

MOLYBDENUM METALLIZATION AND FILL TECHNIQUES FOR LOGIC AND MEMORY

CROSS-REFERENCES

- 5 **[0001]** A PCT Request Form is filed concurrently with this specification as part of the present application. Each application that the present application claims benefit of or priority to as identified in the concurrently filed PCT Request Form is incorporated by reference herein in their entireties and for all purposes.

BACKGROUND

- 10 **[0002]** Deposition of conductive materials an integral part of many semiconductor fabrication processes. These materials may be used for horizontal interconnects, vias between adjacent metal layers, contacts between metal layers and devices, and as lines in memory devices.

- 15 **[0003]** The background description provided herein is for the purposes of generally presenting the context of the disclosure. Work of the presently named inventors, to the extent it is described in this background section, as well as aspects of the description that may not otherwise qualify as prior art at the time of filing, are neither expressly nor impliedly admitted as prior art against the present disclosure.

SUMMARY

- 20 **[0004]** Provided herein are methods and related apparatus for deposition of a molybdenum in a feature. In some embodiments, the methods include single chamber metallization processes that include both plasma and thermal processing and the use of different molybdenum precursors. Related apparatuses are also provided.

- 25 **[0005]** One aspect of the disclosure relates to a method including: providing a feature to be filled with molybdenum, the feature including a metal-containing bottom and dielectric sidewalls; selectively depositing molybdenum on the metal-containing bottom to partially fill the feature, leaving exposed dielectric sidewalls; depositing a conformal molybdenum liner on the exposed sidewalls and molybdenum; and filling the feature with molybdenum.

- 30 **[0006]** In some embodiments, the operations are performed in a single chamber. In some embodiments, the method further includes, prior to selectively depositing molybdenum on the metal-containing bottom, exposing the metal-containing bottom to a metal halide to remove oxide from the metal-containing bottom. In some embodiments, the method further

includes, prior to selectively depositing molybdenum on the metal-containing bottom, exposing the metal-containing bottom to a reducing plasma to remove oxide from the metal-containing bottom. In some embodiments selectively depositing molybdenum on the metal-containing bottom includes a thermal atomic layer deposition (ALD) processing using a molybdenum halide precursor. In some embodiments, depositing a conformal molybdenum liner includes a thermal ALD or plasma enhanced ALD process using a molybdenum oxyhalide.

[0007] In some embodiments, depositing a conformal molybdenum liner includes a plasma enhanced ALD process using a molybdenum oxyhalide. In some embodiments, the metal-containing bottom includes titanium. In some embodiments, the metal-containing bottom includes molybdenum. In some embodiments, filling the feature with molybdenum includes an integration process including etching molybdenum. In some embodiments, filling the feature with molybdenum includes an integration process including inhibiting molybdenum deposition.

[0008] Another aspect of the disclosure relates to an apparatus including: a multi-station chamber, wherein each station includes a substrate support configured to support a substrate, a showerhead configured to inlet gases to a volume above substrate support, and a plasma generator configured to generate a plasma between the substrate support and showerhead; and a controller having instructions for: inletting pulses of a molybdenum halide and a reducing agent to a first station housing a substrate to selectively deposit molybdenum in feature to be filled with molybdenum, the feature including a metal-containing bottom and dielectric sidewalls to fill the feature, leaving exposed dielectric sidewalls; transferring the substrate to a second station; inletting pulses of a molybdenum oxyhalide and a reducing agent, generating a plasma during the reducing agent pulses, to deposit a conformal liner in the feature; transferring the substrate to a third station; and inletting a molybdenum-containing precursor to continue fill of the feature.

[0009] Yet another aspect of the disclosure relates to a method including: providing a substrate including a feature to be filled with molybdenum to a chamber, the feature having one or more openings; depositing a conformal thin film of molybdenum in the feature; non-conformally treating the conformal thin film to increase etch rate, wherein the treatment is preferably applied at portions of the conformal thin film proximate to the one or more openings relative to portion the conformal thin film further from the one or more openings; non-conformally etching the conformal thin film; and depositing molybdenum in the feature.

[0010] In some embodiments, the feature is a wordline feature of a 3D NAND structure. In some embodiments, the wordline feature is having a first opening and a second opening, the first opening and the second opening being at opposite ends of the feature.

[0011] In some embodiments, the first opening opens to a first vertical structure of the 3D NAND structure and the second opening opens to a second vertical structure and wherein the feature is fluidically accessible via the first and second vertical structures. In some embodiments, the feature is further defined by constrictions formed by pillars of the 3D NAND structures.

[0012] In some embodiments, non-conformally treating the conformal thin film to increase etch rate includes oxidization or nitridation.

[0013] In some embodiments, the method further includes, prior after non-conformally etching the conformal film, treating the feature.

[0014] In some embodiments, the method further includes, after depositing molybdenum in the feature, non-conformally etching molybdenum, wherein molybdenum is preferentially etched proximate to the one or more openings.

[0015] In some embodiments, depositing a conformal thin film of molybdenum in the feature includes depositing a molybdenum-containing liner from a molybdenum precursor and ammonia. In some embodiments, depositing the conformal thin film of molybdenum further including depositing a conformal layer of molybdenum on the molybdenum-containing liner from a molybdenum precursor and hydrogen.

[0016] Another aspect of the disclosure relates to an apparatus including: a multi-station chamber, wherein each station includes a substrate support configured to support a substrate, a showerhead configured to inlet gases to a volume above substrate support, and a plasma generator configured to generate a plasma between the substrate support and showerhead; and a controller having instructions for depositing a conformal thin film of molybdenum in a feature; non-conformally treating the conformal thin film to increase etch rate, wherein the treatment is preferably applied at portions of the conformal thin film proximate to the one or more openings relative to portion the conformal thin film further from the one or more openings; non-conformally etching the conformal thin film; and depositing molybdenum in the feature.

[0017] These and other aspects of the disclosure are described in more detail below with reference to the Figures.

BRIEF DESCRIPTION OF DRAWINGS

- [0018] Figures 1A and 1B are schematic examples of material stacks that include Mo layers according to various embodiments.
- [0019] Figures 2A–2L are schematic examples of various structures into which molybdenum may be deposited in accordance with disclosed embodiments.
- [0020] Figure 3 is a schematic example of a features that are filled to contact underlying metals.
- [0021] Figure 4 is a schematic example of an molybdenum-on-molybdenum integration scheme.
- [0022] Figure 5 is a process flow diagram illustrating example operations in a method for interconnect metallization.
- [0023] Figure 6A shows cross-sectional representations of a feature during various stages of the process of Figure 5.
- [0024] Figure 6B shows examples of sub-processes that may be performed for single chamber interconnect metallization.
- [0025] Figures 6C–6G show a schematic illustrations of another example of single chamber metallization.
- [0026] Figures 7–9 are timing diagrams of examples of pulsed CVD processes.
- [0027] Figure 10A shows an example of molybdenum deposition by an atomic layer deposition (ALD) process.
- [0028] Figure 10B shows nucleation delay for deposition of molybdenum on various surfaces.
- [0029] Figure 11 shows an example of a process for filling a feature using a molybdenum precursor concentration gradient.
- [0030] Figure 12 shows examples of deposition-etch-deposition and deposition-inhibition-deposition processes on a vertically-oriented features.
- [0031] Figure 13 is a flow chart that depicts a method blended deposition and etch in accordance with certain disclosed embodiments.
- [0032] Figure 14 is a process diagram show operations in a deposition-etch-deposition method of filling wordline features of a 3D NAND structure.
- [0033] Figure 15A illustrates certain operations of the process of Figure 14.
- [0034] Figure 15B shows examples of sub-processes that may be performed for single chamber metallization including deposition-etch-deposition processes.
- [0035] Figure 16 depicts a schematic illustration of an embodiment of an ALD process

station.

[0036] Figure 17A and Figure 17B show examples of semiconductor processing tools.

[0037] Figure 18 provides an examples of a solid precursor delivery system.

DETAILED DESCRIPTION

5 [0038] In the following description, numerous specific details are set forth to provide a thorough understanding of the presented embodiments. The disclosed embodiments may be practiced without some or all of these specific details. In other instances, well-known process operations have not been described in detail to not unnecessarily obscure the disclosed embodiments. While the disclosed embodiments will be described in conjunction
10 with the specific embodiments, it will be understood that it is not intended to limit the disclosed embodiments.

