ATOMIC LAYER ETCHING OF TUNGSTEN FOR ENHANCED TUNGSTEN DEPOSITION FILL

BACKGROUND

[0001] Semiconductor fabrication processes often involve deposition of metals, such as tungsten, into features, such as vias or trenches, to form contacts or interconnects. However, as devices shrink, features become smaller and harder to fill, particularly in advanced logic and memory applications.

SUMMARY

[0002] Provided herein are methods of filling features on substrates. One aspect involves a method of filling features on a substrate by (a) depositing a first amount of a metal in a feature; and (b) directionally etching the metal at or near an opening of the feature relative to an interior region of the feature by (i) modifying the surface of the deposited metal by exposing the metal to a halogen-containing gas; and (ii) exposing the modified surface to an activation gas to selectively etch the metal. The method may further include repeating (a) and (b).

[0003] In various embodiments, the metal contains one of titanium, tantalum, nickel, cobalt, or molybdenum. In some embodiments, the metal contains tungsten.

[0004] In some embodiments, the halogen-containing gas is selected from the group consisting of chlorine, bromine, iodine, sulfur hexafluoride, silicon tetrafluoride, boron trichloride, or combinations thereof. In some embodiments, the activation gas is an inert gas, such as neon, krypton, argon, or combinations thereof.

[0005] The method may further include applying a bias during at least one of (i) and (ii). The bias power may be less than a threshold bias power. The bias power may be less than about 80Vb.

[0006] In various embodiments, (b) includes a self-limiting reaction. In some embodiments, the substrate includes features having different size openings. The feature may an aspect ratio of at least 3:1. In some embodiments, the opening is less than 20 nm wide.

[0007] In some embodiments, (a) and (b) are performed without breaking vacuum. In some embodiments, (a) and (b) are performed in the same chamber. In some embodiments, (a) and (b)

are performed in different chambers of the same tool.

[0008] The method may further include igniting a plasma during at least one of (i) and (ii). The plasma power may be between about 0W and about 1000W.

[0009] Another aspect may involve a method including (a) partially filling a feature with tungsten; (b) directionally etching tungsten at or near the opening of the feature by exposing the ~~substrate~~ feature to alternating pulses of a halogen-containing gas and an activation gas; and (c) filling the feature with tungsten.

[0010] In some embodiments, a bias is applied during (b). In some embodiments, the bias is applied during (b) at a threshold bias power.

[0011] In various embodiments, (a) and (b) are performed without breaking vacuum. In some embodiments, (a) and (b) are performed in the same chamber. The method may further include repeating (a) and (b). Filling the feature may include repeating (a) and (b).

[0012] The tungsten may be deposited by CVD. In some embodiments, the tungsten is deposited by ALD. The tungsten may be deposited by exposing the ~~substrate~~ feature to alternating pulses of a tungsten-containing precursor and a reducing agent. The tungsten may be deposited using a chlorine-containing tungsten precursor. In some embodiments, the tungsten is fluorine-free tungsten.

[0013] Another aspect involves an apparatus for processing semiconductor substrates, the apparatus including: a process chamber including a showerhead and a substrate support, a plasma generator, and a controller having at least one processor and a memory, whereby the at least one processor and the memory are communicatively connected with one another, the at least one processor is at least operatively connected with ~~the~~ flow-control hardware, and the memory stores machine-readable instructions for: introducing a tungsten-containing precursor and a reducing agent to the chamber to deposit tungsten on a substrate; introducing a halogen-containing gas to modify the surface of the tungsten; and introducing an activation gas and igniting a plasma to etch at least part of the modified surface of tungsten.

[0014] The substrate support may include a bias, and the memory may further store machine-readable instructions for setting the bias power less than about 80 Vb during (iii). In some embodiments, the memory further stores machine-readable instructions for igniting a plasma during (ii).

32 (Institute of Plasma Physics, Nagoya University, Japan, 1983).

[0059] The figure shows the calculated normal incidence sputter yield of tungsten with argon ~~atoms~~ ions versus argon ion energy (or threshold bias power). The calculation used a value of 32 eV for the sputter threshold. Slightly above the threshold, namely at 40 eV argon ion energy, the sputter yield seems to be about 0.001 atoms/ion. However, at 80 eV ion energy, it has increased by a factor of 30. This example curve indicates the maximum argon ion energy sufficient to etch the metal while preventing sputtering of ~~argon~~ tungsten on the substrate. While Figure 4 provides a qualitative representation of a sputter threshold curve, a sputter threshold may be experimentally determined for a particular system and maximum tolerable sputter yield. For one system, sputtering of tungsten is observed at 80 Vb for argon ions. It will be understood that the unit "Vb" or "V_b" or "V_{bias}" is a unit of volts, and "b" or "bias" is used to characterize that the power is for the bias power. As such, the bias power during tungsten removal using argon ions may be set at less than about 80 Vb, or less than about 50 Vb, or between about 50 Vb and 80 Vb. In some embodiments, operation 335 may be performed above the threshold bias power if some small amount of sputtering is tolerable. There may also be a removal threshold voltage, below which removal does not occur, depending on the particular process. It should be noted that the sputter threshold varies according to the metal, metal compound, or other material to be etched.

