pure metal conductor, e.g., a MoO_xN_y layer may be deposited as a nucleation layer prior to deposition of a Mo layer. In other embodiments, the metal oxynitride layer may have a different metal than that of the pure conductor, e.g., a W layer may be deposited on a Mo-containing nucleation layer or a Mo layer may be deposited on a W-containing nucleation layer.

[0067] While Figures 1A and 1B show examples of metallization stacks, the methods and resulting stacks are not so limited. For example, in some embodiments, the nucleation layer may be deposited directly on SiO_2, silicon, or other semiconductor substrate as a template for metal growth. Further, while W or Mo growth on the nucleation layers is described above, the nucleation layers may serve as a template for low resistivity growth of other metals, such as, cobalt (Co), ruthenium (Ru), nickel (Ni), and alloys including these metals such as MoW. Still further, the nucleation layer may be any appropriate metal oxynitride or metal nitride layer, including MoO_xN_y, Mo nitride, tungsten oxynitride, WN, nickel nitride, etc.

[0068] The material stacks described above and further below may be implemented in a variety of structures. Figures 2A and 2B provide examples of structures in which the stacks may be employed. Figure 2A depicts a schematic example of wordlines 210 in a 2D NAND structure 223. The wordlines 210 are separated by oxide layers 211 as pillars with gaps 235 between them on substrate 200. In Figure 2B, a detail of the interface between a wordline 210 and oxide layer 211 is shown including a layer of Al_2O_3 204 and a nucleation layer 208 is shown. In some embodiments, the nucleation layer 208 may be deposited directly on the oxide layer 211 or on a Al_2O_3 204 or other barrier layer as described herein. The nucleation layers may be between about 10Å and 100Å, or 10Å and 50Å, for example, for deposition of a wordline 210 of between about 10 nm and 100 nm thick, or about 5 nm thick or less.

[0069] Figure 3A is a process flow diagram illustrating operations in a method of depositing a conductive material in accordance with certain disclosed embodiments. In operation 301, a substrate having an oxide surface and/or a barrier layer surface (which may be on an oxide surface) is provided. Examples of process conditions and features of operation 301 are provided further below with respect to Figure 3B. In operation 360, the oxide-metal interface is modulated to prevent defects in the oxide. Example methods for performing operation 360 are described below with respect to Figures 3B and 3C. In operation 370, a metal layer is formed over the substrate whereby the metal is in contact with the oxide surface or barrier layer surface. Example embodiments for performing operation 370 are further described below with respect to Figures 3B and 3C.

[0070] In Figure 3A, operations 360 and 370 may be performed at the same time; or in order of operation 360 first followed by operation 370; or operation 370 first followed by operation 360; or a combination of operations 360 and 370 may be performed together (such as alternately; or

oxygen-containing gases include oxygen. Example nitrogen-containing gases include nitrogen and NH_3. Additive gases may be continuously flowed, flowed only with the Mo precursor, flowed only with the reducing agent, flowed only with the purge gas, or periodically without being synchronized to either precursor doses, reducing agent doses, or purge gas operations.

[0106] Another technique which may be performed alone or in combination with the above technique is to change the process conditions. For example, temperature or pressure may be modulated to retain oxygen, nitrogen, and other component elements in the metal oxynitride layer. In various embodiments, operation 305 may be performed at a temperature up to about 650°C, or less than about 350°C, or between about 200°C and about 550°C, or between about 250°C and about 350°C to retain impurities in the film. In some embodiments, the chamber pressure can be between about 5 Torr and about 90 Torr.

[0107] Another technique for retaining impurity content in the nucleation layer is to change the morphology of the film. An amorphous films is more likely to reduce diffusion of impurities out of the film and thus reduce the likelihood of oxygen or other elements from the dielectric from diffusing out of the dielectric, thereby reducing the chances of trapped charge from escaping the dielectric and causing data loss. The morphology may be modulated by reducing the temperature of the substrate during film deposition and bulk molybdenum deposition.