[0039] The subscripts “x” and “y” are used throughout the disclosure to denote a number greater than 0 that forms a stable compound. However, it should be noted that the lack of an “x” or other subscript (e.g., in titanium nitride (TiN) or titanium oxynitride (TiON)) does
15 not imply a particular atomic ratio.

[0040] Provided herein are methods of filling features with molybdenum (Mo) that may be used for logic and memory applications. The Mo films may be deposited in semiconductor substrate features such as vias and trenches. The Mo films may be deposited to line features as liner layers and/or to fill features.

20 [0041] In some embodiments, the methods involve bottom-up deposition of Mo in a feature. Bottom-up deposition refers to growth that is mostly or wholly from a feature bottom relative to the feature sidewalls. Bottom-up deposition is distinguished from filling a feature by nucleation and growth on all feature surfaces. This results in conformal growth and can result in the formation of a void and/or seam in the feature. For example, a void
25 may form as growth at the top of the feature can pinches off the feature. A seam can form in the center of a feature as film grows inward from the sidewalls. Bottom-up deposition can avoid formation of voids and seams in the feature during the fill process. References to bottom-up deposition can include be inside-out deposition for horizontally-oriented features in which growth proceeds from the interior of a feature outward.

30 [0042] While described chiefly in the context of Mo, the methods may be used for deposition of other metals including W, Co, and Ru. For some applications, molybdenum offers several benefits over other metals such as cobalt (Co), ruthenium (Ru), and tungsten (W): (i) barrier-less and liner-less molybdenum film deposition is more feasible on oxides and nitrides as compared to deposition of cobalt, ruthenium, and tungsten, (ii) Mo resistivity

scaling is better than that of tungsten, (iii) Mo intermixing with underlying Co is not expected compared to Ru intermixing with Co at temperatures less than 450°C, and (iv) there is relatively easy Mo integration into current W schemes compared to copper and ruthenium.

5 [0043] Figures 1A and 1B are schematic examples of material stacks that include Mo layers according to various embodiments. Figures 1A and 1B illustrate the order of materials in examples of particular stacks and may be used with any appropriate architecture and application, as described further below. Figure 1A shows a first material stack 111 featuring a substrate 102 and a molybdenum layer 108 deposited thereon. The substrate 102
10 may be a silicon or other semiconductor wafer, e.g., a 200-mm wafer, a 300-mm wafer, or a 450-mm wafer, including wafers having one or more layers of material, such as dielectric, conducting, or semi-conducting material deposited thereon. In some embodiments, the substrate 102 may be or include silicon (Si) or silicon germanium (SiGe). The methods may also be applied to form metallization stack structures on other substrates, such as glass,
15 plastic, and the like.

[0044] The stack 111 has a dielectric layer 104 on the substrate 102. The dielectric layer 104 may be deposited directly on a semiconductor surface (e.g., a Si or SiGe surface) of the substrate 102, or there may be any number of intervening layers. For example, the substrate 102 may include any number of layers deposited in various arrangements on a
20 semiconductor surface.

[0045] Examples of dielectric layers include doped and undoped silicon oxide, silicon nitride, and aluminum oxide layers, with specific examples including doped or undoped layers of silicon nitride (SiN), silicon dioxide (SiO₂), and aluminum oxide (Al₂O₃). The stack 111 has a layer 106 disposed between the molybdenum layer 108 and the dielectric
25 layer 104. The layer 106 may be a diffusion barrier and/or an adhesion layer, for example. A diffusion barrier is a layer that prevents diffusion of species between layers. An adhesion layer is a layer that promotes adhesion of a layer to an underlying layer. Examples of diffusion barrier and adhesion layers include titanium nitride (TiN), titanium/titanium nitride (Ti/TiN), tungsten (W), tungsten nitride (WN), and tungsten carbon nitride (WCN).
30 The molybdenum layer 108 is the main conductor of the structure. In some embodiments, the molybdenum layer 108 may include multiple bulk layers deposited at different conditions. The molybdenum layer 108 may or may not include a molybdenum nucleation layer. In the depicted example of Figure 1A, the molybdenum layer 108 is deposited directly on the layer 106. In other embodiments (not depicted), the molybdenum layer 108 may be

deposited on a separate layer such as a growth initiation layer that includes another material, such as a tungsten (W) or W-containing growth initiation layer. The growth initiation layer may be used to facilitate nucleation and growth of the molybdenum layer 108.

[0046] Figure 1B shows another example of a stack 121. In this example, the stack 121 includes the substrate 102, dielectric layer 104, with molybdenum layer 108 deposited directly on the dielectric layer 104, without an intervening diffusion barrier or adhesion layer. The molybdenum layer 108 is as described with respect to Figure 1A. By using molybdenum as the main conductor, low resistivity thin films can be obtained. Examples of low resistivity thin films include films with resistivity less than 40 $\mu\text{Ohm-cm}$ at 60 angstroms thickness and less than 15 $\mu\text{Ohm-cm}$ at 200 angstroms thickness.

[0047] In some embodiments, a stack (not shown) may include the substrate, a conductive layer, and a molybdenum layer deposited onto the conductive layer. As used herein, a conductive layer is a layer having a conductivity of at least $10^4 \Omega^{-1}\text{-cm}^{-1}$ at room temperature. Examples include molybdenum on a metal layer (e.g., a W layer, or another Mo layer). In these embodiments, there is no dielectric layer between the molybdenum layer and the conductive layer. Similarly, the stack may include molybdenum deposited directly on a metal compound layer. Examples include molybdenum on a metal nitride layer (e.g., TiN, WN, or MoN). In still some other embodiments of a stack (not shown), the stack may include a substrate and a molybdenum layer deposited directly on the substrate, including directly on a semiconducting surface, on a dielectric surface, or on a conductive surface. Figures 1A and 1B illustrate examples of the order of materials in a particular stack and may be used with any appropriate architecture and application, with examples described further below.

[0048] The methods described herein are performed on a substrate that may be housed in a chamber. The substrate may be a silicon or other semiconductor wafer, including wafers having one or more layers of material, such as dielectric, conducting, or semiconducting material deposited thereon. The methods are not limited to semiconductor substrates and may be performed to fill any feature with molybdenum.

[0049] Substrates may have features such as vias or contact holes, which may be characterized by one or more narrow and/or re-entrant openings, constrictions within the feature, and high aspect ratios. A feature may be formed in one or more of the above-described stacks or layers within a stack. For example, the feature may be formed at least partially in a dielectric layer. In some embodiments, a feature may have an aspect ratio of at least about 2:1, at least about 4:1, at least about 6:1, at least about 10:1, at least about

25:1, or higher. One example of a feature is a hole or via in a semiconductor substrate or a layer on the substrate.

[0050] Figure 2A depicts a schematic example of a DRAM architecture, including a Mo buried wordline (bWL) 208 in a silicon substrate 202. The Mo bWL is formed in a trench etched in the silicon substrate 202. Lining the trench is a conformal barrier layer 206 and an insulating layer 204. The conformal barrier layer 206 is disposed between the insulating layer 204 and the silicon substrate 202. In this example, the insulating layer 204 may be a gate oxide layer formed from a high-k dielectric material such as a silicon oxide or silicon nitride material. In some embodiments disclosed herein, the conformal barrier layer 206 is TiN or a tungsten-containing layer, such as WN or WCN layer. In some embodiments, a conformal tungsten-containing growth initiation layer (not shown) may be present between the conformal barrier layer 206 and the molybdenum bWL 208. Alternatively, the molybdenum bWL 208 may be deposited directly on a TiN or other diffusion barrier. In some embodiments, one or both of layers 204 and 206 is not present.

[0051] The bWL structure shown in Figure 2A is one example of an architecture that includes a molybdenum fill layer. During fabrication of the bWL, molybdenum is deposited into a feature that may be defined by an etched recess in the silicon substrate 202 that is conformally lined with layers 206 and/or 204, if present.

