- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}I$;
- the mono-substituted TSA precursor wherein X is a isocyanate –NCO (i.e., being $(SiH_3)_2N\text{-}SiH_2\text{-}NCO$);
- the mono-substituted TSA precursor wherein X is an amino group [$–NR^1R^2$];
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}NMe_2$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}NMeEt$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}NEt_2$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}NiPr_2$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}NHiPr$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}NMeiPr$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}NEtiPr$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}NHtBu$;
- the mono-substituted TSA precursor not being $(SiH_3)_2\text{-}N\text{-}SiH_2\text{-}N(SiH_3)(SiH_2(NHEt))$ (i.e., when $X=NR^1R^2$ and R^1 is SiH_3 and R^2 is NHEt);
- the mono-substituted TSA precursor wherein X is $–N(SiR_3)_2$, wherein each R is independently selected from a halogen, H, or a C_1-C_4 alkyl group;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}N(SiCl_3)_2$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}N(SiBr_3)_2$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}N(SiI_3)_2$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}N(SiH_3)_2$;
- the mono-substituted TSA precursor being $(SiH_3)_2\text{-}N\text{-}SiH_2\text{-}N(SiH_3)(SiH_2Cl)$;
- the mono-substituted TSA precursor being $(SiH_3)_2\text{-}N\text{-}SiH_2\text{-}N(SiH_3)(SiH_2(NEt_2)$;
- the mono-substituted TSA precursor being $(SiH_3)_2\text{-}N\text{-}SiH_2\text{-}N(SiH_3)(SiH_2(NiPr_2)$;
- the mono-substituted TSA precursor being $(SiH_3)_2\text{-}N\text{-}SiH_2\text{-}N(SiH_3)(SiH_2(NHtBu)$;
- the mono-substituted TSA precursor being $(SiH_3)_2\text{-}N\text{-}SiH_2\text{-}N(SiH_3)(SiH_2OEt)$;
- the mono-substituted TSA precursor being $(SiH_3)_2\text{-}N\text{-}SiH_2\text{-}N(SiH_3)(SiH_2OiPr)$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}N(SiMe_3)_2$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}NH(SiMe_3)$;
- the mono-substituted TSA precursor being $(SiH_3)_2N\text{-}SiH_2\text{-}N(SiEt_3)_2$;
- the mono-substituted TSA precursor being $(SiH_3)_2\text{-}N\text{-}SiH_2\text{-}N(SiMe_2Et)_2$;
- the mono-substituted TSA precursor being $(SiH_3)_2\text{-}N\text{-}SiH_2\text{-}N(SiMe_2iPr)_2$;

- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Mn;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw W;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Ni;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw K;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Na;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Sr;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Th;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Sn;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Ti;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw U;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw V;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 500 ppbw Zn;
- the Si-containing film forming organosilane composition comprising between approximately 0 ppmw and approximately 500 ppmw Cl;
- the Si-containing film forming composition comprising between approximately 0 ppmw and approximately 500 ppmw Br;
- the Si-containing film forming composition comprising between approximately 0 ppmw and approximately 500 ppmw I;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w TSA;

- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w $(SiH_3)_2$-N-SiH_2X, wherein X is Cl, Br, or I;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w $(SiH_3)_2$-N-$SiHX_2$, wherein X is Cl, Br, or I;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w SiH_4;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w SiH_3X, wherein X is Cl, Br, or I;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w SiH_2X_2, wherein X is Cl, Br, or I;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w SnX_2, wherein X is Cl, Br, or I;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w SnX_4, wherein X is Cl, Br, or I;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w HX, wherein X is Cl, Br, or I;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w NH_3;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w NH_4X, wherein X is Cl, Br, or I;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w ROH, wherein R is C_1-C_4 alkyl group;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w NH_2R, wherein R is a C_1-C_4 alkyl group;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w NR_2H, wherein R is a C_1-C_4 alkyl group;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w HN=R, wherein R is a C_1-C_4 alkyl group;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w tetrahydrofuran (THF);
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w ether;

- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w pentane;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w cyclohexane;
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w heptane; or
- the Si-containing film forming composition comprising between approximately 0.0% w/w and 0.1% w/w toluene.

[0007] 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 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 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 $(H_3Si)_2N\text{-}SiH_2(NEt_2)$,;
- the Si-containing film forming composition being $(H_3Si)_2N\text{-}SiH_2(NiPr_2)$;
- the Si-containing film forming composition being $(H_3Si)_2N\text{-}SiH_2Cl$; and
- the Si-containing film forming composition being $(H_3Si)_2N\text{-}SiH_2(N(SiMe_3)_2$.

