

Method of forming dielectric films, new precursors and their use in the semi-conductor manufacturing

The invention relates to metal-containing film forming composition comprising a precursor of Niobium or Vanadium and a method of forming a Nb or Vanadium-containing film on one or more substrates via vapor deposition processes using the Niobium, Vanadium containing film forming compositions.

Metal Oxide films, such as Niobium Oxide (Nb_2O_5), have been extensively utilized in various fields of technology. Traditionally these oxides have been applied as resistive films used as high-k materials for insulating layers. For instance, a thin layer of Nb_2O_5 between two ZrO_2 dielectric layers is expected to help significantly reduce leakage current and stabilize the cubic/tetragonal phase of the ZrO_2 , affording higher k values in the current MIM capacitor of a DRAM (Alumina, J. Vac. Sci. Technol A 4 (6), 1986 and Microelectronic Engineering 86 (2009) 1789-1795). A thin layer of V_2O_5 may behave similarly.

Metal Nitride films, such as Niobium Nitride, Vanadium Nitride (NbN_x , VN_x wherein x is approximately 1) have been extensively utilized in various fields of technology. Traditionally these nitrides have been applied as hard and decorative coatings but during the past decade they have increasingly been used as diffusion barrier and adhesion/glue layers in microelectronic devices [Applied Surface Science 120 (1997) 199-212].

Mixed oxides containing Nb is also of high interest in energy storage applications for instance as thin, highly ionic conductive, interface layers between active cathode material and electrolyte in all-solid-state batteries and Li-ion batteries [US7993782B2]. For instance, a thin layer of Lithium Niobate deposited on active cathode materials in the right crystalline phase has been reported to reduce reaction resistance and increase battery power output [US 2020/0075956 A1]. Lithium Niobate is of particular interest as an interface layer because it displays a significantly higher ionic conductivity [Electrochem. Commun. 2007, 9, 1486–1490]. Vapor phase deposition such as Atomic Layer Deposition has been reported to be a viable technique to deposit such stabilizing interface layers onto low Cobalt Cathodes Materials [ACS Appl. Mater. Interfaces 2018, 10, 1654–1661].

NbCl_5 for instance has been examined as a niobium source for Atomic Layer Epitaxial

growth of NbN_x , but the process required Zn as a reducing agent [Applied Surface Science 82/83 (1994) 468-474]. NbN_x films were also deposited by atomic layer deposition using NbCl_5 and NH_3 [Thin Solid Films 491 (2005) 235-241]. The chlorine content showed strong temperature dependence, as the film deposited at 500°C was almost chlorine free, while the chlorine content was 8 % when the deposition temperature was as low as 250°C. The high melting point of NbCl_5 also makes this precursor difficult to use in the vapor deposition process.

As an example for VN_x , $\text{V}(\text{NMe}_2)_4$ has been examined as a vanadium source for chemical vapor deposition of VN_x [Chemical Vapor Deposition of Vanadium, Niobium, and Tantalum Nitride Thin Films by Fix et al., Chem. Mater. 1993, 5, 614-619]. VN_x films were also deposited by plasma enhanced atomic layer deposition using $\text{V}(\text{NEtMe})_4$ and NH_3 . [Low Temperature Plasma-Enhanced Atomic Layer Deposition of Thin Vanadium Nitride Layers for Copper Diffusion Barriers by Rampelberg et al., Appl. Phys. Lett., 102, 111910 (2013)].

Gust et al. disclose the synthesis, structure, and properties of niobium and tantalum imido complexes bearing pyrazolato ligands and their potential use for the growth of tantalum nitride films by CVD (Polyhedron 20 (2001) 805-813).

Elorriaga et al. disclose asymmetric niobium guanidines as intermediates in the catalytic guanylation of amines (Dalton Transactions, 2013, Vol. 42, Issue 23 pp. 8223-8230).

Tomson et al. disclose the synthesis and reactivity of the cationic Nb and Ta monomethyl complexes $[(\text{BDI})\text{MeM}(\text{NtBu})][\text{X}]$ ($\text{BDI}=2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{-N-C(Me)CH-C(Me)-N(2, 6-iPr}_2\text{C}_6\text{H}_3)$; $\text{X}=\text{MeB}(\text{C}_6\text{F}_5)_3$ or $\text{B}(\text{C}_6\text{F}_5)_4$) (Dalton Transactions 2011 Vol. 40, Issue 30, pp. 7718-7729).

