary alkylamino-substituted halocarbosilane precursors having 3 alkylamino groups are all asymmetric and include:



or:



wherein R^1 and R^2 is each independently H, a C1-C6 alkyl group, a C1-C6 alkenyl group, or a C3-C10 aryl or heterocycle group. Preferably, R_1 and R_2 is each independently H, Me, Et, nPr, iPr, Bu, or Am. R_1 and R_2 may be joined to form a cyclic chain on one N atom or on adjacent N atoms. For example, NR_1R_2 may form pyridine, pyrrole, pyrrolidine, morpholine, or imidazole ring structures or $R_1-N-Si-N-R_2$ may form an amidinate or diketiminate structure.

Exemplary tri-alkylamino substituted precursors include $(NMe_2)_3Si-CH_2-SiCl_3$, $(NMe_2)_3Si-CH_2-SiBr_3$, $(NMe_2)_3Si-CH_2-SiI_3$, $(NMe_2)_3Si-CH_2-SiF_3$, $(NEt_2)_3Si-CH_2-SiCl_3$, $(NEt_2)_3Si-CH_2-SiBr_3$, $(NEt_2)_3Si-CH_2-SiI_3$, $(NEt_2)_3Si-CH_2-SiF_3$, $(NMeEt)_3Si-CH_2-SiCl_3$, $(NMeEt)_3Si-CH_2-SiBr_3$, $(NMeEt)_3Si-CH_2-SiI_3$, $(NMeEt)_3Si-CH_2-SiF_3$, $(NEtH)_3Si-CH_2-SiCl_3$, $(NEtH)_3Si-CH_2-SiBr_3$, $(NEtH)_3Si-CH_2-SiI_3$, $(NEtH)_3Si-CH_2-SiF_3$, $(NiPrH)_3Si-CH_2-SiCl_3$, $(NiPrH)_3Si-CH_2-SiBr_3$, $(NiPrH)_3Si-CH_2-SiI_3$, or $(NiPrH)_3Si-CH_2-SiF_3$.

Alternatively, the exemplary tri-alkylamino substituted precursors include $(NMe_2)_2ClSi-CH_2-SiCl_2(NMe_2)$, $(NMe_2)_2BrSi-CH_2-SiBr_2(NMe_2)$, $(NMe_2)_2ISi-CH_2-SiI_2(NMe_2)$, $(NMe_2)_2FSi-CH_2-SiF_2(NMe_2)$, $(NEt_2)_2ClSi-CH_2-SiCl_2(NEt_2)$, $(NEt_2)_2BrSi-CH_2-SiBr_2(NEt_2)$, $(NEt_2)_2ISi-CH_2-SiI_2(NEt_2)$, $(NEt_2)_2FSi-CH_2-SiF_2(NEt_2)$, $(NMeEt)_2ClSi-CH_2-SiCl_2(NMeEt)$, $(NMeEt)_2BrSi-CH_2-SiBr_2(NMeEt)$, $(NMeEt)_2ISi-CH_2-SiI_2(NMeEt)$, $(NMeEt)_2FSi-CH_2-SiF_2(NMeEt)$, $(NEtH)_2ClSi-CH_2-SiCl_2(NEtH)$, $(NEtH)_2BrSi-CH_2-SiBr_2(NEtH)$, $(NEtH)_2ISi-CH_2-SiI_2(NEtH)$, $(NEtH)_2FSi-CH_2-$

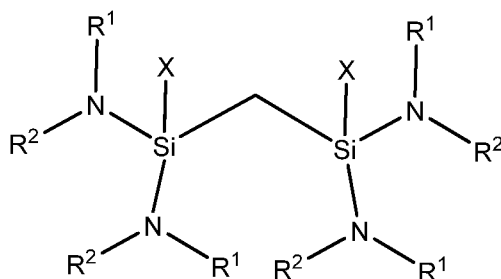
SiF₂(NEtH), (NiPrH)₂ClSi-CH₂-SiCl₂(NiPrH), (NiPrH)₂BrSi-CH₂-SiBr₂(NiPrH), (NiPrH)₂ISi-CH₂-SiI₂(NiPrH), or (NiPrH)₂FSi-CH₂-SiF₂(NiPrH).

At approximately -78 °C to approximately room temperature (approx. 25°C), 6 equivalents of amine are mixed with or dissolved in a nonpolar solvent.

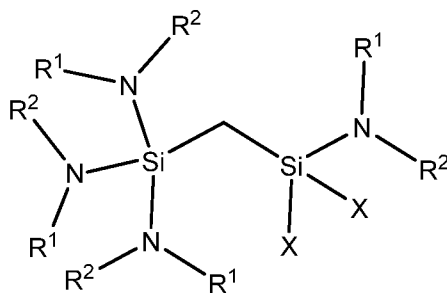
1,1,1,3,3,3-hexachloro-1,3-disilapropane is slowly added to form the desired compound. The reactants are commercially available or may be synthesized according to J. Organomet. Chem. 92, 1975 163-168.

Alternatively, at approximately -78°C to approximately room temperature (approx. 25°C), alkyl lithium is combined with a primary or secondary amine (NH₂R or NHR₂) in a solvent, such as ether or any other polar solvents, to form lithium amide. The lithium amide may be isolated and 3 equivalents reacted with one equivalent 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired compound. Alternatively, 3 equivalents of the lithium amide solution may be added to one equivalent of 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired compound.

Exemplary alkylamino-substituted halocarbosilane precursors having 4 alkylamino groups include symmetric molecules having the formula:



or asymmetric molecules having the formula:



wherein R¹ and R² is each independently H, a C1-C6 alkyl group, a C1-C6 alkenyl group, or a C3-C10 aryl or heterocycle group. Preferably, R₁ and R₂ is each independently H, Me, Et, nPr, iPr, Bu, or Am. R₁ and R₂ may be joined to form a cyclic chain on one N atom or on adjacent N atoms. For example, NR₁R₂ may

form pyridine, pyrrole, pyrrolidine, morpholine, or imidazole ring structures or $R_1-N-Si-N-R_2$ may form an amidinate or diketiminate structure.

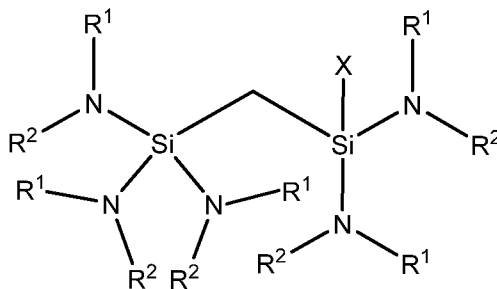
Exemplary assymetrical tetra-alkylamino substituted precursors include
 5 $(NMe_2)_3Si-CH_2-SiCl_2(NMe_2)$, $(NMe_2)_3Si-CH_2-SiBr_2(NMe_2)$, $(NMe_2)_3Si-CH_2-SiI_2(NMe_2)$, $(NMe_2)_3Si-CH_2-SiF_2(NMe_2)$, $(NEt_2)_3Si-CH_2-SiCl_2(NEt_2)$, $(NEt_2)_3Si-CH_2-SiBr_2(NEt_2)$, $(NEt_2)_3Si-CH_2-SiI_2(NEt_2)$, $(NEt_2)_3Si-CH_2-SiF_2(NEt_2)$, $(NMeEt)_3Si-CH_2-SiCl_2(NMeEt)$, $(NMeEt)_3Si-CH_2-SiBr_2(NMeEt)$, $(NMeEt)_3Si-CH_2-SiI_2(NMeEt)$,
 10 $(NMeEt)_3Si-CH_2-SiF_2(NMeEt)$, $(NEtH)_3Si-CH_2-SiCl_2(NEtH)$, $(NEtH)_3Si-CH_2-SiBr_2(NEtH)$, $(NEtH)_3Si-CH_2-SiI_2(NEtH)$, $(NEtH)_3Si-CH_2-SiF_2(NEtH)$, $(NiPrH)_3Si-CH_2-SiCl_2(NiPrH)$, $(NiPrH)_3Si-CH_2-SiBr_2(NiPrH)$, $(NiPrH)_3Si-CH_2-SiI_2(NiPrH)$, or $(NiPrH)_3Si-CH_2-SiF_2(NiPrH)$.

Exemplary symetrical tetra-alkylamino substituted precursors include
 15 $(NMe_2)_2ClSi-CH_2-SiCl(NMe_2)_2$, $(NMe_2)_2BrSi-CH_2-SiBr(NMe_2)_2$, $(NMe_2)_2ISi-CH_2-SiI(NMe_2)_2$, $(NMe_2)_2FSi-CH_2-SiF(NMe_2)_2$, $(NEt_2)_2ClSi-CH_2-SiCl(NEt_2)_2$, $(NEt_2)_2BrSi-CH_2-SiBr(NEt_2)_2$, $(NEt_2)_2ISi-CH_2-SiI(NEt_2)_2$, $(NEt_2)_2FSi-CH_2-SiF(NEt_2)_2$, $(NMeEt)_2ClSi-CH_2-SiCl(NMeEt)_2$, $(NMeEt)_2BrSi-CH_2-SiBr(NMeEt)_2$, $(NMeEt)_2ISi-CH_2-SiI(NMeEt)_2$, $(NMeEt)_2FSi-CH_2-SiF(NMeEt)_2$, $(NEtH)_2ClSi-CH_2-SiCl(NEtH)_2$, $(NEtH)_2BrSi-CH_2-SiBr(NEtH)_2$, $(NEtH)_2ISi-CH_2-SiI(NEtH)_2$, $(NEtH)_2FSi-CH_2-SiF(NEtH)_2$, $(NiPrH)_2ClSi-CH_2-SiCl(NiPrH)_2$, $(NiPrH)_2BrSi-CH_2-SiBr(NiPrH)_2$,
 20 $(NiPrH)_2ISi-CH_2-SiI(NiPrH)_2$, or $(NiPrH)_2FSi-CH_2-SiF(NiPrH)_2$.

