

CLAIMS

What is claimed is:

1. A method of forming a substantially carbon-free metal-containing layer on a semiconductor substrate, the method comprising:
 - (a) introducing a metal-containing precursor into a processing chamber housing the semiconductor substrate, wherein the metal-containing precursor is a halide-free, carbonyl-free compound that comprises at least one ligand, bound to a metal selected from the group consisting of molybdenum and tungsten, wherein the halide-free, carbonyl-free compound does not include metal-carbon bonds and metal-oxygen double bonds; and
 - (b) reacting the metal-containing precursor with at least one reactant in an absence of plasma to form a metal-containing layer on the semiconductor substrate, wherein the formed metal-containing layer is a substantially carbon-free molybdenum-containing or tungsten-containing layer that has a carbon content of less than about 5 atomic %, wherein the layer is selected from the group consisting of Mo, W, MoN, WN, MoON, WON, MoB, WB, MoSi, WSi layer and combinations thereof.
2. The method of claim 1, wherein the formed metal-containing layer has a carbon content of less than about 2 atomic %.
3. The method of claim 1, wherein the metal-containing precursor does not include beta-hydrogen atoms.
4. The method of claim 1, wherein the formed metal-containing layer is selected from the group consisting of Mo, MoN, and MoON.
5. The method of claim 1, wherein the metal-containing precursor is selected from the group consisting of precursors 1-16, wherein each R and R₁ is independently selected from the group consisting of an alkyl, fluoroalkyl, and alkylsilyl, wherein R does not include beta hydrogen bonds, n is 1-4 and m is 1-4.

6. The method of claim 1, wherein the metal-containing precursor is a compound selected from compounds 17-20.
7. The method of claim 1, further comprising:
 - (c) treating the formed metal-containing layer with a nitrogen-containing reactant and increasing nitrogen content in the metal-containing layer.
8. The method of claim 7, wherein the treated metal-containing layer is a MoN layer having a work function of greater than about 4.9 eV.
9. The method of claim 7, wherein the treated metal-containing layer is a MoN layer having nitrogen content of at least about 25 atomic %.
10. The method of claim 7, wherein the treated metal-containing layer is a MoN layer having a work function of greater than about 5.0 eV.
11. The method of claim 7, wherein (c) comprises treating the semiconductor substrate with a plasma formed in a process gas comprising the nitrogen-containing reactant.
12. The method of claim 1, further comprising:
 - (c) densifying the formed metal-containing layer by treating the metal-containing layer with a plasma formed in a process gas comprising H₂.
13. The method of claim 1, wherein in (b) the reaction between the metal-containing precursor and the at least one reactant occurs on the surface of the semiconductor substrate.
14. The method of claim 13, wherein (a) comprises:
 - forming a layer of the metal-containing precursor on the surface of the semiconductor substrate and removing the non surface-bound metal-containing precursor from the processing chamber; and wherein (b) comprises:

introducing the at least one reactant into the processing chamber and reacting with the metal-containing precursor on the surface of the semiconductor substrate.

15. The method of claim 1, wherein the substantially carbon-free metal-containing layer is a diffusion barrier layer or a liner layer.

16. The method of claim 1, wherein the method comprises forming the substantially carbon-free metal-containing layer having a work function of greater than about 5.0 eV in a pMOS device.

17. The method of claim 1, wherein forming the substantially carbon-free metal layer having a work function of greater than about 5.0 eV, comprises treating the semiconductor substrate after (b) with a plasma-activated nitrogen-containing reactant, to increase nitrogen content in the metal-containing layer.

18. The method of claim 1, wherein the substantially carbon-free metal layer is formed in (b) at a temperature of less than about 450 °C.

19. The method of claim 1, wherein the method comprises repeating (a) and (b), such that the method comprises between about 1 – 100 cycles, wherein each cycle comprises (a) and (b).

20. The method of claim 1, wherein the at least one reactant is selected from the group consisting of H_2 , NH_3 , and N_2H_4 .

21. The method of claim 1, wherein (b) comprises reacting the metal-containing precursor with H_2 .

22. A semiconductor device comprising: a substantially carbon-free metal-containing liner layer, wherein the metal is selected from the group consisting of molybdenum and tungsten, and wherein carbon content in the substantially carbon-free metal containing layer is less than about 3 atomic %, wherein the substantially carbon-free metal liner layer has a thickness of less than about 50 Å, a resistivity of

less than about $3,000 \mu \cdot \text{cm}^{-1}$, and is positioned between a dielectric layer and a conductive layer.