DE102006037955 discloses tantalum- and niobium-compounds having the formula $\text{R}^4\text{R}^5\text{R}^6\text{M}(\text{R}^1\text{NNR}^2\text{R}^3)_2$, wherein M is Ta or Nb; $\text{R}^1\text{-R}^3=\text{C}_{1-12}$ alkyl, C_{5-12} cycloalkyl, C_{6-10} aryl, alkenyl, C_{1-4} triorganosilyl; and $\text{R}^4\text{-R}^6=\text{halo}$, (cyclo)alkoxy, aryloxy, siloxy, BH_4 , allyl, indenyl, benzyl, cyclopentadienyl, CH_2SiMe_3 , silylamido, amido, or imino.

Maestre et al. discloses the reaction of the cyclopentadienyl-silyl-amido titanium compound with group 5 metal monocyclopentadienyl complexes to form $\text{NbCp}(\text{NH}(\text{CH}_2)_2\text{-NH}_2)\text{Cl}_3$ and $\text{NbCpCl}_2(\text{N}-(\text{CH}_2)_2\text{-N})$.

Gibson et al. discloses the ligand exchange reaction and kinetic study with Mo, Nb complexes including the $\text{Nb}(=\text{NtBu})\text{Cp}(\text{OiPr})_2$, $\text{Nb}(=\text{NtBu})\text{Cp}(\text{OtBu})_2$ (Dalton

Transactions (2003), (23), 4457-4465).

Today, there is a need for providing liquid or low melting point (<50°C. at standard pressure), highly thermally stable, Niobium and Vanadium containing precursor molecules suitable for vapor phase film deposition with controlled thickness and composition at high temperature.

According to the invention, certain precursors have been found suitable for the deposition of Nb and V containing thin films by ALD processes and to have the following advantages:

- They are liquid at room temperature or having a melting point lower than 50°C,
- They are thermally stable to enable proper distribution (gas phase or direct liquid injection) without particles generation,
- They are thermally stable to allow wide self-limited ALD window, allowing deposition of a variety of Nb and V containing films, by using one or a combination of co-reactants. The co-reactant can typically be selected from an oxidizing agent, such as O₂, O₃, H₂O, H₂O₂, alcohols, or a nitriding agent such as ammonia, amines, polyamines, hydrazines, NO. Such co-reactant may be plasma activated or not

They can also be used in combination with another precursor to deposit mixed films.

- More particularly, these precursors are suitable to be used with precursors of group IV and other group V elements, as well as with phosphorous or lithium compounds for energy storage applications for instance.

According to a first embodiment, the invention relates to a Metal-containing film forming composition comprising a precursor having the formula:



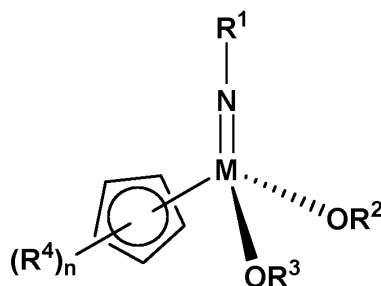
Wherein, M = V or Nb or Ta; R¹-R³ = independently H or C1-C10 alkyl group;

L = Substituted or unsubstituted cyclopentadienes, cyclohexadienes,

- cycloheptadienes, cyclooctadienes, fluorenes, indenenes, fused ring systems, propene, butadiene, pentadienes, hexadienes, heptadienes; m = 0 or 1.

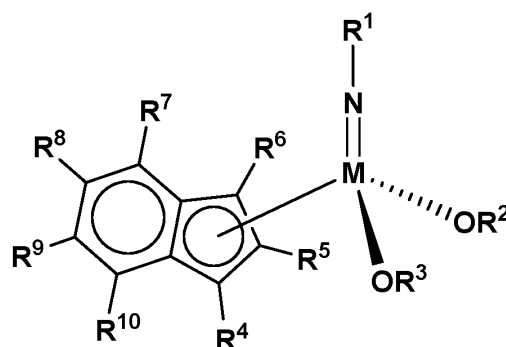
According to other particular embodiments, the invention concerns:

- A Metal-containing film forming composition as defined above, wherein R^1 is H, R^2 is tBu; R^3 and R^4 are Et.
- A Metal-containing film forming composition as defined above, wherein R^1 is H, R^2 , R^3 and R^4 are tBu.
- A Metal-containing film forming composition as defined above, wherein R^1 is H, R^2 is tBu; R^3 and R^4 are sBu.
- A Metal-containing film forming composition as defined above, wherein M is Vanadium.
- A Metal-containing film forming composition as defined above, wherein M is Niobium.
- A Metal-containing film forming composition of formula:



wherein each R^4 is H or a C1-C10 alkyl group or a fluoro group; $n \leq 5$.