At approximately -78 °C to approximately room temperature (approx. 25°C), 8 equivalents of amine are mixed with or dissolved in a nonpolar solvent. 1,1,1,3,3,3-hexachloro-1,3-disilapropane is slowly added to form the desired compound. The reactants are commercially available or may be synthesized
 25 according to J. Organomet. Chem. 92, 1975 163-168.

Alternatively, at approximately -78°C to approximately room temperature (approx. 25°C), alkyl lithium is combined with a primary or secondary amine (NH_2R or NHR_2) in a solvent, such as ether or any other polar solvents, to form lithium amide. The lithium amide may be isolated and 4 equivalents reacted with
 30 one equivalent 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired compound. Alternatively, 4 equivalents of the lithium amide solution may be added to one equivalents of 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired compound.

Exemplary alkylamino-substituted halocarbo-silane precursors having 5
alkylamino groups are all asymmetric and include:



wherein R^1 and R^2 is each independently H, a C1-C6 alkyl group, a C1-C6 alkenyl
group, or a C3-C10 aryl or heterocycle group. Preferably, R_1 and R_2 is each
independently H, Me, Et, nPr, iPr, Bu, or Am. R_1 and R_2 may be joined to form a
cyclic chain on one N atom or on adjacent N atoms. For example, NR_1R_2 may
form pyridine, pyrrole, pyrrolidine, morpholine, or imidazole ring structures or R_1 -N-
Si-N- R_2 may form an amidinate or diketiminate structure.

Exemplary penta-alkylamino substituted precursors include $(NMe_2)_3Si-CH_2-$
 $SiCl(NMe_2)_2$, $(NMe_2)_3Si-CH_2-SiBr(NMe_2)_2$, $(NMe_2)_3Si-CH_2-SiI(NMe_2)_2$, $(NMe_2)_3Si-$
 $CH_2-SiF(NMe_2)_2$, $(NEt_2)_3Si-CH_2-SiCl(NEt_2)_2$, $(NEt_2)_3Si-CH_2-SiBr(NEt_2)_2$, $(NEt_2)_3Si-$
 $CH_2-SiI(NEt_2)_2$, $(NEt_2)_3Si-CH_2-SiF(NEt_2)_2$, $(NMeEt)_3Si-CH_2-SiCl(NMeEt)_2$,
 $(NMeEt)_3Si-CH_2-SiBr(NMeEt)_2$, $(NMeEt)_3Si-CH_2-SiI(NMeEt)_2$, $(NMeEt)_3Si-CH_2-$
 $SiF(NMeEt)_2$, $(NEtH)_3Si-CH_2-SiCl(NEtH)_2$, $(NEtH)_3Si-CH_2-SiBr(NEtH)_2$, $(NEtH)_3Si-$
 $CH_2-SiI(NEtH)_2$, $(NEtH)_3Si-CH_2-SiF(NEtH)_2$, $(NiPrH)_3Si-CH_2-SiCl(NiPrH)_2$,
 $(NiPrH)_3Si-CH_2-SiBr(NiPrH)_2$, $(NiPrH)_3Si-CH_2-SiI(NiPrH)_2$, or $(NiPrH)_3Si-CH_2-$
 $SiF(NiPrH)_2$.

At approximately -78 °C to approximately room temperature (approx. 25°C),
10 equivalents of amine are mixed with or dissolved in a nonpolar solvent. One
equivalent of 1,1,1,3,3,3-hexachloro-1,3-disilapropane is slowly added to form the
desired compound. The reactants are commercially available or may be
synthesized according to J. Organomet. Chem. 92, 1975 163-168.

Alternatively, at approximately -78°C to approximately room temperature
(approx. 25°C), alkyl lithium is combined with a primary or secondary amine
(NH_2R or NHR_2) in a solvent, such as ether or any other polar solvents, to form
lithium amide. The lithium amide may be isolated and 5 equivalents reacted with
one equivalent of 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired
compound. Alternatively, 5 equivalents of the lithium amide solution may be

added to one equivalent of the 1,1,1,3,3,3-hexachloro-1,3-disilapropane to form the desired compound.

For all of the synthesis processes, one of ordinary skill in the art will recognize that Si-C bonds are not affected by the reactants used for amination of the silicon, and that the addition of alkyl groups on the Si atoms in a molecule having a disilapropane backbone may be achieved by selecting the starting disilapropane halide having the selected alkyl ligands on the silicon. For instance, the synthesis of $\text{Me}(\text{NMe}_2)\text{ClSi-CH}_2\text{-SiCl}(\text{NMe}_2)\text{Me}$ would proceed under similar conditions as the synthesis of $(\text{NMe}_2)_2\text{ClSi-CH}_2\text{-SiCl}(\text{NMe}_2)_2$, using 1,1,3,3-tetrachloro-1,3-dimethyldisilapropane in place of 1,1,1,3,3,3-hexachlorodisilapropane and half the amount of amine.

To ensure process reliability, the silicon-containing film forming compositions may be purified by continuous or fractional batch distillation or sublimation prior to use to a purity ranging from approximately 93% w/w to approximately 100% w/w, preferably ranging from approximately 99% w/w to approximately 100% w/w. The silicon-containing film forming compositions may contain any of the following impurities: undesired congeneric species; solvents; chlorinated metal compounds; or other reaction products. In one alternative, the total quantity of these impurities is below 0.1% w/w.

The concentration of each of hexane, substituted hexane, pentane, substituted pentane, dimethyl ether, or anisole in the purified silicon-containing film forming composition may range from approximately 0% w/w to approximately 5% w/w, preferably from approximately 0% w/w to approximately 0.1% w/w. Solvents may be used in the composition's synthesis. Separation of the solvents from the precursor may be difficult if both have similar boiling points. Cooling the mixture may produce solid precursor in liquid solvent, which may be separated by filtration. Vacuum distillation may also be used, provided the precursor product is not heated above approximately its decomposition point.

In one alternative, the disclosed Si-containing film forming compositions contain less than 5% v/v, preferably less than 1% v/v, more preferably less than 0.1% v/v, and even more preferably less than 0.01% v/v of any of its undesired congeneric species, reactants, or other reaction products. This alternative may provide better process repeatability. This alternative may be produced by distillation of the halocarbosilane precursor.

In another alternative, the disclosed Si-containing film forming compositions may contain between 5% v/v and 50% v/v of one or more of its congeneric species, reactants, or other reaction products, particularly when the mixture provides improved process parameters or isolation of the target compound is too difficult or expensive. For example, a mixture of reaction products may produce a stable, liquid mixture suitable for spin-on or vapor deposition.

The concentration of trace metals and metalloids in the purified silicon-containing molecules may each range from approximately 0 ppb to approximately 100 ppb, and more preferably from approximately 0 ppb to approximately 10 ppb.

The disclosed Si-containing film forming compositions may be delivered to a semiconductor processing tool by the disclosed Si-containing film forming composition delivery devices. **FIGS. 1 and 2** show two embodiments of the disclosed delivery devices **1**.

FIG. 1 is a side view of one embodiment of the Si-containing film forming composition delivery device **1**. In **FIG. 1**, the disclosed Si-containing film forming composition **10** are contained within a container **20** having two conduits, an inlet conduit **30** and an outlet conduit **40**. One of ordinary skill in the precursor art will recognize that the container **20**, inlet conduit **30**, and outlet conduit **40** are manufactured to prevent the escape of the gaseous form of the Si-containing film forming composition **10**, even at elevated temperature and pressure.

Suitable valves include spring-loaded or tied diaphragm valves. The valve may further comprise a restrictive flow orifice (RFO). The delivery device **1** should be connected to a gas manifold and in an enclosure. The gas manifold should permit the safe evacuation and purging of the piping that may be exposed to air when the delivery device **1** is replaced so that any residual amount of the pyrophoric material does not react. The enclosure should be equipped with sensors and fire control capability to control the fire in the case of a pyrophoric material release, such as SiH_4 . The gas manifold should also be equipped with isolation valves, vacuum generators, and permit the introduction of a purge gas at a minimum.

The delivery device **1** must be leak tight and be equipped with valves that do not permit escape of even minute amounts of the material. The delivery device **1** fluidly connects to other components of the semiconductor processing tool, such as the gas cabinet disclosed above, via valves **35** and **45**. Preferably, the

container **20**, inlet conduit **30**, valve **35**, outlet conduit **40**, and valve **45** are made of 316L EP or 304 stainless steel. However, one of ordinary skill in the art will recognize that other non-reactive materials may also be used in the teachings herein and that any corrosive Si-containing film forming composition **10** may
5 require the use of more corrosion-resistant materials, such as Hastelloy or Inconel.

