To avoid using halides, SiO_2 ALD has been attempted using a variety of reactants such as alkoxysilanes, aminosilanes and isocyanates, using a variety of different catalysts and reaction conditions. These methods suffer from a number of disadvantages, such as requiring large reactant exposures, long deposition times or resulting in contamination of the deposited film.

SUMMARY ~~OF THE INVENTION~~

A class of organometallic compounds is provided. The compounds correspond in structure to Formula 1:

$$(A)_x\text{-}M\text{-}(OR^3)_{4-x}$$

wherein:

A is selected from the group consisting of $-NR^1R^2$, $-N(R^4)(CH_2)_nN(R^5R^6)$,

$-N{=}C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, halo and Y;

R^1 and R^2 are independently selected from the group consisting of H and a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms, with the proviso that at least one of R^1 and R^2 must be other than H;

R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms;

Y is selected from the group consisting of a 3- to 13-membered heterocyclic radical containing at least one nitrogen atom;

R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms;

M is selected from the group consisting of Si, Ge, Sn, Ti, Zr and Hf;

x is an integer from 1 to 3; and

n is an integer from 1 to 4.

In an aspect, there is provided a method for forming a metal oxide film by an atomic layer deposition (ALD process, the ALD method comprising the steps of:

a. Providing at least one substrate having functional O-H groups covering the surface,

b. delivering to said substrate at least one compound of Formula 1 in the gaseous phase~~,;,-:~~

$(A)_x\text{-}M\text{-}(OR^3)_{4-x}$

wherein:

A is selected from the group consisting of $-NMe_2$, $-N(R^4)(CH_2)_nN(R^5R^6)$, $-N=C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, and Y;

R^1 is independently selected from the group consisting of a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms;

R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms;

Y is selected from the group consisting of a 3- to 13-membered heterocyclic radical containing at least one nitrogen atom;

R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms;

M is selected from the group consisting of Si, Ge, Sn;

x is an integer from 1 to 3; and

n is an integer from 1 to 4;

with the proviso that the compound of Formula 1 is not diacetoxy-ditbutoxysilane, and

with the proviso that when A is $-NMe_2$, R^3 is methyl or ethyl,

c. purging the substrate with purge gas,

d. delivering to said substrate an oxygen source in the gaseous phase,

e. purging the substrate with purge gas,

f. repeating steps b) through e) until a desired thickness of metal oxide has been deposited.

Such compounds may be useful as precursors for metal oxide vapour phase deposition. The compounds of the invention comprise one or more ligands which are strong Lewis bases. Exemplary bases comprise acetates, halides and neutral, nitrogen-containing species with high proton affinity such as phosphazenes, amidines and guanidines.

CLAIMS

What is claimed is:

1. An organometallic compound of Formula 1:

$$(A)_x\text{-}M\text{-}(OR^3)_{4-x}$$

wherein:

A is selected from the group consisting of -NR^1R^2, -$N(R^4)(CH_2)_nN(R^5R^6)$, -N=$C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, halo and Y;

R^1 and R^2 are independently selected from the group consisting of H and a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms, with the proviso that at least one of R^1 and R^2 must be other than H;

R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms;

Y is selected from the group consisting of a 3- to 13-membered heterocyclic radical containing at least one nitrogen atom;

R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms;

M is selected from the group consisting of Si, Ge, Sn, Ti, Zr and Hf;

x is an integer from 1 to 3; and

n is an integer from 1 to 4.

2. The compound of claim 1, wherein M is selected from the group consisting of Si, Ge and Sn.

3. The compound of claim 2, wherein M is Si.

4. The compound of claim 3, wherein A is selected from the group consisting of $-NR^1R^2$, $-N(R^4)(CH_2)_nN(R^5R^6)$, $-N=C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, halo and Y.

5. The compound of claim 4, wherein A is selected from the group consisting of acetate, tetraethylguanidinyl, dimethylethylenediaminyl, bromo, iodo, $-NR^1R^2$ and Y.

6. The compound of claim 5, wherein A is $-NR^1R^2$.

7. The compound of claim 6, wherein R^1 and R^2 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms.

8. The compound of claim 7, wherein wherein R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl.

9. The compound of claim 5, wherein A is Y.

10. The compound of claim 9, wherein Y is selected from the group consisting of aziridinyl, azetidinyl, pyrrolidinyl, pyrrolyl, piperidinyl, pyridinyl, azepanyl, and azepinyl.

11. The compound of claim 10, wherein Y is selected from the group consisting of aziridinyl, azetidinyl and pyrrolidinyl.

12. The compound of claim 8 or 11, wherein R^1 and R^2 are independently selected from the group consisting of H and a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms, with the proviso that at least one of R^1 and R^2 must be other than H.

13. The compound of claim 12, wherein R^1 and R^2 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms.

14. The compound of claim 13, wherein R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl.

15. The compound of claim 8 or 11, wherein R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms.

16. The compound of claim 15, wherein R^3 is a linear or branched acyclic alkyl group having from 1 to 4 carbon atoms.

17. The compound of claim 16, wherein R^3 is selected from the group consisting of methyl and ethyl.

18. The compound of claim 17, wherein R^3 is a methyl group.

19. The compound of claim 8 or 11, wherein R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms.

20. The compound of claim 19, wherein R^4, R^5, R^6 and R^7 are independently selected from the group consisting of methyl and ethyl.

21. The compound of claim 5 wherein R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl, Y is pyrrolidinyl, and R^3 is selected from the group consisting of methyl and ethyl.