[0008] Also disclosed are methods of depositing a Si-containing layer on a substrate. The composition disclosed above is introduced into a reactor having a substrate disposed therein. At least part of the mono-substituted TSA precursor is deposited onto the substrate to form the Si-containing layer using a vapor deposition method. The disclosed methods may have one or more of the following aspects:

- introducing into the reactor a vapor comprising a second precursor;

term “sequentially” refers to the atomic layer deposition process of repetitively reacting a precursor with a substrate to form a reacted layer followed by reacting a reactant with the reacted layer. This may be accomplished either by separate and sequential injection of the precursor followed by the reactant or by rotating the substrate below, or showerhead above, a substrate so that the portions of the substrate are sequentially contacted by the precursor then (sequentially) the reactant.

[0023] 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.).

[0024] Please note that the films or layers deposited, such as silicon oxide, are listed throughout the specification and claims without reference to their proper stoichiometry (i.e., SiO_2). The layers may include pure (Si) layers, silicide (M_oSi_p) layers, carbide (Si_oC_p) layers, nitride (Si_kN_l) layers, oxide (Si_nO_m) layers, or mixtures thereof; wherein M is an element and k, l, m, n, o, and p inclusively range from 1 to 6. For instance, cobalt silicide is Co_kSi_l, where k and l each range from 0.5 to 5. Similarly, any referenced layers may also include a Silicon oxide layer, 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 SiO_2 or SiO_3. The silicon oxide layer may be a silicon oxide based dielectric material, such as organic based or silicon oxide based low-k dielectric materials such as the Black Diamond II or III material by Applied Materials, Inc. Alternatively, any referenced silicon-containing layer may be pure silicon. Any silicon-containing layers may also include dopants, such as B, C, P, As and/or Ge.

[0025] Any and all ranges recited herein are inclusive of their endpoints (i.e., x=1 to 4 includes x=1, x=4, and x=any number in between), irrespective of whether the term “inclusively” is used.

Brief Description of the Drawings

[0026] 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 figure wherein:

[0027] **FIG. 1** is a side view of one embodiment of the Si-containing film forming composition delivery device **1**;

[0028] **FIG. 2** is a side view of a second embodiment of the Si-containing film forming composition delivery device **1**;

[0029] **FIG 3** is a diagram of the Picosun R200 PEALD 8" deposition tool used to perform the depositions in Examples 4-6;

[0030] **FIG 4** is a graph of the ALD growth rate of silicon oxide films as a function of the number of precursor pulses using the precursor $(SiH_3)_2N$-SiH_2-$NiPr_2$ (TSA-$NiPr_2$);

[0031] **FIG 5** is a graph of the ALD growth rate of silicon oxide thin film as a function of the temperature using the precursor TSA-$NiPr_2$;

[0032] **FIG 6** is a graph of the ALD growth rate of silicon oxide films as a function of the number of precursor pulses and the temperature using the precursor $(SiH_3)_2N$-SiH_2-$N(SiH_3)_2$;

[0033] **FIG 7** is a graph of the ALD growth rate of silicon oxide films as a function of the number of precursor pulses using the precursor $(SiH_3)_2N$-SiH_2-NEt_2 (TSA-NEt_2);

[0034] **FIG 8** is a graph of the ALD growth rate of silicon oxide films as a function of substrate temperature using the precursor $(SiH_3)_2N$-SiH_2-Cl (TSA-Cl);

[0035] **FIG 9** is a X-ray Photoelectron Spectroscopy (XPS) graph showing the film composition of a film deposited by thermal low vapor pressure CVD using TSA-Cl and NH_3 at 1 torr, 550°C, and a precursor to NH_3 ratio of 1:20. Cl was below the detection limit of the analyser (< ~ 1%). The deposition rate was 10 Ang/min and the Refractive Index of the obtained film was 2.1. For comparison, films obtained in the same conditions with TSA had a RI of 2.2 (silicon rich) and a similar deposition rate;

[0036] **FIG 10** is a graph demonstrating the comparative wet etch rate of silicon oxide films deposited using 25 W plasma and 100 W plasma normalized against thermally grown silicon oxide (Th-Ox);

[0037] **FIGS 11 a and b** are Scanning Electron Microscope (SEM) images showing the SiN film obtained by PE-ALD with TSA-Cl / N_2 plasma at 250°C, indicating a high step coverage in a 5:1 high aspect ratio structure. The pictures are taken at the top and middle/bottom of the trench structure;

[0038] **FIGS 12 a and b** are SEM images showing the silicon oxide film obtained by spatial ALD with TSA-$NiPr_2$ / O_2 plasma at 60 cycles per minute, 100°C, indicating a perfect step coverage in a 22:1 high aspect ratio structure. A clear underlying Ta_2O_5 layer was added for contrast enhancement. The pictures are taken at the top and bottom of the trench structure; and

substituted TSA structure is close to that of oligomers formed during flowable process.