23. A semiconductor device of claim 21, wherein the substantially carbon-free metal-containing layer is a diffusion barrier layer.

24. A semiconductor device of claim 21, wherein the substantially carbon-free metal-containing layer has a resistivity of less than about $1,000 \mu \cdot \text{cm}^{-1}$.

25. A semiconductor device of claim 21, wherein the substantially carbon-free metal-containing layer has a resistivity of less than about $600 \mu \cdot \text{cm}^{-1}$.

26. A semiconductor device of claim 21, wherein the substantially carbon-free metal-containing layer is a Mo or MoN layer.

27. A semiconductor device comprising a gate electrode, wherein the gate electrode comprises a substantially carbon free metal-containing layer, wherein carbon content in the substantially carbon free metal-containing layer is less than about 3 atomic %, and wherein the substantially carbon-free metal-containing layer has a work function of greater than 4.9 eV, and comprises a metal selected from the group consisting of molybdenum and tungsten.

28. The semiconductor device of claim 27, wherein the substantially carbon free metal-containing layer is a MoN layer.

29. The semiconductor device of claim 27, wherein the substantially carbon free metal-containing layer has a work function of greater than about 5.0 eV.

30. The semiconductor device of claim 27, wherein the substantially carbon free metal-containing layer has a thickness of between about 5 – 50 Å.

31. The semiconductor device of claim 27, wherein the semiconductor device is a pMOS device selected from the group consisting of a planar pMOS device, a FinFET pMOS device, and a gate all around (GAA) pMOS device.

32. An apparatus for forming a substantially carbon-free metal-containing layer on a semiconductor substrate, the apparatus comprising:

(a) a deposition processing chamber having a substrate support, and an inlet for an introduction of a metal-containing precursor and a second inlet for an introduction of at least one reactant;

(b) a plasma treatment processing chamber, different from the deposition processing chamber, wherein the plasma treatment processing chamber comprises a substrate support and an inlet for introducing a plasma treatment reactant; and

(c) a controller comprising program instructions for:

(i) causing a surface-limited reaction between a metal-containing precursor and at least one reactant in the deposition process chamber in an absence of plasma to form a layer of a substantially carbon-free metal-containing material, wherein the metal is selected from the group consisting of molybdenum and tungsten;

(ii) causing transfer of the semiconductor substrate from the deposition processing chamber to the plasma treatment processing chamber without exposing the semiconductor substrate to an ambient atmosphere; and

(iii) causing treatment of the substantially carbon-free metal-containing material by a plasma-activated plasma treatment reactant.

33. The apparatus of claim 32, wherein the plasma treatment reactant is a nitrogen-containing reactant and/or H₂, and wherein (iii) comprises instructions for forming a remote plasma in a process gas comprising the nitrogen-containing reactant and/or H₂.

34. A flow mixer for mixing a carrier gas and a metal-containing precursor, the flow mixer comprising:

(a) an outer fluidic conduit comprising, an inlet for admitting the carrier gas into the outer fluidic conduit, a mixing zone for mixing the carrier gas with the metal-containing precursor and an outlet for removing the carrier gas mixed with the metal-containing precursor from the outer fluidic conduit;

(b) an inner fluidic conduit positioned at least partially inside the outer conduit, wherein the inner fluidic conduit comprises an inlet for admitting the metal-containing precursor into the inner fluidic conduit, and an outlet configured to release

the metal-containing precursor into the outer fluidic conduit, wherein a distance from the inlet of the inner fluidic conduit to the inlet of the outer fluidic conduit is greater than a distance from the outlet of the inner fluidic conduit to the inlet of the outer fluidic conduit, thereby supporting opposing flows of the carrier gas and of the metal-containing precursor in the flow mixer, wherein the distances refer to distances in a z-direction.

35. The flow mixer of claim 34, wherein the outlet from the inner fluidic conduit comprises a flow diverter, configured to divert flow of the metal-containing precursor before the metal-containing precursor flow mixes with the carrier gas flow in the outer fluidic conduit, such that the diverted flow of the metal-containing precursor retains a velocity component opposing the velocity direction of the carrier gas flow in the outer fluidic conduit.