[0052] Figures 2B–2H are additional schematic examples of various structures into which molybdenum may be deposited in accordance with disclosed embodiments. Figure 2B shows an example of a cross-sectional depiction of a vertical feature 201 to be filled with Mo. The feature can include a feature hole 205 in a silicon substrate 202. The feature hole 205 may have an underlayer 203 lining the sidewall or interior of the feature hole 205 and may form the interior surfaces. The feature hole 205 or other feature may have a dimension near the opening, e.g., an opening diameter or line width of between about 10 nm to 500 nm, for example, between about 25 nm and about 300 nm. The feature hole 205 can be referred to as an unfilled feature or simply a feature. The vertical feature 201, and any feature, may be characterized in part by an axis 218 that extends through the length of the feature, with vertically-oriented features having vertical axes and horizontally-oriented features having horizontal axes. The underlayer 203 can be, for example, a diffusion barrier layer, an adhesion layer, a nucleation layer, a combination of thereof, or any other applicable material. Non-limiting examples of underlayers can include dielectric layers and conducting layers. Examples of dielectric materials include oxides, such as SiO₂ and Al₂O₃; nitrides, such as SiN; carbides, such as nitrogen-doped silicon carbide (NDC) and oxygen-doped

silicon carbide (ODC); and low k dielectrics, such as carbon-doped SiO₂. In particular implementations, an underlayer can be one or more of titanium, titanium nitride, tungsten nitride, titanium aluminide, tungsten, and molybdenum. In some embodiments, the underlayer is tungsten-free. In some embodiments, the underlayer is molybdenum-free.

5 [0053] In some embodiments, features are wordline features in a 3D NAND structure. For example, a substrate may include a wordline structure having an arbitrary number of wordlines (e.g., 50 to 450) with vertical channels at least 200Å deep. Examples of wordline features are described further below. Another example of a feature is a trench in a substrate or layer. Features may be of any depth. In various embodiments, the feature may have an
10 underlayer, such as a barrier layer or adhesion layer. Non-limiting examples of underlayers include dielectric layers and conducting layers, e.g., silicon oxides, silicon nitrides, silicon carbides, metal oxides, metal nitrides, metal carbides, and metal layers.

[0054] Figure 2C shows an example of a vertical feature 201 that has a re-entrant profile. A re-entrant profile is a profile that narrows from a bottom, closed-end, or interior of the
15 feature to the feature opening. According to various implementations, the profile may narrow gradually and/or include an overhang at the feature opening. Figure 2C shows an example of the latter, with an underlayer 213 lining the sidewall or interior surfaces of the feature hole 205. Similar to Figure 2B, the underlayer 213 can be a diffusion barrier layer, an adhesion layer, a nucleation layer, a combination of thereof, or any other applicable
20 material. Non-limiting examples of under-layers can include dielectric layers and conducting layers. The underlayer 213 forms an overhang 215 such that the underlayer 213 is thicker near the opening of the vertical feature 201 than inside the vertical feature 201.

[0055] In some implementations, features having one or more constrictions within the feature may be filled. Figure 2D shows examples of views of various filled features having
25 constrictions. Each of the examples (a), (b), and (c) in Figure 2D includes a constriction 209 at a midpoint within the feature. The constriction 209 can be, for example, between about 15 nm-20 nm wide. Constrictions can cause pinch off during deposition of molybdenum in the feature using conventional techniques, with deposited metal blocking further deposition past the constriction before that portion of the feature is filled, resulting
30 in voids in the feature. Example (b) further includes an overhang 215 (such as, a liner/barrier overhang) at the feature opening. Such an overhang could also be a potential pinch-off point. Example (c) includes a constriction 212 further away from the field region than the overhang 215 in example (b).

[0056] Horizontal features, such as in 3-D memory structures, can also be filled.

Figure 2E shows an example of a horizontal feature 250 that includes a constriction 251. For example, horizontal feature 250 may be a word line in a 3-D NAND (also referred to as vertical NAND or VNAND) structure. In some implementations, the constrictions can be due to the presence of pillars in a 3D NAND or other structure. Figure 2F presents a cross-sectional side view of a 3-D NAND structure 210 (formed on a silicon substrate 202) having 3-D NAND stacks (left 225 and right 226), central vertical structure 230, and a plurality of stacked horizontal wordline features 220 with openings 222 on opposite sidewalls 240 of central vertical structure 230. Note that Figure 2F displays two “stacks” of the exhibited 3-D NAND structure 210, which together form the “trench-like” central vertical structure 230. However, in certain embodiments, there may be more than two such stacks arranged in sequence and running spatially parallel to one another, the gap between each adjacent pair of stacks forming a central vertical structure 230, like that explicitly illustrated in Figure 2F. In this embodiment, the horizontal wordline features 220 are 3-D memory wordline features that are fluidically accessible from the central vertical structure 230 through the openings 222. Although not explicitly indicated in the figure, the horizontal wordline features 220 present in both the 3-D NAND stacks 225 and 226 shown in Figure 2F (i.e., the left 3-D NAND stack 225 and the right 3-D NAND stack 226) are also accessible from the other sides of the stacks (far left and far right, respectively) through similar vertical structures formed by additional 3-D NAND stacks (to the far left and far right, but not shown). Each 3-D NAND stack 225, 226 contains a stack of wordline features that are fluidically accessible from both sides of the 3-D NAND stack through a central vertical structure 230. In the particular example schematically illustrated in Figure 2F, each 3-D NAND stack contains 6 pairs of stacked wordlines. However a 3-D NAND memory layout may contain any number of vertically stacked pairs of wordlines.

[0057] The wordline features in a 3-D NAND stack can be formed by depositing an alternating stack of silicon oxide and silicon nitride layers, and then selectively removing the nitride layers leaving a stack of oxides layers having gaps between them. These gaps are the wordline features. Any number of wordlines may be vertically stacked in such a 3-D NAND structure so long as there is a technique for forming them available, as well as a technique available to successfully accomplish (substantially) void-free fills of the vertical features. Thus, for example, a VNAND stack may include between 2 and 512 horizontal wordline features, between 2 and 256 horizontal wordline features, between 8 and 128 horizontal wordline features, or between 16 and 64 horizontal wordline features, and so forth (the listed ranges understood to include the recited endpoints).

[0058] Figure 2G presents a cross-sectional top-down view of the same 3-D NAND structure 210 shown in the side view in Figure 2F with the cross-section taken through the horizontal section 260 as indicated by the dashed horizontal line in Figure 2F. The cross-section of Figure 2G illustrates several rows of pillars 255, which are shown in Figure 2F to run vertically from the base of the substrate 202 to the top of the 3-D NAND structure 210. In some embodiments, the pillars 255 are formed from a polysilicon material and are structurally and functionally significant to the 3-D NAND structure 210. In some embodiments, such polysilicon pillars may serve as gate electrodes for stacked memory cells formed within the pillars. The top-view of Figure 2G illustrates that the pillars 255 form constrictions in the openings 222 to wordline features 220. Fluidic accessibility of wordline features 220 from the central vertical structure 230 via openings 222 (as indicated by the arrows in Figure 2G) is inhibited by pillars 255. In some embodiments, the size of the horizontal gap between adjacent polysilicon pillars is between about 1 and 20 nm. This reduction in fluidic accessibility increases the difficulty of uniformly filling wordline features 220 with material. The structure of wordline features 220 and the challenge of uniformly filling them with molybdenum material due to the presence of pillars 255 is further illustrated in Figures 2H, 2I, and 2J.

[0059] Figure 2H exhibits a vertical cut through a 3-D NAND structure similar to that shown in Figure 2F, but here focused on a single pair of wordline features 220 and additionally schematically illustrating a fill process which resulted in the formation of a void 275 in the filled wordline features 220. Figure 2I also schematically illustrates void 275, but in this figure illustrated via a horizontal cut through pillars 255, similar to the horizontal cut exhibited in Figure 2G. Figure 2J illustrates the accumulation of molybdenum material around the constriction-forming pillars 255, the accumulation resulting in the pinch-off of openings 222, so that no additional molybdenum material can be deposited in the region of voids 275. Apparent from Figures 2H and 2I is that void-free molybdenum fill relies on migration of sufficient quantities of deposition precursor down through central vertical structure 230, through openings 222, past the constricting pillars 255, and into the furthest reaches of wordline features 220, prior to the accumulated deposition of molybdenum around pillars 255 causing a pinch-off of the openings 222 and preventing further precursor migration into wordline features 220. Similarly, Figure 2J exhibits a single wordline feature 220 viewed cross-sectionally from above and illustrates how a generally conformal deposition of molybdenum material begins to pinch-off the interior of wordline feature 220 due to the fact that the significant width of pillars 255 acts to partially block, and/or narrow,

and/or constrict what would otherwise be an open path through wordline feature 220. (It should be noted that the example in Figure 2J can be understood as a 2-D rendering of the 3-D features of the structure of the pillar constrictions shown in Figure 2I, thus illustrating constrictions that would be seen in a plan view rather than in a cross-sectional view.)

