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Published:

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(54) Title: SI-CONTAINING FILM FORMING COMPOSITIONS FOR ALD/CVD OF SILICON-CONTAINING FILMS

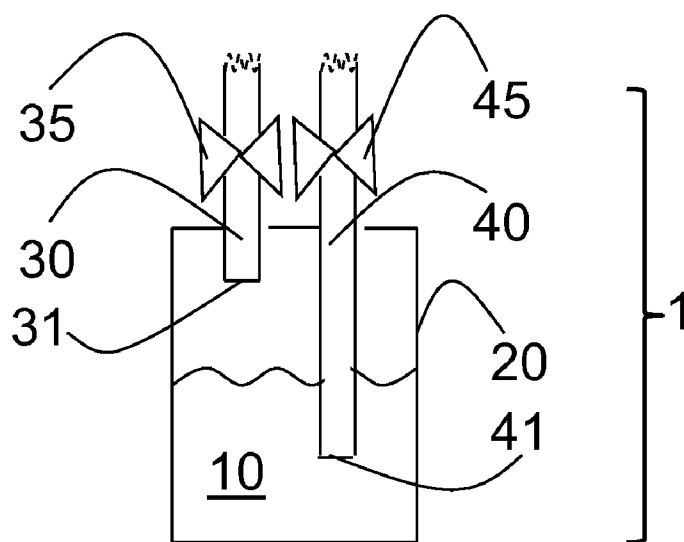


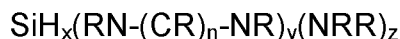
FIG 1

(57) Abstract: Si-containing film forming compositions, methods of synthesizing the same, and methods of using the same to deposit silicon-containing films using vapor deposition processes are disclosed. The disclosed Si-containing film forming compositions comprise organosilane precursors have the formula $\text{SiH}_x(\text{RN}-(\text{CR})_n-\text{NR})_y(\text{NRR})_z$, wherein each R is independently selected from the group consisting of H, a C_1 to C_6 alkyl group, and a C_3 - C_{20} aryl or heterocycle group; $n = 1$ or 3 ; $x = 0, 1$, or 2 ; $y = 1$ or 2 ; and $z = 1, 2$, or 3 ; and $x+y+z = 4$, provided that x is not equal to 2 when $y=2$.

5 Cross Reference to Related Applications

10 Technical Field

15 The disclosed Si-containing film forming compositions comprise organosilane precursors having the formula:



20 2; and $z = 1, 2$, or 3 ; and $x+y+z = 4$, provided that $x \neq 2$ when $y=2$.

Si-containing thin films are used widely in the semiconductor, photovoltaic, liquid-crystal display-thin-film transistor (LCD-TFT), flat panel-type device, refractory material, or aeronautic industries. Si-containing thin films may be used, for example, as dielectric materials having electrical properties which may be insulating (SiO_2 , SiN , SiCN , SiCOH , 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 Atomic layer deposition (ALD) process), lower

process temperatures, reactivity with various oxidants and low film contamination, in addition to high deposition rates, conformality and consistency of films produced.

Organoaminosilanes have been used as precursors for CVD of Si-containing films. US 7192626 to Dussarrat *et al.* discloses the use of trisilylamine $N(SiH_3)_3$ for deposition of SiN films. Other organoaminosilane precursors include diisopropylaminosilane $[SiH_3(NiPr_2)]$ and analogous $SiH_3(NR_2)$ compounds disclosed in, for example, US 7875312 to Thridandam *et al.* and phenylmethyaminosilane $[SiH_3(NPhMe)]$ and related substituted silylanilines disclosed in, for example, EP 2392691 to Xiao *et al.*

WO2006/097525 to Dussarrat *et al.* disclosed another related class of Si precursors for CVD of Si-containing films given by a general formula $(R^1R^2N)_xSiH_{4-x}$ wherein x is an integer between 1 and 4 and the substituent R is H, C_1-C_6 linear, branched, or cyclic carbon chains.

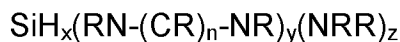
Hunks *et al.* disclose a wide range of Si-containing precursors in US2010/0164057, including silicon compounds having the formula $R_{4-x}SiL_x$, wherein x is an integer having a value from 1 to 3, R may be selected from the group consisting of H, branched and unbranched C_1-C_6 alkyl, C_3-C_8 cycloalkyl, and C_6-C_{13} aryl groups, and L may be selected from the group consisting of isocyanato, methylethylketoxime, trifluoroacetate, triflate, acyloxy, β -diketiminato, β -di-iminato, amidinate, guanidinate, alkylamino, hydride, alkoxide, or formate ligands. Pinnavaia *et al.* claim a method for the preparation of a porous synthetic, semi-crystalline hybrid organic-inorganic silicon oxide composition from silicon acetylacetonate and silicon 1,3-diketone precursors (US6465387).

Dussarrat *et al.* disclosed silicon amidinate precursors in WO2014/015232 A1 having the form $H_3Si(amd)$ and silicon β -diketiminato precursors in WO2014015237 A1.

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.

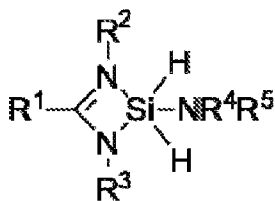
Summary

Disclosed are Si-containing film forming compositions comprising organosilane precursors having the formula:

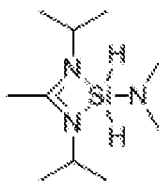


wherein each R is independently selected from the group consisting of H, a C₁ to C₆ alkyl group, and a C₃-C₂₀ aryl or heterocycle group; n = 1 or 3; x=0, 1, or 2; y = 1 or 2; and z = 1, 2, or 3; and x+y+z = 4, provided that x≠2 when y=2. The disclosed Si-containing film forming compositions may have one or more of the following aspects:

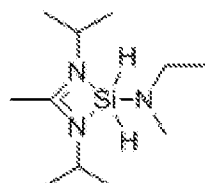
- When n = 1, x = 1 or 2, y = 1 or 2, and z = 1 or 2, the organosilane precursor contains amidinate, amido and hydride functional groups;
- When n = 3, x = 1 or 2, y = 1 or 2, and z = 1 or 2, the organosilane precursor contains β-diketimate, amido and hydride functional groups;
- n = 1;
- x = 2;
- y = 1;
- z = 1;
- the organosilane precursor having the formula:



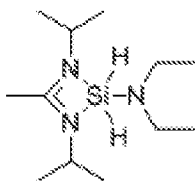
- R¹ and R² and/or R¹ and R³ and/or R⁴ and R⁵ being joined to form cyclic chains;
- the organosilane precursor being:



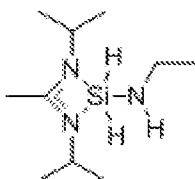
- the organosilane precursor being:



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- the organosilane precursor being:

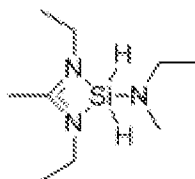


- the organosilane precursor being:

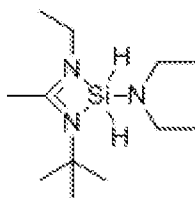


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- the organosilane precursor being:

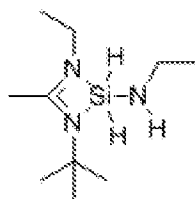


- the organosilane precursor being:

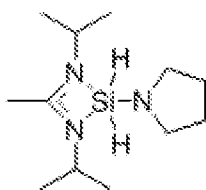


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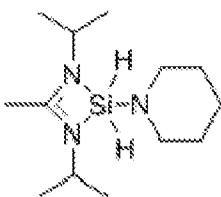
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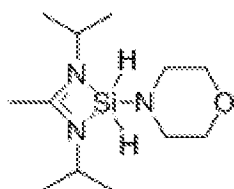
- the organosilane precursor being:



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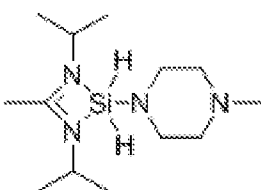


- the organosilane precursor being:



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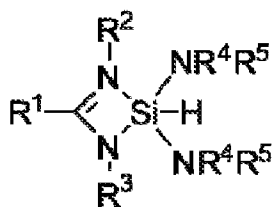
- the organosilane precursor being:



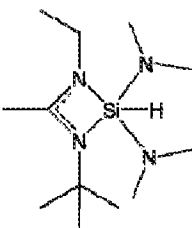
- $x = 1$;
- $z = 2$;

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- the organosilane precursor having the formula:

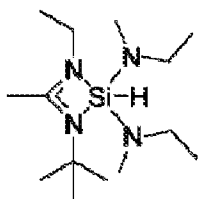


- R^1 and R^2 and/or R^1 and R^3 and/or R^4 and R^5 being joined to form cyclic chains;
- the organosilane precursor being:

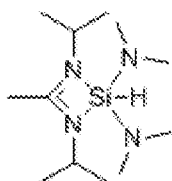


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- the organosilane precursor being:

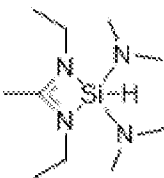


- the organosilane precursor being:



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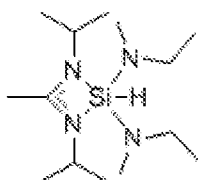
- the organosilane precursor being:



- the organosilane precursor being:

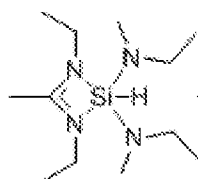


- the organosilane precursor being:

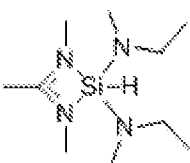


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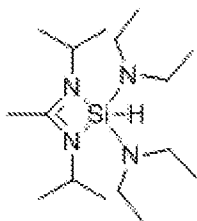
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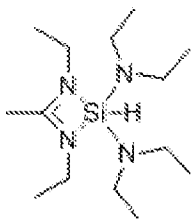
- the organosilane precursor being:



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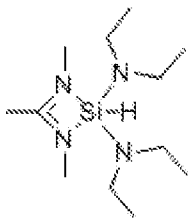


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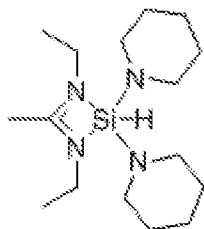


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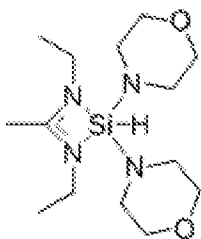
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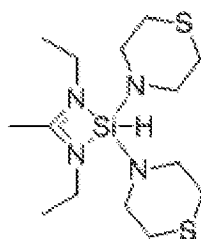


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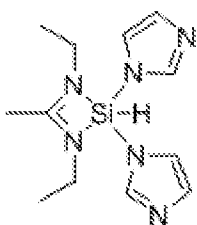


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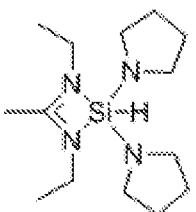
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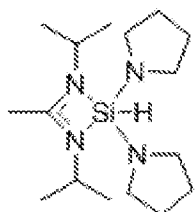
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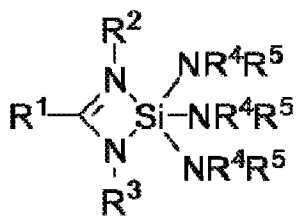
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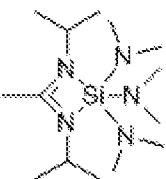
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- the organosilane precursor being:



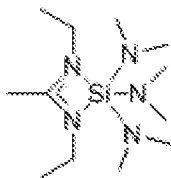
- $x = 0$;
- $z = 3$;
- the organosilane precursor having the formula:



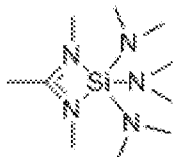
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- R^1 and R^2 and/or R^1 and R^3 and/or R^4 and R^5 being joined to form cyclic chains;
 - the organosilane precursor being:



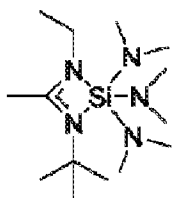
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- the organosilane precursor being:



- the organosilane precursor being:

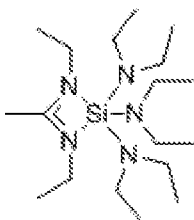


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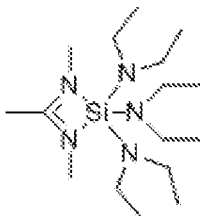


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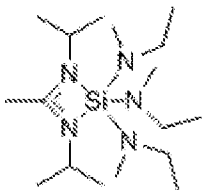


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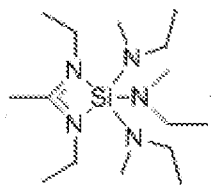


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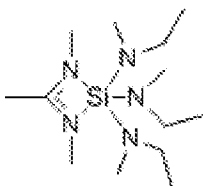
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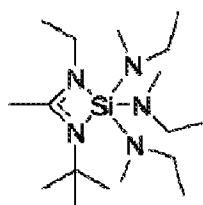
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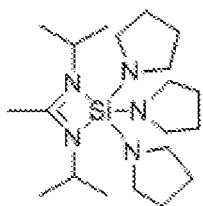


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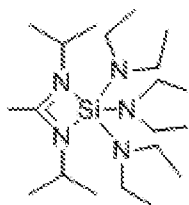


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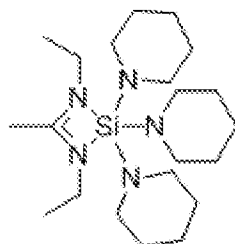


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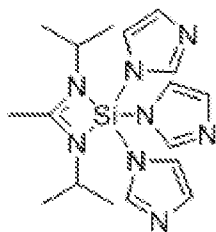


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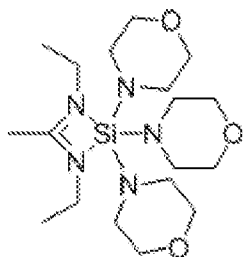
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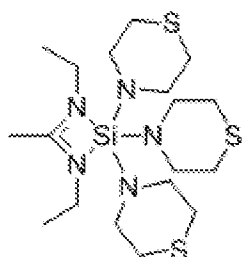
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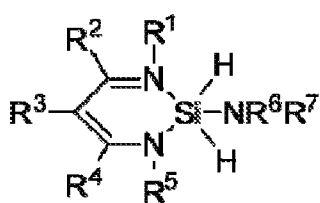


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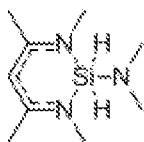
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- $n = 3$;
- $x = 2$;
- $z = 1$;
- the organosilane precursor having the formula:



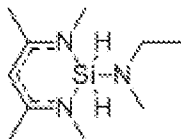
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- R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 and/or R^4 and R^5 and/or R^6 and R^7 being joined to form cyclic chains;
- the organosilane precursor being:

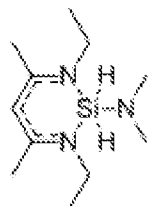


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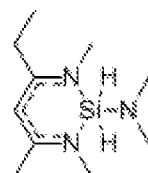
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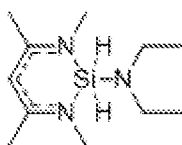


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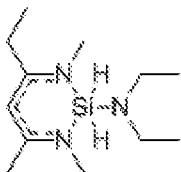


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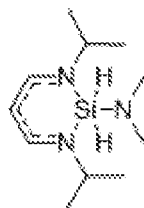


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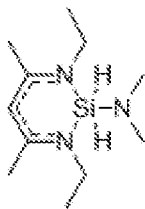


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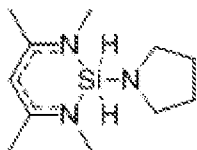
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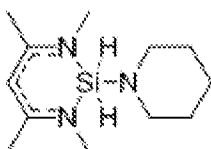
- the organosilane precursor being:



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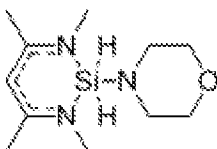


- the organosilane precursor being:

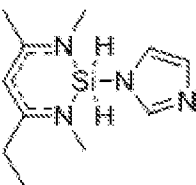


5

- the organosilane precursor being:

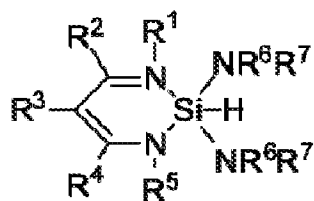


- the organosilane precursor being:



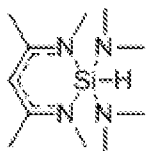
10

- $x = 1$;
- $z = 2$;
- the organosilane precursor having the formula:

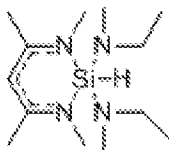


15

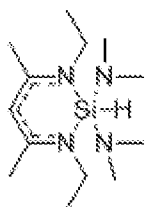
- R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 and/or R^4 and R^5 and/or R^6 and R^7 being joined to form cyclic chains;
- the organosilane precursor being:



- the organosilane precursor being:

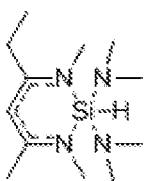


- the organosilane precursor being:

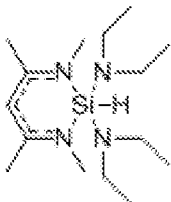


5

- the organosilane precursor being:

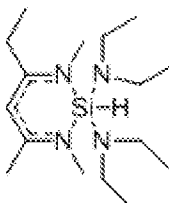


- the organosilane precursor being:

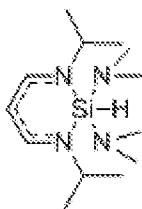


10

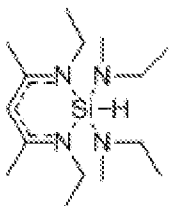
- the organosilane precursor being:



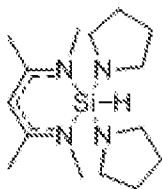
- the organosilane precursor being:



- the organosilane precursor being:

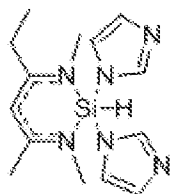


- the organosilane precursor being:



5

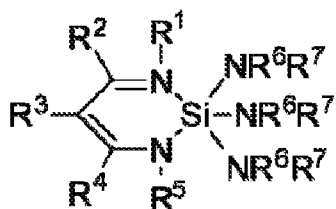
- the organosilane precursor being:



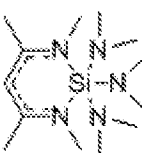
- $x = 0$;
- $z = 3$;

10

- the organosilane precursor having the formula:



- R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 and/or R^4 and R^5 and/or R^6 and R^7 being joined to form cyclic chains;
- the organosilane precursor being:



15

- the organosilane precursor being:

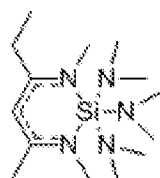


- the organosilane precursor being:

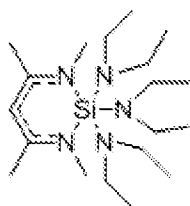


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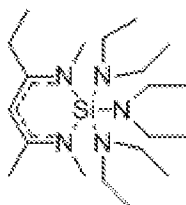
- the organosilane precursor being:



- the organosilane precursor being:



- the organosilane precursor being:

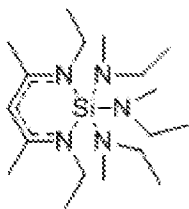


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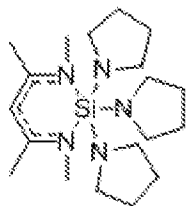
- the organosilane precursor being:



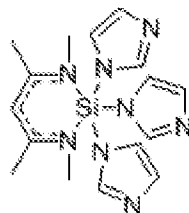
- the organosilane precursor being:



- the organosilane precursor being:



- the organosilane precursor being:

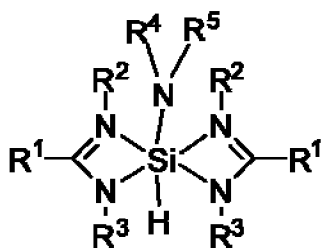


5

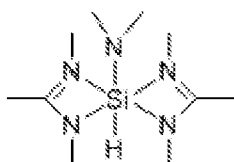
- $n = 1$;
- $x = 1$;
- $y = 2$;
- $z = 1$;

10

- the organosilane precursor having the formula:

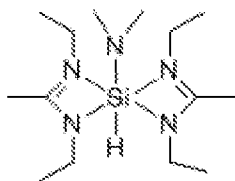


- R^1 and R^2 and/or R^1 and R^3 and/or R^4 and R^5 being joined to form cyclic chains;
- the organosilane precursor being:

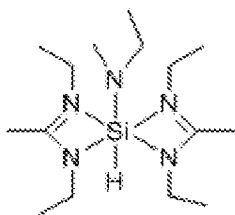


15

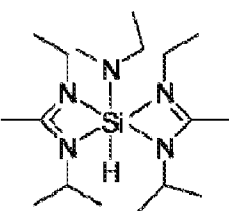
- the organosilane precursor being:



- the organosilane precursor being:

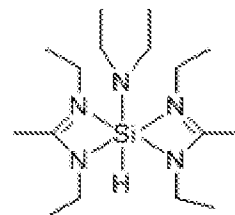


- the organosilane precursor being:

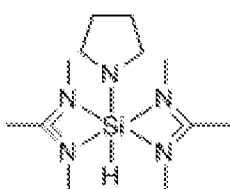


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- the organosilane precursor being:

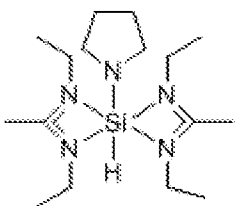


- the organosilane precursor being:

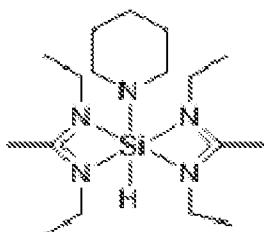


10

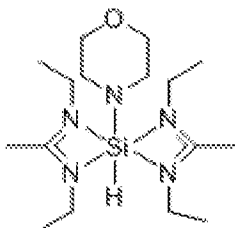
- the organosilane precursor being:



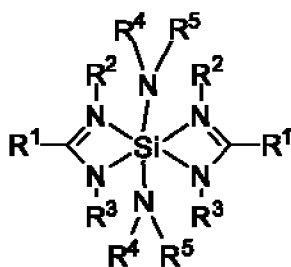
- the organosilane precursor being:



- the organosilane precursor being:

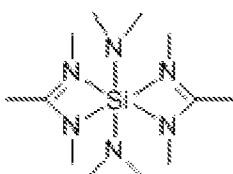


- $x = 0$;
- $z = 2$;
- the organosilane precursor having the formula:

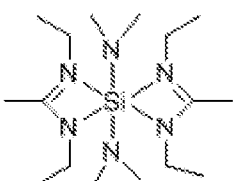


- R^1 and R^2 and/or R^1 and R^3 and/or R^4 and R^5 being joined to form cyclic chains;

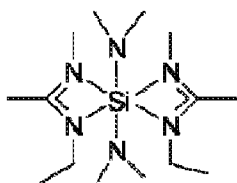
- the organosilane precursor being:



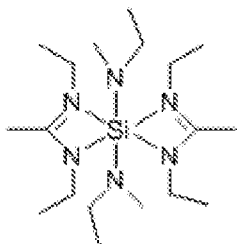
- the organosilane precursor being:



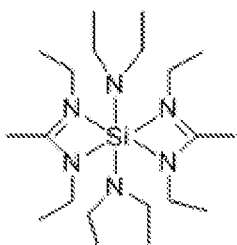
- the organosilane precursor being:



- the organosilane precursor being:

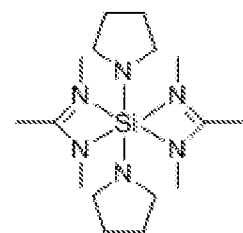


- the organosilane precursor being:

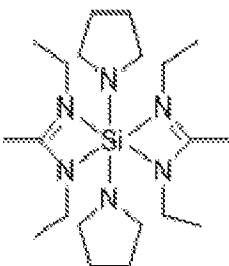


5

- the organosilane precursor being:

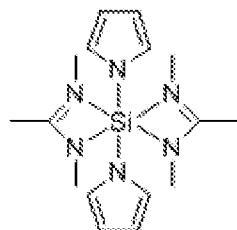


- the organosilane precursor being:

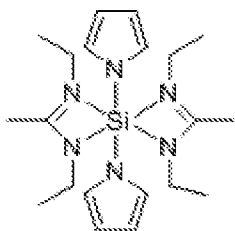


10

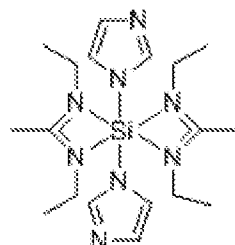
- the organosilane precursor being:



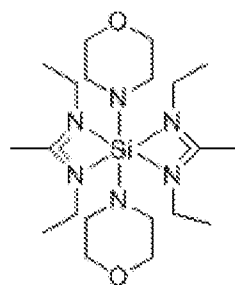
- the organosilane precursor being:



- the organosilane precursor being:

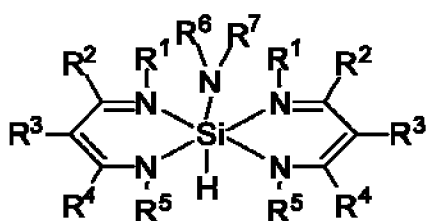


- 5
- the organosilane precursor being:

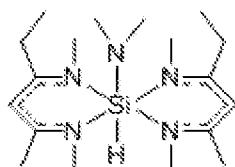


- $n = 3$;
- $x = 1$;
- $z = 1$;

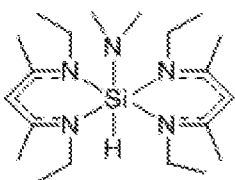
- 10
- the organosilane precursor having the formula:



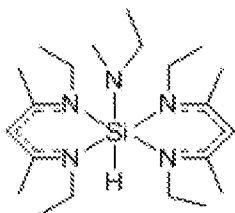
- R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 and/or R^4 and R^5 and/or R^6 and R^7 being joined to form cyclic chains;
- the organosilane precursor being:



- the organosilane precursor being:

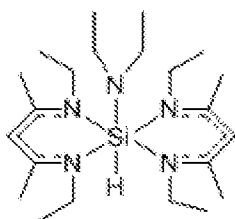


- the organosilane precursor being:

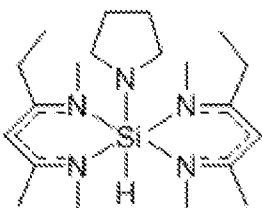


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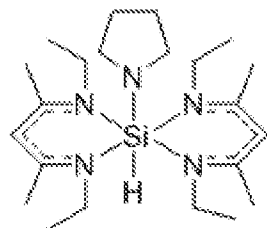
- the organosilane precursor being:



- the organosilane precursor being:

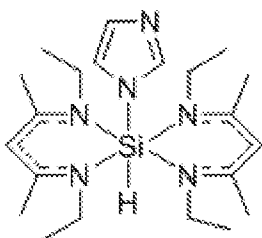


- the organosilane precursor being:

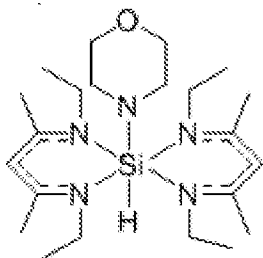


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- the organosilane precursor being:

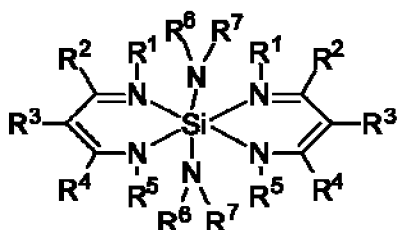


- the organosilane precursor being:

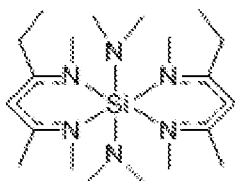


- $x = 0$;
- $z = 2$;

- 5
- the organosilane precursor having the formula:

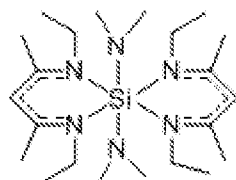


- R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 and/or R^4 and R^5 and/or R^6 and R^7 being joined to form cyclic chains;
- the organosilane precursor being:

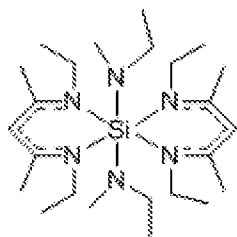


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- the organosilane precursor being:

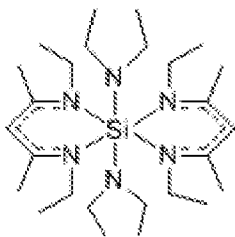


- the organosilane precursor being:

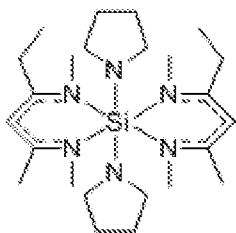


15

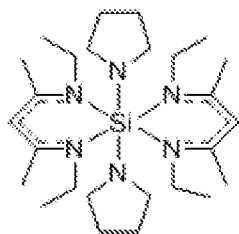
- the organosilane precursor being:



- the organosilane precursor being:

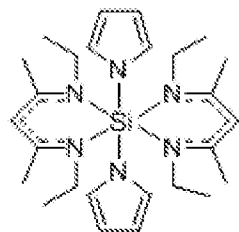


- the organosilane precursor being:

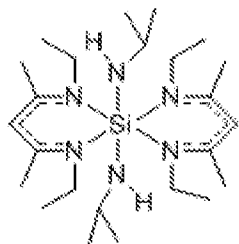


5

- the organosilane precursor being:

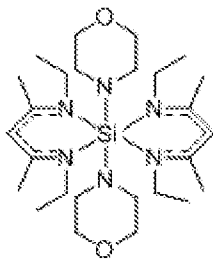


- the organosilane precursor being:

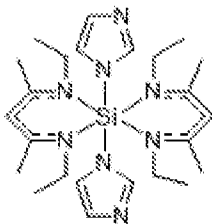


10

- the organosilane precursor being:



- the organosilane precursor being:



- the Si-containing film forming composition comprising between approximately 95% w/w and approximately 100% w/w of the organosilane precursor ;
- the Si-containing film forming composition comprising between approximately 5 % w/w and approximately 50% w/w of the organosilane precursor ;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Al;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw As;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Ba;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Be;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Bi;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Cd;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Ca;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Cr;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Co;

- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Cu;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Ga;
- 5 • the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Ge;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Hf;
- 10 • the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Zr;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw In;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Fe;
- 15 • the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Pb;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Li;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Mg;
- 20 • the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Mn;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw W;
- 25 • the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Ni;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw K;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Na;
- 30 • the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Sr;

- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Th;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Sn;
- 5 • the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Ti;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw U;
- 10 • the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw V;
- the Si-containing film forming composition comprising between approximately 0 ppbw and approximately 100 ppbw Zn;
- the Si-containing film forming composition comprising between approximately 0 ppmw and approximately 100 ppmw Cl;
- 15 • the Si-containing film forming composition comprising between approximately 0 ppmw and approximately 100 ppmw Br; and
- the Si-containing film forming composition comprising between approximately 0 ppmw and approximately 100 ppmw I.