[0108] Although certain disclosed embodiments may involve modulating the first few cycles of ALD of operation 305, in some embodiments, most or all cycles of ALD in operation 305 may be modulated. Any combination of modulated ALD cycles may be performed, including alternating between modulated and non-modulated cycles, such as performing a few cycles of low temperature ALD followed by a few cycles of high temperature ALD and repeating this sequentially, to improve throughput.

[0109] Exposure times for gases used to deposit the nucleation layer may vary depending on flow rates. Non-limiting examples of exposure times range from about 0.1 seconds to about 10 seconds, or between about 0.1 seconds and about 20 seconds for each gas. For alternating pulses of treatments, each pulse may have any of the above exposure times.

[0110] Exposure times for NH_3 and hydrogen gas exposure depend on the particular application and can range widely. In some embodiments, hydrogen gas exposure may be at least about 30 seconds or longer. Non-limiting examples of exposure times include between about 0.1 second and about 60 seconds, between about 0.1 second and about 50 seconds, and at least about 30 seconds. For example, in some embodiments, NH_3 and hydrogen may be simultaneously flowed to the substrate for at least about 30 seconds, or between about 0.1 second and about 50 seconds.

[0111] Exposure times for an oxygen-containing Mo precursor (such as one having a formula

CLAIMS

1. A method for processing substrates, the method comprising:
providing a substrate having an oxide material thereon;
depositing at least a portion of an elemental molybdenum layer over the oxide material using a first atomic layer deposition (ALD) process by exposing the oxide material to alternating pulses of a first oxygen-containing molybdenum precursor and a first reducing agent using a first set of process conditions; and
modulating the first set of process conditions to increase non-molybdenum content when depositing the portion of the elemental molybdenum layer.

2. The method of claim 1, wherein the first set of process conditions comprise using a flow rate of at least about 1000 sccm of the first reducing agent during the first ALD process.

3. The method of claim 1, wherein the first set of process conditions comprise exposing the substrate to the first reducing agent for at least 1 second during a cycle of the first ALD process.

4. The method of claim 1, further comprising prior to depositing the portion of the elemental molybdenum layer, exposing the oxide material to a soak gas selected from the group consisting of boron-containing gases, tungsten-containing gases, fluorine-containing gases, oxygen-containing gases, chlorine-containing gases, and combinations thereof.

5. The method of claim 1, further comprising, prior to depositing the portion of the elemental molybdenum layer, exposing the oxide material to alternating pulses of a boron-containing gas and a tungsten-containing gas.

6. The method of claim 5, wherein the boron-containing gas comprises diborane (B_2H_6) and the tungsten-containing gas comprises tungsten hexafluoride (WF_6).

7. The method of claim 1, further comprising prior to depositing the portion of the elemental molybdenum layer, depositing a first layer on the oxide material using a second oxygen-containing molybdenum precursor and a second reducing agent using a second ALD process on the oxide material under a second set of process conditions.

8. The method of claim 7, wherein the second reducing agent is a nitrogen-containing gas, hydrogen, or combinations thereof.

9. The method of claim 7, wherein the second set of process conditions comprises depositing at least the portion of the elemental molybdenum layer at a substrate temperature less than about 400°C.

10. The method of claim 7, wherein at least one of the first and the second oxygen-containing molybdenum precursor is a molybdenum oxyhalide.

11. The method of claim 10, wherein the first oxygen-containing molybdenum precursor is a molybdenum oxyhalide, and wherein the first set of process conditions comprise using a hydrogen to molybdenum oxyhalide precursor ratio of between about 100:1 and about 10,000:1.

12. The method of claim 7, wherein the second set of process conditions comprises increasing flow of a nitrogen-containing gas during the second ALD process.

13. The method of claim 7, further comprising flowing nitrogen during depositing of the first layer.

14. The method of claim 7, further comprising soaking the substrate having the oxide material thereon with a soak gas prior to depositing the first layer.

15. The method of claim 14, wherein the soak gas is selected from the group consisting of oxygen, ammonia (NH_3), and nitrogen.

16. The method of claim 7, further comprising soaking the substrate having the oxide material thereon with a soak gas after depositing the first layer.