36. The flow mixer of claim 35, wherein the flow diverter comprises two parallel flow restrictor plates, configured to restrict the flow of the metal-containing precursor between the plates.

37. The flow mixer of claim 34, wherein the flow mixing zone has a length of at least about 127 mm in z-direction.

38. The flow mixer of claim 34, wherein a ratio of a length of the flow mixing zone in z-direction to an inner diameter of the outer fluidic conduit is at least 2.

39. The flow mixer of claim 34, wherein a ratio of a length of the flow mixing zone in z-direction to an inner diameter of the outer fluidic conduit is at least 3.

40. The flow mixer of claim 34, wherein the outer fluidic conduit further comprises a restriction zone, downstream from the mixing zone, wherein the restriction zone is configured to restrict the mixed flow into a plurality of non-communicating conduits.

41. The flow mixer of claim 34, wherein the outer fluidic conduit and the inner fluidic conduit comprise a substantially coaxial portion.

42. The flow mixer of claim 34, wherein a ratio of an inner diameter of the outer fluidic conduit to an inner diameter of the inner fluidic conduit is between about 1.5 - 10.
43. The flow mixer of claim 34, wherein an inner diameter of the outer fluidic conduit is about 40.5 mm, and an inner diameter of the inner fluidic conduit is about 4.8 mm.
44. The flow mixer of claim 34, wherein the flow mixer has a length in z-direction of between about 102-508 mm.
45. The flow mixer of claim 34, wherein the flow mixer comprises a material selected from the group consisting of aluminum, stainless steel, and a ceramic
46. The flow mixer of claim 34, wherein the outlet of the outer fluidic conduit is configured to be connected to a showerhead of a deposition apparatus.
47. A deposition apparatus for depositing metal containing layers comprising the flow mixer of claim 34.
48. A method of depositing a metal-containing layer on a semiconductor substrate, the method comprising:
- (a) mixing a metal-containing precursor with a carrier gas in the flow mixer of claim 34; and
 - (b) delivering the formed mixture to a processing chamber and reacting the metal-containing precursor with a reactant to form the metal-containing layer on the semiconductor substrate.
49. A multi-plenum showerhead for delivery of a plurality of reactants to a processing chamber, the multi-plenum showerhead comprising:
- (a) a showerhead faceplate comprising a first plurality of conduits for delivery of a first reactant and a second plurality of conduits for delivery of a second

reactant, wherein the first plurality of conduits is configured to be fluidically isolated from the second plurality of conduits; and

(b) a showerhead housing positioned about the perimeter of the showerhead faceplate, wherein the showerhead faceplate is releasably attached to the showerhead housing.

50. The multi-plenum showerhead of claim 49, wherein the showerhead comprises a plurality of fasteners configured to releasably attach the showerhead faceplate to the showerhead housing.

51. The multi-plenum showerhead of claim 49, wherein the first plurality of conduits comprises openings with a diameter of less than about 1 mm.

52. The multi-plenum showerhead of claim 49, wherein the first plurality of conduits comprises openings with a diameter of about 0.5 mm.

53. The multi-plenum showerhead of claim 49, wherein the multi-plenum showerhead is a dual-plenum showerhead.

54. The multi-plenum showerhead of claim 49, wherein the showerhead housing comprises a conduit that fluidically connects with a first plurality of conduits of the showerhead faceplate.

55. The multi-plenum showerhead of claim 49, wherein the showerhead housing comprises a heater.

56. The multi-plenum showerhead of claim 49, wherein the face plate comprises a material selected from the group consisting of aluminum, stainless steel and a ceramic..

57. A faceplate for a showerhead for a deposition apparatus, wherein the faceplate comprises a first plurality of conduits for delivery of a first reactant and a second plurality of conduits for delivery of a second reactant, wherein the first plurality of

conduits is configured to be fluidically isolated from the second plurality of conduits, and wherein the faceplate is configured to be releasably attachable to a showerhead housing.

58. A deposition apparatus for depositing a metal-containing layer on a semiconductor substrate, wherein the deposition apparatus comprises a multi-plenum showerhead of claim 49.

59. The method of claim 1, further comprising:

applying photoresist to the semiconductor substrate;

exposing the photoresist to light;

patterning the photoresist and transferring the pattern to the semiconductor substrate; and

selectively removing the photoresist from the semiconductor substrate.