5 [0060] Three-dimensional structures may need longer and/or more concentrated exposure to precursors to allow the innermost and bottommost areas to be filled. Three-dimensional structures can be particularly challenging when employing molybdenum halide and/or molybdenum oxyhalide precursors because of their proclivity to etch, with longer and more concentrated exposure allowing for more etch as parts of the structure.

10 [0061] Figures 2K and 2L show examples of an asymmetric trench structure DRAM bWL. Some fill processes for DRAM bWL trenches can distort the trenches such that the final trench width and resistance R_s are significantly non-uniform. Figure 2K shows an unfilled feature 261 and filled feature 265 that exhibits line bending after fill. In this example, the features are a narrow asymmetric trench structure DRAM bWL. As shown, multiple
15 features 283 are depicted on a substrate. These features 283 are spaced apart, and in some embodiments, adjacent features have a pitch between about 20 nm and about 60 nm or between about 20 nm and 40 nm. The pitch is defined as the distance between the middle axis of one feature to the middle axis of an adjacent feature. The unfilled features 261 may be generally V-shaped, as shown in feature 283, having sloped sidewalls where the width
20 of the feature narrows from the top of the feature to the bottom of the feature. The features widen from the feature bottom 273b to the feature top 273a. After some fill operations, line bending may be observed within the filled feature 265. In some situations, a cohesive force between opposing surfaces of a trench pulls the trench sides together, as depicted by arrows 267. This phenomenon is illustrated in Figure 2L and may be characterized as “zipping up”
25 the feature. As the feature 283 is filled, more force is exerted from a center axis 299 of the feature 283, causing line bending. For example, molybdenum may be deposited on the sidewalls of the feature 283. Deposited molybdenum 284a and 284b on sidewalls of feature 283 thereby interact in close proximity, where molybdenum-molybdenum bond radius r is small, thereby causing cohesive interatomic forces between the smooth growing surfaces of
30 molybdenum and pulling the sidewalls together, thereby causing line bending.

[0062] Provided below are methods of filling features with molybdenum. The methods described herein include surface treatment and deposition operations, which may be used to fill substrate features such as those described above. As described above, molybdenum offers several benefits over other metals. Examples of feature fill for horizontally-oriented

and vertically-oriented features are described below. It should be noted that in at least most cases, the examples are applicable to both horizontally-oriented and vertically-oriented features. Horizontally-oriented features generally refer to features oriented such that the feature axis is parallel to the plane of the substrate surface. Vertically-oriented features generally refer to features oriented such that the feature axis is orthogonal to the plane of the substrate surface.

[0063] In some embodiments, methods of filling features that include exposing a feature to a metal halide, e.g., a molybdenum halide, prior to feature fill are described. The metal halide can etch, deposit, and/or otherwise treat material on the feature bottom and/or sidewalls.

[0064] In some embodiments, the methods are used to fill features to contact an underlying metal. An example of such a feature is shown in Figure 3. At 301, an unfilled feature 312 is shown. The unfilled feature 312 is formed in an oxide layer 305 and is to be filled with Mo to make contact with an underlying metal-containing layer 303. The unfilled feature 312 is defined by sidewall surfaces 315 and bottom surface 317. The metal-containing layer may be, e.g., an elemental metal or a metal silicide in some embodiments.

[0065] According to various embodiments, the sidewall surfaces 315 and the bottom surface 317 may be the same or different materials. In some embodiments, the oxide layer 305 may be exposed to form the sidewall surfaces 315. Similarly, the underlying metal-containing layer 303 may be exposed to form the bottom surface 317. In some embodiments, surface oxidation may result in the bottom surface 317 being a metal oxide. In some embodiments, a liner layer (not shown) may be formed on the sidewall and/or bottom of the feature to form the sidewall surfaces 315 and/or bottom surface 317. Examples of liner layers include TiN, WN, and WCN. In some embodiments, a liner layer may be a molybdenum-containing liner layer such as a molybdenum nitride (MoN) layer.

[0066] In some embodiments, the sidewall surfaces 315 and bottom surface 317 are different. In a subsequent deposition operation, Mo may be deposited at conditions under which it preferentially nucleates on the bottom surface 317. This can promote bottom-up fill and prevent the formation of voids.

[0067] Examples of underlying metals and/or bottom surfaces include TiN, titanium aluminum carbide (TiAlC), Ti, W, Co, Mo, Ru, Cu, nickel (Ni), iridium (Ir), rhodium (Rh), tantalum (Ta), and tantalum nitride (TaN).

[0068] The methods described herein address various challenges that occur as feature size decreases. For example, void-free gap fill becomes more challenging in small features due

to deeper features, re-entrant profiles near the feature openings, and/or insufficient growth selectivity between feature bottom metal surfaces and sidewall dielectric surfaces. Smaller features can lead to more frequent pattern misalignment. An example of a misaligned feature is shown at 350 in which the unfilled feature 312 is not centered over the underlying metal 303. As a result, the bottom surface 317 includes metal and dielectric material.

[0069] In some embodiments, the methods may be used in molybdenum-on-molybdenum integration schemes. An example of such an integration scheme is shown in Figure 4. A layer 401 includes dielectric 402 and Mo 403. An etch stop layer (ESL) 404 is disposed over the layer 401. The ESL 404 may be SiN, for example. A dielectric layer 405 is deposited over the ESL 404. The dielectric layer 405 is then patterned and etched, with the etch stopping at the ESL 404 (not shown). The ESL 404 is then removed from the feature 412 forming the unfilled feature 412.

[0070] A Mo-containing layer 410 may be formed at the surface of Mo 403 during the previous processing operations. The Mo-containing layer 410 is generally an amorphous layer. It is relatively thin, e.g., on the order of 0.5 nm to 3 nm. It may contain various impurities such as oxygen, nitrogen, and/or other halogens. While surface oxidation can be removed by a hydrogen (H₂) plasma, the Mo-containing layer 410 is generally resistant to H₂ plasma. If left in the device, it can cause higher resistance at the interface between Mo 403 and the subsequently deposited Mo film. A surface treatment may be performed prior to deposition of Mo in a feature. According to various embodiments, the surface treatment involves exposure to a molybdenum halide. In some embodiments, the molybdenum halide is provided without a co-reactant, and no deposition occurs. In some embodiments, the molybdenum halide is provided with a co-reactant. A thin layer of Mo may be deposited.

[0071] In some embodiments, the feature includes dielectric surfaces such as dielectric sidewall surfaces. The surface treatment may inhibit growth on the dielectric surfaces, enhancing selectivity during subsequent deposition on the conductive surfaces. In some embodiments, the feature as provided includes a Mo-containing layer as described above. The surface treatment can remove this layer, yielding a clean Mo surface for deposition and Mo-Mo interconnect formation.

Interconnect Metallization

[0072] Figure 5 is a process flow diagram illustrating example operations in a method for interconnect metallization. The process begins with an operation 501 in which a feature

having dielectric sidewalls and a metal-containing contact is provided. The metal-containing contact may be at the bottom of the feature with the dielectric sidewalls extending from the feature opening to the metal-containing contact. The feature may be provided to a processing chamber. In some embodiments, one or more processing operations may occur in the processing chamber to form the feature having dielectric sidewalls and a metal-containing contact.

[0073] Examples of dielectric sidewalls include silicon-containing layers such as oxides and nitrides. Examples of metal-containing contacts include metals and metal compound films. The metal-containing contact may be generally conductive, having a conductivity of at least $10^4 \Omega^{-1}\text{-cm}^{-1}$ at room temperature. Examples include TiN, TiAlC, W, Co, Mo, Ru, Cu, Ni, Rh, Ir, Ta, Ti, TiSi_x, RuSi_x, NiPtSi_x, TiSiN, MoSi_x, CoSi_x, and TaN.

[0074] In some embodiments, a surface oxide is present on the metal-containing contact. Still further, in some embodiments, a layer containing other impurities is present on the metal-containing contact. An example is an amorphous Mo-containing layer described as with reference to Figure 4.