[0042] The disclosed mono-substituted TSA precursors contain two or three hydrogen atoms directly bonded to each Si atom. These Si-H bonds help increase the volatility of the precursor, which is important for vapor deposition processes.

[0043] When X is a halide, exemplary Si-containing film forming compositions include $(SiH_3)_2$-N-SiH_2Cl, $(SiH_3)_2$-N-SiH_2Br, or $(SiH_3)_2$-N-SiH_2I. Halides are known for their high reactivity. Applicants believe that the halide on the disclosed mono-substituted TSA precursors may help to improve volatility and the deposition rate as compared to the non-halogenated analogs. These compositions may be synthesized according to the reaction: $SnX_4 + N(SiH_3)_3 \rightarrow N(SiH_3)_2(SiH_2X) + SnX_2\downarrow + HX$, wherein X is Cl, Br, or I (see *J. Chem. Soc. Dalton Trans.* 1975, p.1624). Alternatively, dihalosilane [SiH_2X_2, wherein X is Cl, Br, or I] and monohalosilane [SiH_3X, wherein X is Cl, Br, or I] may be introduced continuously in the gas phase in a 1/20 to ¼ ratio and at room temperature with 400 sccm of NH_3 in a flow-through tubular reactor as described by Miller in U.S. Pat. No. US 8,669,387. The reaction of NH_3 with 2 equivalents of monohalosilane produces mostly disilylamine (DSA). DSA then reacts with the dihalosilane to form $(SiH_3)_2$-N-SiH_2X and HX, wherein X is Cl, Br, or I. One of ordinary skill in the art would recognize that the reaction may take place in two steps (first forming DSA from the monohalosilane and NH_3 and second adding dihalosilane) or in one step (combining the monohalosilane, dichlorosilane, and NH_3 in one step).

[0044] When X is an isocyanato group [–NCO], exemplary Si-containing film forming compositions include $(SiH_3)_2$-N-SiH_2(NCO). This composition may be synthesized using dehydrogenerative coupling according to the method disclosed by Taniguchi *et al*. in Angewandte Communications, Angew. Chem. Int. Ed. 2013, 52, 1-5, the teachings of which are incorporated herein by reference. More particularly, $(SiH_3)_3N$ may be reacted with urea (NH_2CONH_2) to form $(SiH_3)_2$-N-SiH_2(NCO)+H_2 in the presence of gold nanoparticles supported on alumina.

[0045] When X is an amino group [$–NR^1R^2$], exemplary Si-containing film forming compositions include $(SiH_3)_2$-N-$SiH_2(NMe_2)$, $(SiH_3)_2$-N-SiH_2(NMeEt), $(SiH_3)_2$-N-$SiH_2(NEt_2)$, $(SiH_3)_2$-N-$SiH_2(NiPr_2)$, $(SiH_3)_2$-N-SiH_2(NHiPr), $(SiH_3)_2$-N-SiH_2(NMeiPr), $(SiH_3)_2$-N-SiH_2(NEtiPr), $(SiH_3)_2$-N-SiH_2(NHtBu), $(SiH_3)_2$-N-$SiH_2[N(SiH_3)_2]$, $(SiH_3)_2$-N-$SiH_2[N(SiH_3)(SiH_2Cl)]$, $(SiH_3)_2$-N-$SiH_2[N(SiH_3)(SiH_2(NEt_2))]$, $(SiH_3)_2$-N-

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**.

[0073] 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 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.

[0074] The disclosed Si-containing film forming compositions may be suitable for the deposition of Si-containing films by various ALD or CVD processes and may have the following advantages:

- liquid at room temperature or having a melting point lower than 50°C;
- thermally stable to enable proper distribution (gas phase or direct liquid injection) without particles generation; and/or
- suitable reactivity with the substrate to permit a wide self-limited ALD window, allowing deposition of a variety of Si -containing films.