Also disclosed is a Si-containing film forming composition delivery device
20 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;
- 25 • 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; and
- 30 • further comprising a diaphragm valve on the inlet and the outlet.

Also disclosed are methods of depositing a Si-containing layer on a substrate. The Si-containing film forming composition disclosed above is introduced into a

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

- 5 • introducing into the reactor a vapor comprising a second precursor;
- an element of the second precursor being selected from the group consisting of group 2, group 13, group 14, transition metal, lanthanides, and combinations thereof;
- the element of the second precursor being selected from Mg, Ca, Sr, Ba, Zr, Hf, Ti, Nb, Ta, Al, Si, Ge, Y, or lanthanides;
- 10 • introducing a reactant into the reactor;
- the reactant being selected from the group consisting of O₂, O₃, H₂O, H₂O₂, NO, NO₂, a carboxylic acid, radicals thereof, and combinations thereof;
- the reactant being plasma treated oxygen;
- 15 • the reactant being ozone;
- the Si-containing layer being a silicon oxide layer;
- the reactant being selected from the group consisting of H₂, 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 Me₂SiH₂, Et₂SiH₂, MeSiH₃, EtSiH₃), hydrazines (such as N₂H₄, MeHNNH₂, MeHNNHMe), organic amines (such as NMeH₂, NEtH₂, NMe₂H, NEt₂H, NMe₃, NEt₃, (SiMe₃)₂NH), pyrazoline, pyridine, B-containing molecules (such as B₂H₆, 9-borabicyclo[3,3,1]nonane, trimethylboron, triethylboron, borazine), alkyl metals (such as
- 20 trimethylaluminum, triethylaluminum, dimethylzinc, diethylzinc), radical species thereof, and mixtures thereof;
- the reactant being selected from the group consisting of H₂, NH₃, SiH₄, Si₂H₆, Si₃H₈, SiH₂Me₂, SiH₂Et₂, N(SiH₃)₃, hydrogen radicals thereof, and mixtures thereof;
- 30 • the reactant is selected from the group consisting of SiHCl₃, Si₂Cl₆, Si₂HCl₅, Si₂H₂Cl₄, and cyclo-Si₆H₆Cl₆;
- the reactant being HCDS or PCDS;
- the vapor deposition method being a chemical vapor deposition process;

- the vapor deposition method being an ALD process;
- the vapor deposition method being a spatial ALD process;
- the silicon-containing layer being Si;
- the silicon-containing layer being SiO₂;
- 5 • the silicon-containing layer being SiN;
- the silicon-containing layer being SiON;
- the silicon-containing layer being SiCN; and
- the silicon-containing layer being SiCOH.

Also disclosed are methods of forming Si-containing films on substrates. A
 10 solution comprising any of the Si-containing film forming compositions disclosed
 above is contacted with the substrate and the Si-containing film formed via a spin
 coating, spray coating, dip coating, or slit coating technique. The disclosed methods
 may include the following aspects:

- the Si-containing film forming composition comprising ethanol;
- 15 • the Si-containing film forming composition comprising isopropanol;
- forming the Si-containing film via a spin coating technique;
- forming the Si-containing film via a spray coating technique;
- forming the Si-containing film via a dip coating technique;
- forming the Si-containing film via a slit coating technique;
- 20 • annealing the Si-containing film; or
- laser treating the Si-containing film.

Notation and Nomenclature

Certain abbreviations, symbols, and terms are used throughout the following
 25 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” mean $\pm 10\%$ of the value
 stated.

As used herein, the term “independently” when used in the context of
 30 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.

5 As used herein, the term “alkyl group” refers to saturated functional groups containing exclusively carbon and hydrogen atoms. Further, the term “alkyl group” refers to linear, branched, or cyclic alkyl groups. Examples of linear alkyl groups include without limitation, methyl groups, ethyl groups, n-propyl groups, n-butyl groups, etc. Examples of branched alkyls groups include without limitation, t-butyl.
10 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
15 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);
20 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-
25 N-C(Me)-N-R amidinate ligand, with R being an alkyl group (e.g., iPr_{amd} is iPr-N-C(Me)-N-iPr).

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

30 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., SiO_2 , SiO_3 , Si_3N_4). The layers may include pure (Si) layers, carbide (SiO_Cp) 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 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.

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.).

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:

FIG 1 is a side view of one embodiment of the Si-containing film forming composition chemistry delivery device disclosed herein;

FIG 2 is a side view of a second embodiment of the Si-containing film forming delivery device disclosed herein;

FIG 3 is a graph demonstrating the percentage of mass loss as a function of temperature in an open cup thermogravimetric analysis of purified $\text{SiH}(\text{NMe}_2)_2(\text{iPr-AMD})$ and $\text{SiH}_3(\text{iPr-AMD})$; and

FIG 4 is a graph showing the deposition rate and index of refraction as a function of temperature for the Si containing films deposited by PEALD using $\text{SiH}(\text{NMe}_2)_2(\text{iPr-AMD})$.

Description of Preferred Embodiments

Disclosed are Si-containing film forming compositions comprising organosilane precursors having the following formula:



wherein each R is independently selected from the group consisting of H, a C₁ to C₆ alkyl group, and a C₃-C₂₀ aryl or heterocycle group; n = 1 or 3; x=0, 1, or 2; y = 1 or 2; and z = 1, 2 or 3; and x+y+z = 4, provided that x≠2 when y=2.

As illustrated below, the disclosed organosilane precursors may have a
5 pentacoordinate or hexacoordinate silicon (+IV) center.

When y=1 in formula (I), the RN-(CR)_n-NR ligand bonds to the silicon atom via its two N atoms, resulting in a precursor with a pentacoordinate Si(IV) center. The (RN-(CR)_n-NR) ligand forms a chelated ring structure with the silicon via one or three CR(s) (n = 1 or 3). The carbon atom(s) in the backbone of the bidentate monoanionic
10 ligand may be sp² hybridized, resulting in a delocalized charge across the ligand. The carbon atoms may independently be substituted by H, C₁-C₆ alkyl groups, or C₃-C₂₀ aryl or heterocycle groups.

When y=2 in formula (I), each of the two (RN-(CR)_n-NR) ligands bond to the silicon atom via the two N atoms, resulting in a precursor with a hexacoordinate
15 Si(IV) center. The hexacoordinate organosilane compounds contain two ring structures, each formed by the bonds between the two nitrogens of the (RN-(CR)_n-NR) ligand with the silicon atom. The carbon atoms in the (RN-(CR)_n-NR) ligands may be sp² hybridized, resulting in a delocalized charge across the monoanionic ligand. Alternatively, the carbon atoms in the (RN-(CR)_n-NR) ligands may be sp³
20 hybridized or some combination of sp² and sp³ hybridized, resulting in a negative charge on one nitrogen in each ring structure and a neutral charge on the other nitrogen in the same ring structure. Each of the nitrogen and carbon atoms may independently be substituted by H, C₁-C₆ alkyl groups, or C₃-C₂₀ aryl or heterocycle groups.

25 The disclosed organosilane precursors may be more reactive with the substrate and/or any co-reactants than other Si +IV precursors due to hypercoordination at the silicon atom. In other words, although the silicon atom is +IV, the monoanionic chelating ligand results in a total of 5 or 6 bonds to the silicon atom.

30 The disclosed organosilane precursor may contain one or two hydrogen atoms directly bonded to the Si atom. These Si-H bonds may help increase the volatility of the precursor, which is important for vapor deposition processes. The disclosed organosilane precursors contain no Si-halogen bonds, which is important

because halogens may damage other layers in the substrate (e.g., low k layers, copper interconnect layers, etc.). 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 Si-halogen containing precursors because the H atoms occupy less surface area, resulting in more molecules on the substrate surface.

The disclosed organosilane precursor may contain one, two, or three amino groups directly bonded to the Si atom. These Si-N bonds may help increase thermal stability of the precursor, which is also important for vapor deposition processes. The amino group may also help incorporate N and C atoms into the resulting film, which may make the resulting layer more resistant to any subsequent etching processes.

One of ordinary skill in the art will recognize that the volatility provided by the Si-H bonds competes directly with the thermal stability provided by the amino groups. Applicants believe that at least $\text{SiH}(\text{NMe}_2)_2(\text{iPr-amd})$, $\text{SiH}_2(\text{NMe}_2)(\text{iPr-amd})$, and $\text{SiH}_2(\text{NEt}_2)(\text{iPr-amd})$ successfully balance those competing characteristics.

One of ordinary skill in the art will recognize that embodiments in which $n=1$ may produce precursors having higher volatility and lower melting points, being more suitable for vapor deposition. Embodiments in which $n=3$ may also be suitable for vapor deposition when the resulting silicon-containing film also contains carbon. Embodiments in which $n=3$ may also be suitable for casting deposition methods, such as spin-on or dip coating.

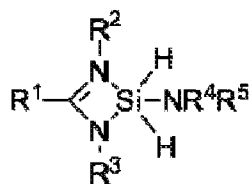
Preferably, the disclosed Si-containing film forming compositions have suitable properties for vapor depositions methods, such as high vapor pressure, low melting point (preferably being in liquid form at room temperature), low sublimation point, and high thermal stability.

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;
- suitable reactivity with the substrate to permit a wide self-limited ALD window, allowing deposition of a variety of Si-, Ge- and Sn-containing

films, including ternary or quaternary materials, by using one or a combination of reactants (selected from the group comprising of H_2 , NH_3 , O_2 , H_2O , O_3 , SiH_4 , Si_2H_6 , Si_3H_8 , $SiH(NMe_2)_3$ (TriDMAS or TDMAS), $SiH_2(NMe_2)_2$ (BDMAS), $SiH_2(N(Et)_2)_2$ (BDEAS), $SiH(N(Et)_2)_3$ (TDEAS), $SiH(NEtMe)_3$ (TEMAS), $(SiH_3)_3N$, $(SiH_3)_2O$, an aluminum-containing precursor such as trimethyl aluminum (TMA), (*tert*-butylimido)tris(diethylamido) tantalum (TBTDET), tantalum tetraethoxide dimethylaminoethoxide (TAT-DMAE), polyethylene terephthalate (PET), (*tert*-butylimido)bis(dimethylamino)niobium (TBTDEN), polyethylene naphthalate (PEN), lanthanide-containing precursors such as $Ln(tmhd)_3$ (lanthanide (2,2,6,6-tetramethyl-3,5-heptanedione)₃)).

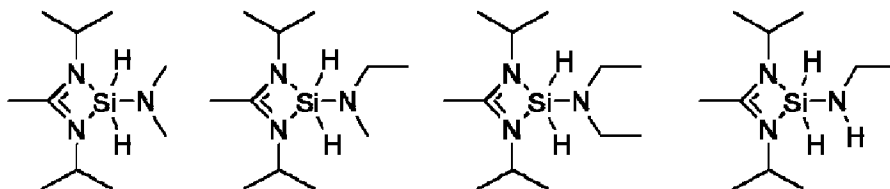
When $n = 1$, $x = 2$, $y = 1$ and $z = 1$ in formula (I), exemplary organosilane precursors contain amidinate, amido and hydride functional groups and have the structural formula:

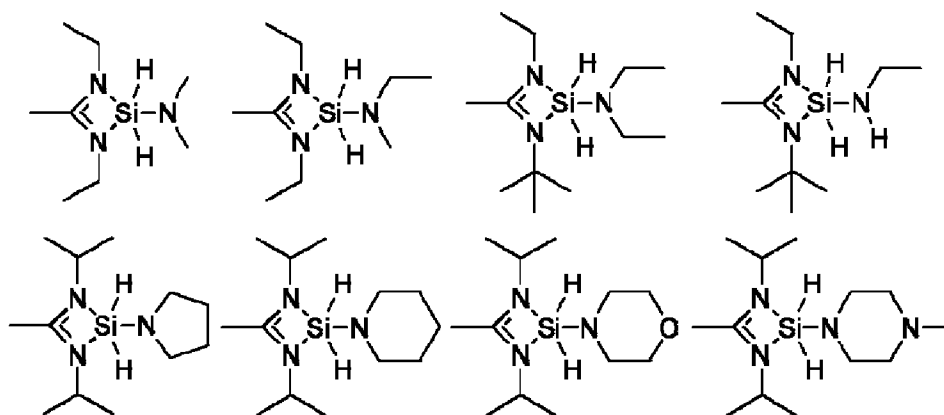


wherein R^1 , R^2 , R^3 , R^4 and R^5 may each independently be H, a C_1 to C_6 alkyl group, or a C_3 - C_{20} aryl or heterocycle group, and R^1 and R^2 and/or R^1 and R^3 and/or R^4 and R^5 being joined to form cyclic chains.