In **FIG. 1**, the end **31** of inlet conduit **30** is located above the surface of the Si-containing film forming composition **10**, whereas the end **41** of the outlet conduit **40** is located below the surface of the Si-containing film forming composition **10**. In this embodiment, the Si-containing film forming composition
10 **10** is preferably in liquid form. An inert gas, including but not limited to nitrogen, argon, helium, and mixtures thereof, may be introduced into the inlet conduit **30**. The inert gas pressurizes the container **20** so that the liquid Si-containing film forming composition **10** is forced through the outlet conduit **40** and to components in the semiconductor processing tool (not shown). The semiconductor processing
15 tool may include a vaporizer which transforms the liquid Si-containing film forming composition **10** into a vapor, with or without the use of a carrier gas such as helium, argon, nitrogen or mixtures thereof, in order to deliver the vapor to a chamber where a wafer to be repaired is located and treatment occurs in the vapor phase. Alternatively, the liquid Si-containing film forming composition **10**
20 may be delivered directly to the wafer surface as a jet or aerosol.

FIG. 2 is a side view of a second embodiment of the Si-containing film forming composition delivery device **1**. In **FIG. 2**, the end **31** of inlet conduit **30** is located below the surface of the Si-containing film forming composition **10**,
25 whereas the end **41** of the outlet conduit **40** is located above the surface of the Si-containing film forming composition **10**. **FIG. 2** also includes an optional heating element **25**, which may increase the temperature of the Si-containing film forming composition **10**. The Si-containing film forming composition **10** may be in solid or liquid form. An inert gas, including but not limited to nitrogen, argon, helium, and mixtures thereof, is introduced into the inlet conduit **30**. The inert gas flows
30 through the Si-containing film forming composition **10** and carries a mixture of the inert gas and vaporized Si-containing film forming composition **10** to the outlet conduit **40** and to the components in the semiconductor processing tool.

Both **FIGS. 1 and 2** include valves **35** and **45**. One of ordinary skill in the art will recognize that valves **35** and **45** may be placed in an open or closed

position to allow flow through conduits **30** and **40**, respectively. Either delivery device **1** in **FIGS. 1 or 2**, or a simpler delivery device having a single conduit terminating above the surface of any solid or liquid present, may be used if the Si-containing film forming composition **10** is in vapor form or if sufficient vapor pressure is present above the solid/liquid phase. In this case, the Si-containing film forming composition **10** is delivered in vapor form through the conduit **30** or **40** simply by opening the valve **35** in **FIG. 1** or **45** in **FIG. 2**, respectively. The delivery device **1** may be maintained at a suitable temperature to provide sufficient vapor pressure for the Si-containing film forming composition **10** to be delivered in vapor form, for example by the use of an optional heating element **25**.

While **FIGS. 1 and 2** disclose two embodiments of the Si-containing film forming composition delivery device **1**, one of ordinary skill in the art will recognize that the inlet conduit **30** and outlet conduit **40** may both be located above or below the surface of the Si-containing film forming composition **10** without departing from the disclosure herein. Furthermore, inlet conduit **30** may be a filling port. Finally, one of ordinary skill in the art will recognize that the disclosed Si-containing film forming compositions **10** may be delivered to semiconductor processing tools using other delivery devices, such as the ampoules disclosed in WO 2006/059187 to Jurcik *et al.*, without departing from the teachings herein.

The disclosed alkylamino-substituted halocarbosilane precursors in the Si-containing film forming compositions may prove useful as monomers for the synthesis of carbosilane based oligomers or polymers. The carbosilane based oligomers or polymers may be formed by partial hydrolysis or ammonolysis of the disclosed Si-containing film forming compositions. The carbosilane based oligomers or polymers may further comprise a solvent, pH regulators, surfactants, or combinations thereof. The carbosilane based oligomers or polymers may be used to form spin-on dielectric film formulations. The spin-on dielectric film formulations may be used to make various silicon containing films, such as insulating films, patternable films, hard masks, lithography transfer layers, or for anti-reflective films. For example, the carbosilane based oligomers or polymers may be applied to a substrate to form a film. Typically, the substrate is rotated to evenly distribute the carbosilane based oligomers or polymers across the substrate. One of ordinary skill in the art will recognize that the viscosity of the carbosilane based oligomers or polymers will contribute as to whether rotation of

the substrate is necessary. The resulting film may be heated under an inert gas, such as Argon, Helium, or nitrogen or under a reactive gas like H₂, O₂, O₃, steam, NH₃, or a mixture thereof, in order to achieve a modification of the average film composition. The heating of the film may happen in one or preferably two
5 successive steps at different temperatures. Other means of increasing the connectivity may be used in addition to or in replacement of a heating step, such as application of electron beams or ultraviolet radiation to the resulting film. The reactive groups of the disclosed alkylamino-substituted halocarbosilane precursors (*i.e.*, no direct Si-C bonds except the bonds to the central carbon
10 atoms) may increase the connectivity of the oligomer or polymer obtained by hydrolysis and intermolecular condensation to form siloxane bridges, or by ammonolysis and intermolecular condensation to form silazane bridges.

The Si-containing film forming compositions may also be used for vapor deposition methods. The disclosed methods provide for the use of the Si-
15 containing film forming compositions 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: introducing the vapor of the disclosed Si-containing film forming compositions into a reactor having at least one substrate disposed therein: and using a vapor
20 deposition process to deposit at least part of the disclosed alkylamino-substituted halocarbosilane precursor onto the substrate to form a Si-containing layer.

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, Zr, Ti, Nb, B, P,
25 Mg, Al, Sr, Y, Ba, As, Sb, Bi, lanthanides (such as Er), or combinations thereof.

The disclosed methods of forming silicon-containing layers on substrates may be useful in the manufacture of semiconductor, photovoltaic, LCD-TFT, or flat panel type devices. The disclosed Si-containing film forming compositions may deposit Si-containing films using any vapor deposition methods known in the art.
30 Examples of suitable vapor deposition methods include chemical vapor deposition (CVD) or atomic layer deposition (ALD). Exemplary CVD methods include thermal CVD, plasma enhanced CVD (PECVD), pulsed CVD (PCVD), low pressure CVD (LPCVD), sub-atmospheric CVD (SACVD) or atmospheric pressure CVD (APCVD), hot-wire CVD (HWCVD, also known as cat-CVD, in which a hot wire serves as an

energy source for the deposition process), radicals incorporated CVD, and combinations thereof. Exemplary ALD methods include thermal ALD, plasma enhanced ALD (PEALD), spatial isolation ALD, hot-wire ALD (HWALD), radicals incorporated ALD, and combinations thereof. Super critical fluid deposition may also be used. The disclosed methods may also be used in the flowable PECVD deposition processes described in U.S. Pat. App. Pub. No. 2014/0051264 to Applied Materials, Inc., the contents of which is incorporated herein in its entirety. The deposition method is preferably ALD, spatial ALD, or PE-ALD.

The vapor of the Si-containing film forming compositions 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 alkylamino-substituted halocarbosilane precursor onto the substrate. In other words, after introduction of the vaporized Si-containing film forming compositions into the chamber, conditions within the chamber are such that at least part of the alkylamino-substituted halocarbosilane 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 optimal deposition temperature range for each alkylamino-substituted halocarbosilane precursor may be determined experimentally to achieve the desired result.

The temperature of the reactor may be controlled by controlling the temperature of the substrate holder and/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. A substrate is generally defined as the material on which a process is conducted. The substrates may be any suitable substrate used in semiconductor, photovoltaic, flat panel, or LCD-TFT device manufacturing. Examples of suitable substrates include wafers, such as silicon, silica, glass, plastic, Ge, or GaAs wafers. The wafer may have one or more layers of differing materials deposited on it from a previous manufacturing step. For example, the wafers may include silicon layers (crystalline, amorphous, porous, etc.), silicon oxide layers, silicon nitride layers, silicon oxy nitride layers, carbon doped silicon oxide (SiCOH) layers, or combinations thereof. Additionally, the wafers may include copper layers, tungsten layers or metal layers (e.g. platinum, palladium, nickel, rhodium, or gold). The wafers may include barrier layers, such as manganese, manganese oxide, tantalum, tantalum nitride, etc. Plastic layers, such as poly(3,4-ethylenedioxythiophene)poly (styrenesulfonate) [PEDOT:PSS] may also be used. The layers may be planar or patterned. 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 (e.g., $x \leq 4$). In some embodiments, the substrate may include layers of 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. The disclosed processes may deposit the silicon-containing layer directly on the wafer or directly on one or more than one (when patterned layers form the substrate) of the layers on top of the wafer. Furthermore, one of ordinary skill in the art will recognize that the terms "film" or "layer" used herein refer to a thickness of some material laid on or spread over a surface and that the surface may be a trench or a line. Throughout the specification and claims, the wafer and any associated layers thereon are referred to as substrates. 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, Ru, and Si type substrates, such as polysilicon or crystalline silicon substrates.

The disclosed Si-containing film forming compositions 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 alkylamino-substituted halocarbosilane 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 Si-containing film forming compositions are introduced into a reactor in vapor form by conventional means, such as tubing and/or flow meters. The composition in vapor form may be produced by vaporizing the neat or blended composition 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 composition 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 composition may be vaporized by passing a carrier gas into a container containing the composition or by bubbling the carrier gas into the composition. The carrier gas may include, but is not limited to, Ar, He, or N₂, and mixtures thereof. Bubbling with a carrier gas may also remove any dissolved oxygen present in the neat or blended composition. The carrier gas and composition are then introduced into the reactor as a vapor.

If necessary, the container may be heated to a temperature that permits the Si-containing film forming composition 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 Si-containing film forming compositions vaporized.