[0060] In some embodiments, the chamber may be purged after a removal operation. Purge processes may be any of those used for a purge after operation 315.

[0061] Returning to Figure 3, operations 315 and 335 may be optionally repeated as necessary to fill the feature. In operation 307, it is determined whether the feature has been sufficiently filled. If not, operations 303 and 305 may be repeated. In some embodiments, operation 303 is repeated and the feature may be sufficiently filled such that operation 305 may not be performed again. In some embodiments, operations 303 and 305 are performed until features are sufficiently filled. In some embodiments, features may be sufficiently filled after performing operation 303 in one of the repeated operations, such that operation 305 is not performed after features are filled. In some embodiments, operations 303 and 305 are performed in the same chamber. In some embodiments, operations 303 and 305 are performed in the same tool. In some embodiments, operations 303 and 305 are performed without breaking vacuum. In some embodiments, repeated cycles of operation 303 may involve different deposition methods and

precursors than in prior cycles of operation 303. For example, in one process, tungsten may be deposited into a feature by ALD, ALE may be performed to etch the deposited tungsten to open the feature, and tungsten deposition may be repeated by this time performing CVD of tungsten using a tungsten-containing precursor and a reducing agent to completely fill the feature. In another example, tungsten is deposited by alternating pulses of WF_6 and ~~BH_4~~ B_2H_6, the tungsten at or near the opening of a feature may be etched by alternating pulses of Cl_2 and Ar in the presence of a plasma and applying a bias, and tungsten may be deposited by simultaneous exposure to WCl_5 and H_2.

[0062] Figure 5 provides an example diagram of a timing scheme that may be performed in accordance with disclosed embodiments. Process 500 includes deposition cycle 520A, etch cycle 505A, and a repeated deposition cycle 520B and etch cycle 505B. Deposition cycle 520A includes W CVD phase 503A, which may correspond to operation ~~503~~ 303 of Figure 3. Although a CVD deposition is provided in Figure 5, in some embodiments, this operation may involve cyclic deposition of a metal, such as by ALD. In W CVD phase 503A, the carrier gas may be flowed, while the modification chemistry flow is turned off and the removal gas is turned off. CVD Precursors may be continuously flowed to deposit tungsten and the bias is turned off. Etch cycle 505A may correspond to operations 315 and 335 of Figure 3. Etch cycle 505A includes a surface modification 515A, which may correspond to operation 315 of Figure 3. During surface modification 515A, the modification chemistry is flowed with a carrier gas while the removal gas and CVD precursor flows are turned off. The bias may be on, as shown in Figure 5. Following surface modification 515A may be a purge phase 525A, which, as described above, is an optional operation. During purge phase 525A, the carrier gas is continuously flowed to remove any modification chemistry that did not adsorb onto the substrate. Accordingly, modification chemistry, removal gas, and CVD precursor flows are turned off, and the bias is also turned off. In removal phase 535A, the carrier gas is continuously flowed while the removal gas is flowed, while the modification chemistry and CVD precursor flows are turned off. The bias may also be turned on during removal phase 535A. Removal phase 535A may correspond to operation 335 of Figure 3. In various embodiments, a plasma is ignited during this phase. Purge phase 545A may involve flowing a carrier gas while modification chemistry, removal gas, and CVD precursor flows are turned off, and the bias is also turned off.

[0063] In accordance with operation 307 of Figure 3, the operations may be repeated as shown

aligned, the wafer 726 is moved by the front-end robot 732 into an airlock 730. Because the airlock 730 has the ability to match the environment between an ATM 740 and a VTM 738, the wafer 726 is able to move between the two pressure environments without being damaged. From the airlock 730, the wafer 726 is moved by robot 722 through VTM 738 and into one of the processing modules 720a-720d. In order to achieve this wafer movement, the robot 722 uses end effectors 724 on each of its arms. Once the wafer 726 has been processed, it is moved by robot 722 from the processing modules 720a-720d to the airlock 730. From here, the wafer 726 may be moved by the front-end robot 732 to one of the FOUPs 734 or to the aligner 744.

[0083] It should be noted that the computer controlling the wafer movement can be local to the cluster architecture, or can be located external to the cluster architecture in the manufacturing floor, or in a remote location and connected to the cluster architecture via a network. A controller as described above with respect to Figure 6 may be implemented with the tool in Figure 7.