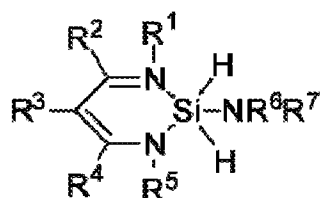
Exemplary amino(amidinate)silanes having the formula

$H_2Si[RN(CR)NR](NRR)$ include:





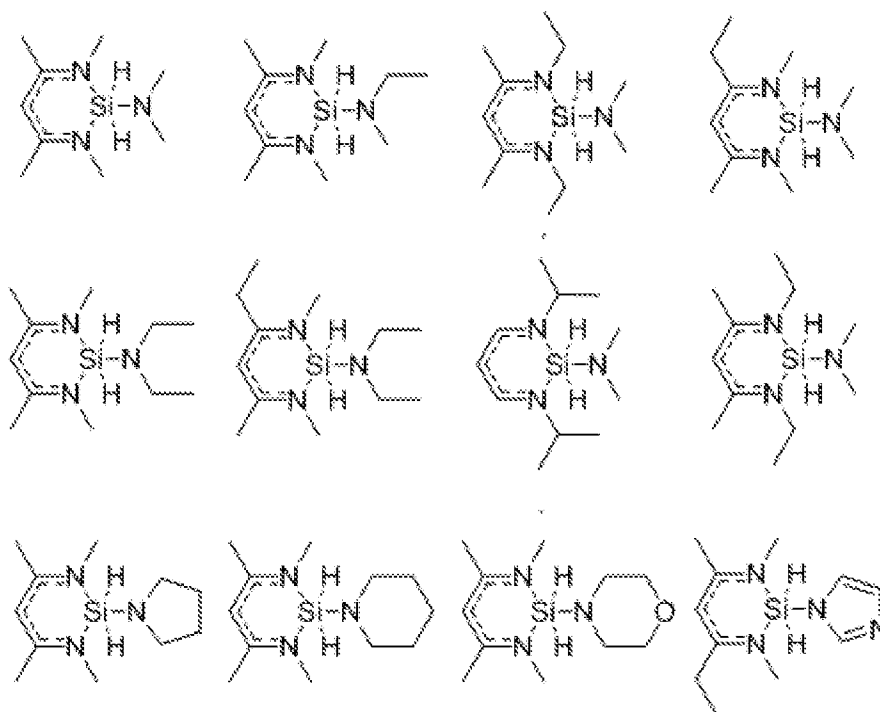
When $n = 3$, $x = 2$, $y = 1$ and $z = 1$ in formula (I), exemplary organosilane precursors contain β -diketiminato, amido and hydride functional groups and have the structural formula:



wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 may each independently be H, a C_1 to C_6 alkyl group, or a C_3 - C_{20} aryl or heterocycle group, and R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 and/or R^4 and R^5 and/or R^6 and R^7 being joined to form cyclic chains.

Exemplary amino(β -diketiminato)silanes having the formula

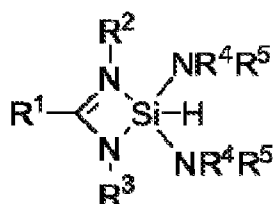
HSi[RN(CR)₃NR](NRR)₂ include:



The $\text{H}_2\text{Si}[\text{RN}(\text{CR})_n\text{NR}](\text{NRR})$, with $n = 1$ or 3 , precursors may be synthesized by combining a hydrocarbon solution of SiX_2H_2 , wherein X is Cl , Br , I , or triflate (SO_3CF_3), with a neat or hydrocarbon solution of the first ligand compound, either $\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$ or $\text{Li}[\text{NRR}]$, followed by addition of a neat or hydrocarbon solution of the second ligand compound, either $\text{Li}[\text{NRR}]$ or $\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$, under atmosphere of nitrogen, the outlet of the mixing flask being connected to an oil bubbler to inhibit backflow of air and moisture. A second synthesis route to the disclosed $\text{H}_2\text{Si}[\text{RN}(\text{CR})_n\text{NR}](\text{NRR})$ precursors is by combining a hydrocarbon solution of SiX_2H_2 , wherein X is Cl , Br , I , or triflate (SO_3CF_3), with a neat or hydrocarbon solution of the protonated first ligand ($\text{HRN}(\text{CR})_n\text{NR}$ or HNRR) followed by a neat or hydrocarbon solution of the protonated second ligand (HNRR or $\text{HRN}(\text{CR})_n\text{NR}$), performed under an inert atmosphere. Alternatively, the disclosed $\text{H}_2\text{Si}[\text{RN}(\text{CR})_n\text{NR}](\text{NRR})$ precursors may be synthesized by reaction of $\text{SiH}_n\text{Cl}_{4-n}$ wherein $n = 0$ or 1 , with sequentially one equivalent each of the first and second ligand compounds ($\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$ or $\text{Li}[\text{NRR}]$) followed by subsequent reduction using a selected metal hydride, such as lithium aluminum hydride (LAH). In all three synthesis routes, the resulting solution may be stirred at room temperature overnight.

Exemplary hydrocarbon solutions suitable for these synthesis methods include diethyl ether, pentane, hexane, or toluene. The resulting suspension is filtered and the resulting solution distilled to remove solvent. Purification of the resulting liquid or solid is carried out by distillation or sublimation, respectively. Except for the ligand compounds $\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$ or $\text{Li}[\text{NRR}]$ all of the starting materials are commercially available. The ligand compounds may be synthesized by combining a hydrocarbon solution of metalorganic salt (*i.e.*, alkyl lithium) to a hydrocarbon solution of the appropriate amine, amidine, or β -diketimine.

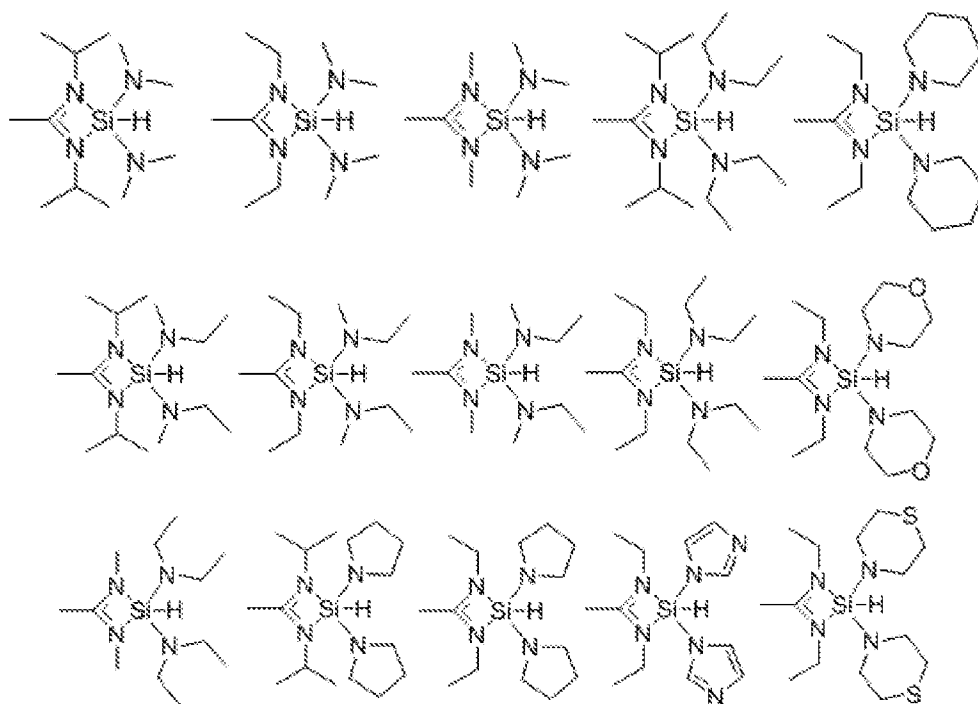
When $n = 1$, $x = 1$, $y = 1$ and $z = 2$ in formula (I), exemplary organosilane precursors contain amidinate, amido and hydride functional groups and have the structural formula:



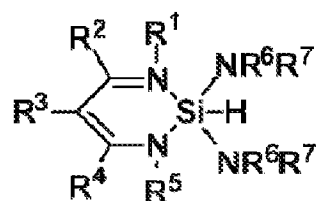
wherein R^1 , R^2 , R^3 , R^4 and R^5 may each independently be H, a C_1 to C_6 alkyl group, or a C_3 - C_{20} aryl or heterocycle group, and R^1 and R^2 and/or R^1 and R^3 and/or R^4 and R^5 being joined to form cyclic chains.

Exemplary amino(amidinate)silanes having the formula

5 $HSi[RN(CR)NR](NRR)_2$ include:



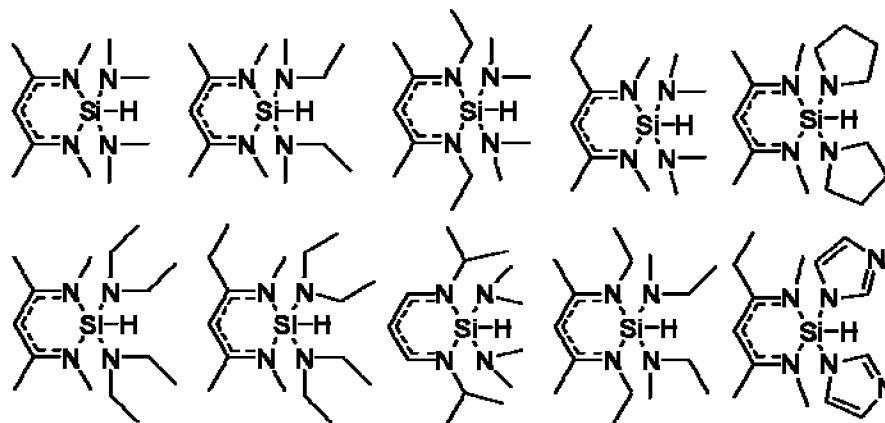
10 When $n = 3$, $x = 1$, $y = 1$ and $z = 2$ in formula (I), exemplary organosilane precursors contain β -diketiminato, amido and hydride functional groups and have the structural formula:



15 wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 may each independently be H, a C_1 to C_6 alkyl group, or a C_3 - C_{20} aryl or heterocycle group, and R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 and/or R^4 and R^5 and/or R^6 and R^7 being joined to form cyclic chains.

Exemplary diamino(β -diketiminato)silanes having the formula

$HSi[RN(CR)_3NR](NRR)_2$ include:



The $\text{HSi}[\text{RN}(\text{CR})_n\text{NR}](\text{NRR})_2$ precursors, with $n=1$ or 3 , may be synthesized by combining a hydrocarbon solution of SiX_3H , wherein X is Cl , Br , I , or triflate (SO_3CF_3), with a neat or hydrocarbon solution of the first ligand compound,

5 $\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$ or $\text{Li}[\text{NRR}]$ followed by addition of a neat or hydrocarbon solution of the second ligand compound, $\text{Li}[\text{NRR}]$ or $\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$, under atmosphere of nitrogen, the outlet of the mixing flask being connected to an oil bubbler to inhibit backflow of air and moisture. A second synthetic route to the disclosed

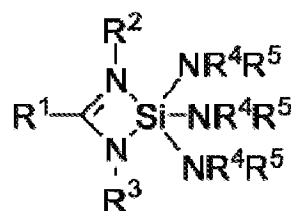
$\text{HSi}[\text{RN}(\text{CR})_n\text{NR}](\text{NRR})_2$ precursors is by combining a hydrocarbon solution of

10 SiX_3H , wherein X is Cl , Br , I , or triflate (SO_3CF_3), with a neat or hydrocarbon solution of the protonated first ligand ($\text{HRN}(\text{CR})_n\text{NR}$ or HNRR) followed by a neat or hydrocarbon solution of the protonated second ligand (HNRR or $\text{HRN}(\text{CR})_n\text{NR}$) performed under an inert atmosphere. Alternatively, the disclosed

15 $\text{HSi}[\text{RN}(\text{CR})_n\text{NR}](\text{NRR})_2$ precursors may be synthesized by reaction of SiCl_4 with sequentially one equivalent of the first ligand and two equivalents of the second ligand compounds ($\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$ or $\text{Li}[\text{NRR}]$) followed by subsequent reduction using a selected metal hydride such as LAH . In all three synthesis routes, the resulting solution may be stirred at room temperature overnight.

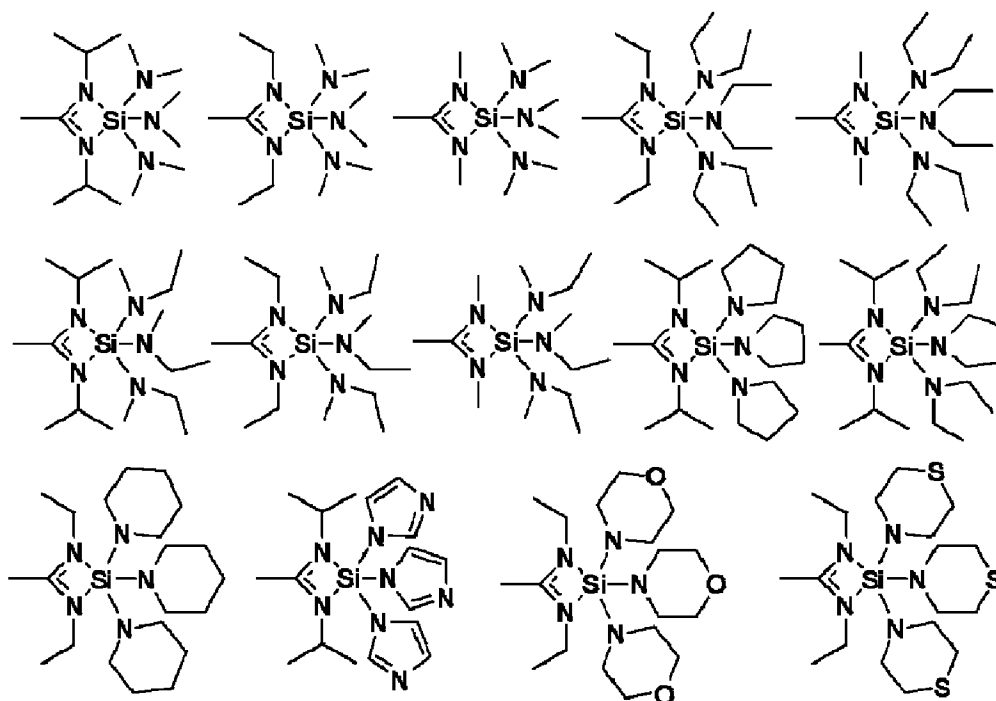
Exemplary hydrocarbon solutions suitable for these synthesis methods
 20 include diethyl ether, pentane, hexane, or toluene. The resulting suspension is filtered and the resulting solution distilled to remove solvent. Purification of the resulting liquid or solid is carried out by distillation or sublimation, respectively. Except for the ligand compounds $\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$ or $\text{Li}[\text{NRR}]$ all of the starting materials are commercially available. The ligand compound may be synthesized by
 25 combining a hydrocarbon solution of metalorganic salt (*i.e.*, alkyl lithium) to a hydrocarbon solution of the appropriate amine, amidine, or β -diketimine.

When $n = 1$, $x = 0$, $y = 1$ and $z = 3$ in formula (I), exemplary organosilane precursors contain amidinate and amido functional groups and have the structural formula:



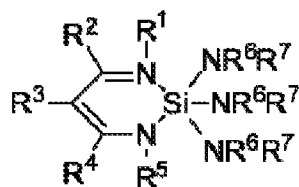
- 5 wherein R^1 , R^2 , R^3 , R^4 and R^5 may each independently be H, a C_1 to C_6 alkyl group, or a C_3 - C_{20} aryl or heterocycle group, and R^1 and R^2 and/or R^1 and R^3 and/or R^4 and R^5 being joined to form cyclic chains.