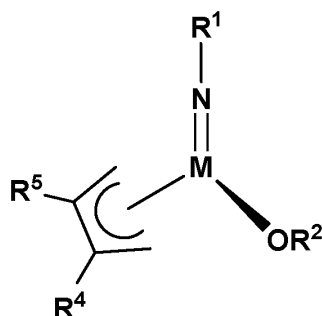
- The Metal-containing film forming composition of formula:



wherein each R^4 to R^{10} is independently H or a C1-C10 alkyl group or a fluoro group.

- The Metal-containing film forming composition of formula:

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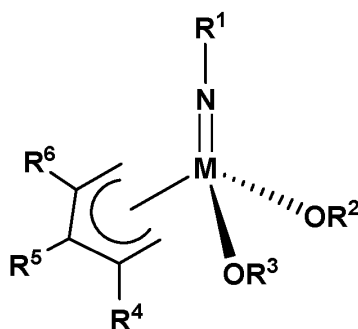


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wherein each R^4 to R^6 is independently H or a C1-C10 alkyl group, or a fluoro group.

- The Metal-containing film forming composition of formula:

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wherein each R^4 to R^6 is independently H or a C1-C10 alkyl group, or a fluoro group.

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- A method of forming a Metal-containing film, the method comprising introducing into a reactor having a substrate therein a vapor of the Metal-containing film forming composition as defined above; and depositing at least part of the precursor onto the substrate.
- A method as defined above, further comprising introducing a reactant into the reactor.
- A method as defined above, wherein the reactant is selected from the group consisting of O_2 , O_3 , H_2O , H_2O_2 , NO , N_2O , NO_2 , TMPO, oxygen radicals thereof, and mixtures thereof.

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- A method as defined above, wherein M = Nb and the Niobium-containing film forming composition and the reactant are introduced into the chamber sequentially and the reactor is configured for atomic layer deposition.
- A method as defined above wherein the substrate is a cathode active material powder.
- A method as defined above wherein the substrate is a cathode material consisting of a cathode active material powder, a conductive carbon and a binder material deposited onto a current collector foil.
- A method as defined above, wherein the substrate is ZrO₂ and the Niobium-containing film forming composition is used to form a DRAM capacitor.
- The method, further comprising plasma treating the reactant.
- According to another embodiment, the invention relates to a method of manufacturing a thin interface layer into a Lithium-ion or into an all-solid-state-batteries device. The thin layer is a Niobium containing oxide layer deposited by Atomic Layer Deposition using the Nb precursor of the invention having the formula:



R¹-R³ = independently H or C1-C10 alkyl group;

L = Substituted or unsubstituted cyclopentadienes, cyclohexadienes, cycloheptadienes, cyclooctadienes, fluorenes, indenenes, fused ring systems, propene, butadiene, pentadienes, hexadienes, heptadienes; m = 0 or 1; and a co-reactant onto a cathode active material in the form of a powder, or onto a cathode. The co-reactant can be selected from the list consisting of O₂, O₃, H₂O, H₂O₂, NO, NO₂, H₂O or a NO_x, trimethylphosphate, diethyl phosphoramidate, a sulfate or any other oxygen containing species. The thin layer can be a niobium containing ternary or quaternary oxide, such as LiNbO, LiNb(M)O, NbMO with M being selected from the list consisting of Zr, Ti, Co, W, Ta, V, Sr, Ba, La, Y, Sc, Mn, Ni, Mo. The thin interface layer can be deposited directly onto the cathode active material for instance in a fluidized bed ALD-reactor. The cathode active material is the main element in the composition of cathode battery cells. The cathode materials are for example Cobalt, Nickel and Manganese in the crystal structure such as the layered structure forms a multi-metal oxide material in which lithium is inserted. The cathode active material may preferably

be a "NMC" (a lithium nickel manganese cobalt oxide), a NCA (a lithium nickel cobalt aluminum oxide), a LNO (a lithium nickel oxide) a LMNO (a lithium manganese nickel oxide), or a LFP (a lithium iron phosphate). For instance, the cathode active material can be NMC622 or NMC811. The thin interface layer may be done on the electrode active material powder, on electrode active material porous materials, on different shapes of electrode active materials, or in pre-formed electrodes in which the electrode active material may be already associated with conductive carbons and/or binders and may already be supported by a current collector foil.