17. The method of claim 7, wherein less than half of the first layer is converted to a converted elemental molybdenum layer during or prior to the first ALD process.

18. The method of claim 17, wherein the converted elemental molybdenum layer contains more than 1 (atomic) % impurities.

19. The method of claim 18, wherein the impurities are selected from the group consisting of oxygen, chlorine, nitrogen, and combinations thereof.20. The method of any of claims 7-19, wherein the first layer is a crystalline layer.

21. The method of any of claims 7-19, wherein the first layer is an amorphous layer.

22. The method of any of claims 7-19, wherein the first ALD process and the second ALD

process are performed in the same chamber and without exposure to air.

23. The method of any of claims 7-19, wherein the first layer is a template for metal grain growth in the elemental molybdenum layer.

24. The method of any of claims 7-19, wherein the second ALD process is performed at a temperature less than 400°C.

25. The method of claim 24, wherein the first ALD process is performed at the same temperature as the second ALD process.

26. The method of claim 24, wherein the elemental molybdenum layer is a gradient film, wherein at least a first set of cycles of the first ALD process is performed at a temperature less than about 400°C and at least a last set of cycles of the first ALD process is performed at a temperature greater than 400°C.

27. The method of any of claims 7-19, wherein deposition of the first layer and deposition of the elemental molybdenum layer are performed in the same chamber.

28. The method of claim 27, wherein deposition of the first layer and deposition of the elemental molybdenum layer are performed in different stations of the same chamber.

29. The method of any of claims 7-19, wherein deposition of the first layer is performed in a first chamber and deposition of the elemental molybdenum layer is performed in a second chamber.

30. The method of any of claims 7-19, further comprising exposing the first layer to air prior to deposition of the elemental molybdenum layer.

31. The method of any of claims 1-19, wherein the elemental molybdenum layer is crystalline.

32. The method of any of claims 1-19, wherein the elemental molybdenum layer contains less than 1 (atomic) % impurities.

33. The method of any of claims 1-19, wherein the elemental molybdenum layer is elemental molybdenum.

34. An apparatus for processing substrates, the apparatus comprising:

first and second process chambers each configured to house a substrate;

a substrate support in each of the first and the second process chambers;

gas inlets configured to direct gas into each of the first and the second process chambers via one or more showerheads;

a heater configured to heat the substrate support in each process chamber; and

a controller comprising program instructions for:

(a) causing sequentially inletting of an oxygen-containing molybdenum precursor and a nitrogen-containing gas into the first process chamber while a substrate is housed in the first process chamber;

(b) after (a), causing transfer of the substrate to the second process chamber;

(c) after (b), causing sequentially inletting of an oxygen-containing molybdenum precursor and hydrogen into the second process chamber while the substrate is housed in the second process chamber; and

(d) causing implementation of one or more of the program instructions selected from the group consisting of:

causing nitrogen to be inletted into the first process chamber when the substrate is housed in the first process chamber,

causing temperature of the substrate support in the second process chamber to be at two different temperatures while the substrate is housed in the second process chamber,

causing delivery of a soak gas to the first process chamber before or after sequentially inletting the oxygen-containing molybdenum precursor and the nitrogen-containing gas into the first process chamber, and

causing reduced flow of hydrogen into the second process chamber while the substrate is housed in the second process chamber.

35. An apparatus for processing substrates, the apparatus comprising:

a process chamber configured to house a substrate;

a substrate support in the process chambers;

a first gas box comprising a gas source for containing hydrogen gas;

a second gas box comprising a gas source for containing a molybdenum-containing gas;

a third gas box comprising a gas source for containing a boron-containing or tungsten-containing gas;

gas inlets configured to direct gas from each of the first gas box, second gas box, and third gas box into the process chamber via one or more showerheads; and

a heater configured to heat the substrate support in each process chamber.

36. The apparatus of any of claims 34 and 35, wherein at least one of the one or more showerheads is a single plenum showerhead.

37. The apparatus of any of claims 34 and 35, wherein at least one of the one or more showerheads is a dual plenum showerhead.

38. The apparatus of claim 35, wherein the process chamber is a chamber within a multi-chamber apparatus.