Exemplary tris(amino)amidinosilanes having the formula $Si[RN(CR)NR](NRR)_3$ include:



10

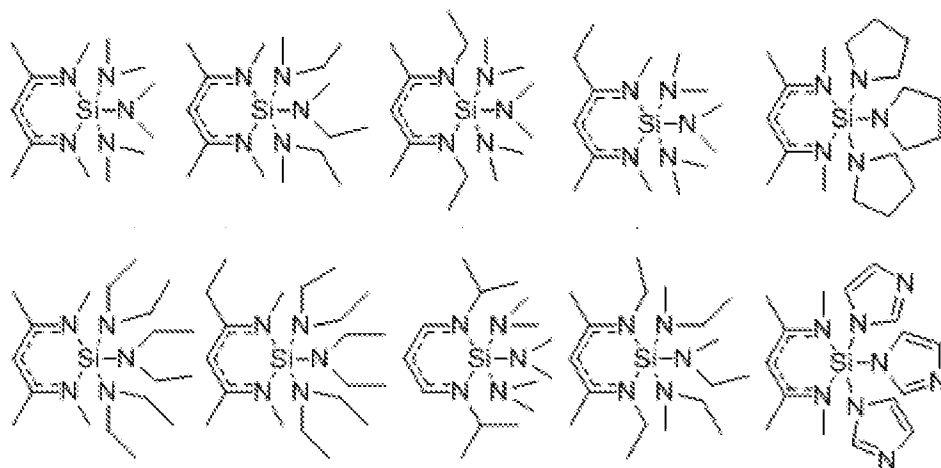
When $n = 3$, $x = 0$, $y = 1$ and $z = 3$ in formula (I), exemplary organosilane precursors contain β -diketiminato and amido functional groups and have the structural formula:



wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 may each independently be H, a C_1 to C_6 alkyl group, or a C_3 - C_{20} aryl or heterocycle group, and R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 and/or R^4 and R^5 and/or R^6 and R^7 being joined to form cyclic chains.

Exemplary triamino(β -diketiminato)silanes having the formula

5 $Si[RN(CR)_3NR](NRR)_3$ include:

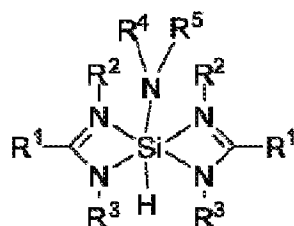


The $Si[RN(CR)_nNR](NRR)_3$ precursors, with $n=1$ or 3 , may be synthesized by combining a hydrocarbon solution of SiX_4 , wherein X is Cl, Br, I, or triflate (SO_3CF_3), with a neat or hydrocarbon solution of the first ligand compound, $Li[RN(CR)_nNR]$ or $Li[NRR]$, followed by addition of a neat or hydrocarbon solution of the second ligand compound, $Li[NRR]$ or $Li[RN(CR)_nNR]$, under atmosphere of nitrogen, the outlet of the mixing flask being connected to an oil bubbler to inhibit backflow of air and moisture. A second synthetic route to the disclosed $Si[RN(CR)_nNR](NRR)_3$ precursors is by combining a hydrocarbon solution of SiX_4 , wherein X is Cl, Br, I, or triflate (SO_3CF_3), with a neat or hydrocarbon solution of the protonated first ligand ($HRN(CR)_nNR$ or $HNRR$) followed by a neat or hydrocarbon solution of the protonated second ligand ($HNRR$ or $HRN(CR)_nNR$) performed under an inert atmosphere.

Exemplary hydrocarbon solutions suitable for these synthesis methods include diethyl ether, pentane, hexane, or toluene. The resulting suspension is filtered and the resulting solution distilled to remove solvent. Purification of the resulting liquid or solid is carried out by distillation or sublimation, respectively. Except for the ligand compounds $Li[RN(CR)_nNR]$ or $Li[NRR]$ all of the starting materials are commercially available. The ligand compound may be synthesized by

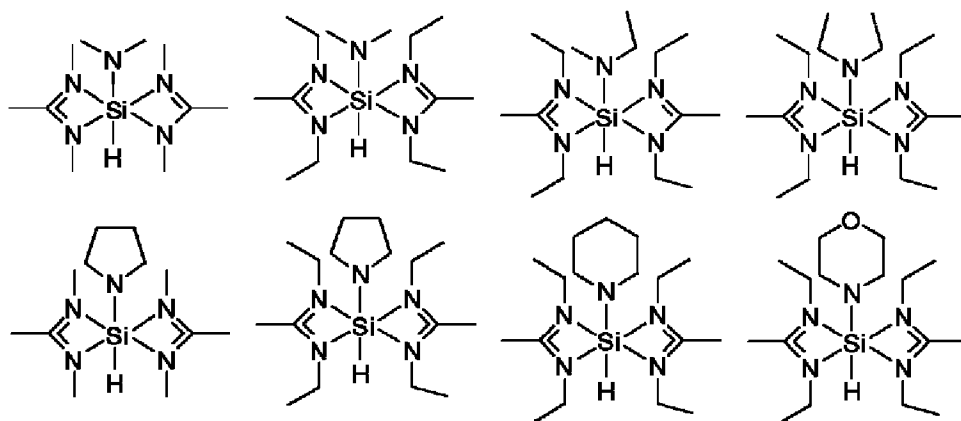
combining a hydrocarbon solution of metalorganic salt (*i.e.*, alkyl lithium) to a hydrocarbon solution of the appropriate amine, amidine, or β -diketimine.

When $n = 1$, $x = 1$, $y = 2$ and $z = 1$ in formula (I), exemplary organosilane precursors contain amidinate, amido, and hydride functional groups and have the structural formula:

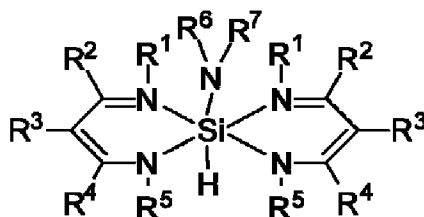


wherein R^1 , R^2 , R^3 , R^4 and R^5 may each independently be H, a C_1 to C_6 alkyl group, or a C_3 - C_{20} aryl or heterocycle group, and R^1 and R^2 and/or R^1 and R^3 and/or R^4 and R^5 being joined to form cyclic chains.

Exemplary bis(amidinato)aminosilanes having the formula $HSi[RN(CR)NR]_2(NRR)$ include:

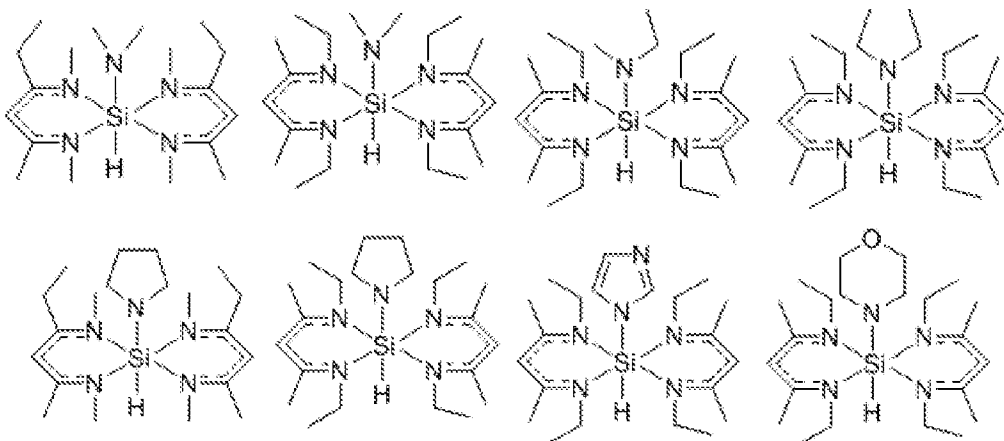


When $n = 3$, $x = 1$, $y = 2$ and $z = 1$ in formula (I), exemplary organosilane precursors contain β -diketiminato, amido, and hydride functional groups and have the structural formula:



wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 may each independently be H, a C_1 to C_6 alkyl group, or a C_3 - C_{20} aryl or heterocycle group, and R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 and/or R^4 and R^5 and/or R^6 and R^7 being joined to form cyclic chains.

Exemplary bis(β -diketiminato)aminosilanes having the formula $\text{HSi}[\text{RN}(\text{CR})_3\text{NR}]_2(\text{NRR})$ include:

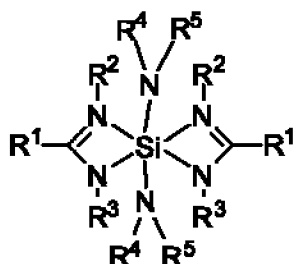


5 The $\text{HSi}[\text{RN}(\text{CR})_n\text{NR}]_2(\text{NRR})$ precursors, with $n=1$ or 3 , may be synthesized by combining a hydrocarbon solution of SiX_3H , wherein X is Cl , Br , I , or triflate (SO_3CF_3), with a neat or hydrocarbon solution of the first ligand compound, $\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$ or $\text{Li}[\text{NRR}]$, followed by addition of a neat or hydrocarbon solution of the second ligand compound, $\text{Li}[\text{NRR}]$ or $\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$, under atmosphere of
10 nitrogen, the outlet of the mixing flask being connected to an oil bubbler to inhibit backflow of air and moisture. A second synthetic route to the disclosed $\text{HSi}[\text{RN}(\text{CR})_n\text{NR}]_2(\text{NRR})$ precursors is by combining a hydrocarbon solution of SiX_3H , wherein X is Cl , Br , I , or triflate (SO_3CF_3), with a neat or hydrocarbon solution of the protonated first ligand ($\text{HRN}(\text{CR})_n\text{NR}$ or HNRR) followed by a neat or
15 hydrocarbon solution of the protonated second ligand (HNRR or $\text{HRN}(\text{CR})_n\text{NR}$), performed under an inert atmosphere. Alternatively, the disclosed $\text{HSi}[\text{RN}(\text{CR})_n\text{NR}]_2(\text{NRR})$ precursors may be synthesized by reaction of SiCl_4 with sequentially one equivalent of the first ligand and two equivalents of the second ligand compounds ($\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$ or $\text{Li}[\text{NRR}]$) followed by subsequent reduction using a selected
20 metal hydride such as LAH . In all three synthesis routes, the resulting solution may be stirred at room temperature overnight.

Exemplary hydrocarbon solutions suitable for these synthesis methods include diethyl ether, pentane, hexane, or toluene. The resulting suspension is filtered and the resulting solution distilled to remove solvent. Purification of the
25 resulting liquid or solid is carried out by distillation or sublimation, respectively. Except for the ligand compounds $\text{Li}[\text{RN}(\text{CR})_n\text{NR}]$ or $\text{Li}[\text{NRR}]$ all of the starting materials are commercially available. The ligand compound may be synthesized by

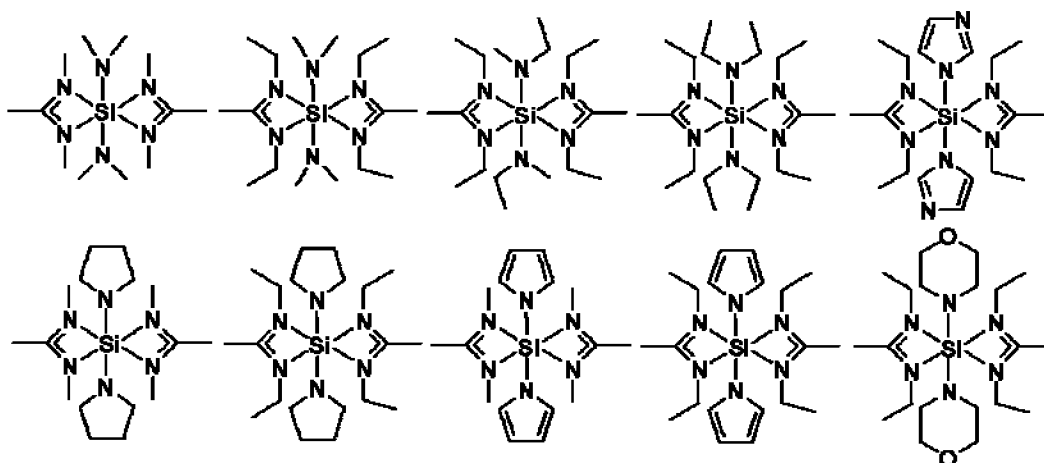
combining a hydrocarbon solution of metalorganic salt (*i.e.*, alkyl lithium) to a hydrocarbon solution of the appropriate amine, amidine, or β -diketimine.

When $n = 1$, $x = 0$, $y = 2$ and $z = 2$ in formula (I), exemplary organosilane precursors contain amidinate and amido functional groups and have the structural formula:

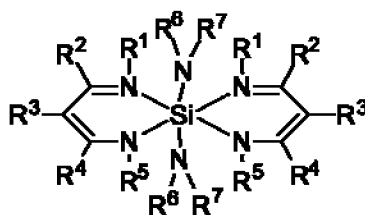


wherein R^1 , R^2 , R^3 , R^4 and R^5 may each independently be H, a C_1 to C_6 alkyl group, or a C_3 - C_{20} aryl or heterocycle group, and R^1 and R^2 and/or R^1 and R^3 and/or R^4 and R^5 being joined to form cyclic chains.

Exemplary bis(amidinato)diaminosilanes having the formula $Si[RN(CR)NR]_2(NRR)_2$ include:



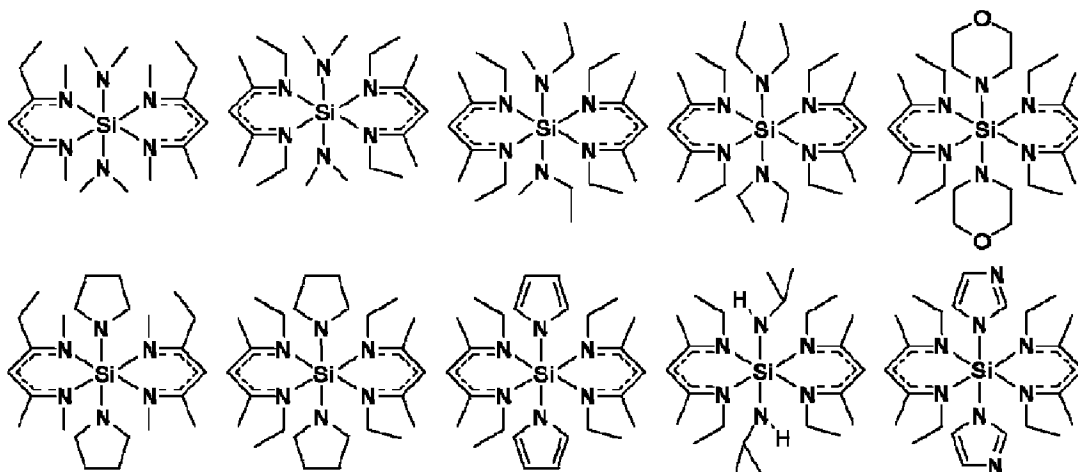
When $n = 3$, $x = 0$, $y = 2$ and $z = 2$ in formula (I), exemplary organosilane precursors contain β -diketiminato and amido functional groups and have the structural formula:



wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 may each independently be H, a C_1 to C_6 alkyl group, or a C_3 - C_{20} aryl or heterocycle group, and R^1 and R^2 and/or R^2 and R^3 and/or R^3 and R^4 and/or R^4 and R^5 and/or R^6 and R^7 being joined to form cyclic chains.