The following examples are an illustration of the various embodiments of the present invention, without being a limitation.

Example 1

Synthesis of Niobium tButyl Imido Cyclopentadienyl Ethoxy, $\text{Nb(=NtBu)Cp(OEt)}_2$

To a solution of $\text{Nb(=NtBu)Cp(NMe}_2)_2$ (2g, 6.3mmol) in 30 mL of Toluene at -78°C , was added dropwise a solution of Ethyl alcohol (0.58g, 12.6mmol). After stirring the mixture at room temperature for 12h, the solvent was removed under vacuum to give yellow oil. The material was then purified by distillation up to 100°C at 25mTorr to give 1.34g (66.6%) of yellow oil. The material was characterized by NMR ^1H (δ , ppm, C_6D_6): 6.18 (s, 5H), 4.54 (q, 4H), 1.28 (t, 6H), 1.16 (s, 9H).

The purified product left a 2.1% residual mass during open-cup TGA analysis measured at a temperature rising rate of $10^\circ\text{C}/\text{min}$ in an atmosphere which flows nitrogen at 200mL/min. These results are shown in Fig 1, which is a TGA graph illustrating the percentage of weight upon temperature increase. Onset temperature of melting (-3.8°C) and decomposition(317.3°C) of the product were measured by Differential scanning calorimetry(DSC), which are shown in Fig 4.

Example 2

Synthesis of Niobium tButyl Imido Cyclopentadienyl tButoxy, $\text{Nb(=NtBu)Cp(OtBu)}_2$

To a solution of $\text{Nb(=NtBu)Cp(NMe}_2)_2$ (2g, 6.3mmol) in 30 mL of Toluene at -78°C , was added dropwise a solution of tert-Butyl alcohol (0.93g, 12.6mmol). After stirring the mixture at room temperature for 12h, the solvent was removed under vacuum to give yellow oil. The material was then purified by distillation up to 100°C at 25mTorr to give

2.0g (84.6%) of yellow oil. The material was characterized by NMR ^1H (δ , ppm, C_6D_6): 6.17 (s, 5H), 1.32 (s, 18H), 1.21 (s, 9H).

The purified product left a 0.6% residual mass during open-cup TGA analysis measured at a temperature rising rate of $10^\circ\text{C}/\text{min}$ in an atmosphere which flows nitrogen at 200mL/min. These results are shown in Fig 2, which is a TGA graph illustrating the percentage of weight upon temperature increase. Onset temperature of melting (34.5°C) and decomposition (285.1°C) of the product were measured by Differential scanning calorimetry (DSC), which are shown in Fig 5.

10 Example 3

Synthesis of Niobium tButyl Imido Cyclopentadienyl sButoxy $\text{Nb}(=\text{NtBu})\text{Cp}(\text{OsBu})_2$

To a solution of $\text{Nb}(=\text{NtBu})\text{Cp}(\text{NMe}_2)_2$ (2g, 6.3mmol) in 30 mL of Toluene at -78°C , was added dropwise a solution of sec-Butyl alcohol (0.93g, 12.6mmol). After stirring the mixture at room temperature for 12h, the solvent was removed under vacuum to give yellow oil. The material was then purified by distillation up to 125°C at 25mTorr to give 1.75g (74%) of yellow oil. The material was characterized by NMR ^1H (δ , ppm, C_6D_6): 6.19 (s, 5H), 4.49 (m, 2H), 1.61 (m, 2H), 1.49 (m, 2H), 1.31 (d, 3H), 1.26 (d, 3H), 1.18 (s, 9H), 0.99 (t, 6H).

The purified product left a 1.3% residual mass during open-cup TGA analysis measured at a temperature rising rate of $10^\circ\text{C}/\text{min}$ in an atmosphere which flows nitrogen at 200mL/min. These results are shown in Fig 3, which is a TGA graph illustrating the percentage of weight upon temperature increase. Onset temperature of decomposition (318.6°C) of the product were measured by Differential scanning calorimetry (DSC), which are shown in Fig 6.

25 Other examples:

1. $\text{Nb}(=\text{NtBu})(\text{RCp})(\text{OEt})_2$ can be synthesized from the way below.