In addition to the disclosed Si-containing film forming compositions, a reaction gas may also be introduced into the reactor. The reaction gas may be an oxidizing agent such as one of O₂; O₃; H₂O; H₂O₂; oxygen containing radicals such as O[•] or OH[•]; NO; NO₂; carboxylic acids such as formic acid, acetic acid, propionic acid; radical species of NO, NO₂, or the carboxylic acids; para-formaldehyde; and mixtures thereof. Preferably, the oxidizing agent is selected from the group consisting of O₂, O₃, H₂O, H₂O₂, NO, N₂O, NO₂, a diol (such as ethylene glycol or hydrated hexafluoroacetone), oxygen containing radicals thereof such as O[•] or OH[•], 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, a reaction gas may be selected, such as one of H₂, H₂CO, NH₃, (SiH₃)₃N, hydridosilanes (such as SiH₄, Si₂H₆, Si₃H₈, Si₄H₁₀, Si₅H₁₀, Si₆H₁₂), chlorosilanes and chloropolysilanes (such as SiHCl₃, SiH₂Cl₂, SiH₃Cl, Si₂Cl₆, Si₂HCl₅, Si₃Cl₈), alkylsilanes (such as (CH₃)₂SiH₂, (C₂H₅)₂SiH₂, (CH₃)SiH₃, (C₂H₅)SiH₃), hydrazines (such as N₂H₄, MeHNNH₂, MeHNNHMe), organic amines (such as N(CH₃)H₂, N(C₂H₅)H₂, N(CH₃)₂H, N(C₂H₅)₂H, N(CH₃)₃, N(C₂H₅)₃, (SiMe₃)₂NH), diamines (such as ethylene diamine, dimethylethylene diamine, tetramethylethylene diamine), aminoalcohols (such as ethanolamine [HO-CH₂-CH₂-NH₂], bis ethanolamine [HN(C₂H₅OH)₂] or tris ethanolamine[N(C₂H₅OH)₃]), pyrazoline, pyridine, B-containing molecules (such as B₂H₆, 9-borabicyclo[3,3,1]nonane, trimethylboron, triethylboron, borazine, substituted borazine, dialkylaminoboranes), alkyl metals (such as trimethylaluminum, triethylaluminum, dimethylzinc, diethylzinc), radical species thereof, and mixtures thereof.

The reaction gas may be treated by a plasma, in order to decompose the reaction gas into its radical form. N₂ 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.

5 When the desired silicon-containing film also contains another element, such as, for example and without limitation, Ta, Hf, Zr, Ti, Nb, P, B, Mg, Al, Sr, Y, Ba, As, Sb, Bi, lanthanides (such as Er), or combinations thereof, the co-reactants may include an element-containing precursor which is selected from, but not limited to, element-containing alkyls, such as $\text{Ln}(\text{RCp})_3$, element-containing
10 amines, such as $\text{Nb}(\text{Cp})(\text{NtBu})(\text{NMe}_2)_3$, and any combination thereof.

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

 The Si-containing film forming compositions 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
20 example, the Si-containing film forming composition may be introduced in one pulse and two additional element 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 Si-containing film forming composition. The co-reactant may be passed through a
25 plasma system localized or remotely from the reaction chamber, and decomposed to radicals. Alternatively, the Si-containing film forming composition may be introduced to the reaction chamber continuously while other element 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
30 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 Si-containing film forming composition 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 chemical vapor deposition type process, the vapor phase of a Si-containing film forming composition and a reaction gas, such as H₂, are simultaneously introduced into the reaction chamber, where they react to deposit the desired SiC film on the substrate.

In one non-limiting exemplary atomic layer deposition type process, the vapor phase of a Si-containing film forming composition is introduced into the reaction chamber, where at least part of the alkylamino-substituted halocarbosilane chemi- or physisorbs on the substrate. Excess Si-containing film forming composition 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 chemi- or physisorbed alkylamino-substituted halocarbosilane 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/metalloid oxide film (i.e., SiMO_x, wherein x may be 0-4 and M is Ta, Hf, Zr, Ti, Nb, P, B, Mg, Al, Sr, Y, Ba, As, Sb, Bi, lanthanides (such as Er), or combinations thereof), the two-step process above may be followed by introduction of a second vapor of an element-containing precursor into the reaction chamber. The element-containing precursor will be selected based on the nature of the silicon element oxide film being deposited (i.e., the element may be Ta, Hf, Zr, Ti, Nb, P, B, Mg, Al, Sr, Y, Ba, As, Sb, Bi, or a lanthanide). After introduction into the reaction chamber, the element-containing precursor chemi- or physisorbs on the silicon oxide substrate. Any excess element-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 chemi- or physisorbed element-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 Si-containing film forming composition, element-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 Si-containing film forming composition and one pulses of the element-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 dense SiCN films may be deposited via an ALD or modified ALD process using the disclosed Si-containing film forming compositions and a halosilane compound having the formula $\text{Si}_a\text{H}_{2a+2-b}\text{X}_b$, 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 $-\text{Si}_c\text{H}_{2c-d}\text{X}_d-$, 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 N-containing co-reactant, such as NH_3 . Vapors of the disclosed Si-containing film forming compositions 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. As described in PCT Pub No WO2011/123792, the order of the introduction of the precursors may be varied and the deposition may be performed with or without the NH_3 co-reactant in order to tune the amounts of carbon and nitrogen in the SiCN film.

In yet another alternative, a silicon-containing film may be deposited by the flowable PECVD method disclosed in U.S. Pat. App. Pub. No. 2014/0051264 using

the disclosed Si-containing film forming compositions and a radical nitrogen- or oxygen-containing co-reactant. The radical nitrogen- or oxygen-containing co-reactant, such as NH_3 or H_2O respectively, is generated in a remote plasma system. The radical co-reactant and the vapor phase of the disclosed compositions are introduced into the reaction chamber where they react and deposit the initially flowable film on the substrate. Applicants believe that the carbon atom between the two Si atoms and the nitrogen atoms of the alkylamino groups in the disclosed alkylamino-substituted halocarbosilane precursors help to further improve the flowability of the deposited film, resulting in films having less voids.

In yet another alternative, a thin film containing silicon, oxygen and carbon may be deposited on a substrate via ALD by performing a cycle a predetermined number of times, the cycle including supplying the disclosed Si-containing film forming composition and a first catalytic gas to the substrate and supplying an oxidizing gas and a second catalytic gas to the substrate as disclosed in US Pat App Pub No 2014/287596 to Hitachi Kokusai Electric, Inc. and L'Air Liquide, Société Anonyme pour l'Etude et l'Exploitation des Procédés Georges Claudes, the content of which is incorporated herein in its entirety. For example, the disclosed Si-containing film forming composition may replace BTCSM in paragraphs 0095-0151: supply disclosed Si-containing film forming composition and pyridine gas; remove residual gas; supply H_2O and pyridine gas; remove residual gas; repeat a predetermined number of times to obtain the desired thickness of the SiOC layer. Applicants believe that the disclosed Si-containing film forming compositions may help to keep the Si-C-Si backbone in the resulting Si-containing film, which may be shown by a Fourier Transfer Infrared spectrum of the resulting film. Additionally, the H_2O oxidizing gas helps to remove any potential halide impurities from the disclosed Si-containing film forming composition from the film.

In yet another alternative, a thin film containing silicon, oxygen and carbon may be deposited on a substrate by performing two cycles a predetermined number of times, the first cycle including supplying the disclosed Si-containing film forming composition and a first catalytic gas to the substrate and supplying an oxidizing gas and a second catalytic gas to the substrate as discussed above, followed by a second cycle including supplying a non-halogenated silane and a first catalytic gas to the substrate and supplying an oxidizing gas and a second catalytic gas to the substrate. The non-halogenated silane may include SiH_4 , Si_2H_6 , $\text{H}_x\text{Si}(\text{NR}_2)_{4-x}$, with

x being 1-3 and R being an alkyl group, such as $\text{H}_2\text{Si}(\text{NEt}_2)_2$, or $\text{R}_3\text{Si-CH}_2\text{-SiR}_3$, wherein R is independently H or an alkylamino group, but is not a halide. For example, the process may comprise: supply of disclosed Si-containing film forming composition and pyridine gas; remove residual gas; supply H_2O and pyridine gas; remove residual gas; supply non-halogenated silane, such as $(\text{Me}_2\text{N})_3\text{Si-CH}_2\text{-Si}(\text{NMe}_2)_3$, and pyridine gas; remove residual gas; supply H_2O and pyridine gas; remove residual gas; repeat a predetermined number of times to obtain the desired thickness of the SiOC layer. The second cycle is halide free and may result in production of less HCl byproduct, which may better maintain the Si-C-Si backbone in the resulting Si-containing film.

The silicon-containing films resulting from the processes discussed above may include Si, SiO_2 , SiN, SiON, SiC, SiOC, SiCN, SiCOH, or MSiO_x , wherein 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 judicious selection of the appropriate halocarbosilane 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.

Examples

The following non-limiting examples are provided to further illustrate embodiments of the invention. However, the examples are not intended to be all inclusive and are not intended to limit the scope of the inventions described herein.

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Example 1: Synthesis of $(\text{Me}_2\text{N})_2\text{ClSi-CH}_2\text{-SiCl(NMe}_2)_2$



A 200mL Schlenk flask equipped with a reflux condenser is charged with 1,1,1,3,3,3-hexakis(dimethylamino)-1,3-disilapropane (39.1g, 0.123 mol) followed by slow addition of bis(trichlorosilyl)methane (17.4g, 0.062 mol) with stirring to yield a colorless liquid. Initially some fuming was observed. After completing the addition, the reaction temperature is increased to 60°C for 7 hours. At the end of the workday, heating is removed and the reaction stirred at room temperature overnight (14 hrs). The following day, the reaction is heated again at 60°C for 7 hours to yield a colorless liquid. GCMS analysis indicates the reaction is complete with ca. 84% of the desired product.