[0075] Silicon nitride and silicon oxide containing films (referred to as SiO_xN_y) may be deposited by CVD or ALD using one or a combination of reactants selected from the group consisting of N_2, H_2, NH_3, O_2, H_2O, H_2O_2, O_3, NO, NO_2, N_2O, a carboxylic acid, an alcohol, a diol, hydrazines (such as N_2H_4, $MeHNNH_2$, MeHNNHMe), organic amines (such as $NMeH_2$, $NEtH_2$, NMe_2H, NEt_2H, NMe_3, NEt_3, $(SiMe_3)_2NH$), pyrazoline, pyridine, diamines (such as ethylene diamine), a combination thereof, and the plasma product thereof.

[0076] Ternary or quarternary films may be deposited using the Si-containing film forming compositions with one or several other precursors containing elements selected from As, B, P, Ga, Ge, Sn, Sb, Al, In, or a transition metal precursor, and possibly one or more reactant listed above. Typical precursors that may be used along with the disclosed Si-containing film forming compositions are selected from the families of :

- Metal Halides (for example, $TiCl_4$, TiI_4, $TaCl_5$, $HfCl_4$, $ZrCl_4$, $AlCl_3$, NbF_5, *etc.*) ;
- Alkyls (Al, Ge, Ga, In, Sb, Sn, Zn), such as trimethylaluminum, diethylzinc, triethylgallium;
- Hydrides (GeH_4, alanes, *etc.*);
- Alkylamides (metals of group IV and V transition metals);
- Imido group (metals of group V and VI);
- Alkoxides (metals of group IV, V);
- Cyclopentadienyls (Ru, Co, Fe, Group IV transition metals, lanthanides *etc.*);
- Carbonyls (ex: Ru, Co, Fe, Ni);
- Amidinates and guanidinates (ex : Co, Mn, Ni, Cu, Sc, *etc.*);
- Beta-diketonates (ex : Sc, Cu, lanthanides) ;
- Beta-diketoimines (Cu, Ni, Co, *etc.*);
- Bis-trialkylsilylamides (Ni, Co, Fe, *etc.*);
- Oxo groups (RuO_4, $WOCl_4$, $PO(OEt)_3$, $AsO(OEt)_3$, *etc.*);
- Or heteroleptic molecules having a combination of the above ligands.

[0077] The disclosed Si-containing film forming compositions may also be used in conjunction with another silicon source, such as a halosilane (possibly selected from SiH_3Cl, SiH_2Cl_2, $SiHCl_3$, $SiCl_4$, $SiBr_4$, SiI_4, $SiHI_3$, SiH_2I_2, SiH_3I, SiF_4), a polysilane SiH_xH_{2x+2}, or a cyclic polysilane SiH_xH_{2x}, a halo-polysilane (Si_xCl_{2x+2}, $Si_xH_yCl_{2x+2-y}$, such as HCDS, OCTS, PCDS, MCDS (monochlorodisilane or Si_2H_5Cl), DCDS (dichlorodisilane or $Si_2H_4Cl_2$), or a carbosilane having a Si-$(CH_2)_n$-Si backbone, with n= 1 or 2.

[0078] Also disclosed are methods of using the disclosed Si-containing film forming compositions for vapor deposition methods, including various CVD and ALD methods. The disclosed methods provide for the use of the disclosed Si-containing film forming compositions for deposition of silicon-containing films, preferably silicon nitride (SiN) films, silicon-oxide (SiO) films, and nitrogen doped silicon-oxide films.

[0089] Alternatively, the ALD process may be carried at a substrate temperature being set below a self-decomposition temperature of the precursor. One of ordinary skill in the art would recognize how to determine the self-decomposition temperature of the precursor.

[0090] The reactor contains one or more substrates onto which the films will be deposited. 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 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, photoresist layers, anti-reflective layers, or combinations thereof. Additionally, the wafers may include copper layers or noble metal layers (*e.g.* platinum, palladium, rhodium, or gold). The layers may include oxides which are used as dielectric materials in MIM, DRAM, STT RAM, PC-RAM or FeRam technologies (*e.g.*, ZrO_2 based materials, HfO_2 based materials, TiO_2 based materials, rare earth oxide based materials, ternary oxide based materials such as strontium ruthenium oxide (SRO), *etc.*) or nitride-based films (*e.g.*, TaN) that are used as an oxygen barrier between copper and the low-k layer. The wafers may include barrier layers, such as manganese, manganese oxide, *etc.* Plastic layers, such as poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) may also be used. The layers may be planar or patterned. For example, the layer may be a patterned photoresist film made of hydrogenated carbon, for example CH_x, wherein x is greater than zero. 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. In many instances though, the preferred substrate utilized may be selected from copper, silicon oxide, photoresist, hydrogenated carbon, TiN, SRO, Ru, and Si type substrates, such as polysilicon or

tetrachlorodisilane, and one or more reactants to form Si, SiCN, or SiCOH films. PCT Publication Number WO2011/123792 discloses a SiN layer (not a Si or SiCOH layer), and the entire contents of which are incorporated herein in their entireties.

