

WHAT IS CLAIMED IS:

1. A method for forming a molybdenum-containing film, the method comprising:
 - A. thermally depositing a first film comprising an elemental metal on a surface of a substrate at a first temperature less than or equal to about 400°C, wherein the elemental metal is tungsten, molybdenum, or a combination thereof; and
 - B. thermally depositing a second film on at least a portion of the first film at a second temperature of greater than about 400°C, wherein the second film comprises a reaction product of a molybdenum-containing precursor with a reducing agent.
2. A method for forming a molybdenum-containing film, the method comprising:
 - A. thermally depositing a first film comprising an elemental metal on a surface of a substrate at a first temperature less than or equal to about 400°C, wherein the elemental metal is selected from the group consisting of ruthenium, cobalt, and a combination thereof; and
 - B. thermally depositing a second film on at least a portion of the first film at a second temperature of greater than about 400°C, wherein the second film comprises a reaction product of a molybdenum-containing precursor with a reducing agent.
3. The method of claim 1, wherein the first film comprises elemental molybdenum and the first film has a thickness of greater than or equal to about 2 nm.
4. The method of claim 1 or claim 3, wherein the first film comprises elemental molybdenum and has a thickness of about 2 nm to about 10 nm.
5. The method of any one of claims 1, 3, or 4, wherein the first film comprises elemental molybdenum and the first film has a conductivity of less than or equal to about 200 $\mu\Omega$.cm.
6. The method of claim 2, wherein the first film comprises elemental ruthenium and the first film has a thickness of greater than or equal to about 2 nm.

7. The method of any one of claims 1 or 3 to 5, wherein the thermally depositing the first film comprises delivering a first metal-containing precursor and a co-reactant to the substrate, wherein the first metal-containing precursor is a molybdenum halide or molybdenum hexacarbonyl.
8. The method of claim 7, wherein the molybdenum halide is MoCl_5 or MoF_6 .
9. The method of claim 2 or claim 6, wherein the thermally depositing the first film comprises delivering a first metal-containing precursor and a co-reactant to the substrate, wherein the first metal-containing precursor is a ruthenium-containing precursor.
10. The method of claim 9, wherein the ruthenium-containing precursor is η^4 -2,3-dimethylbutadiene ruthenium tricarbonyl $((\text{DMBD})\text{Ru}(\text{CO})_3)$ or (ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl) $(\text{EtBz})\text{Ru}(\text{EtCHD})$.
11. The method of any one of the previous claims wherein the thermally depositing the second film comprises delivering the molybdenum-containing precursor and a reducing agent to the substrate, wherein the molybdenum-containing precursor is a molybdenum halide or a molybdenum oxyhalide.
12. The method of claim 11, wherein molybdenum halide is MoCl_5 or MoF_6 , and the molybdenum oxyhalide is MoOCl_4 or MoO_2Cl_2 .
13. The method of any one of the previous claims, wherein the reducing agent is hydrogen or hydrogen plasma.
14. The method of any one of the previous claims, wherein the co-reactant is selected from the group consisting of 1,4-di-trimethylsilyl-2-methyl-cyclohexa-2,5-diene (CHD), 1,4-bis-trimethylsilyl-1,4-dihydropyrazine (DHP), 1-trimethylsilylcyclohexa-2,5-diene,

nitrogen plasma, ammonia plasma, oxygen, air, water, ozone, NH_3 , H_2 , hydrazine, alkyldiazine, and a combination thereof.

15. The method of any one of the previous claims, wherein the first temperature is less than or equal to about 300°C .

16. The method of any one of the previous claims, wherein the first temperature is about 225°C to about 290°C .

17. The method of any one of the previous claims, wherein the second temperature is about 400°C to about 600°C .

18. The method of any one of the previous claims, wherein the second temperature is about 450°C to about 500°C .

19. The method of any one of the previous claims, wherein the second film is substantially continuous and conformal.

20. The method of any one of the previous claims, wherein the second film has a resistivity of less than or equal to about $200\ \mu\Omega\text{-cm}$.

21. The method of any of the previous claims, wherein the thermally depositing the first film is performed at a pressure of about 0.1 Torr to about 6 Torr.

22. The method of any of the previous claims, wherein the thermally depositing the second film is performed at a pressure of about 1 Torr to about 100 Torr.

23. The method of any of the previous claims, wherein the thermally depositing the second film is performed at a pressure of about 5 Torr to about 10 Torr.

24. The method of any one of the previous claims, wherein the first film is thermally deposited by chemical vapor deposition or atomic layer deposition.
25. The method of any one of the previous claims, wherein the second film is thermally deposited by chemical vapor deposition or atomic layer deposition.
26. The method of any one of the previous claims, wherein the substrate comprises one or more of silicon oxide, aluminum oxide, titanium nitride, tungsten nitride, tungsten carbon nitride, and tantalum nitride.
27. The method of any one of the previous claims, wherein the first film and the second film are deposited in a same reaction vessel.
28. The method of any one of the previous claims, wherein the first film and the second film are deposited in different reaction vessels.