[0075] In some embodiments, an etch operation to remove a liner layer from at least the sidewalls of the feature is performed prior to operation 501. For example, a feature may include a TiN liner layer conformally coating the bottom and sidewalls. An etch may be performed to remove the TiN layer from the sidewalls, exposing dielectric material. The sidewall surfaces are then silicon oxide or other dielectric material.

[0076] In an operation 503, a pre-treatment is performed. Operation 503 can remove surface oxide and/or etch residue, for example. Examples of etch residue include fluorocarbons and hydrocarbon polymers. According to various embodiments, operation 503 involves exposure to a molybdenum halide gas and/or a plasma clean.

[0077] A plasma clean may be remotely generated or generated in-situ. In some embodiments, operation 503 involves exposure to a reducing plasma such as a H₂ plasma. In some embodiments, operation 503 treats the dielectric sidewalls. For example, it may remove organic materials and/or reduce oxygen in the dielectric sidewalls. This can improve subsequent Mo growth selectivity on a metal-containing surface with respect to the sidewalls.

[0078] In some embodiments, the clean involves exposure to a molybdenum halide gas, e.g., MoCl₅. This may be a plasma-free operation. Plasma-free refers to the operation performed without activating a plasma. Exposure to a molybdenum halide can remove impurities from the metal contact. For example, in embodiments in which an amorphous

Mo-containing layer as described above with respect to Figure 4 is present, it can remove all or at least a portion of the layer. In the same or other embodiments, exposure to a molybdenum halide inhibits nucleation on the dielectric sidewall surfaces.

[0079] In some embodiments, a molybdenum chloride compound is used. Molybdenum-containing compounds are also referred to herein as Mo-containing precursors or Mo precursors. Molybdenum chlorides are given by the formula MoCl_x , where x is 2, 3, 4, 5, or 6, and include molybdenum dichloride (MoCl_2), molybdenum trichloride (MoCl_3), molybdenum tetrachloride (MoCl_4), molybdenum pentachloride (MoCl_5), and molybdenum hexachloride (MoCl_6). In some embodiments, MoCl_5 or MoCl_6 are used. While the description chiefly refers to MoCl_x compounds, in other embodiments, other molybdenum halides may be used. Molybdenum halide precursors are given by the formula MoX_z , where X is a halogen (fluorine (F), chlorine (Cl), bromine (Br), or iodine (I)) and z is 2, 3, 4, 5, or 6. Examples of MoX_z precursors include molybdenum fluoride (MoF_6). In some embodiments, a non-fluorine-containing MoX_z precursor is used to prevent fluorine etch or incorporation. In some embodiments, a non-bromine-containing and/or a non-iodine-containing MoX_z precursor is used to prevent etch or bromine or iodine incorporation.

[0080] In some embodiments, operation 503 involves exposure to the molybdenum halide compound without a co-reactant gas. In such embodiments, the molybdenum halide may be pulsed or delivered in a continuous dose. For examples, MoCl_5 may be pulsed with argon (Ar) or other inert gas for a certain number of cycles. Alternatively, a continuous dose of MoCl_5 can be delivered followed by an Ar purge.

[0081] In some embodiments, operation 503 involves exposure to the molybdenum halide compound with a co-reactant gas to deposit Mo. The co-reactant is generally H_2 , though other reducing agents as described below may be used. In one example sequence, MoCl_5 pulses are alternated with H_2 pulses with intervening purge gas pulses. In another example, MoCl_5 pulses are alternated with H_2 pulses with no intervening purge gas pulses. In another example sequence, MoCl_5 pulses are alternated with H_2 pulses with a purge gas pulse directly after only one of the reactant gases in each cycle. In another example sequence, MoCl_5 is flowed with H_2 . In the further example sequence, the co-flowed reactants are pulsed with an alternating Ar pulse. In another example sequence, H_2 gas may be flowed into the chamber and is continuously flowing into the chamber while MoCl_5 is intermittently flowing into the chamber. In any of these examples, another molybdenum halide and/or another inert gas may be used instead of MoCl_5 and Ar, respectively. In some embodiments, sequences with a co-reactant may be employed when metals besides Mo are at the feature

bottom. In such embodiments, a Mo surface layer may be formed facilitating subsequent Mo growth. For example, if a W, Co, or Ru layer is at the feature bottom, operation 503 may be used to form a thin Mo surface layer.

[0082] In addition to or instead of any of the operations described above, operation 503 can involve an atomic layer clean with a chlorine-based plasma, a hydrogen fluoride (HF) vapor clean, an ammonium fluoride (NH₄F) clean, or a treatment using other reducing agents. These operations may be used to reduce oxide off a feature surface.

[0083] The process continues at operation 505 with selective deposition of a Mo pre-fill layer on the metal-containing contact. The selective deposition deposits a layer on the metal-containing without significant deposition on the dielectric sidewalls.

[0084] In some embodiments, this operation involves reaction using a molybdenum halide or a molybdenum oxyhalide precursor. In some embodiments, MoCl₅ is used as it has good selectivity as described below.

[0085] Process conditions such as the precursor gas, the reducing agent, substrate temperature, process pressure, and exposure time may affect the selectivity of the Mo film being deposited. Different precursor gases may have different process windows in which Mo film may be selectively deposited. For example, MoCl₅ is selective while MoO₂Cl₂ is not, i.e., under the same temperature and pressure conditions, the precursor gas of MoCl₅ may deposit Mo only on a conductive surface and not on a dielectric surface while a precursor gas of MoO₂Cl₂ will deposit Mo on both conductive and dielectric surfaces. Generally speaking, MoCl₅ gas has a large process window, i.e., large temperature and pressure range, where the precursor gas retains its selectivity. For example, MoCl₅ may be selectively deposited on a metal material with respect to a dielectric material where the process temperature is 300°C to 800°C. In some embodiments, the substrate temperature is 350°C to 550°C. Generally speaking, higher process temperatures and higher process pressures reduce the selectivity of the deposited film. For example, at higher temperatures, a precursor gas such as MoCl₅ may lose its selectivity and deposit Mo film on both a metal surface and dielectric surface within a feature.

[0086] In some embodiments, operation 505 can be a thermal or plasma-based process. In some embodiments, operation 505 is a plasma-enhanced ALD (PEALD) or plasma enhanced CVD (PECVD) process using a molybdenum halide precursor. In some embodiments, the molybdenum halide precursor is MoCl₅. Hydrogen (H₂) or other reducing agent may be used for the PEALD or PECVD deposition.

[0087] In some embodiments, operation 505 can be a thermal process. It can be easier to

achieve selectivity with a thermal process. In some such embodiments, operation 505 can involve a pulsed chemical vapor deposition (pulsed CVD) process. Pulsed CVD processes for selective deposition of a molybdenum are described further below with reference to Figures 7–9.

5 [0088] Figure 6A shows cross-sectional representations of a feature during various stages of the process of Figure 5. The feature including a conductive bottom material 602 and dielectric sidewalls 604 is provided to a processing tool, where it undergoes a pre-treatment operation as described with reference to operation 503 of Figure 5. After pretreatment, the surface of the conductive bottom material may be free of oxide and other residues, for
10 example. A selective deposition is then performed to deposit Mo 606 at the bottom of the feature. The selective deposition forms Mo on the conductive bottom material 602 without significant deposition on the dielectric sidewalls 604. This depicts an example of feature after operation 505 of Figure 5 with a layer of Mo in the feature without deposition on the sidewalls above the layer.

15 [0089] Returning to Figure 5, a conformal Mo liner is deposited in an operation 507. The conformal Mo liner is deposited by a non-selective method that deposits on both the Mo pre-fill layer and the dielectric sidewalls. In some embodiments, MoO_2Cl_2 may be used to deposit a conformal layer. The deposition may be a PEALD deposition using MoO_2Cl_2 . Above about 400°C , thermal ALD may be used to deposit a conformal layer using MoO_2Cl_2 .
20 In some embodiments, MoCl_5 may be used with a PEALD to deposit the conformal layer. This is shown in Figure 6A, with conformal Mo liner 608 deposited in the feature.

[0090] Returning to Figure 5, the process may continue with fill of the feature with Mo in an operation 509. The same or different Mo precursor may be used for operations 507 and 509. Operation 509 may include one or more deposition, inhibition, and etch operations
25 as described further below. The sequence of these operations as well as the precursor used can depend on the feature profile. For example, if the feature is re-entrant, one or more etch and/or inhibition operations may be used to tailor the fill. For less challenging structures, such as V-shaped structures, PEALD using MoO_2Cl_2 may be used, for example. These structures may also be filled using a pulsed CVD process in some embodiments. Further
30 description of possible fill techniques of re-entrant features is described below. Figure 6A shows the structure after the fill, with bulk Mo film 601 in the feature.

