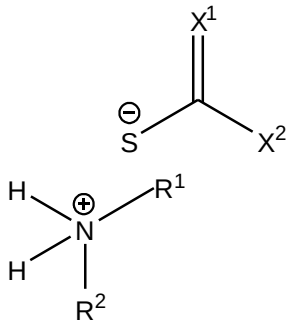
[00077] In another embodiment, a method of forming a metal-containing film on a substrate surface comprises: during an ALD process, exposing a substrate to a vapor phase metal complex according to one or more of the embodiments described herein (*e.g.*, corresponding in structure to Formula (III)), such that a layer is formed on the surface comprising the metal complex bound to the surface by the metal center (*e.g.,* hafnium); during an ALD process, exposing the substrate having bound metal complex with a co-reactant such that an exchange reaction occurs between the bound metal complex and co-reactant, thereby dissociating the bound metal complex and producing a first layer of elemental metal on the surface of the substrate; and sequentially repeating the ALD process and the treatment.

[00078] The reaction time, temperature and pressure are selected to create a metal-surface interaction and achieve a layer on the surface of the substrate. The reaction conditions for the ALD reaction will be selected based on the properties of the metal complex. The deposition can be carried out at atmospheric pressure but is more commonly carried out at a reduced pressure. The vapor pressure of the metal complex should be low enough to be practical in such applications. The substrate temperature should be low~~high~~ enough to keep the bonds between the metal atoms at the surface intact and to prevent thermal decomposition of gaseous reactants. However, the substrate temperature should also be low~~high~~ enough to keep the source materials (*i.e.,* the reactants) in the gaseous phase and to provide sufficient activation energy for the surface reaction. The appropriate temperature depends on various parameters, including the particular metal complex used and the pressure. The properties of a specific metal complex for use in the ALD deposition methods disclosed herein can be evaluated using methods known in the art, allowing selection of appropriate temperature and pressure for the reaction. In general, lower molecular weight and the presence of functional groups that increase the rotational entropy of the ligand sphere result in a melting point that yields liquids at typical delivery temperatures and increased vapor pressure.

[00079] A metal complex for use in the deposition methods will have all of the requirements for sufficient vapor pressure, sufficient thermal stability at the selected substrate temperature and sufficient reactivity to produce a reaction on the surface of the substrate without unwanted impurities in the thin film. Sufficient vapor pressure ensures that molecules

CLAIMS

1. A compound corresponding in structure to Formula I:



(I)

wherein

R^1 and R^2 are each independently a C_1–C_{20}-alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group;

X^1 is O or S; and

X^2 is selected from the group consisting of R^3, NR^4R^5, $–SR^6$, and $–OR^7$; wherein R^3, R^4, R^5, R^6, and R^7 each independently are a C_1–C_{20}-alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group; and wherein at least one of R^1 and R^4 are dodecyl.

2. The compound of claim 1, wherein R^1, R^2, R^3, R^4, R^5, R^6, and R^7 are each independently a C_1–C_{15}-alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group.

~~3. The compound of claim 1 or claim 2, wherein R^1, R^2, R^3, R^4, R^5, R^6, and R^7 are each independently a C_1–C_{12}-alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group.~~

4~~3~~. The compound of ~~any one of~~ claim~~s~~ 1 ~~to 3~~or 2, wherein X^2 is NR^4R^5.

~~5~~4. The compound of any one of claims 1, 2, or ~~to~~ ~~3~~4, wherein R^1 is a C_1–C_{15}-alkyl, R^2 is C_1–C_4-alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group; X^1 is S; and X^2 is NR^4R^5, wherein R^4 is a C_1–C_{15}-alkyl, R^5 is C_1–C_4-alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group.

~~5~~6. The compound of any one of claims 1, 2, 3, or ~~to~~ ~~4~~5, wherein the ~~complex~~ compound corresponding in structure to Formula (I) is N-dodecyl-N-methyl carbamodithioic acid N-dodecyl-N-methylammonium salt.

~~7~~6. A method of forming a metal-containing film, the method comprising:

forming a blocking layer on a first substrate surface by a first deposition process, the first deposition process comprising vaporizing the compound of any one of claims 1, 2 or 3 to ~~5~~6; 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;

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

~~8. A method of forming a metal-containing film, the method comprising:~~

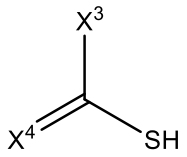
~~forming a blocking layer on a first portion of a substrate by a first deposition process, the first deposition process comprising exposing the substrate to the compound of any one of claims 1 to 6; and~~

~~forming the metal-containing film on a second portion of the substrate by a second deposition process, the second deposition process comprising exposing the substrate to at least one metal complex;~~

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

~~9~~7. A method of forming a metal-containing film, the method comprising:

forming a blocking layer on a first substrate surface by a first deposition process, the first deposition process comprising vaporizing a compound corresponding in structure to Formula II:



(II)

wherein

X^3 is selected from the group consisting of R^8, NR^9R^{10}, $–SR^{11}$, and $–OR^{12}$; wherein R^8, R^9, R^{10}, R^{11}, and R^{12} are each independently a $C_1–C_{20}$-alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group; and

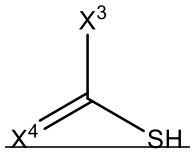
X^4 is O or S; and

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;

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

~~10. 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 deposition process, the first deposition process comprising exposing the substrate to a compound corresponding in structure to Formula II:~~



~~(II)~~

~~wherein~~

~~X^3 is selected from the group consisting of R^8, NR^9R^{10}, SR^{11}, and OR^{12}; wherein R^8, R^9, R^{10}, R^{11}, and R^{12} are each independently a C_1–C_{20}-alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group; and~~

~~X^4 is O or S; and~~

~~forming the metal-containing film on a second portion of the substrate by a second deposition process, the second deposition process comprising exposing the substrate to at least one metal complex;~~

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

~~11~~8. The method of claim ~~9~~7 ~~or claim 10~~, wherein R^8, R^9, R^{10}, R^{11}, and R^{12} are each independently a C_1–C_{15}-alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group.

~~12. The method of any one of claims 9 to 11, wherein R^8, R^9, R^{10}, R^{11}, and R^{12} are each independently a C_1–C_{10}-alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group.~~

~~13~~9. The method of ~~any one of~~ claim~~s~~ ~~9~~ 7 or 8~~to 12~~, wherein X^3 is R^8.

~~14~~10. The method of ~~any one of~~ claim~~s~~ ~~9~~ 7 ~~to 12~~or 8, wherein X^3 is NR^9R^{10}.

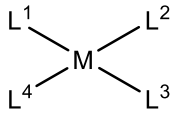
~~15~~11. The method of ~~any one of~~ claim~~s~~ ~~9~~7, ~~10~~ ~~and~~ or ~~14~~10, wherein X^3 is NR^9R^{10}; X^4 is S; R^9 is a C_1–C_4-alkyl and R^{10} is a C_1–C_{12}-alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group.

12~~16~~. The method of any one of claims ~~9~~7, ~~10, 14~~10, and ~~15~~11, wherein the compound corresponding in structure to Formula (II) is N-dodecyl-N-methyl carbamodithioic acid.

~~17~~13. The method of ~~any one of~~ claim~~s~~ ~~9~~ 7 ~~to 12~~or 8, wherein X^3 is $–SR^{11}$.

~~18~~14. The method of ~~any one of~~ claim~~s~~ ~~9~~ 7 ~~to 12~~or 8, wherein X^3 is $–OR^{12}$.

~~19~~15. The method of any one of claims ~~7~~6, 7, 8, or 9 to ~~18~~14, wherein the metal complex corresponds in structure to Formula III:



(III)

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.

~~20~~16. The method of any one of claims 6, 7, 8, or 9~~7~~to ~~19~~15, wherein the metal complex is $(MeCp)_2Hf(OMe)(Me)$.

~~21~~17. The method of any one of claims 6, 7, 8, or 9~~7~~to ~~20~~16, wherein the metal of the metal-containing film is present in an amount of less than about 15 at.% on the blocking layer.

~~22~~18. The method of any one of claims 6, 7, 8, or 9~~7, 9, and 11~~ to ~~21~~17, wherein the first substrate surface and the second substrate surface are present on the same substrate or on different substrates.

~~23~~19. The method of any one of claims 6, 7, 8, or 9~~7~~ to ~~22~~18, wherein the metal material comprises W, Co, Cu or a combination thereof.

~~24~~20. The method of any one of claims 6, 7, 8, or 9~~7~~ to ~~23~~19, 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.

~~25~~21. The method of any one of claims 6, 7, 8, or 9~~7~~ to ~~24~~20, wherein the compound corresponding in structure to Formula (I), the compound corresponding in structure to Formula (II), or a combination thereof is delivered at a temperature of less than about 150°C.

~~26. The method of any one of claims 7 to 25, wherein first deposition process and the second deposition process are independently chemical vapor deposition or atomic layer deposition.~~

~~27. The method of claim 26, wherein the chemical vapor deposition is pulsed chemical vapor deposition, continuous flow chemical vapor deposition, or liquid injection chemical vapor deposition.~~

~~28. The method of claim 26, wherein the atomic layer deposition is liquid injection atomic layer deposition or plasma-enhanced atomic layer deposition.~~

~~29. The method of any one of claims 7 to 28, wherein the metal complex is delivered to a substrate in pulses alternating with pulses of an oxygen source.~~

~~30. The method of claim 29, 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.~~

~~31~~22. The method of any one of claims 6, 7, 8, or 9~~7~~ to 21~~ to 30~~, 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.

~~32~~23. The method of any one of claims 6, 7, 8, or 9~~7~~to 21 or~~to~~ 22~~31~~, wherein the method is used for a DRAM or CMOS application.