[0096] When the desired silicon-containing film also contains another element, such as, for example and without limitation, Ti, Hf, Zr, Ta, Nb, V, Al, Sr, Y, Ba, Ca, As, B, P, Sb, Bi, Sn, Ge, lanthanides (such as Er), or combinations thereof, another precursor may include a metal-containing precursor which is selected from, but not limited to:

- Metal Halides (*e.g.,* $TiCl_4$, TiI_4, $TaCl_5$, $HfCl_4$, $ZrCl_4$, $AlCl_3$, NbF_5, *etc.*);
- Alkyls (Al, Ge, Ga, In, Sb, Sn, Zn), such as trimethylaluminum, diethylzinc, triethylgallium;
- Hydrides (GeH_4, alanes, *etc.*);
- Alkylamides (metals of group IV and V transition metals);
- Imido group (metals of group V and VI);
- Alkoxides (metals of group IV, V);
- Cyclopentadienyls (Ru, Co, Fe, Group IV transition metals, lanthanides, *etc.*);
- Carbonyls (ex: Ru, Co, Fe, Ni);
- Amidinates and guanidinates (ex : Co, Mn, Ni, Cu, Sc, *etc.*);
- Beta-diketonates (*e.g.,:* Sc, Cu, lanthanides) ;
- Beta-diketoimines (Cu, Ni, Co, etc.);
- Bis-trialkylsilylamides (Ni, Co, Fe, *etc.*);
- Oxo groups (RuO_4, $WOCl_4$, $PO(OEt)_3$, $AsO(OEt)_3$, *etc.*);
- Heteroleptic molecules having a mixed set of ligands selected from the above families.

[0097] The Si-containing film forming compositions and one or more reactants may be introduced into the reaction chamber simultaneously (*e.g.,* CVD), sequentially (*e.g.,* ALD), or in other combinations. For example, the Si-containing film forming composition may be introduced in one pulse and two additional metal sources may be introduced together in a separate pulse (*e.g.,* modified ALD). Alternatively, the reaction chamber may already contain the reactant prior to introduction of the Si-containing film forming composition. The reactant may be passed through a 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 metal sources

on the oxidation state of M. One of ordinary skill in the art will recognize that by judicial selection of the appropriate mono-substituted TSA precursor and reactants, the desired film composition may be obtained.

[00108] 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 to 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 reactive 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. When the deposition process is a FCVD, the curing step is preferably an oxygen curing step, carried out at a temperature lower than 600°C. The oxygen containing atmosphere may contain H_2O or O_3. Alternatively, the substrate may be removed from the reaction chamber, with the annealing/flash annealing process being performed in a separate apparatus.

Examples

[00109] 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.

[00110] The examples described herein are TSA based precursors, *i.e.*, mono-substituted TSA.

Example 1: Synthesis of $(SiH_3)_2N\text{-}SiH_2\text{-}NiPr_2$ and of $(SiH_3)_2N\text{-}SiH_2\text{-}NEt_2$

[00111] 300g of diisopropylamine (3.0mol) was charged to a 1-liter filter flask equipped with an overhead mechanical stirrer, a nitrogen bubbler, a chiller and a hydride scrubber as a reactor. 60g (0.4mol) of chlorotrisilylamine was charged to a dropping funnel. The dropping funnel was affixed to the reactor. A nitrogen sweep

then reacted with n-BuLi in a n-hexane solvent to form $(Me_2SiH)_2N$-Li. Chlorodimethyl dimethylaminosilane [$ClSiMe_2(NMe_2)$] is added to the mixture to then form the $(Me_2SiH)_2NSiMe_2(NMe_2)$ product.

