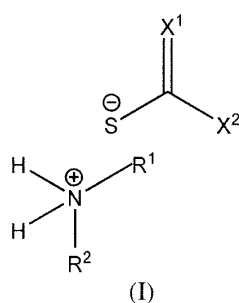


WHAT IS CLAIMED IS:

1. A compound corresponding in structure to Formula I:



5 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

10 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.

15 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.

20 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. The compound of any one of claims 1 to 3, wherein X^2 is NR^4R^5 .

5. The compound of any one of claims 1 to 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.

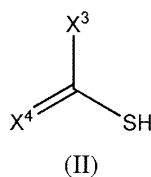
6. The compound of any one of claims 1 to 5, wherein the complex corresponding in structure to Formula (I) is N-dodecyl-N-methyl carbamodithioic acid N-dodecyl-N-methylammonium salt.

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 the compound of any one of claims 1 to 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. 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:

5



10

wherein

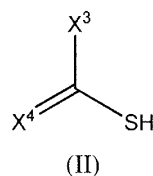
X^3 is selected from the group consisting of R^8 , NR^9R^{10} , $-\text{SR}^{11}$, and $-\text{OR}^{12}$; wherein R^8 , R^9 , R^{10} , R^{11} , and R^{12} are each independently a C_1 – C_{20} -alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and
15 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
20 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
25 corresponding in structure to Formula II:



5 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

10 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;

15 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. The method of claim 9 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.

20 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.

25 13. The method of any one of claims 9 to 12, wherein X^3 is R^8 .

14. The method of any one of claims 9 to 12, wherein X^3 is NR^9R^{10} .

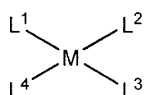
15. The method of any one of claims 9, 10 and 14, wherein X^3 is NR^9R^{10} ; X^4 is S; R^9 is a C_1 – C_4 -alkyl and R^{10} is a C_1 – C_{12} -alkyl, each optionally substituted with one or more of a trifluoromethyl group, a hydroxyl group, a nitrile group, an alkoxy group, and an amino group.

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

17. The method of any one of claims 9 to 12, wherein X^3 is $-SR^{11}$.

10 18. The method of any one of claims 9 to 12, wherein X^3 is $-OR^{12}$.

19. The method of any one of claims 7 to 18, wherein the metal complex corresponds in structure to Formula III:



(III)

15 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

20. The method of any one of claims 7 to 19, wherein the metal complex is $(MeCp)_2Hf(OMe)(Me)$.

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

25

22. The method of any one of claims 7, 9, and 11 to 21, wherein the first substrate surface and the second substrate surface are present on the same substrate or on different substrates.
- 5 23. The method of any one of claims 7 to 22, wherein the metal material comprises W, Co, Cu or a combination thereof.
24. The method of any one of claims 7 to 23, wherein the dielectric material comprises SiO₂, SiN, or a combination thereof, or the metal oxide material comprises HfO₂,
10 ZrO₂, SiO₂, Al₂O₃, or a combination thereof.
25. The method of any one of claims 7 to 24, 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.
- 15 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.
- 20 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
25 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 H₂O, H₂O₂, O₂, ozone, air, *i*-PrOH, *t*-BuOH, and N₂O.
31. The method of any one of claims 7 to 30, further comprising vaporizing at least
5 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. The method of any one of claims 7 to 31, wherein the method is used for a
10 DRAM or CMOS application.