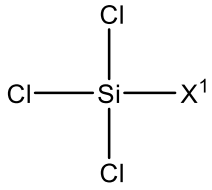
WHAT IS CLAIMED IS:

1. A method of forming a metal-containing film, the method comprising:

forming a blocking layer on a first substrate surface by a first vapor phase deposition process or a first liquid phase deposition process,

wherein the first vapor phase deposition process comprises vaporizing a compound corresponding in structure to Formula (I):



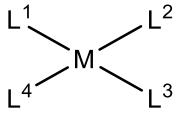
(I)

wherein

X^1 is R^1 or R^2R^3; wherein R^1 is a C_1–C_{20}-alkyl, optionally substituted with one or more trichlorosilyl group; R^2 is a C_1–C_{20}-alkylene group optionally substituted with one or more halogen; and R^3 is selected from the group consisting of a nitrile group, an ethenyl group, a halogen, a triflouromethyl group, an acetoxy group, a methoxyethoxy group, and a phenoxy group; and

wherein the first liquid phase deposition process comprises contacting the first substrate surface with a solution comprising the compound corresponding in structure to Formula (I); and

forming the metal-containing film on a second substrate surface by a second deposition process, the second deposition process comprising vaporizing at least one metal complex corresponding in structure to Formula II:



(II)

wherein M is Hf; and

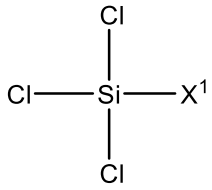
L^1, L^2, L^3, and L^4 are each independently selected from the group consisting of a C_1–C_8-alkyl group, a C_1–C_8-alkoxy group, and a Cp group optionally substituted with at least one C_1–C_8-alkyl;

wherein the first substrate surface comprises a dielectric material or a metal oxide material and the second substrate surface comprises a metal material.

2. A method of forming a metal-containing film, the method comprising:

forming a blocking layer on a first portion of a substrate by a first vapor phase deposition process or a first liquid phase deposition process,

wherein the first vapor phase deposition process comprises vaporizing a compound corresponding in structure to Formula (I):



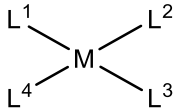
(I)

wherein

X^1 is R^1 or R^2R^3; wherein R^1 is a C_1–C_{20}-alkyl, optionally substituted with one or more trichlorosilyl group; R^2 is a C_1–C_{20}-alkylene group optionally substituted with one or more halogen; and R^3 is selected from the group consisting of a nitrile group, an ethenyl group, a halogen, a triflouromethyl group, an acetoxy group, a methoxyethoxy group, and a phenoxy group; and

wherein the first liquid phase deposition process comprises contacting the first portion of the substrate with a solution comprising the compound corresponding in structure to Formula (I); and

forming the metal-containing film on a second portion of the substrate by a second deposition process, the second deposition process comprising vaporizing at least one metal complex corresponding in structure to Formula II:



(II)

wherein M is Hf; and

L^1, L^2, L^3, and L^4 are each independently selected from the group consisting of a C_1–C_8-alkyl group, a C_1–C_8-alkoxy group, and a Cp group optionally substituted with at least one C_1–C_8-alkyl;

wherein the first portion of the substrate comprises a dielectric material or a metal oxide material and the second portion of the substrate comprises a metal material.

3. The method of claim 1 or claim 2, wherein R^1 is a C_1–C_{15}-alkyl, optionally substituted with one or more of a trichlorosilyl group.

4. The method of any one of the previous claims, wherein R^1 is a C_1–C_{12}-alkyl, each optionally substituted with one or more of a trichlorosilyl group.

5. The method of any one of the previous claims, wherein R^2 is a C_1–C_{15}-alkylene.

6. The method of any one of the previous claims, wherein R^2 is a C_1–C_{12}-alkylene.

7. The method of any one of the previous claims, wherein the compound corresponding in structure to Formula (I) is selected from the group consisting of:

n-octyltrichlorosilane;
dodecyltrichlorsilane;
11-cyanoundecyltrichlorosilane;
11-acetoxyundecyltrichlorosilane;
(tridecafluoro-1,1,2,2-tetrahydrooxtyl)trichlorosilane;
10-undecenyltrichlorosilane;
11-bromoundecyltrichlorosilane;
11-(2-methoxyethoxy)undecyltrichlorosilane;
11-phenoxyundecyltrichlorosilane; and
1,2-bis(trichlorosilyl)decane.

8. The method of any one of the previous claims, wherein the metal complex is $(MeCp)_2Hf(OMe)(Me)$.

9. The method of any one of the previous claims, wherein the metal of the metal-containing film is present in an amount of less than about 15 at.% on the blocking layer.

10. The method of any one of claims 1 and 3 to 9, wherein the first substrate surface and the second substrate surface are present on the same substrate or on different substrates.

11. The method of any one of the previous claims, wherein the metal material comprises W, Co, Cu or a combination thereof.

12. The method of any one of the previous claims, wherein the dielectric material comprises SiO_2, SiN, or a combination thereof, or the metal oxide material comprises HfO_2, ZrO_2, SiO_2, Al_2O_3, or a combination thereof.

13. The method of any one of the previous claims, wherein first vapor phase deposition process and the second deposition process are independently chemical vapor deposition or atomic layer deposition.

14. The method of claim 13, wherein the chemical vapor deposition is pulsed chemical vapor deposition, continuous flow chemical vapor deposition, or liquid injection chemical vapor deposition.

15. The method of claim 13, wherein the atomic layer deposition is liquid injection atomic layer deposition or plasma-enhanced atomic layer deposition.

16. The method of any one of claims 1 to 12, wherein the first liquid phase deposition process comprises dipping the first substrate surface or the first portion of the substrate surface in the solution comprising the compound of Formula (I) one or more times.

17. The method of any one of the previous claims, wherein the metal complex is delivered to a substrate in pulses alternating with pulses of an oxygen source.

18. The method of claim 17, wherein the oxygen source is selected from the group consisting of H_2O, H_2O_2, O_2, ozone, air, *i*-PrOH, *t*-BuOH, and N_2O.

19. The method of any one of the previous claims, further comprising vaporizing at least one co-reactant selected from the group consisting of hydrogen, hydrogen plasma, oxygen, air, water, ammonia, a hydrazine, a borane, a silane, ozone, and a combination of any two or more thereof.

20. The method of any the previous claims, wherein the method is used for a DRAM or CMOS application.