[00120] One of ordinary skill in the art would recognize that the synthesis method described in Example 1 would not be suitable to produce the molecules disclosed herein containing the $(SiH_3)_2N$- moiety. DNF's proposed synthesis method would require the synthesis and isolation of the amine $(SiH_3)_2NH$ followed by its treatment with the strong base, tBuLi, in liquid phase. It is well known in the literature that the $(SiH_3)_2NH$ amine may be prepared and handled in its gas phase, but is not stable in liquid phase and decomposes even at 0°C. See, e.g., "Silicon-nitrogen compounds. VI. Preparation and properties of disilazane"; Aylett, Bernard J.; Hakim, M. J.; Journal of the Chemical Society [Section] A: Inorganic, Physical, Theoretical, 1969, 4, 639-642. More particularly, $(SiH_3)_2NH$ rapidly disproportionates in the presence of a weak base, such as liquid NH_3. *Id.* Therefore, one of ordinary skill in the art would recognize that a much stronger base, such as ^tBuLi, would cause even faster disproportionation. As a result, one of ordinary skill in the art would not expect success in the synthesis of the required $(SiH_3)_2NLi$ intermediate salt, which is necessary for the next step in the synthesis.

[00121] The method described in Example 1 of WO2015/190749 for the preparation of amines with the formula $(SiHR_2)_2NH$ implies the reaction of chlorosilanes $SiHR_2Cl$ with NH_3 in stoichiometric amount. In the case of SiH_3X (X = Cl, Br, I), Stock *et al.* reported the impossibility of isolating gaseous $(SiH_3)_2NH$ by this method because the reaction did not stop at the bis-substituted product and formed the tris-substituted amine $(SiH_3)_3N$. *See, e.g.*, Stock, A. and Somieski, C.; *Chem. Ber.*, **1921**, *54B*, 740. All of the aforementioned arguments, together with the total absence of any reference describing the formation of a lithium silylamide with more than one hydride in each silicon atom, prove that it is not feasible to prepare $(SiH_3)_2N$- or $(SiH_2R)_2N$- containing aminosilanes by the synthetic route described in WO2015/190749.

[00122] In contrast, as shown in Examples 1-3, Applicants have successfully synthesized the disclosed $(SiH_3)_2N$-containing compounds by using $(SiH_3)_2N$-SiH_2Cl as a starting material.

Example 4

[00123] The following PEALD testing was performed using a Picosun R200 PEALD 8" deposition tool with a 4" wafer. The vapor of the mono-substituted TSA precursor was delivered to the Picosun tool as shown in **FIG 3**.

[00124] ALD tests were performed using $(SiH_3)_2N\text{-}SiH_2\text{-}NiPr_2$ as the silicon-containing film forming composition **10**, which was placed in an ampoule heated to 70ºC and O_2 plasma as oxidizing reactant. Typical ALD conditions were used with the reactor **50** pressure fixed at ~9 hPa (1 hPa=100 Pa=1mbar). Two 0.1-second pulses of the precursor vapor were introduced into the deposition chamber via overpressure in the ampoule using the 3-way pneumatic valve **51**. The 0.1-second pulses were separated by a 0.5 second pause. A 4-second N_2 purge removed any excess precursor. A 16-second plasma O_2 pulse was followed by a 3-second N_2 purge. The process was repeated until a minimum thickness of 300 Angstrom was obtained. Depositions were performed with the substrate heated to 70°C, 150°C, and 300°C. Real self limited ALD growth behavior was validated as shown in **FIG 4** by increasing the number of precursor pulses within a given cycle.

[00125] ALD tests were also performed using the prior art $SiH_2(NEt_2)_2$ precursor as the Si-containing film forming composition **10**, which was placed in an ampoule heated to 60ºC and O_2 plasma as oxidizing reactant. Applicants believe that $SiH_2(NEt_2)_2$ is currently used to deposit SiO_2 in several commercial processes. Typical ALD conditions were used with the reactor pressure fixed at ~9 hPa (1 hPa=100 Pa=1mbar). Two 0.1-second pulses of the precursor vapor were introduced into the deposition chamber via overpressure in the ampoule using the 3-way pneumatic valve. The 0.1-second pulses were separated by a 0.5 second pause. A 4-second N_2 purge removed any excess precursor. A 16-second plasma O_2 pulse was followed by a 3-second N_2 purge. The process was repeated until a minimum thickness of 300 Ang was reached. Depositions were performed at 70°C, 150°C, 200°C, and 300°C. As shown in **FIG 5**, the growth per cycle decreased with increasing temperature.

Table 2 summarizes the results:

	$SiH_2(NEt_2)_2$	$(SiH_3)_2N\text{-}SiH_2\text{-}NiPr_2$
Growth rate 70°C[1]	1.42 Ang/cycle	3.10 Ang/cycle
Growth rate 300°C[1]	0.98 Ang/cycle	2.05 Ang/cycle
Wet Etch Rate 70°C[2]	9.4 Ang/sec	8.8 Ang/sec

pulses of the precursor vapor were introduced into the deposition chamber via overpressure in the ampoule using the 3-way pneumatic valve. The 0.1-second pulses were separated by a 0.5 second pause. A 4-second N_2 purge removed any excess precursor. An 11-second plasma NH_3 pulse was followed by a 3-second purge. The entire process (precursor – plasma O_2 – precursor – plasma NH_3) was repeated until the thickness reached at least 300 Ang. Depositions were performed at 150°C.