Exemplary bis(β -diketiminato)diaminosilanes having the formula

5 $Si[RN(CR)_3NR]_2(NRR)_2$ include:



The $Si[RN(CR)_nNR]_2(NRR)_2$ precursors, with $n=1$ or 3 , may be synthesized by combining a hydrocarbon solution of SiX_4 , wherein X is Cl, Br, I, or triflate (SO_3CF_3), with a neat or hydrocarbon solution of the first ligand compound, $Li[RN(CR)_nNR]$ or $Li[NRR]$, followed by addition of a neat or hydrocarbon solution of the second ligand compound, $Li[NRR]$ or $Li[RN(CR)_nNR]$, under atmosphere of nitrogen, the outlet of the mixing flask being connected to an oil bubbler to inhibit backflow of air and moisture. A second synthetic route to the disclosed $Si[RN(CR)_nNR]_2(NRR)_2$ precursors is by combining a hydrocarbon solution of SiX_4 , wherein X is Cl, Br, I, or triflate (SO_3CF_3), with a neat or hydrocarbon solution of the protonated first ligand ($HRN(CR)_nNR$ or $HNRR$) followed by a neat or hydrocarbon solution of the protonated second ligand ($HNRR$ or $HRN(CR)_nNR$), performed under an inert atmosphere. In both synthesis routes, the resulting solution may be stirred at room temperature overnight.

Exemplary hydrocarbon solutions suitable for these synthesis methods include diethyl ether, pentane, hexane, or toluene. The resulting suspension is filtered and the resulting solution distilled to remove solvent. Purification of the resulting liquid or solid is carried out by distillation or sublimation, respectively. Except for the ligand compounds $Li[RN(CR)_nNR]$ or $Li[NRR]$ all of the starting materials are commercially available. The ligand compound may be synthesized by

combining a hydrocarbon solution of metalorganic salt (*i.e.*, alkyl lithium) to a hydrocarbon solution of the appropriate amine, amidine, or β -diketimine.

To ensure process reliability, the disclosed Si-containing film forming compositions may be purified by continuous or fractional batch distillation prior to use to a purity ranging from approximately 95% w/w to approximately 100% w/w, preferably ranging from approximately 98% w/w to approximately 100% w/w. One of ordinary skill in the art will recognize that the purity may be determined by H NMR or gas or liquid chromatography with mass spectrometry. The Si-containing film forming compositions may contain any of the following impurities: carbodiimides, alkylamines, dialkylamines, alkyimines, cyclopentadiene, dicyclopentadiene, THF, ether, pentane, cyclohexane, heptanes, toluene, chlorinated metal compounds, lithium, sodium, potassium, lithium amidinate, sodium amidinate, or potassium amidinate. Preferably, the total quantity of these impurities is between 0.0% w/w and 0.1% w/w. The purified compositions may be produced by recrystallization, sublimation, distillation, and/or passing the gas or liquid through a suitable adsorbent, such as a 4A molecular sieve.

The concentration of each solvent (such as THF, ether, pentane, cyclohexane, heptanes, and/or toluene), in the purified Si-containing film forming compositions 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 composition may be difficult if both have similar boiling points. Cooling the composition may produce solid precursor in liquid solvent, which may be separated by filtration. Vacuum distillation may also be used, provided the composition is not heated above approximately its decomposition point.

The disclosed Si-containing film forming compositions contain between approximately 0% v/v and approximately 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 homo or heteroleptic silane side products or starting materials. This embodiment may provide better process repeatability. This embodiment may be produced by distillation of the Si-containing film forming composition.

Alternatively, the disclosed Si-containing film forming compositions may comprise between approximately 5% w/w to approximately 50% w/w of one

organosilane precursor with the balance of the composition comprising a second organosilane precursor, particularly when the mixture provides improved process parameters or isolation of the target organosilane precursor is too difficult or expensive. For example, the disclosed Si-containing film forming compositions may be 40/60 % w/w of $\text{SiH}_2(\text{NMe}_2)(\text{iPr-amd})$ and $\text{SiH}(\text{NMe}_2)_2(\text{iPr-amd})$. The mixture may produce a stable, liquid composition suitable for spin-on or vapor deposition.

The concentration of trace metals and metalloids in the purified Si-containing film forming compositions may each range independently from approximately 0 ppbw to approximately 100 ppbw, and more preferably from approximately 0 ppbw to approximately 10 ppbw. These metal or metalloid impurities include, but are not limited to, Aluminum(Al), Arsenic(As), Barium(Ba), Beryllium(Be), Bismuth(Bi), Cadmium(Cd), Calcium(Ca), Chromium(Cr), Cobalt(Co), Copper(Cu), Gallium(Ga), Germanium(Ge), Hafnium(Hf), Zirconium(Zr), Indium(In), Iron(Fe), Lead(Pb), Lithium(Li), Magnesium(Mg), Manganese(Mn), Tungsten(W), Nickel(Ni), Potassium(K), Sodium(Na), Strontium(Sr), Thorium(Th), Tin(Sn), Titanium(Ti), Uranium(U), Vanadium(V) and Zinc(Zn). The concentration of X (where X = Cl, Br, I) in the purified Si-containing film forming composition may range between approximately 0 ppmw and approximately 100 ppmw and more preferably between approximately 0 ppmw to approximately 10 ppmw.

The 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 compositions **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.

For pyrophoric compositions, as determined by section 33.3.1 of the United Nations Recommendations on the Transport of Dangerous Goods Manual of Tests and Criteria, 5th Edition (2009), the delivery device must be leak tight and be

equipped with valves that do not permit even minute amounts of the material. Suitable valves include spring-loaded or tied diaphragm valves. The valve may further comprise a restrictive flow orifice (RFO). The delivery device 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 is replaced so that any residual amounts 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. 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 fluidly connects to other components of the semiconductor processing tool, such as the gas cabinet disclosed above, via valves **35** and **45**. Preferably, the delivery device **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 compositions **10** may 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 **11** of the Si-containing film forming composition **10**, whereas the end **41** of the outlet conduit **40** is located below the surface **11** of the Si-containing film forming composition **10**. In this embodiment, the Si-containing film forming composition **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 delivery device **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 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** 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 **11** of the Si-containing film forming composition **10**, whereas the end **41** of the outlet conduit **40** is located above the surface **11** 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**. In this embodiment, 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 bubbles 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 on 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 **11** 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 composition 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.

Also disclosed are methods of using the disclosed Si-containing film forming compositions for vapor or casting deposition methods. The disclosed methods provide for the use of the Si-containing film forming compositions for deposition of silicon-containing films. The disclosed methods may be useful in the manufacture of semiconductor, photovoltaic, LCD-TFT, flat panel type devices, refractory materials, or aeronautics.

The disclosed methods for forming a silicon-containing layer on a substrate include: placing a substrate in a reactor, delivering into the reactor a vapor including the disclosed Si-containing film forming composition, and contacting the vapor with the substrate (and typically directing the vapor to the substrate) to form a silicon-containing layer on the surface of the substrate.

The methods may include forming a bimetal-containing layer on a substrate using the vapor deposition process and, more specifically, for deposition of SiMO_x films wherein x is 4 and M is Ta, Hf, Nb, Mg, Al, Sr, Y, Ba, Ca, As, Sb, Bi, Sn, Pb, Co, lanthanides (such as Er), or combinations thereof. The disclosed methods may be useful in the manufacture of semiconductor, photovoltaic, LCD-TFT, or flat panel type devices. An oxygen source, such as O_3 , O_2 , H_2O , NO, H_2O_2 , acetic acid, formalin, para-formaldehyde, oxygen radicals thereof, and combinations thereof, but preferably O_3 or plasma treated O_2 , may also be introduced into the reactor.

The disclosed Si-containing film forming compositions may be used to deposit silicon-containing films using any deposition methods known to those of skill in the art. Examples of suitable deposition methods include chemical vapor deposition (CVD) or atomic layer deposition (ALD). Exemplary CVD methods include thermal CVD, 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, plasma enhanced CVD (PECVD) including but not limited to flowable PECVD, 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 deposition method is preferably ALD, PE-ALD, or spatial ALD in order to provide suitable step coverage and film thickness control.

The vapor of the Si-containing film forming composition is generated and then introduced into a reaction chamber containing a substrate. The temperature and the pressure in the reaction chamber and the temperature of the substrate are held at conditions suitable for vapor deposition of at least part of the organosilane precursor onto the substrate. In other words, after introduction of the vaporized composition into the reaction chamber, conditions within the reaction chamber are adjusted such that at least part of the organosilane precursor is deposited onto the substrate to form the Si-containing layer. One of ordinary skill in the art will recognize that “at least part of the organosilane precursor is deposited” means that some or all of the precursor reacts with or adheres to the substrate. Herein, a 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 or CVD reaction chamber. The reaction chamber may be maintained at a pressure ranging from about 0.5mTorr to about 20Torr for all ALD and subatmospheric CVD processes. Subatmospheric CVD and atmospheric CVD pressures may range up to 760Torr (atmosphere). In addition, the temperature within the reaction chamber may range from about 20°C to about 600°C. One of ordinary skill in the art will recognize that the temperature may be optimized through mere experimentation to achieve the desired result.

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

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

5 temperature of the substrate remains less than or equal to 500°C.

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

10 substrates include wafers, such as silicon, silica, glass, 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.

15 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, or FeRam technologies (e.g., ZrO₂ based materials, HfO₂ based materials, TiO₂ based materials, rare earth oxide based materials, ternary oxide based materials such as strontium ruthenium oxide

20 [SRO], etc.) or from 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

25 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. The substrate may be patterned to

30 include vias or trenches having high aspect ratios. For example, a conformal Si-containing film, such as SiO₂, may be deposited using any ALD technique on a through silicon via (TSV) having an aspect ratio ranging from approximately 20:1 to approximately 100:1. Furthermore, one of ordinary skill in the art will recognize that

the terms “film” or “layer” used interchangeably 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
5 substrate utilized may be selected from hydrogenated carbon, TiN, SRO, Ru, and Si type substrates, such as polysilicon or crystalline silicon substrates. For example, a silicon nitride film may be deposited onto a Si layer. In subsequent processing, alternating silicon oxide and silicon nitride layers may be deposited on the silicon nitride layer forming a stack of multiple SiO₂/SiN layers used in 3D NAND gates.

10 The disclosed Si-containing film forming compositions may comprise the organosilane precursor 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. Alternatively, the Si-containing film forming composition may
15 comprise a solvent suitable for casting deposition, such as naphtha, methylisobutylketone (MIBK), n-methylisobutylketone (NMIBK), or combinations thereof. One of ordinary skill in the art will recognize that the casting deposition solution may further comprise pH regulators or surfactants. The precursors may be present in varying concentrations in the solvent. For example, the resulting
20 concentration may range from approximately 0.05M to approximately 2M. One of ordinary skill in the art will recognize that the molarity of the casting deposition solution is directly proportional to the desired film thickness and may adjust the molarity accordingly.

For vapor deposition, the Si-containing film forming compositions are
25 delivered 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 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 composition may be fed in liquid state
30 to a vaporizer where it is vaporized before it is introduced into the reactor. Alternatively, the composition may be vaporized by passing a carrier gas into a container containing the composition or by bubbling of 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 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 composition vaporized.

In addition to the disclosed Si-containing film forming compositions, a reactant may also be introduced into the reactor. The reactant 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, oxygen containing radicals thereof such as O· or OH·, and mixtures thereof. Preferably, when an ALD process is performed, the reactant is plasma treated oxygen, ozone, or combinations thereof. When an oxidizing agent is used, the resulting silicon containing film will also contain oxygen.

Alternatively, the reactant may be a reducing agent such as one of H₂, NH₃, (SiH₃)₃N, hydridosilanes (for example, SiH₄, Si₂H₆, Si₃H₈, Si₄H₁₀, Si₅H₁₀, Si₆H₁₂), chlorosilanes and chloropolysilanes (for example, SiHCl₃, SiH₂Cl₂, SiH₃Cl, Si₂Cl₆, Si₂HCl₅, Si₃Cl₈), alkylsilanes (for example, (CH₃)₂SiH₂, (C₂H₅)₂SiH₂, (CH₃)SiH₃, (C₂H₅)SiH₃), hydrazines (for example, N₂H₄, MeHNNH₂, MeHNNHMe), organic amines (for example, N(CH₃)H₂, N(C₂H₅)H₂, N(CH₃)₂H, N(C₂H₅)₂H, N(CH₃)₃, N(C₂H₅)₃, (SiMe₃)₂NH), pyrazoline, pyridine, B-containing molecules (for example, B₂H₆, 9-borabicyclo[3,3,1]nonane, trimethylboron, triethylboron, borazine), alkyl metals (such as trimethylaluminum, triethylaluminum, dimethylzinc, diethylzinc), radical species thereof, and mixtures thereof. Preferably, the reducing agent is H₂, NH₃, SiH₄, Si₂H₆, Si₃H₈, SiH₂Me₂, SiH₂Et₂, N(SiH₃)₃, hydrogen radicals thereof, or mixtures thereof. Preferably, the reducing agent is SiHCl₃, Si₂Cl₆, Si₂HCl₅, Si₂H₂Cl₄, and cyclo-Si₆H₆Cl₆. When a reducing agent is used, the resulting silicon containing film may be pure Si.

The reactant may be treated by plasma, in order to decompose the reactant 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 50W to about 500W, preferably from about 100W to about 200W. The plasma
5 may be generated or present within the reactor itself. Alternatively, the plasma may generally be at a location removed from the reactor, for instance, in a remotely located plasma system. One of skill in the art will recognize methods and apparatus suitable for such plasma treatment.

The disclosed Si-containing film forming compositions may also be used with
10 a halosilane or polyhalodisilane, such as hexachlorodisilane pentachlorodisilane, 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.

When the desired silicon-containing film also contains another element, such
15 as, for example and without limitation, Ta, Hf, Nb, Mg, Al, Sr, Y, Ba, Ca, As, Sb, Bi, Sn, Pb, Co, lanthanides (such as Er), or combinations thereof, the reactants may include a second precursor which is selected from, but not limited to, alkyls, such as Ln(RCp)₃ or Co(RCp)₂, amines, such as Nb(Cp)(NtBu)(NMe₂)₃ and any combination thereof.

20 The Si-containing film forming composition 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
25 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 reactants are introduced by pulse
30 (e.g., pulsed-CVD). In each example, a pulse may be followed by a purge or evacuation step to remove excess amounts of the component introduced. In each example, the pulse may last for a time period ranging from about 0.01s to about 10s, alternatively from about 0.3s to about 3s, alternatively from about 0.5s to about 2s.