EXPERIMENTAL

EXPERIMENT 1

[0084] Etch rate of tungsten was plotted against chlorination bias power for etch with chlorine adsorption and no argon ~~sputtering~~ ion bombardment, as well as for an atomic layer etch (ALE) process with chlorine adsorption with argon ~~sputtering~~ ion bombardment. The results are plotted in Figure 8. The dotted line depicts the etch rate of tungsten versus chlorination bias (e.g., the bias power during chlorine adsorption) for a process involving adsorbing chlorine and igniting a plasma at 900W, and no argon ~~sputtering~~ ion bombardment. The solid line depicts the etch rate of tungsten versus chlorination bias for a process involving adsorbing chlorine and igniting a plasma at 900W, followed by an argon bombardment with a bias power of 60V. A chlorination bias threshold voltage as shown in Figure 8 is at about 60V. Note where a chlorination bias is less than 60V, tungsten is not etched without using ion bombardment of argon. Where a chlorination bias is greater than 60V, the etch rate of tungsten without argon ion bombardment is much lower than that of the process with argon ion bombardment. These results suggest that argon ion bombardment may be used to modulate the etch rate of tungsten by ALE methods in various embodiments whereby 1) chlorine is being adsorbed onto the tungsten substrate without etching during chlorination, and 2) the bias

CLAIMS

~~What is claimed is:~~

1. An apparatus for processing semiconductor substrates, the apparatus comprising:

one or more process chambers, each process chamber comprising a showerhead and a substrate support,

a plasma generator, and

a controller having at least one processor and a memory,

wherein the at least one processor and the memory are communicatively connected with one another,

the at least one processor is at least operatively connected with ~~the~~ flow-control hardware, and

the memory stores machine-readable instructions for:

(i) introducing a tungsten-containing precursor and a reducing agent to one of the one or more process chambers to deposit tungsten on a substrate;

(ii) introducing a halogen-containing gas to modify the surface of the tungsten; and

(iii) introducing an activation gas and igniting a plasma to etch at least part of the modified surface of tungsten.

2. The apparatus of claim 1, wherein the memory further stores machine-readable instructions for igniting a plasma during (ii).

3. The apparatus of claim 1, wherein the substrate support comprises a bias, and the memory further stores machine-readable instructions for setting the bias power less than about 80 Vb during (iii).

4. The apparatus of claim 1, wherein (ii) and (iii) are performed without breaking vacuum.

5. The apparatus of claim 1, wherein (ii) and (iii) are performed in the same process chamber.

17. The method of claim 11, wherein the substrate comprises features having different size openings.

18. The method of claim 11, wherein (a) and (b) are performed without breaking vacuum.

19. The method of claim 11, wherein (a) and (b) are performed in the same chamber.

20. The method of claim 18, wherein (a) and (b) are performed in different chambers of the same tool.

21. The method of claim 11, wherein the activation gas is selected from a group consisting of neon, krypton, and argon.

22. The method of any of claims 11-21, further comprising igniting a plasma during at least one of (i) and (ii).

23. The method of any of claims 11-21, wherein the feature has an aspect ratio of at least 3:1.

24. The method of any of claims 11-21, wherein the opening is less than 20 nm wide.

25. The method of any of claims 11-21, further comprising repeating (a) and (b).

26. The method of any of claims 11-21, wherein the halogen-containing gas is selected from the group consisting of chlorine, bromine, iodine, sulfur hexafluoride, silicon tetrafluoride, boron trichloride, and combinations thereof.

27. The method of claim 22, wherein the plasma power is between about 0W and about 1000W.

28. The method of claim 14, wherein the bias power is less than about 80Vb.

29. A method comprising:

(a) partially filling a feature with tungsten;

(b) directionally etching tungsten at or near the opening of the feature by exposing the ~~substrate~~ feature to alternating pulses of a halogen-containing gas and an activation gas; and

(c) filling the feature with tungsten.

30. The method of claim 29, wherein a bias is applied during (b).

31. The method of claim 29, wherein a bias is applied during (b) at a threshold bias power.

32. The method of claim 29, wherein (a) and (b) are performed without breaking vacuum.

33. The method of claim 29, wherein (a) and (b) are performed in the same chamber.

34. The method of any of claims 29-33, further comprising repeating (a) and (b).

35. The method of any of claims 29-33, wherein filling the feature comprises repeating (a) and (b).

36. The method of any of claims 29-33, wherein the tungsten is deposited by CVD.

37. The method of any of claims 29-33, wherein the tungsten is deposited by ALD.

38. The method of any of claims 29-33, wherein the tungsten is deposited by exposing the ~~substrate~~ feature to alternating pulses of a tungsten-containing precursor and a reducing agent.

39. The method of any of claims 29-33, wherein the tungsten is deposited using a chlorine-containing tungsten precursor.

40. The method of any of claims 29-33, wherein the tungsten is fluorine-free tungsten.