[00128] The resulting SiO_2 film had a wet etch rate of 3.2 Ang/sec using 0.1% v/v HF (determined by ellipsometry) and N concentration of ~1%. Such a low etch rate is found to be beneficial for spacer-based double patterning to enable a low edge roughness in the transfer layer when the ALD-deposited silicon oxide film is used as a mask. The person of ordinary skill in the art would recognize that the Oxygen to Nitrogen content in the obtained film can be tuned by adjusting the number, sequence or/and duration of the O containing reactant and N containing reactant pulses. Applicant believes that a N concentration of approximately 0.5 atomic % to approximately 5 atomic % in an SiO_2 film is beneficial for the spacer-defined patterning applications.

Example 6

[00129] ALD tests were performed using the $(SiH_3)_2N\text{-}SiH_2\text{-}N(SiH_3)_2$, which was placed in an ampoule heated to 26ºC and O_2 plasma as oxidizing reactant. Typical ALD conditions were used with the reactor pressure fixed at ~9 hPa. Three 0.1-second pulses of the precursor vapor were introduced into the deposition chamber via overpressure in the ampoule using the 3-way pneumatic valve. The 0.1-second pulses were separated by a 0.5 second pause. A 4-second N_2 purge removed any excess precursor. A 16-second plasma O_2 pulse was followed by a 3-second N_2 purge. The entire process (precursor – plasma O2 –) was repeated until the thickness reached at least 300 Ang. As shown in **FIG 6**, the growth per cycle increased with increasing deposition temperatures from 150°C to 300°C. **FIG 6** also shows comparative growth per cycle results of five 0.1-second pulses versus three 0.1-second pulses. Both were approximately 0.6 angstroms/cycle, indicating true ALD saturation because the larger amounts of precursor introduced via 5 pulses do not result in a higher growth rate than the film produced by 3 pulses.

[00130] The growth rate was approximately 0.58 Ang/cycle at 150°C and resulted in a film having a refractive index of 1.45. For comparison, attempts to grow a SiO_2 film by ALD using pure TSA in similar conditions have not yielded any films, thus proving the benefit of the chemical functionalization to enhance the reactivity with the surface hydroxyl groups.

Example 7

[00131] ALD tests were performed using $(SiH_3)_2N\text{-}SiH_2\text{-}NEt_2$ as the silicon-containing film forming composition **10**, which was placed in an ampoule heated to 70ºC and O_2 plasma as oxidizing reactant. Typical ALD conditions were used with the reactor **50** pressure fixed at ~9 hPa (1 hPa=100 Pa=1mbar). Two 0.1-second pulses of the precursor vapor were introduced into the deposition chamber via overpressure in the ampoule using the 3-way pneumatic valve **51**. The pulses were separated by a 0.5 second pause. A 4-second N_2 purge removed any excess precursor. A 16-second plasma O_2 pulse was followed by a 3-second N_2 purge. The process was repeated until a minimum thickness of 300 Angstrom was obtained. Depositions were performed with the substrate heated to 150°C. A self limited ALD growth behavior was found as shown in **FIG 7** by increasing the number of precursor pulses to reach a cumulative opening time higher than 0.4 second per cycle.

[00132] As in Example 4, the approximately 3.0 Å/cycle growth rate for films produced by $(SiH_3)_2N\text{-}SiH_2\text{-}NEt_2$ at 150°C is much better than the 1.42 Å/cycle and 0.98 Å/cycle for films produced by $SiH_2(NEt_2)_2$ at 70°C and 300°C, respectively.

Example 8

[00133] ALD tests were performed using $(SiH_3)_2N\text{-}SiH_2\text{-}Cl$ as the silicon-containing film forming composition **10**, which was placed in an ampoule heated to 30ºC and O_2 plasma as oxidizing reactant. $(SiH_3)_2N\text{-}SiH_2\text{-}Cl$ gas a molecular weight of 141.78, is liquid at room temperature and standard pressure, and has a boiling point at standard pressure between approximately 83°C and approximately 85°C.