The resulting mixture is distilled under reduced pressure using a 300mm Vigreux column (50-58°C @ 20mTorr) to afford a colorless liquid. No clear end point is observed. Analysis by GCMS shows improved purity to be 93% (44.7g, 81.3% isolated yield).

The NMR of the final product collected on a 400 MHz instrument is provided in **FIG 3**. $(\text{Me}_2\text{N})_2\text{ClSiCH}_2\text{SiCl(NMe}_2)_2$ in C_6D_6 : ^1H NMR: δ 0.61 (s, 2H, $-\text{CH}_2-$), 2.43 (s, 24H, $-(\text{CH}_3)_2$).

Thermogravimetric analysis (TGA) in open cup conditions produces less than 1% w/w residue. See **FIG 4**.

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Example 2: One Step Synthesis of $(\text{Me}_2\text{N})\text{Cl}_2\text{Si-CH}_2\text{-SiCl}_2(\text{NMe}_2)$



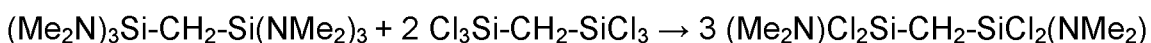
In a 1 L four-necked, round-bottomed flask with two reflux condensers and mechanical stirrer, hexane (500 mL) was cooled to -78 °C in a dry ice / IPA bath. A small Me_2NH cylinder was placed on a balance and set to zero. The cylinder was connected to the Schlenk line (for purging) and one reflux condenser of the reaction flask via bubbler and back-flow safety. The Schlenk line exhaust was connected to a washing bottle containing 30% aq. H_2SO_4 solution and a washing

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bottle containing water before releasing into the fume hood. The reflux condensers were cooled to -20 °C. The cylinder valve was slowly opened and ca. 22 g (0.48 mol, 1.2 eq) of Me₂NH was condensed into hexane. After closing the valve, the line was purged with nitrogen, the cylinder removed, and the connection on the reflux condenser closed. An addition funnel was charged with 250 mL (0.40 mol, 1.0 eq) of nBuLi solution (1.6 M in hexane) in a glovebox. The addition funnel was connected to the reaction flask under a stream of nitrogen. nBuLi was slowly added over 1 h. The addition funnel was rinsed with ca. 40 mL hexane. The mixture was let warm to room temperature during 1.5 h and then stirred at 40 °C for 1 h before using the suspension in the next step.

The freshly prepared Me₂NLi suspension (0.40 mol, 2.0 eq) was cooled to -78 °C in a dry ice / IPA bath. An addition funnel was charged with a solution of Cl₃Si-CH₂-SiCl₃ (56.58 g, 0.20 mol, 1.0 eq) in hexane (50 mL) in a glovebox. The addition funnel was attached to the reaction flask under a stream of nitrogen. The Cl₃Si-CH₂-SiCl₃ solution was slowly added to the suspension over 30 min. The reaction mixture was let warm to room temperature and stirred over night. The product solution was separated from LiCl by transferring into a 1 L round-bottomed flask with magnetic stirring bar via cannula filtration or by filtration over a glass wool filter under nitrogen. The volatiles were removed under reduced pressure. The crude product was distilled using a packed column (T_{bath} = 130 °C, T_{vap} = 42 °C, p = 50 – 200 mTorr). The residue contained mainly (Me₂N)₂ClSi-CH₂-SiCl₂(NMe₂), (Me₂N)₂ClSi-CH₂-SiCl(NMe₂)₂, and (Me₂N)₃Si-CH₂-SiCl(NMe₂)₂. The distilled fractions contained 42.14 g (0.14 mol, 70%) product.

Example 3: Two Step Synthesis of (Me₂N)Cl₂Si-CH₂-SiCl₂(NMe₂)



Preparation of (Me₂N)₃Si-CH₂-Si(NMe₂)₃: The freshly prepared Me₂NLi suspension (0.40 mol, 6.6 eq) was cooled to -78 °C in a dry ice / IPA bath. An addition funnel was charged with a solution of Cl₃Si-CH₂-SiCl₃ (16.98 g, 0.06 mol, 1.0 eq) in hexane (50 mL) in a glovebox. The addition funnel was attached to the reaction flask under a stream of nitrogen. The Cl₃Si-CH₂-SiCl₃ solution was slowly added to the suspension over 30 min. The reaction mixture was let warm to room temperature and stirred over night. The product solution was separated from LiCl

by transferring into a 1 L round-bottomed flask with magnetic stirring bar via cannula filtration or by filtration over a glass wool filter under nitrogen. The volatiles were removed under reduced pressure. The crude product was distilled without column ($T_{\text{bath}} = 130\text{ }^{\circ}\text{C}$, $T_{\text{vap}} = 98 - 107\text{ }^{\circ}\text{C}$, $p = 260\text{ mTorr}$). The distilled fraction contained 19.14 g (0.057 mol, 95%) product.

Preparation of $(\text{Me}_2\text{N})\text{Cl}_2\text{Si-CH}_2\text{-SiCl}_2(\text{NMe}_2)$: $(\text{Me}_2\text{N})_3\text{Si-CH}_2\text{-Si}(\text{NMe}_2)_3$ (54.95 g, 0.164 mol, 1.0 eq) and $\text{Cl}_3\text{Si-CH}_2\text{-SiCl}_3$ (92.91 g, 0.328 mol, 2.0 eq) were mixed in a Schott bottle at room temperature in a glovebox. No exothermicity was observed. The mixture was carefully agitated for a few minutes and then stored in the glove box at room temperature to yield 147.68 g (0.492 mol, 100%) of product. $^1\text{H-NMR}$ analysis showed 90% $(\text{Me}_2\text{N})\text{Cl}_2\text{Si-CH}_2\text{-SiCl}_2(\text{NMe}_2)$, 5% $(\text{Me}_2\text{N})\text{Cl}_2\text{Si-CH}_2\text{-SiCl}_3$, and 5% $(\text{Me}_2\text{N})_2\text{ClSi-CH}_2\text{-SiCl}_2(\text{NMe}_2)$. This ratio did not change, even after heating at $80\text{ }^{\circ}\text{C}$ for 96 h.

Thermogravimetric analysis (TGA) in open cup conditions produces less than 0.5% w/w residue. See **FIG 5**.

Stability testing was performed at room temperature and 80°C for 1 week and 1 month. The stability of the precursor at usage temperature is important. When a precursor is used, its canister may be heated to provide sufficient vapor pressure and film growth rate. Therefore, the precursor needs to be stable at elevated temperatures. None of the samples exhibited any color change. Similarly, **FIG 6** demonstrates that the TGA for the samples did not change.

Example 4: Atomic Layer Deposition

FIG 7 is a schematic diagram of deposition apparatus used for the following testing. The apparatus includes a hotwall tube reactor **100** containing substrate coupons **105**. A pump **110** removes the contents from the hotwall tube reactor **100**.

The vapor of the disclosed Si-containing film forming composition is introduced to the hotwall tube reactor **100** from delivery device **200** via line **201**. An inert gas **205**, such as N_2 , is delivered to the delivery device **200** via line **206**. The inert gas **205** may also be delivered to the reactor **100** via line **207**.

An oxidizing gas may be introduced to the hotwall tube reactor **100** from delivery device **300** via line **301**. When the oxidizing gas is ozone, line **301** may include an ozone generator **303** and ozone monitor **304**. Oxidizing gas may also be delivered to the exhaust **311**.

5 A nitrogen containing gas may be introduced to the hotwall tube reactor **100** from delivery device **400** via line **401**.

One of ordinary skill in the art will recognize that lines **201**, **206**, **207**, **301**, and **401** may include numerous pressure gauges, check valves, valves, and pressure regulators and that additional lines for pressure regulation or by-pass
10 flow have not been included in order to simplify the drawing.

SiOC films were deposited on a Si(100) substrate with native oxide **105** via ALD using $(\text{Me}_2\text{N})\text{Cl}_2\text{Si}-\text{CH}_2-\text{SiCl}_2(\text{NMe}_2)$ as a Si source **200**, water (H_2O) as an oxygen source **300**, and pyridine as a catalyst **400**. The pressure in the reaction furnace **100** of **FIG 7** is controlled at 1 Torr, the temperature at 50°C , and 100
15 sccm of N_2 **205** was continuously flowing. The deposition process includes the following steps: 1) introducing a pulse of the 3 sccm Si source **200** and pyridine **400** to the reaction furnace **100** for 10 seconds, 2) purging the reaction furnace **100** using 1slm of N_2 **205** for 30 seconds, 3) introducing a pulse of 56 sccm H_2O **300** and 33 sccm pyridine **400** to the reaction furnace **100** for 20 seconds, and 4)
20 purging the reaction furnace **100** by 1slm of N_2 **205** for 40 seconds. The sequence from 1) to 4) were repeated for 150 cycles. The deposited layer achieved a thickness of 19.7 nm based on a $1.4 \text{ \AA/cycle}$ growth rate.

FIG 8 is a graph demonstrating the XPS depth profile of the resulting SiOC film, including the 37.4 atomic % of Si, 45.8 atomic % of O, 12.7 atomic % of C,
25 1.6 atomic % Cl, and 1.4 atomic % N.