[0091] Figure 6B shows examples of sub-processes that may be performed for interconnect metallization. In the example of Figure 6B, all of the operations described with reference to Figure 5 or Figure 6B are performed in a single chamber, which may be a multi-

station or single station chamber. Such a chamber may be equipped for delivery of two solid precursors (e.g., MoCl_5 and MoO_2Cl_2). The example of Figure 6B refers to various inhibition and deposition-etch-deposition (DED) operations. These are described more fully below. In other embodiments, any one or more of the operations may occur in different chambers. These may be connected by vacuum in some embodiments.

[0092] Figure 6B describes single chamber interconnect metallization processes, including pre-treatment, selective prefill, conformal liner, and final fill operations. Interconnect metallization may include all of pre-treatment, selective prefill, conformal liner, and final fill operations or a subset of these. For example, a single chamber metallization process may include pre-treatment, selective prefill, followed by a deposition that results in complete fill of the feature. See, e.g., Figure 6B, which shows PECVD using MoO_2Cl_2 for both the conformal liner and the final fill. A PECVD operation performed after pre-treatment and/or selective fill may be used to fill a feature without forming a conformal liner as part of a separate fill operation. This also may be characterized as deposition of a conformal liner continuing until the feature is filled. Examples of other single chamber fill processes include:

Pre-treatment / conformal liner / final fill

Pre-treatment / selective prefill / final fill

Pre-treatment / selective fill (selective deposition is continued until feature fill is complete)

[0093] Any one or more of the sub-processes described may be used for each of pre-treatment, selective prefill, conformal liner, and final fill. Turning to pre-treatment, as described above, the pre-treatment may be a thermal or plasma treatment. An example of a thermal treatment is exposure to a metal halide. This can be a molybdenum halide as described above or another metal halide, such as a tungsten halide. Tungsten hexafluoride (WF_6) or MoF_6 may be used in some embodiments. These pretreatment agents are gases at standard pressure and temperature, allowing delivery at room temperature through a mass flow controller. Direct or remote plasma pre-cleans may be used. Exposure to a reducing plasma such as a H_2 plasma may be performed. For interconnect metallization, the incoming bottom surface may be a conductive surface. Examples include elemental metal films such as tungsten, molybdenum, copper, cobalt, titanium, ruthenium, or metal-containing conductive compounds films such as titanium nitride and tungsten nitride. Sidewall surfaces are dielectric and include silicon oxides, silicon nitrides, silicon carbides, silicon oxycarbides, silicon oxynitrides, aluminum oxides, and the like. The pre-treatment can be

used to remove surface oxides of the conductive surface and/or treat dielectric sidewalls as discussed above.

[0094] Selective prefill, if performed, results in preferential deposition on the conductive surface relative to the dielectric surfaces. In some embodiments, it is performed to reduce the aspect ratio of the feature for subsequent fill. Processes that may be used include thermal deposition using a molybdenum halide, e.g., MoCl₅ or MoF₆. The thermal deposition may be an atomic layer deposition (ALD), a pulsed chemical vapor deposition process (pulsed CVD), or a continuous flow CVD process. ALD is a surface-mediated deposition technique in which doses of the Mo halide precursor and hydrogen (H₂) are sequentially introduced into a deposition chamber, optionally with an argon or other inert gas purge between sequential reactant doses. One or more cycles of sequential doses of the molybdenum precursor and H₂ are used to deposit Mo selectively. In continuous flow thermal CVD, the Mo halide and H₂ are flowed concurrently to the chamber for a gas phase reaction. Pulsed CVD process sequences can involve continuous flow of one or more process gases and pulsed flow of one or more other process gases. Examples of pulsed CVD processes are given below with respect to Figures 7–9.

[0095] Selective deposition on conductive surfaces with respect to dielectric surfaces is an inherent feature using molybdenum halides and hydrogen (H₂) for thermal ALD, thermal CVD, and thermal pulsed CVD at appropriate conditions. As described further below, MoCl₅ and MoF₆ have a large process window, i.e., large temperature and pressure range, where the precursor gas retains its selectivity. For example, MoCl₅ may be used to selectively deposit molybdenum on a metal or metallic conductive material with respect to a dielectric material where the process temperature is 200°C to 800°C, e.g., 250°C to 550°C, or 300°C to 500°C. Generally speaking, higher process temperatures and higher process pressures reduce the selectivity of the deposition. However, selectivity is significantly controlled by precursor identity with molybdenum halides resulting in much greater selectivity than molybdenum oxyhalides. Selectivity can also decrease with the use of stronger reducing agents than hydrogen. These include silane and diborane, for example. In some embodiments, plasma deposition may be used for selective prefill. In such embodiments, the plasma may be a remote plasma, with hydrogen radicals that are generated in a plasma generator remote to the process chamber fed to the reactor. Description of thermal ALD, thermal CVD, and thermal pulsed CVD herein may be modified with hydrogen radicals flowed to the chamber rather than hydrogen gas for selective deposition.

[0096] As noted above, selective deposition refers to deposition that preferentially occurs

on one surface type over another. According to various embodiments, a feature may be provided to the chamber with two material types (e.g., a conductive metal bottom and dielectric sidewalls). In other embodiments, a feature may be provided to the chamber having a single material type that is treated to allow selective deposition. As an example, a feature may be provided with a TiN liner conformally lining the bottom and sidewalls of the feature. It may be exposed to a high temperature molybdenum halide that preferentially etches the TiN layer at top of the surface to form a TiN cup at the feature bottom, exposing dielectric sidewalls at the top of the surface. Molybdenum may then be selectively deposited on the TiN cup. The molybdenum halide exposure may be performed as part of the pre-treatment process described above. In another example, a feature having uniform surface materials may be treated by inhibiting deposition on a portion of the feature. For example, an inhibition treatment may be performed to inhibit deposition at the feature opening.

[0097] Deposition of the conformal liner is typically done by an ALD process rather than CVD to facilitate conformally depositing the liner on the contours of the feature. PEALD or thermal ALD may be used. If the feature has multiple material types (e.g., as in Figure 6A), PEALD with a direct plasma may be used with a molybdenum halide as it will result in conformal, non-selective deposition rather than selective deposition on the conductive surfaces. Example PEALD processes using MoCl_5 may use substrate temperatures of 300°C or more. For molybdenum oxyhalides, either thermal or plasma ALD may be used. For thermal ALD, the temperature is high enough for deposition to occur, e.g., with MoO_2Cl_2 and H_2 , deposition at 450°C or above may be used. For PEALD with MoO_2Cl_2 , a wide range of temperatures may be used. For example, a substrate temperature from 100°C to 600°C may be used.

[0098] If the feature itself is not selective – i.e., it has a uniform material throughout such as previously formed liner film – and that liner film is to be incorporated into the device, the conformal liner may be formed by any ALD process, thermal or plasma, using any molybdenum halide or oxyhalide precursor capable of deposition.

[0099] Examples of final fill subprocesses are also shown in Figure 6B. As indicated above, filling re-entrant structures is more challenging and may employ one or more inhibition or etch processes to achieve fill. In one example depicted in Figure 6B for a re-entrant structure, an fill process with a molybdenum oxyhalide or molybdenum halide can use a deposition-etch-deposition (DED) or deposition-inhibition-deposition (DID) process. As described further below, more complex processes including processes with one or more deposition, etch, inhibition, and de-inhibition processes, may be performed to achieve void

free fill.

[0100] Figure 6B also an inhibition subprocess for molybdenum oxyhalide and molybdenum halide deposition processes. Inhibition refers to inhibiting molybdenum nucleation and is described further below. As an example, halogenating a dielectric material or conductive material will inhibit subsequent nucleation. Examples of halogen-containing inhibitors include NF_3 , BCl_3 , MoCl_5 , and Cl_2 .

[0101] For a DED process, Figure 6B shows examples of two alternative subprocesses – one a discrete intermittent DED and a simultaneous DED. A discrete intermittent DED process may involve a deposition of a first molybdenum film, followed by a partial etch of that film, followed by a second deposition of a molybdenum film. For an ALD process, an etch operation may be performed between any number of deposition cycles to tailor the feature profile. One or more DED processes may be performed during the fill. For a CVD process, the deposition may be stopped and the etched performed at the appropriate time to tailor the feature profile. A simultaneous DED process can involve adding an etchant to the reducing agent to preferentially etch a portion of the film while depositing. As an example, an etchant such as chlorine (Cl_2) can be added to the H_2 gas during a plasma H_2 operation during a PEALD cycle.