[00134] Typical ALD conditions were used with the reactor **50** pressure fixed at ~9 hPa (1 hPa=100 Pa=1mbar). Two 0.1-second pulses of the precursor vapor were introduced into the deposition chamber via overpressure in the ampoule using the 3-way pneumatic valve **51**. The 0.1-second pulses were separated by a 0.5 second pause. A 4-second N_2 purge removed any excess precursor. A 16-second plasma

O_2 pulse was followed by a 3-second N_2 purge. The process was repeated until a minimum thickness of 300 Angstrom was obtained. Depositions were performed with the substrate heated to 100°C, 150°C, 200°C, 250°C, and 300°C. As shown in **FIG 8**, the growth per cycle remained steady (i.e., approximately 2 Å/cycle) with increasing deposition temperatures from 100°C to 300°C.

[00135] The resulting silicon oxide films were deposited at a high deposition rate (approximately 2Å/cycle) at multiple temperatures. These results are beneficial when temperature uniformity is difficult to maintain across the substrate (*i.e.*, for large substrates) or from one substrate to another due to temperature gradients in the reactor.

[00136] The average thickness of the film was also uniform across the wafer. Table 3 summarizes the film uniformity obtained. These results demonstrate extremely good film uniformity.

Experiment Number (Process Conditions)	Deposition Temp. (°C)	Average Thickness (Å)	Non Uniformity[1] (%)	σ^2	3 σ/Average (%)
1272 (1 x 0.1 s)	100	321	1.04	1.66	1.56
1256 (2 x. 0.1 s)	100	329	1.07	1.59	1.45
1271 (3 x 0.1 s)	100	323	0.93	1.34	1.24
1252 (1 x 0.1 s)	150	590	1.30	4.45	2.26
1253 (2 x 0.1 s)	150	585	1.96	6.61	3.39
1267 (1 x 0.1 s)	200	319	0.66	1.09	1.03
1273 (2 x 0.1 s)	200	325	1.15	1.94	1.79
1268 (3 x 0.1 s)	200	324	1.15	2.01	1.87
1263 (1 x 0.1 s)	250	362	0.74	1.37	1.13
1265 (2 x 0.1 s)	250	317	0.88	1.27	1.20

[1] % non-uniformity = [(maximum thickness – minimum thickness)/(2x average)] x 100

[2] σ = standard deviation

Example 9

[00137] Thermal, low pressure CVD tests were performed using $(SiH_3)_2N\text{-}SiH_2\text{-}Cl$ and NH_3 at 1 torr, 550°C, and a precursor to NH_3 ratio of 1:20. **FIG 9** is a X-ray Photoelectron Spectroscopy (XPS) graph showing the resulting film composition. Cl was below the detection limit of the analyser (< ~ 1 atomic %). The deposition rate

What is claimed is:

1. A silicon- and nitrogen-containing film formation process, the process comprising the steps of:

depositing a silicon- and nitrogen-containing film on a substrate by introducing a vapor of a mono-substituted TSA precursor and a nitrogen-containing reactant into a reactor containing the substrate, the mono-substituted TSA precursor having a formula $(SiH_3)_2N\text{-}SiH_2\text{-}X$, wherein X is an amino group [$–NR_2$] and each R is independently selected from the group consisting of H; a C_1-C_6 hydrocarbyl group; or a silyl group [SiR'_3] with each R' being independently selected from H or a C_1-C_6 hydrocarbyl group.

2. The silicon- and nitrogen-containing film formation process of claim 1, wherein X is $NiPr_2$.

3. The silicon- and nitrogen-containing film formation process of claim 1, wherein X is NEt_2.

4. The silicon- and nitrogen-containing film formation process of claim 1, wherein X is $N(SiH_3)_2$.

5. The silicon- and nitrogen-containing film formation process of any one of claims 1 to 4, wherein the nitrogen-containing reactant is selected from the group consisting of ammonia, N_2, N atoms, N radicals, N ions, saturated or unsaturated hydrazine, amines, diamines, ethanolamine, and combinations thereof.

6. The silicon- and nitrogen-containing film formation process of claim 5, wherein the nitrogen-containing reactant is NH_3.

7. The silicon- and nitrogen-containing film formation process of claim 6, wherein the mono-substituted TSA precursor and the nitrogen-containing reactant are introduced into the reactor simultaneously.

8. The silicon- and nitrogen-containing film formation process of claim 5, wherein the nitrogen-containing reactant is plasma N_2.

9. The silicon- and nitrogen-containing film formation process of claim 8, wherein the mono-substituted TSA precursor and the nitrogen-containing reactant are introduced into the reactor sequentially.