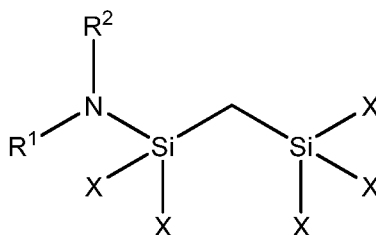
It will be understood that many additional changes in the details, materials, steps, and arrangement of parts, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the
30 art within the principle and scope of the invention as 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.

We claim:

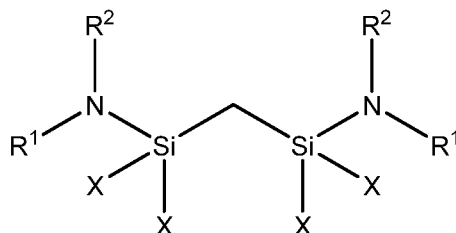
1. A Si-containing film forming composition comprising a halocarbosilane precursor having the formula $R_3Si-CH_2-SiR_3$, wherein each R is independently H, a halide X, an alkyl group, or an alkylamino group, provided that at least one R is a halide X and at least one R is an alkylamino group having the formula NR^1R^2 , wherein R^1 and R^2 is each independently H, a C1-C6 alkyl group, a C1-C6 alkenyl group, or a C3-C10 aryl or heterocycle group.

2. The Si-containing film forming composition of claim 1, wherein R^1 and R^2 is each independently H, Me, Et, nPr, iPr, Bu, Am, or are joined to form a cyclic chain on one N atom or on adjacent N atoms.

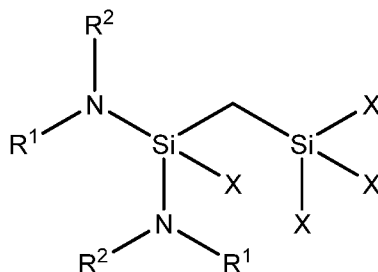
3. The Si-containing film forming composition of claim 1, having the formula:



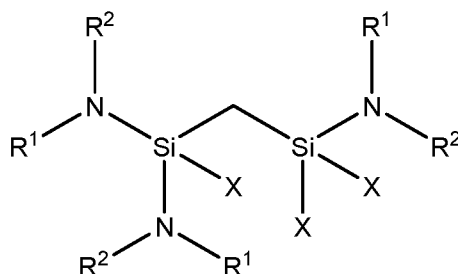
4. The Si-containing film forming composition of claim 1, having the formula:



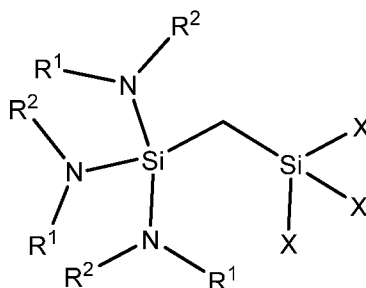
5. The Si-containing film forming composition of claim 1, having the formula:



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

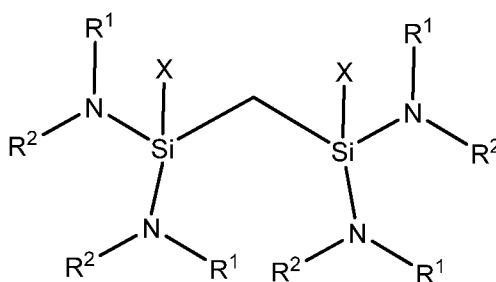


7. The Si-containing film forming composition of claim 1, having the formula:

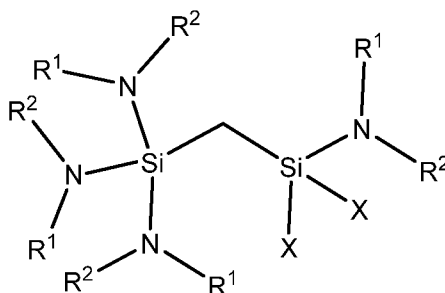


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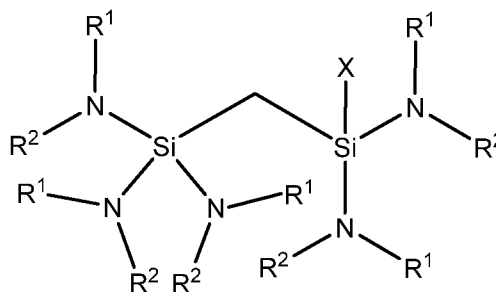
8. The Si-containing film forming composition of claim 1, having the formula:



- 10 9. The Si-containing film forming composition of claim 1, having the formula:



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



11. A process for the deposition of a Silicon-containing film on a substrate,
comprising the steps of: introducing a vapor of the Si-containing film forming
composition of any one of claims 1 to 10 into a reactor having a substrate disposed
therein and depositing at least part of the alkylamino-substituted halocarbosilane
precursor onto the substrate to form the Silicon-containing film.

12. The process of claim 11, further comprising introducing at least one reactant
into the reactor.

13. The process of claim 12, wherein the deposition is plasma enhanced.

14. A process of manufacturing a semiconductor device, the process
comprising:

Introducing a first catalytic gas and a vapor of the Si-containing film forming
composition of any one of claims 1 to 10 into a reactor having a substrate disposed
therein;

Introducing an oxidizing gas and a second catalytic gas into the reactor.

15. The process of claim 14, wherein the catalytic gas is an amine, such as
pyridine or triethylamine.

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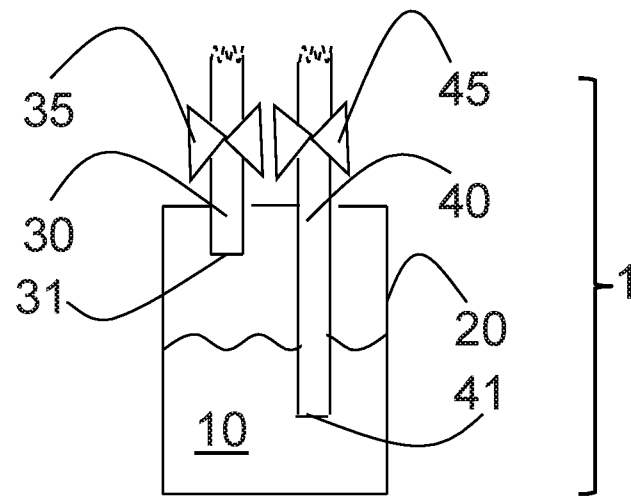


FIG 1

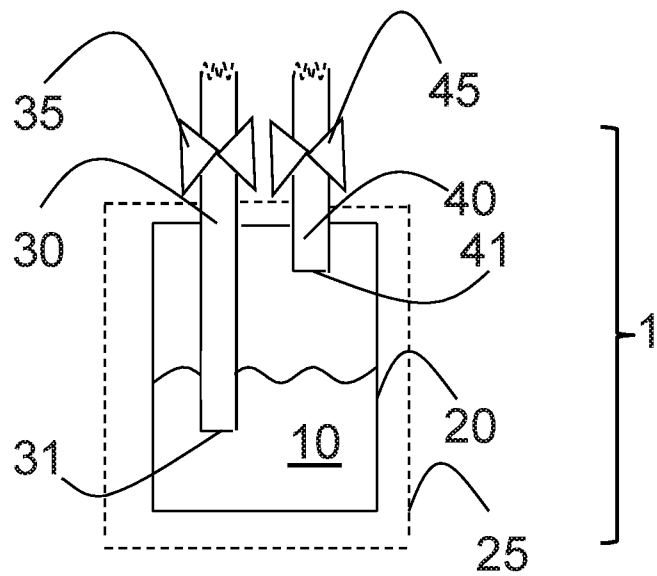


FIG 2

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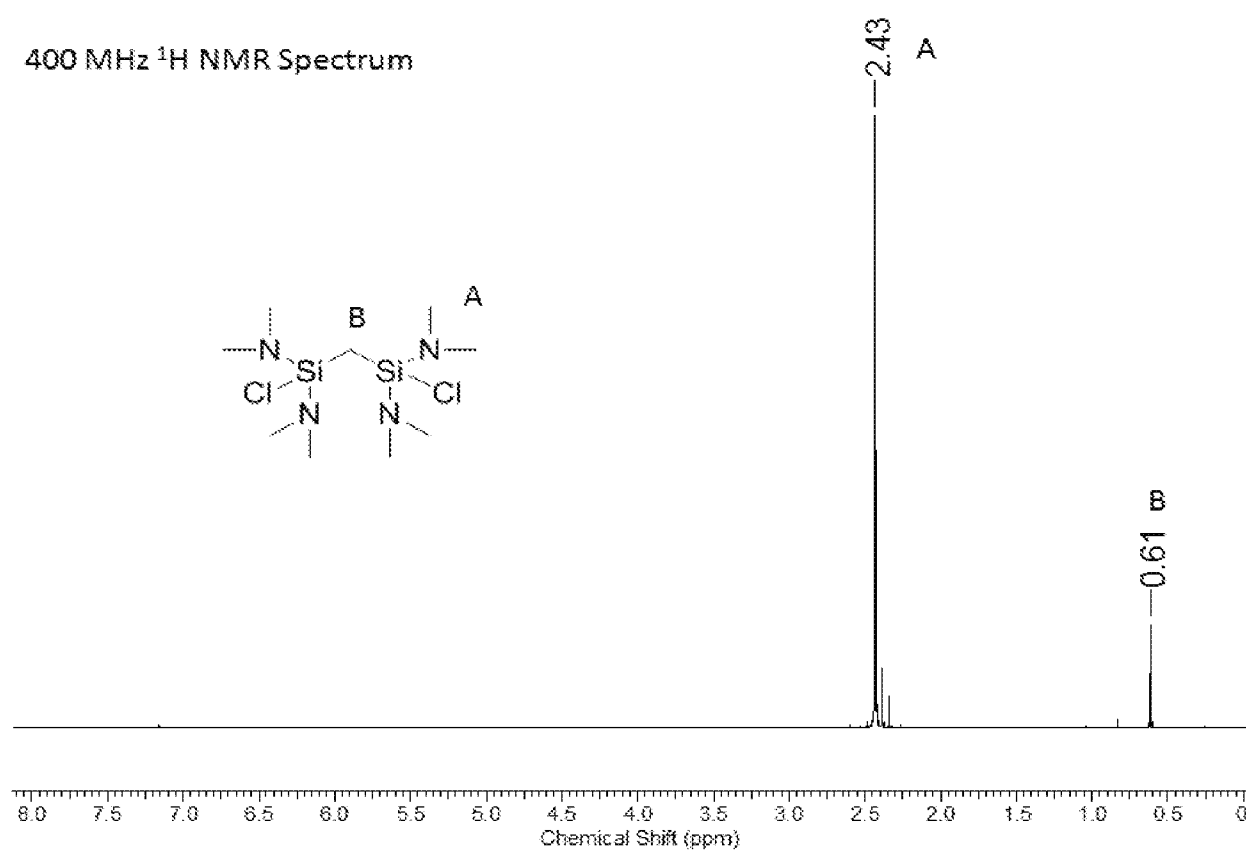
400 MHz ^1H NMR Spectrum