~~22.~~1. A method for forming a metal oxide film by an atomic layer ~~vapour~~ deposition (ALD) process, the ALD method comprising the steps of:

a. Providing at least one substrate having functional O-H groups covering the surface,

b. delivering to said substrate at least one compound of Formula 1 in the gaseous phase~~,~~;~~-~~:

$(A)_x$-M-$(OR^3)_{4-x}$

wherein:

A is selected from the group consisting of $–NMe_2$, -$N(R^4)(CH_2)_nN(R^5R^6)$, -$N=C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, and Y;

R^1 is independently selected from the group consisting of a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms;

R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms;

Y is selected from the group consisting of a 3- to 13-membered heterocyclic radical containing at least one nitrogen atom;

R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms;

M is selected from the group consisting of Si, Ge, Sn;

x is an integer from 1 to 3; and

n is an integer from 1 to 4;

with the proviso that the compound of Formula 1 is not diacetoxy-ditbutoxysilane, and

with the proviso that when A is $–NMe_2$, R^3 is methyl or ethyl,

c. purging the substrate with purge gas,

d. delivering to said substrate an oxygen source in the gaseous phase,

e. purging the substrate with purge gas,

f. repeating steps b) through e) until a desired thickness of metal oxide has been deposited.

~~23.~~2. The method of claim 1~~22~~, wherein M is Si.

~~24. The method of claim 23, wherein A is selected from the group consisting of $-NR^1R^2$, -$N(R^4)(CH_2)_nN(R^5R^6)$, -$N=C(NR^4R^5)(NR^6R^7)$, $OCOR^1$, halo and Y.~~

~~25.~~3. The method of claim 1~~24~~, wherein A is selected from the group consisting of acetate, tetraethylguanidinyl, dimethylethylenediaminyl, ~~bromo, iodo, -NR^{1}R^2-~~ and Y.

~~26. The method of claim 25, wherein A is -NR^{1}R^2.~~

~~27.~~4. The method of claim 1~~26~~, wherein A is OCOR^1, and wherein R^1 ~~and R^2 are~~is independently selected from the group consisting of ~~H and~~ an acyclic alkyl group having from 1 to 4 carbon atoms.

~~28. The method of claim 27, wherein R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl.~~

~~29.~~5. The method of claim 3~~25~~, wherein A is Y, and wherein Y is selected from the group consisting of aziridinyl, azetidinyl, pyrrolidinyl, pyrrolyl, piperidinyl, pyridinyl, azepanyl, and azepinyl.

~~30. The method of claim 29, wherein Y is selected from the group consisting of aziridinyl, azetidinyl, pyrrolidinyl, pyrrolyl, piperidinyl, pyridinyl, azepanyl, and azepinyl.~~

~~31. The method of claim 30, wherein Y is selected from the group consisting of aziridinyl, azetidinyl and pyrrolidinyl.~~

~~32. The method of claim 28 or 31, wherein R^1 and R^2 are independently selected from the group consisting of H and a cyclic or acyclic alkyl group having from 1 to 8 carbon atoms, with the proviso that at least one of R^1 and R^2 must be other than H.~~

~~33. The method of claim 32, wherein R^1 and R^2 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms.~~

~~34. The method of claim 33, wherein R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl.~~

~~35. The method of claim 28 or 31, wherein R^3 is a cyclic or acyclic alkyl group having from 1 to 6 carbon atoms.~~

~~36~~6. The method of claim ~~35~~1, wherein R^3 is a~~n linear or branched~~ acyclic alkyl group having from 1 to 4 carbon atoms.

~~37. The method of claim 36, wherein R^3 is selected from the group consisting of methyl and ethyl.~~

~~38. The method of claim 37, wherein R^3 is a methyl group.~~

~~39. The method of claim 28 or 31, wherein R^4, R^5, R^6 and R^7 are independently selected from the group consisting of H and an acyclic alkyl group having from 1 to 4 carbon atoms.~~

~~40. The method of claim 39, wherein R^4, R^5, R^6 and R^7 are independently selected from the group consisting of methyl and ethyl.~~

~~41~~7. The method of claim ~~25~~3 wherein~~ R^1 and R^2 are independently selected from the group consisting of methyl, ethyl and isobutyl, Y~~ A is pyrrolidinyl, and R^3 is selected from the group consisting of methyl and ethyl.

~~42~~8. The method of claim ~~41~~1, wherein the oxygen source is selected from H_2O in gaseous phase, H_2O_2 in gaseous phase, O_2, O_3 and hydrazine.

~~43. The method of claim 41 wherein the vapour deposition process is chemical vapour deposition.~~

~~44. The method of claim 41 wherein the vapour deposition process is atomic layer deposition.~~

9. The method of claim 1, wherein A is $-NMe_2$.

10. The method of claim 4, wherein R^1 is independently selected from the group consisting of methyl, ethyl and isobutyl.

11. The method of claim 5, wherein Y is selected from the group consisting of aziridinyl, azetidinyl and pyrrolidinyl.

12. The method of claim 6, wherein R^3 is selected from the group consisting of methyl and ethyl.

13. The method of claim 12, wherein R^3 is a methyl group.

14. The method of claim 1, wherein A is $-N(R^4)(CH_2)_nN(R^5R^6)$ or $-N=C(NR^4R^5)(NR^6R^7)$.

15. The method of claim 14, wherein R^4, R^5, R^6 and R^7 are independently selected from the group consisting of methyl and ethyl.