[0102] Simultaneous DED may also be referred to a blended DED, with the deposition and etch operations overlapping in time. Figure 6B also has an example of a molybdenum halide-based blended DED. Unlike a molybdenum oxyhalide such as MoO_2Cl_2 or MoOCl_4 , a molybdenum halide such as MoCl_5 or MoF_6 will etch the deposited molybdenum. An example of a blended process may be to lower the H_2 and/or increase the molybdenum halide flow to have net etch at the feature opening.

[0103] For a V-shape incoming structure, fill is less challenging and can use any appropriate ALD or CVD process, either thermal or plasma-enhanced. CVD processes include continuous flow and pulsed CVD processes. The subprocesses identified under “V-shaped” structures may be performed for any feature that is relatively easy to fill. In some embodiments, these subprocesses may be used as the final fill operation of a more challenging structure that has been partially filled.

[0104] An additional example of single chamber metallization is described with reference to Figures 6C–6F. Figures 6C–6G show a schematic illustrations of another example of single chamber metallization. In Figure 6C, a feature 601 having a TiN liner layer 615 is shown. The feature 601 has a bottom surface 605 and sidewall surfaces 611. In Figure 6A, the TiN liner is the bottom surface 605 and the sidewall surfaces 611. In some embodiment,

the liner layer may be a titanium silicon nitride (TiSixN) liner layer. In some embodiments, the TiN layer 615 may be oxidized on a top surface of the layer. The feature 601 is formed in a dielectric material 613. An underlying stack 610 is below the feature bottom surface 605. In the example shown, the underlying stack 610 has a metal silicide nitride (MSixNy) layer 608 and a metal silicide layer (MSix) 607 connected to a semiconductor layer 606, e.g., silicon (Si) or silicon-germanium (SiGe). This stack 610 may be used in a transistor junction structure. One example of a MSix layer is titanium silicide (TiSix) and a metal silicide nitride (MSixNy) is a titanium silicide nitride (TiSixNy). The TiN liner layer 615 on the bottom surface 605 is used to protect the underlying stack 610 below the feature bottom surface. The TiN liner layer may act as a diffusion barrier, prevent etching of the underlying material, and prevent the underlying material from oxidizing.

[0105] Figure 6D depicts the feature 601 undergoing a pre-treatment, as described above with respect to Figure 6B. Shown is a Mo halide precursor 619 soaking the feature to remove any oxide on the surface. For example, TiNxOy may be cleaned and may leave a TiN layer 615. In addition, a high temperature Mo halide soak etches the TiN layer to removes any TiN layer on the field and may remove part or all of the TiN layer on the substrate sidewall. In the embodiment shown, part of the TiN layer 615 remains on the sidewalls such that the TiN layer is thicker at the bottom portion of the sidewall relative to the upper portion. The TiN layer remains as the bottom surface 605 and may be the thickest portion of the remaining TiN layer in the feature 601. The TiN layer remains as the bottom surface 605 to protect the underlying stack 610 during subsequent processing.

[0106] Figure 6E shows the feature 701 after an initial Mo layer 621 is deposited. The Mo layer 621 is deposited as described above with reference to Figure 6B using an ALD process using a Mo halide precursor such as MoCl₅ with a reducing agent. As shown, the initial Mo layer 621 is selectively deposited on the TiN layer 615 in the feature and covers the sidewalls and the feature bottom. The Mo layer 621 is deposited directly on the TiN layer 615 and not on any dielectric surface.

[0107] Figure 6F shows the feature 602 after a second etch process. The etch process may be similar to the clean and etch process used in Figure 6D. The feature 601 may undergo a soak process with an Mo halide precursor 619. In some embodiments, the soak may be continuous. In still some other embodiments, the soak may be multiple cycles of alternating doses of the Mo halide precursor and a purge gas. The etch in Figure 6F may be a more aggressive etch than the etch shown in Figure 6D. The etch removes the Mo layer and the TiN layer on the sidewalls of the feature. As shown, the dielectric material 613 forms the

sidewall surfaces 611 after the etch. The etch leaves the TiN layer 615 and the Mo layer 621 on the bottom of the feature 601 so that they form the bottom surface 604 and protect the underlying stack 610. The clean removes any oxide or contaminants on the surfaces.

[0108] Figure 6G shows the feature 601 after a Mo gap fill of the feature as described above with respect to Figure 6B. The feature 601 is filled with a Mo fill 623. The TiN layer 615 remains between the Mo fill 623 and the underlying stack 610. The feature 601 may be filled using a thermal or plasma ALD or a CVD process. The fill may be done with a Mo oxyhalide precursor containing oxygen, a Mo halide precursor not containing oxygen, or a combination thereof. In some embodiments, the fill may be a conformal fill followed by gap fill or a bottom-up fill. In some embodiments, the fill may be performed in a single stage deposition, where the fill is continued using the same parameters, such as temperature and pressure, as the initial fill. In some other embodiments, the fill may be performed in multi-stage Mo deposition, where parameters may be changed during the deposition. For example, the deposition at a first stage may have a first temperature. After the first stage, the deposition may continue in a second stage and may have a second temperature higher than the first temperature. The increase in temperature may be used to increase the rate of Mo bulk fill, decreasing processing time. In another example of multi-stage deposition, the Mo precursor and reactant concentrations may be varied at different stages.

Molybdenum Deposition

[0109] Deposition of molybdenum as described herein involves reacting a Mo-containing precursor, also referred to as a molybdenum precursor. In some embodiments, a molybdenum halide compound as described above is used. In methods including surface treatment using a molybdenum halide compound, the same or different compound may be used for deposition.

[0110] In some embodiments, a Mo precursor is a molybdenum chloride (MoCl_x) compound also referred to as a molybdenum chloride precursor or MoCl_x precursor. Molybdenum chloride precursors are given by the formula MoCl_x , where x is 2, 3, 4, 5, or 6, and include molybdenum dichloride (MoCl_2), molybdenum trichloride (MoCl_3), molybdenum tetrachloride (MoCl_4), molybdenum pentachloride (MoCl_5), and molybdenum hexachloride (MoCl_6). In some embodiments, MoCl_5 or MoCl_6 are used. While the description chiefly refers to MoCl_x precursors, in other embodiments, other molybdenum halide precursors may be used. Molybdenum halide precursors are given by the formula MoX_z , where X is a halogen (fluorine (F), chlorine (Cl), bromine (Br), or iodine (I)) and z is 2, 3, 4, 5, or 6. Examples of MoX_z precursors include molybdenum fluoride (MoF_6). In

some embodiments, a non-fluorine-containing MoX_z precursor is used to prevent fluorine etch or incorporation. In some embodiments, a non-bromine-containing and/or a non-iodine-containing MoX_z precursor is used to prevent etch or bromine or iodine incorporation.

5 [0111] In some embodiments, the feature may be filled using a molybdenum oxyhalide precursor. Molybdenum oxyhalide precursors are given by the formula MoO_yX_z , where X is a halogen (fluorine (F), chlorine (Cl), bromine (Br), or iodine (I)), and y and z are numbers greater than 0 such that MoO_yX_z forms a stable compound. Examples of molybdenum oxyhalides include molybdenum dichloride dioxide (MoO_2Cl_2), molybdenum tetrachloride
10 oxide (MoOCl_4), molybdenum tetrafluoride oxide (MoOF_4), molybdenum dibromide dioxide (MoO_2Br_2), and the molybdenum iodides MoO_2I , and $\text{Mo}_4\text{O}_{11}\text{I}$. It should be understood that as used herein the term molybdenum oxyhalide precursor may refer to a molybdenum oxyhalide precursor as described above or a molybdenum-containing oxyhalide precursor that includes molybdenum, oxygen, a halide and one or more other
15 elements. In some embodiments, molybdenum oxyhalide or molybdenum-containing oxyhalides may include multiple different halogens (e.g., F and Cl and/or I and/or Br, etc.). A feature may be filled with molybdenum using a MoX_x precursor, MoO_yX_z precursor, or a combination thereof.