(R = H or C1-C10 alkyl group)

To a solution of $\text{Nb}(=\text{NtBu})(\text{RCp})(\text{NMe}_2)_2$ in Toluene at -78°C , was added dropwise a solution of ethyl alcohol. After stirring the mixture at room temperature for 12h, the solvent was removed under vacuum. The material was then purified by distillation or sublimation to give a final product.

2. $\text{Nb}(=\text{NR})(\text{Cp})(\text{OEt})_2$ can be synthesized from the way below.

($\text{R} = \text{H}$ or C1-C10 alkyl group)

To a solution of $\text{Nb}(=\text{NR})\text{Cp}(\text{NMe}_2)_2$ in Toluene at -78°C , was added dropwise a solution of ethyl alcohol (12.6mmol). After stirring the mixture at room temperature for 12h, the solvent was removed under vacuum. The material was then purified by distillation or sublimation to give a final product.

3. $\text{V}(=\text{NtBu})(\text{Cp})(\text{OEt})_2$ can be synthesized from the way below.

To a solution of $\text{V}(=\text{NtBu})\text{Cp}(\text{NMe}_2)_2$ in Toluene at -78°C , was added dropwise a solution of ethyl alcohol (12.6mmol). After stirring the mixture at room temperature for 12h, the solvent was removed under vacuum. The material was then purified by distillation or sublimation to give a final product.

In addition Fig 7 represents a ThermoGravimetric Analysis (TGA) graph demonstrating the percentage of weight with increasing temperature of Niobium tButyl Imido Cyclopentadienyl Dimethylamido, $\text{Nb}(=\text{NtBu})\text{Cp}(\text{NMe}_2)_2$, which is the precursor chosen as the reference in the state of the art.

The following table illustrates a comparison of the properties of the following precursors:

Compounds	Temperature at 133 Pa
$\text{Nb}(=\text{NtBu})\text{Cp}(\text{OEt})_2$	100 °C
$\text{Nb}(=\text{NtBu})\text{Cp}(\text{OtBu})_2$	105 °C
$\text{Nb}(=\text{NtBu})\text{Cp}(\text{OsBu})_2$	119 °C
$\text{Nb}(=\text{NtBu})\text{Cp}(\text{NMe}_2)(\text{OtBu})$	106 °C
$\text{Nb}(=\text{NtBu})\text{Cp}(\text{NMe}_2)_2$	117 °C
$\text{Nb}(\text{Cp})_2(\text{iPr-amd})_2$	170 °C

Conclusion:

The disclosed precursor compounds offer high thermal stability, high volatility and low viscosity when compared to $\text{Nb}(=\text{NtBu})\text{Cp}(\text{NMe}_2)_2$. These properties enable more effective and efficient vapor deposition process.

Fig 1. is a ThermoGravimetric Analysis (TGA) graph demonstrating the percentage of weight with increasing temperature of Niobium tButyl Imido Cyclopentadienyl Ethoxy, $\text{Nb(=NtBu)Cp(OEt)}_2$.

- 5 **Fig 2.** is a thermoGravimetric Analysis (TGA) graph demonstrating the percentage of weight with increasing temperature of Niobium tButyl Imido Cyclopentadienyl tButoxy, $\text{Nb(=NtBu)Cp(OtBu)}_2$.

Fig 3. Is a thermoGravimetric Analysis (TGA) graph demonstrating the percentage of weight with increasing temperature of Niobium tButyl Imido Cyclopentadienyl sButoxy

- 10 $\text{Nb(=NtBu)Cp(OsBu)}_2$.

Fig 4. Is a differential scanning calorimetry(DSC) of Niobium tButyl Imido Cyclopentadienyl Ethoxy, $\text{Nb(=NtBu)Cp(OEt)}_2$.

Fig 5. Is a differential scanning calorimetry(DSC) of Niobium tButyl Imido Cyclopentadienyl tButoxy, $\text{Nb(=NtBu)Cp(OtBu)}_2$.

- 15 **Fig 6.** Is a differential scanning calorimetry(DSC) of Niobium tButyl Imido Cyclopentadienyl sButoxy $\text{Nb(=NtBu)Cp(OsBu)}_2$.

Fig 7 is a ThermoGravimetric Analysis (TGA) graph demonstrating the percentage of weight with increasing temperature of Niobium tButyl Imido Cyclopentadienyl Dimethylamido, $\text{Nb(=NtBu)Cp(NMe}_2)_2$.