In another alternative, the Si-containing film forming composition and one or more reactants may be simultaneously sprayed from a shower head under which a susceptor holding several wafers is spun (e.g., spatial ALD).

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

Alternatively, if the desired film is a silicon metal oxide film (*i.e.*, SiMO_x , wherein x may be 4 and M is Ta, Hf, Nb, Mg, Al, Sr, Y, Ba, Ca, As, Sb, Bi, Sn, Pb, Co, lanthanides (such as Er), or combinations thereof), the two-step process above may be followed by introduction of a vapor of a second precursor into the reaction chamber. The second precursor will be selected based on the nature of the silicon oxide film being deposited. After introduction into the reaction chamber, the second precursor is contacted with the substrate. Any excess second 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 physi- or chemisorbed second 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, second 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 $M:\text{Si}$ ratio may be obtained. For example, a SiMO_2 film may be obtained by having one pulse of the organosilane precursor and one pulses of the second 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, dense SiCN films may be deposited using an ALD method with hexachlorodisilane (HCDS) or pentachlorodisilane (PCDS), the disclosed Si-containing film forming composition, and an ammonia reactant. The reaction chamber may be controlled at 5 Torr, 550°C, with a 55 sccm continuous flow of Ar. An approximately 10 second long pulse of the Si-containing film forming composition at a flow rate of approximately 1 sccm is introduced into the reaction chamber. The Si-containing film forming composition is purged from the reaction chamber with an approximately 55 sccm flow of Ar for approximately 30 seconds. An approximately 10 second pulse of HCDS at a flow rate of approximately 1 sccm is introduced into the reaction chamber. The HCDS is purged from the reaction chamber with an approximately 55 sccm flow of Ar for approximately 30 seconds. An approximately 10 second long pulse of NH₃ at a flow rate of approximately 50 sccm is introduced into the reaction chamber. The NH₃ is purged from the reaction chamber with an approximately 55 sccm flow of Ar for approximately 10 seconds. These 6 steps are 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 NH₃ reactant in order to tune the amounts of carbon and nitrogen in the resulting SiCN film.

In yet another alternative, a silicon-containing film may be deposited by the flowable PECVD method disclosed in U.S. Patent Application Publication No. 2014/0051264 using the disclosed Si-containing film forming compositions and a radical nitrogen- or oxygen-containing reactant. The radical nitrogen- or oxygen-containing reactant, such as NH₃ or H₂O respectively, is generated in a remote plasma system. The radical reactant and the vapor phase of the disclosed Si-containing film forming compositions are introduced into the reaction chamber where they react and deposit the initially flowable film on the substrate. Applicants believe that the nitrogen atoms of the (RN-(CR)_n-NR) ligand and amino groups in the

disclosed Si-containing film forming compositions help to further improve the flowability of the deposited film, resulting in films having less voids.

Also disclosed are methods of using the disclosed Si-containing film forming compositions in casting deposition methods, such as spin coating, spray coating, dip coating or slit coating techniques. The disclosed methods provide for the use of the Si-containing film forming composition 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: applying the liquid form of the disclosed Si-containing film forming composition on a substrate in a reactor: and forming the Si-containing layer on the substrate. As discussed previously, the liquid form of the disclosed Si-containing film forming composition may be a neat solution of the organosilane precursor or a mixture of the precursor with a solvent and optional pH adjusters or surfactants. The liquid form of the disclosed Si-containing film forming composition may be applied directly to the center of the substrate or may be applied to the entire substrate by spraying. When applied directly to the center of the substrate, the substrate may be spun to utilize centrifugal forces to evenly distribute the composition over the substrate. Alternatively, the substrate may be dipped in the Si-containing film forming composition. The resulting film may be dried at an appropriate temperature for a period of time to vaporize any solvent or volatile components of the film. One of ordinary skill in the art would recognize the appropriate temperature selection based on the solvent to be evaporated. During the vaporization process, a mist of water may be sprayed onto the substrate to promote the hydrolysis reaction of the film.

The disclosed organosilane precursors in the Si-containing film forming compositions may prove useful as monomers for the synthesis of silicon containing polymers. The Si-containing film forming compositions may be used to form spin-on dielectric film formulations, for patternable films, or for anti-reflective films. For example, the disclosed Si-containing film forming compositions may comprise a solvent and applied to a substrate to form a film. If necessary, the substrate may be rotated to evenly distribute the Si-containing film forming composition across the substrate. One of ordinary skill in the art will recognize that the viscosity of the Si-containing film forming compositions 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 and/or under reduced pressure. Alternatively, electron beams or ultraviolet radiation may be applied to the resulting film. The 8-9 hydrolysable groups of the disclosed organodisilane precursors (i.e., the direct Si-Si, Si-N, Si-O, Si-S, or Si-H bonds) may prove useful to increase the connectivity of the polymer obtained.

The silicon-containing films resulting from the processes discussed above may include SiO₂, SiN, SiON, SiCN, SiCOH, or MSiO_x, wherein M is an element such as Hf, Zr, Ti, Nb, Ta, or Ge, and x may be from 0-4, depending of course on the oxidation state of M. One of ordinary skill in the art will recognize that by judicial selection of the appropriate Si-containing film forming composition and 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.

Example 1: Synthesis of $\text{SiH}(\text{NMe}_2)_2(\text{N}^i\text{Pr-AMD})$.

All reaction steps described here are performed under inert atmosphere. A 3-neck round-bottom equipped with a cold liquid addition funnel and a condenser was charged with trichlorosilane (11.3g; 0.08 mol) at 0 °C. To the cold liquid addition funnel (cooled with dry-ice), transfer via cannula tris-(dimethylamino)silane (29.6 g; 0.184 mol). Add tris-(dimethylamino)silane drop-wise to trichlorosilane at 0 °C. After complete addition, allow the reaction to proceed for an additional 30 min. at 0 °C. Rinse the cold liquid addition funnel into the reaction mixture with diethyl ether (300 mL). Via cannula add a solution of *N,N'*-diisopropylamidine (71.5 g; 0.503 mol) in 200 mL of diethyl ether to the cold liquid addition funnel (cooled with dry-ice) and add the solution drop-wise to the reaction mixture. After complete addition, allow the reaction to proceed at room temperature (22 °C) for 1 hour. Via cannula add pentane (100 mL) and filter the mixture through Celite™ brand diatomaceous earth. Assist the filtration and transfer of crude material with additional pentane (2 x 100 mL). Remove solvent under reduced pressure. Take crude material up in pentane (20 mL) and filter through Celite™ brand diatomaceous earth. Assist filtration with additional pentane (2x10 mL). The crude material was purified by distillation to produce a clear colorless oil (60% yield; 37.5 g). ^1H NMR (400MHz, C_6D_6 , 25 °C) $\delta(\text{ppm})$ = 4.79 (s, 1H, SiH), 3.77 (sept, 2H, $\text{NCH}(\text{CH}_3)_2$), 2.47 (s, 12H, $\text{N}(\text{CH}_3)_2$), 1.69 (s, 3H, CCH_3), 1.30 (d, 12H, $\text{NCH}(\text{CH}_3)_2$). A 44 mg sample of the product was placed into an open aluminum pan and the temperature ramped from 25 to 500 C at a rate of 10 °C/min under a dry nitrogen purge flowing at 200 sccm. Less than 1% residue was observed after analysis. (See **FIG 3**)

Example 2: PEALD of SiN Films Using $\text{SiH}(\text{NMe}_2)_2(\text{N}^i\text{Pr-AMD})$

PEALD test were performed using $\text{SiH}(\text{NMe}_2)_2(\text{N}^i\text{Pr-AMD})$ which was placed in a bubbler at 80°C. Typical PEALD conditions were used, such as using nitrogen direct plasma with excitation frequency at 13.56 Mhz, and reactor pressure fixed at 1 Torr. Wafer temperature was measured at 250 °C and deposition was performed on pure silicon wafers. The resulting deposition rate and refractive index are shown in **FIG 4**.

The refractive index values are characteristic of SiN films (1.9-2.0). The film with optimum properties was obtained for 5s pulse. In these conditions, WER was

measured at $12\text{\AA}/\text{min} \pm 2$ (benchmark precursor $\text{SiH}_2(\text{NEt}_2)_2$ deposited film measured at $20.5\text{\AA}/\text{min} \pm 7$). 2.

For the same condition, XPS analysis of the film shows Si rich film with following at%: C1s of 4.215 at%; N1s of 37.77 at%; O1s of 9.55 at%; and Si2p of 47.315 at%. This analysis was performed on the uncapped film at a R&D facility, therefore the oxygen concentration may be due to post deposition air exposure. The wet etch rate and XPS analysis results are similar to those obtained at this facility for commercially successful alkylaminosilanes and indicate that this precursor may have commercial viability.

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

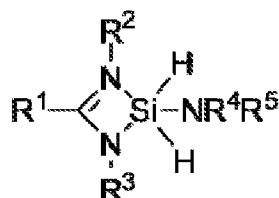
What is claimed is:

1. A Si-containing film forming composition comprising an organosilane precursor having the formula:

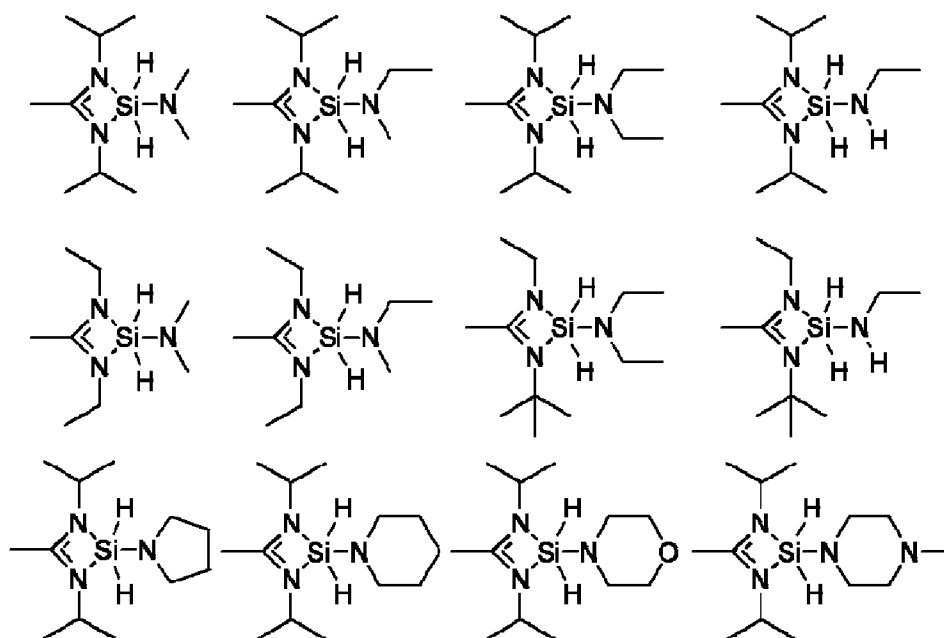


wherein each R is independently selected from the group consisting of H, a C₁ to C₆ alkyl group, and a C₃-C₂₀ aryl or heterocycle group; n = 1 or 3; x=0, 1, or 2; y = 1 or 2; and z = 1, 2, or 3; and x+y+z = 4, provided that x≠2 when y=2.

10 2. The Si-containing film forming composition of claim 1, wherein n = 1, x = 2, y = 1, z = 1, and the organosilane precursor has the formula:

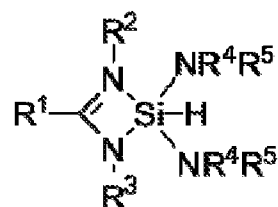


15 3. The Si-containing film forming composition of claim 2, wherein the organosilane precursor is selected from the group consisting of:

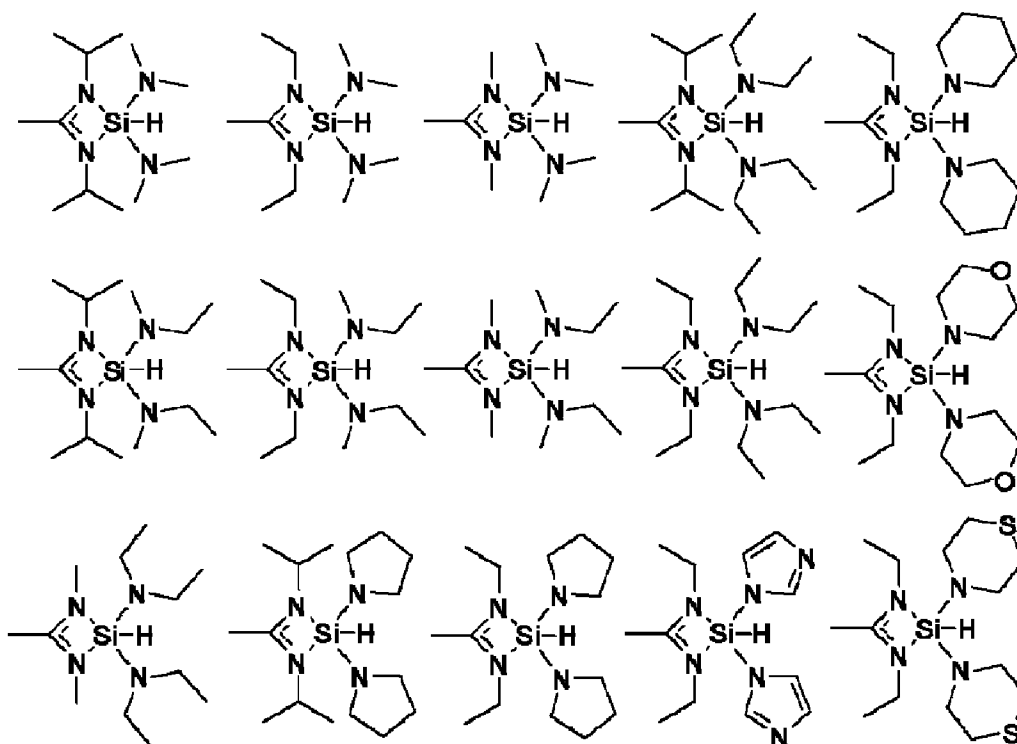


4. The Si-containing film forming composition of claim 3, wherein the organosilane precursor is SiH₂(NMe₂)(iPr-amd) or SiH₂(NEt₂)(iPr-amd).