FIG 3

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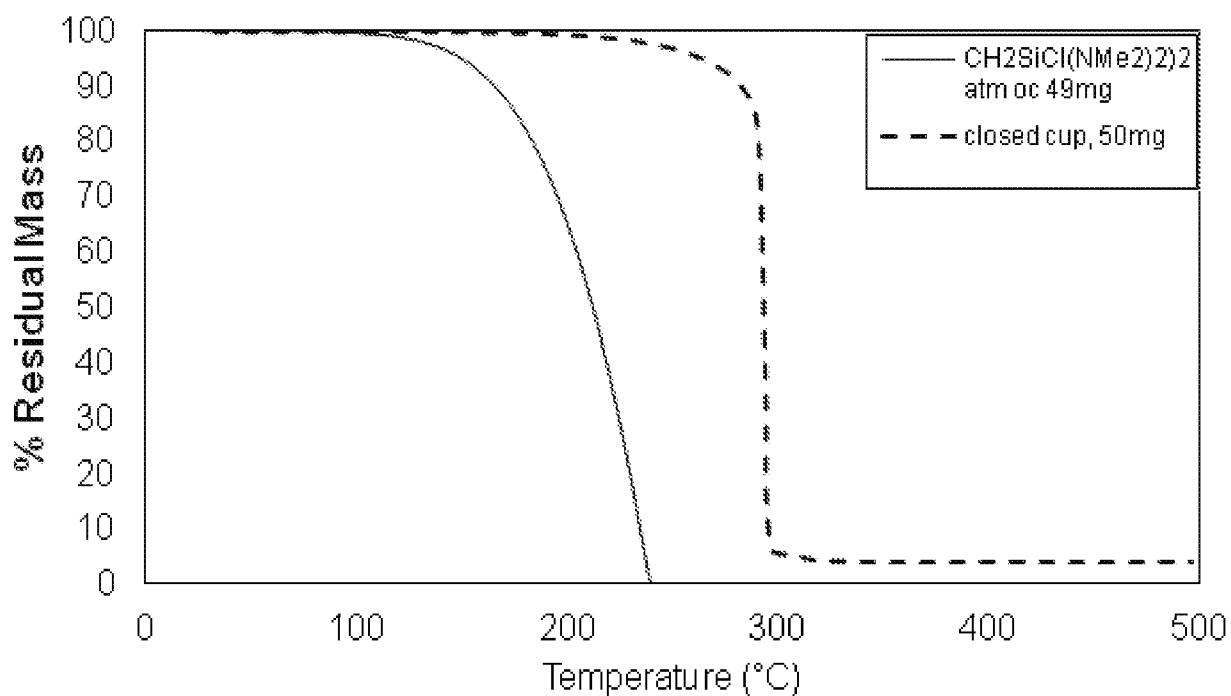
TGA of $\text{CH}_2[\text{SiCl}(\text{NMe}_2)_2]_2$ 

FIG 4

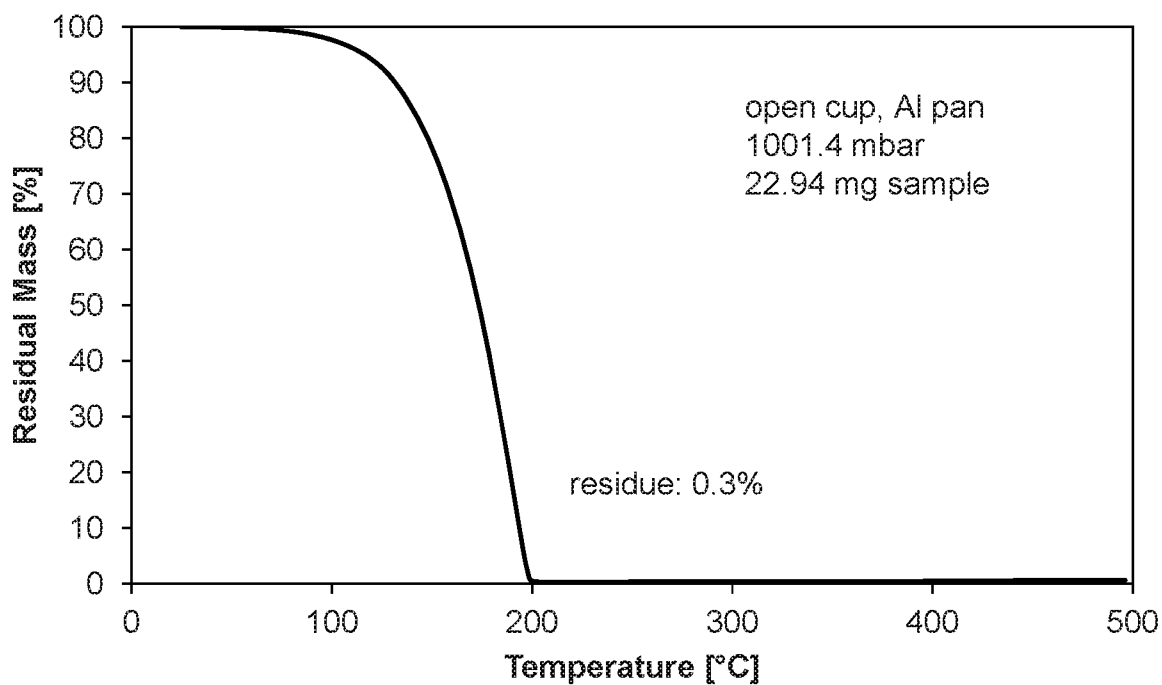
TGA of $(\text{Me}_2\text{N})\text{Cl}_2\text{Si}-\text{CH}_2-\text{SiCl}_2(\text{NMe}_2)$ 

FIG 5

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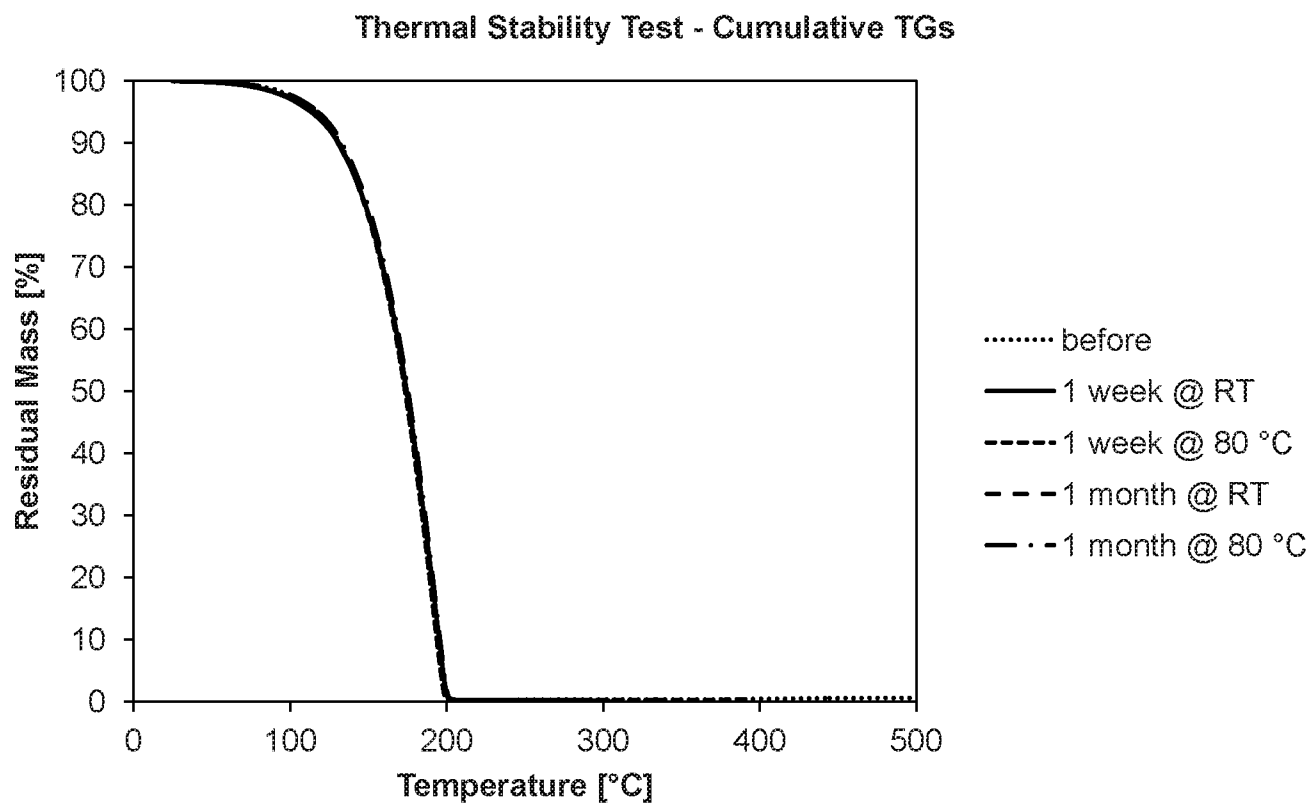