CLAIMS

1. A Metal-containing film forming composition comprising a precursor having the formula:



Wherein, M = V or Nb or Ta; R¹-R³ = independently H or C1-C10 alkyl group;

L = Substituted or unsubstituted cyclopentadienes, cyclohexadienes, cycloheptadienes, cyclooctadienes, fluorenes, indenenes, fused ring systems, propene, butadiene, pentadienes, hexadienes, heptadienes; m = 0 or 1.

2. The Metal-containing film forming composition of claim 1, wherein R¹ is H, R² is tBu; R³ and R⁴ are Et.

15 3. The Metal-containing film forming composition of claim 1, wherein R¹ is H, R², R³ and R⁴ are tBu.

4. The Metal-containing film forming composition of claim 1, wherein R¹ is H, R² is tBu; R³ and R⁴ are sBu.

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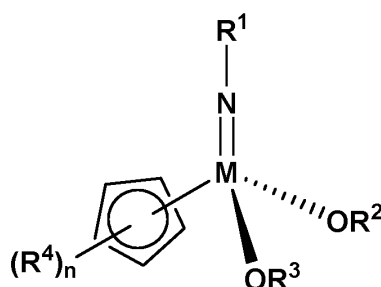
5. The Metal-containing film forming composition of claim 1, 2, 3 or 4 wherein, M is Vanadium.

6. The Metal-containing film forming composition of claim 1, 2, 3 or 4 wherein, M is Niobium.

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7. The Metal-containing film forming composition according to anyone of claims 1 to 6, of formula:

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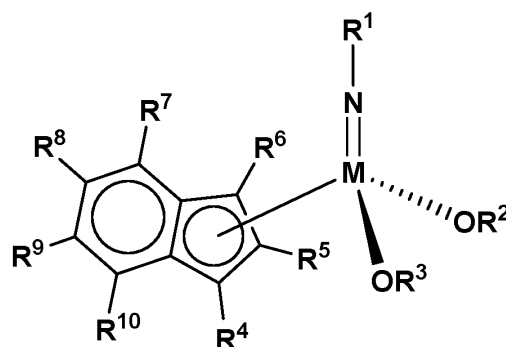


wherein each R^4 is H or a C1-C10 alkyl group or a fluoro group; $n \leq 5$.

8. The Metal-containing film forming composition according to anyone of claims 1 to 6, of formula:

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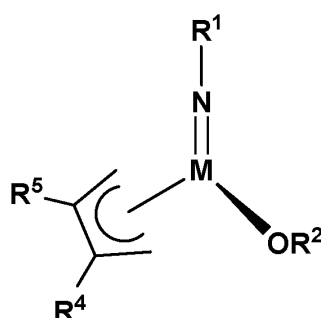


wherein each R^4 to R^{10} is independently H or a C1-C10 alkyl group or a fluoro group.

9. The Metal-containing film forming composition according to anyone of claims 1 to 6, of formula:

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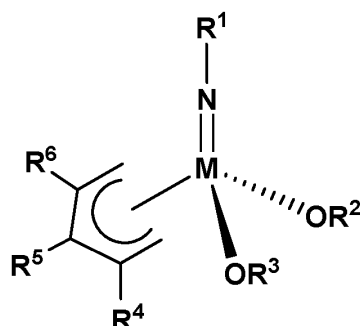


wherein each R^4 to R^6 is independently H or a C1-C10 alkyl group, or a fluoro group.

10. The Metal-containing film forming composition according to anyone of claims 1 to 6, of formula:

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wherein each R^4 to R^6 is independently H or a C1-C10 alkyl group, or a fluoro group.

11. A method of forming a Metal-containing film, the method comprising introducing into a reactor having a substrate therein a vapor of the Metal-containing film forming composition of anyone of claims 1 to 10; and depositing at least part of the precursor onto the substrate.
- 5 12. The method of claim 11, further comprising introducing a reactant into the reactor.
- 10 13. The method of claim 12, wherein the reactant is selected from the group consisting of O₂, O₃, H₂O, H₂O₂, NO, N₂O, NO₂, TMPO, oxygen radicals thereof, and mixtures thereof.
14. The method of claim 12, wherein M is Nb and the Niobium-containing film forming composition and the reactant are introduced into the chamber sequentially
15 and the reactor is configured for atomic layer deposition.
15. The method of claim 11 where the substrate is a cathode active material powder.
- 20 16. The method of claim 11 where the substrate is a cathode material consisting of a cathode active material powder, a conductive carbon and a binder material deposited onto a current collector foil.