5. The Si-containing film forming composition of claim 1, wherein $n = 1$, $x = 1$, $y = 1$, $z = 2$, and the organosilane precursor has the formula:

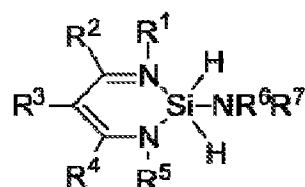


- 5 6. The Si-containing film forming composition of claim 5, wherein the organosilane precursor is selected from the group consisting of:

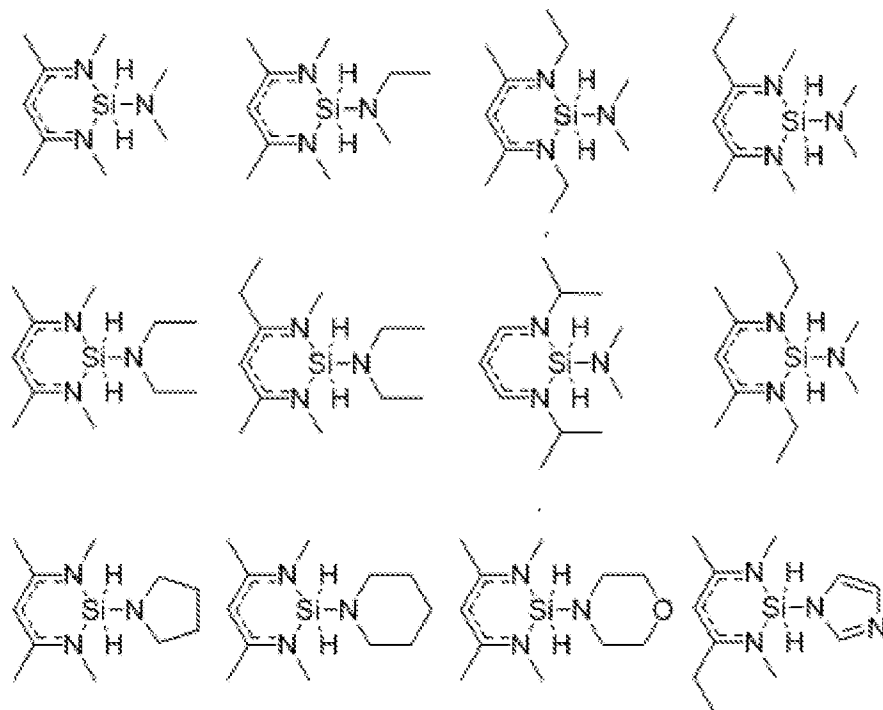


7. The Si-containing film forming composition of claim 6, wherein the
10 organosilane precursor is $\text{SiH}(\text{NMe}_2)_2(\text{iPr-amd})$.

8. The Si-containing film forming composition of claim 1, wherein $n = 3$, $x = 2$, $y = 1$, $z = 1$, and the organosilane precursor has the formula:

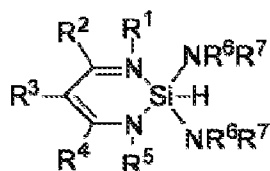


9. The Si-containing film forming composition of claim 8, wherein the organosilane precursor is selected from the group consisting of:



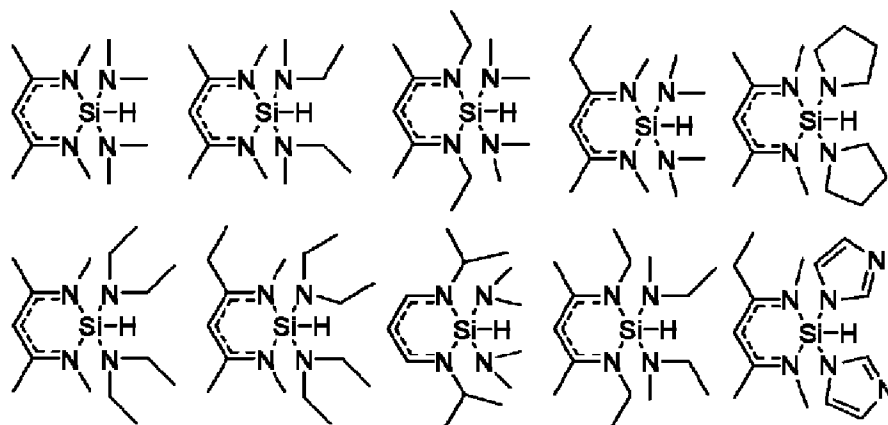
5

10. The Si-containing film forming composition of claim 1, wherein $n = 3$, $x = 1$, $y = 1$, $z = 2$, and the organosilane precursor has the formula:

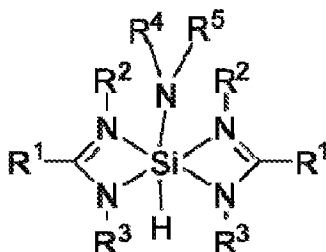


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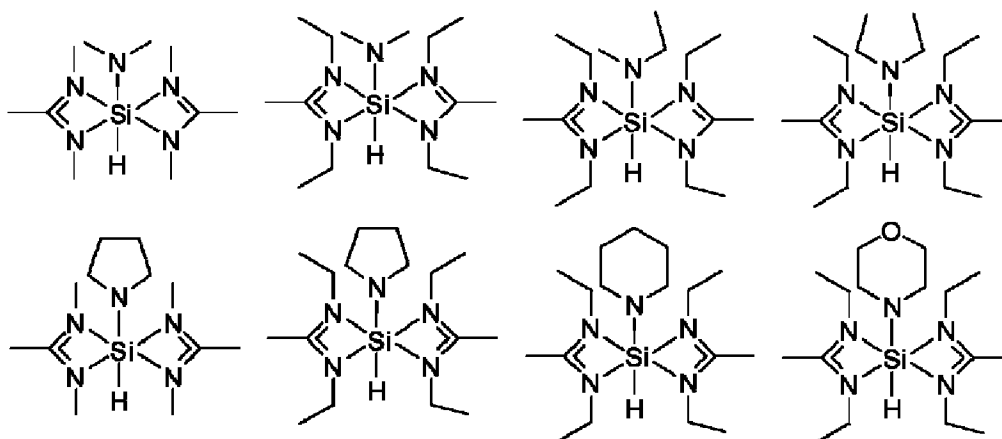
11. The Si-containing film forming composition of claim 10, wherein the organosilane precursor is selected from the group consisting of:



12. The Si-containing film forming composition of claim 1, wherein $n = 1$, $x = 1$, $y = 2$, $z = 1$, and the organosilane precursor has the formula:



13. The Si-containing film forming composition of claim 12, wherein the organosilane precursor is selected from the group consisting of:



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

introducing the Si-containing film forming composition of any one of claims 1 to 13 into a reactor having a substrate disposed therein; and

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

15. The method of claim 14, further comprising introducing into the reactor a reactant, wherein the reactant is selected from the group consisting of H_2 , NH_3 , $(SiH_3)_3N$, hydrosilanes, chlorosilanes, chloropolysilanes, alkylsilanes, hydrazines, organic amines, pyrazoline, pyridine, B-containing molecules, alkyl metals, radical species thereof, and mixtures thereof.

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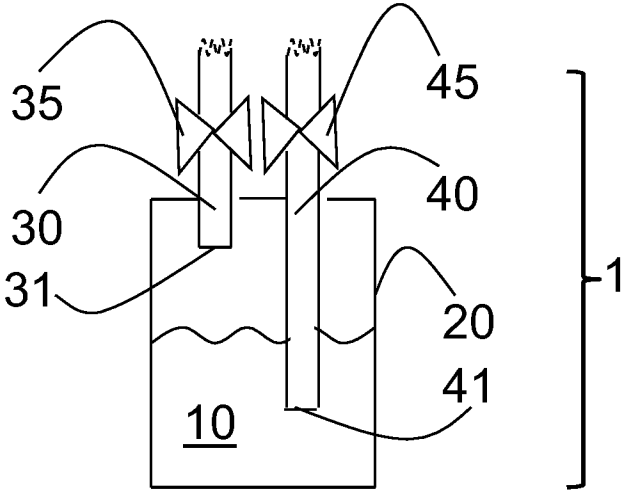


FIG 1

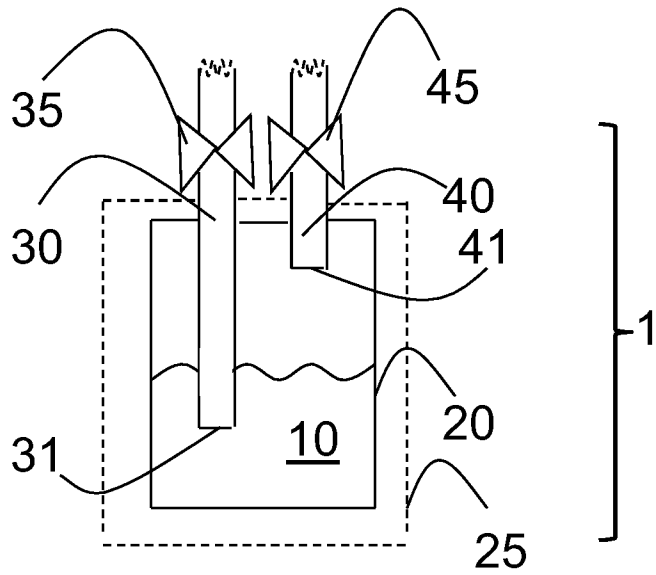


FIG 2

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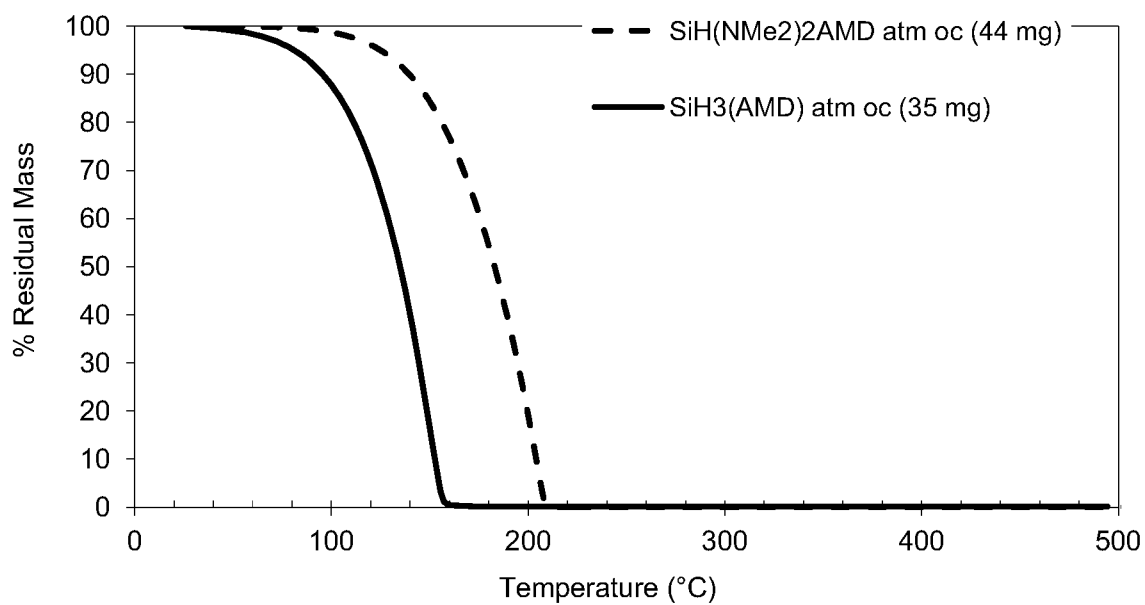


FIG 3

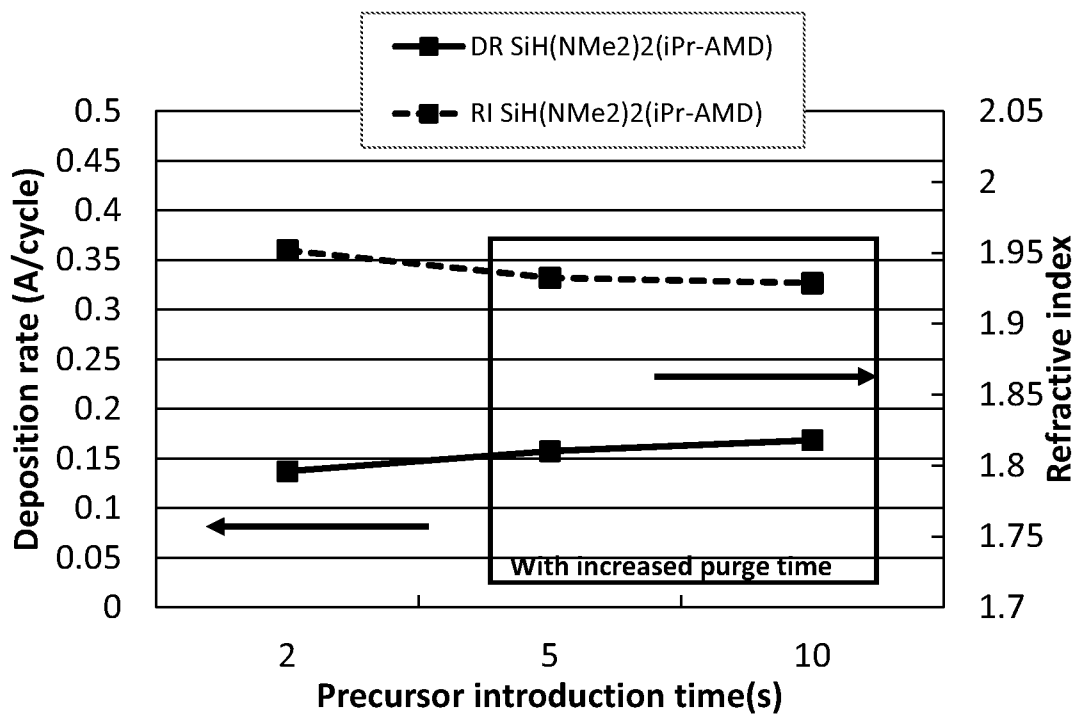


FIG 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/013799**A. CLASSIFICATION OF SUBJECT MATTER****C23C 16/36(2006.01)i, C23C 16/455(2006.01)i, C07F 7/02(2006.01)i, C07F 7/10(2006.01)i, C07F 7/12(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)

C23C 16/36; H01L 23/00; C07F 7/10; B05D 1/00; C07F 7/12; H01L 21/02; C23C 16/18; A01N 3/02; A01N 25/24; C23C 16/455; C07F 7/02

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & keywords: organosilane, precursor, film, silane, silicon, depositing

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-2012-0131114 A (UMT CO., LTD.) 04 December 2012 See paragraphs [0030]-[0048]; claims 1-4.	1-15
A	US 2015-0004317 A1 (AMERICAN AIR LIQUIDE, INC.) 01 January 2015 See paragraph [0089]; claim 4.	1-15
A	US 2014-0264778 A1 (SAMSUNG ELECTRONICS CO., LTD.) 18 September 2014 See paragraphs [0045]-[0057]; claim 1.	1-15
A	US 6113815 A (ELFERSY et al.) 05 September 2000 See column 9, line 49 - column 11, line 8; claims 1 and 5.	1-15
A	PAN, GUIRONG et al., 'Morphology and water resistance of mixed silane films of bis[3-(triethoxysilyl) propyl]tetrasulfide and bis-[trimethoxysilylpropyl]amine', Thin Solid Films, vol. 515, no. 4, 2006, pp.2771-2780 See page 2772.	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

24 August 2016 (24.08.2016)

Date of mailing of the international search report

24 August 2016 (24.08.2016)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea



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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/013799

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US 6113815 A	05/09/2000	US 2003-0180440 A1	25/09/2003