FIG 6

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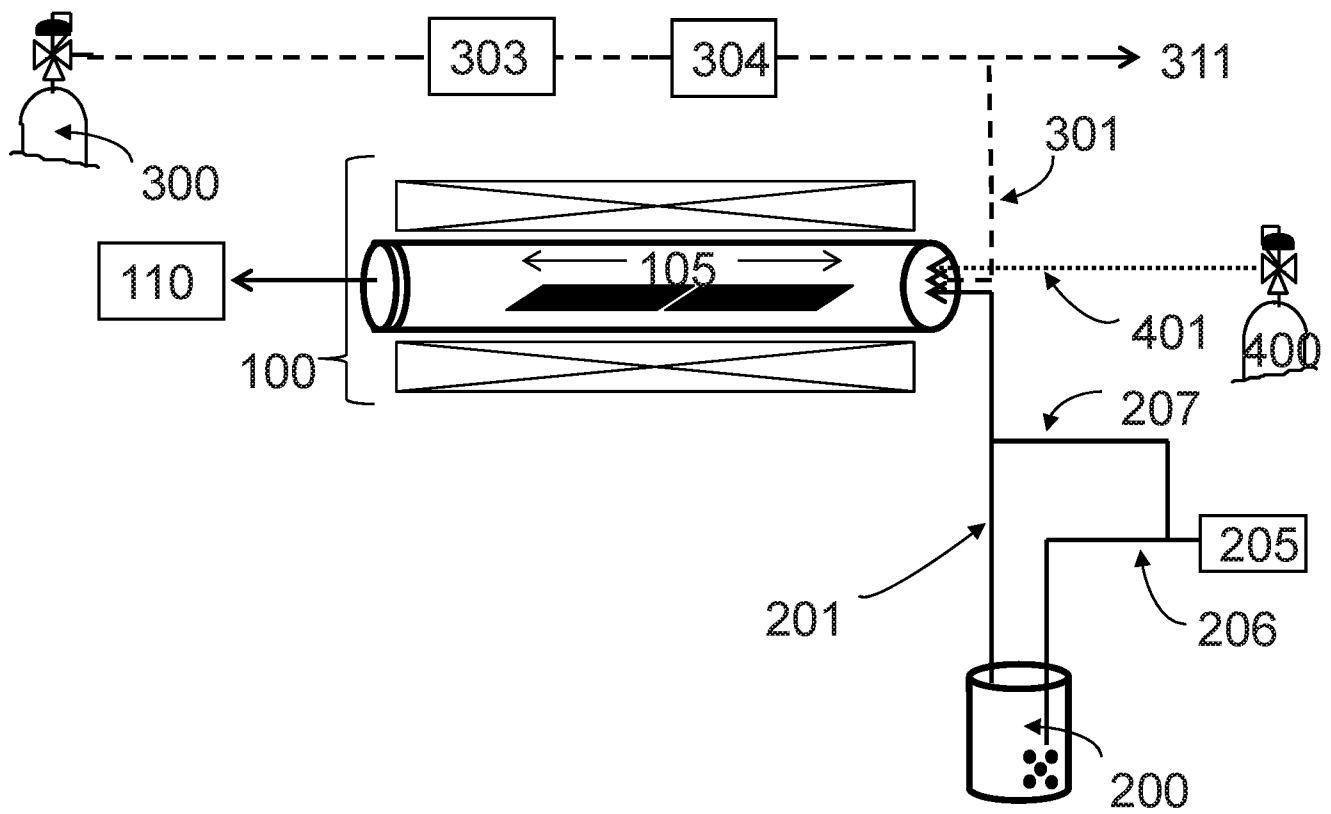


FIG 7

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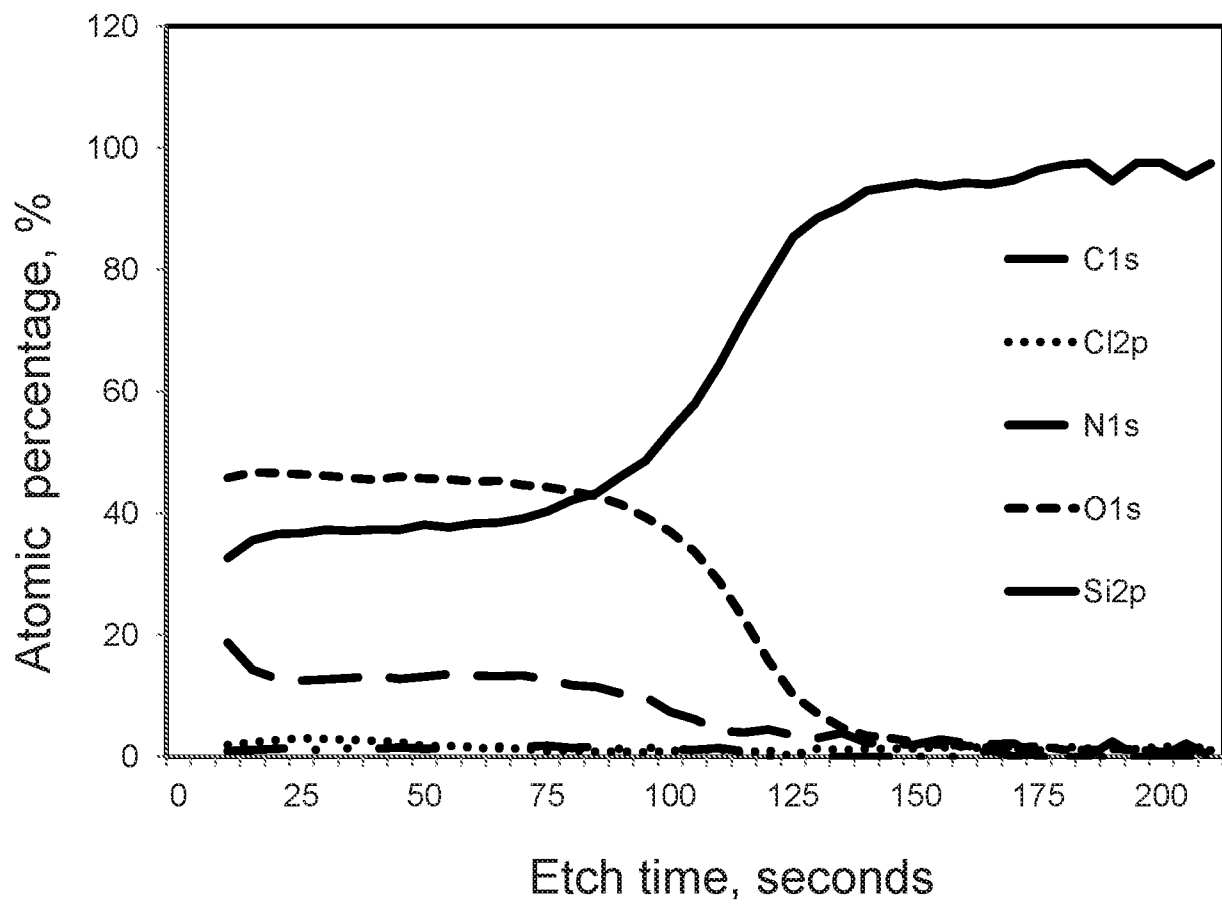


FIG 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/041435

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C23C16/42 (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)

Int.Cl. C23C16/42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2016
 Registered utility model specifications of Japan 1996-2016
 Published registered utility model applications of Japan 1994-2016

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JSTPlus/JST/580(JDreamIII), CPlus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/103282 A2 (L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE) 2011.08.25, & JP 2013-520030 A & CN 102762763 A	1-15
A	US 2013/0319290 A1 (AIR PRODUCTS AND CHEMICALS, INC.) 2013.12.05, & JP 2015-159306 A & CN 103451619 A	1-15
A	JP 2006-96675 A (L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE) 2006.04.13, (Family:none)	1-15



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 another 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

07.10.2016

Date of mailing of the international search report

18.10.2016

Name and mailing address of the ISA/JP

Japan Patent Office

3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan

Authorized officer

YOSHINO, Ryo

Telephone No. +81-3-3581-1101 Ext. 3416

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/041435

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/123792 A2 (L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE) 2011.10.06, & JP 2013-524522 A & CN 102471885 A	1-15
A	US 2006/0165891 A1 (INTERNATIONAL BUSINESS MACHINES CORPORATION) 2006.07.27, & JP 2006-216541 A & CN 1819180 A	1-15
P, A	WO 2016/049154 A1 (L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE) 2016.03.31, (Family:none)	1-15