[0112] For deposition of molybdenum into the feature, the molybdenum precursor may
20 be reacted with a co-reactant. Examples of co-reactants include hydrogen (H_2), silane (SiH_4), diborane (B_2H_6), germane (GeH_4), ammonia (NH_3), and hydrazine (N_2H_4). Ammonia and hydrazine may be used to deposit molybdenum nitrides or molybdenum oxynitrides.

[0113] In some embodiments, deposition of molybdenum may use a plasma-based
25 process. Gas may be fed into a remote or in-situ plasma generator to generate plasma species. Examples of gas that may be used to generate plasma may be a hydrogen-containing gas, such as H_2 , nitrogen-containing gas, such as nitrogen (N_2) and other gases, such as Ar and NH_3 . The plasma species may be inert or react with the molybdenum precursor to form a film.

30 [0114] A feature may be filled with molybdenum by atomic layer deposition (ALD) or chemical vapor deposition (CVD). Thermal ALD or plasma enhanced ALD (PEALD) may be used. Similarly, thermal CVD or plasma enhanced CVD (PECVD) may be used.

[0115] ALD is a surface-mediated deposition technique in which doses of a precursor and a reactant are sequentially introduced into a deposition chamber. One or more cycles of

sequential doses of a molybdenum precursor and reactant may be used to deposit Mo. For example, in the deposition of an initial molybdenum layer (e.g., as in operation 505 or 507 of Figure 5), MoCl₅ may be used as a precursor and H₂ as a reducing agent. Doses of MoCl₅ and H₂ are sequentially introduced into the deposition chamber with a purge gas, such as argon, flowed between. For ALD, the temperature of the substrate and the pressure of the chamber may be controlled. For example, the substrate may be heated between 200°C and 800°C, e.g., between 250°C and 550°C or between 300°C and 500°C between 350°C and 450°C. In some embodiments, the chamber may be pressurized between 10 Torr and 200 Torr, e.g., between 50 Torr and 90 Torr. In some embodiments, the temperature and/or pressure may be used to control the rate of reactions. In some embodiments, the temperature and/or pressure may be used to control selectivity.

[0116] In some embodiments, the Mo precursor is a molybdenum fluoride (MoF_x) compound, also referred to as a molybdenum fluoride precursor or MoF_x precursor. Molybdenum chloride precursors are given by the formula MoF_x, where x is 4, 5, or 6, and include molybdenum tetrafluoride (MoF₄), molybdenum pentafluoride (MoF₅), and molybdenum hexafluoride (MoF₆).

[0117] MoF₆ can be advantageous as it has a boiling point of 34°C. Being a gas at standard pressure and 35°C allows MoF₆ to be delivered through a mass flow controller (MFC) at room temperature, without heating and without condensing and forming particles. However MoF₆ is an aggressive etchant and exposure to MoF₆ during a process can result in etching instead of or in addition to Mo deposition. In some embodiments, deposition using MoF₆ involves providing a flow of MoF₆ in a process gas with the MoF₆ at a molar concentration of 0.01% or less. Concentration may be significantly lower in some embodiments, for example, 0.008% or less, 0.005% or less, or 0.004% or less. These values can also be expressed as parts per million (ppm) of a gas: 100 ppm (100 MoF₆ molecules per 1 million gas particles (atoms, molecules)) or less, 80 ppm or less, or 40 ppm or less. At temperatures between 200°C and 650°C, for example, a molar concentration at or below 0.004% results in CVD deposition when flowed with H₂ and argon. Higher temperatures may be used to favor the deposition reaction and allow higher concentrations of MoF₆, e.g., up to 0.01%. In some embodiments, concentrations may be 0.0039% or .0035% or less. In some embodiments, the MoF₆ concentration is at least 0.00004% or at least 0.0001%. Concentration may be very low with an exposed metal surface to grow on, for example.

[0118] Deposition using MoF₆ with H₂ as reducing agent occurs only at unusually low concentration. As an example, for 0.5 sccm of MoF₆, a total flow rate of 13,500 sccm may

be used, for a MoF₆ concentration of 0.0037%. Deposition using metal halides and hydrogen generally involves much higher concentrations. For example, deposition of molybdenum using molybdenum hexachloride and hydrogen can be performed using concentrations 5 to 10 times higher than those used for MoF₆.

5 [0119] In some embodiments, MoF₆ may be used at higher concentrations and lower temperatures with a reducing agent that is stronger than that of hydrogen. Lower temperatures can reduce or prevent etching with MoF₆; however, at low temperatures H₂ may not result in deposition. Stronger reducing agents such as silane, disilane, polysilanes and diborane may be used for deposition at lower temperatures (e.g., below 200°C). The
10 resulting films may not be pure molybdenum and in some cases are more resistive than those deposited using H₂ as the reducing agent. For these reasons they may not be appropriate for some applications.

[0120] In some embodiments, molybdenum fill may involve CVD. In a CVD process, the molybdenum precursor and reactant are in vapor phase together in the deposition
15 chamber. Generally speaking, a CVD process fills a feature faster than an ALD process. In one example, the precursor may be a molybdenum oxychloride, such as MoO₂Cl₂, and is flowed into the chamber with a reactant, such as H₂. In this example, the wafer is simultaneously exposed to the precursor and reactant, which react and fill features with Mo. In one example, MoF₆ is flowed into the chamber with a reactant, such as H₂. In this
20 example, the wafer is simultaneously exposed to the precursor and reactant, which react and fill features with Mo.

[0121] In still some other embodiments, a feature may be filled using a pulsed CVD process. The pulsed CVD process continuously flows a reactant into a chamber while pulses of a precursor flow into the chamber. For example, H₂ gas may be flowed into the chamber
25 and is continuously flowing into the chamber while the molybdenum-containing precursor is intermittently flowing into the chamber. The temperature of the substrate and pressure in the chamber may be controlled during a CVD operation. Figures 7–9 show examples of pulsed CVD processes. Figure 7 shows a timing schematic illustration that shows various operations that may be performed in accordance with certain disclosed embodiments. Process 701 includes two deposition cycles 710A and 710B but it will be understood that
30 only one cycle or more than two cycles may be performed in accordance with certain disclosed embodiments. In this example, deposition cycles 710A and 710B include the same operations repeated in each cycle but it will be understood that in some embodiments, various operations, or a variety of operations such as those later described with respect to

Figures 8 and 9 may be combined with cycles described here with respect to Figure 7.

[0122] Figure 7 shows various process conditions during each phase – four process conditions are depicted here but it will be understood that other gases, plasma, temperature, pressure, or other conditions may also be present and may vary or be the same across different phases and across different cycles. The process conditions shown in this example include a first hydrogen-containing gas source (which may be a first source of hydrogen gas (H_2)), a second hydrogen-containing gas source (which may be a second source of hydrogen gas (H_2)), argon (which may act as a purge gas, carrier gas, inert gas, or any combination thereof), and molybdenum-containing precursor gas.

[0123] In this example, deposition cycle 710A includes four phases – first phase 720A, first purge phase 740A, second phase 750A, and second purge phase 780A. During first phase 720A, the first hydrogen source gas is turned on, the second hydrogen gas source is turned on, the argon source is turned off, and the molybdenum precursor gas source is turned off. During this operation only hydrogen-containing gas sources may be flowed.

[0124] During first purge phase 740A, the first hydrogen source gas may continue to be on (and may continue to be flowed at the same flow rate), the second hydrogen gas source may be turned off or turned down (e.g., lowered flow rate), argon gas source may be turned on, and molybdenum precursor gas source is still turned off.

[0125] During second phase 750A, the first hydrogen source gas may continue to be on (and may continue to be flowed at the same flow rate), the second hydrogen gas source may continue to be off (or on the lower flow rate), argon gas source may be turned off (or have reduced flow rate), and molybdenum precursor gas source is turned on.

[0126] During second purge phase 780A, the first hydrogen source gas may continue to be on (and may continue to be flowed at the same flow rate), the second hydrogen gas source may be still turned off or turned down (e.g., lowered flow rate), argon gas source may be turned on, and molybdenum precursor gas source is turned off.

[0127] While this process flow shows second hydrogen source turned on followed by molybdenum precursor gas turned on, it will be understood that the alternate may be used instead (e.g., molybdenum precursor gas on, then purge, then second hydrogen source on, then purge).

[0128] Deposition cycle 710A is then repeated in deposition cycle 710B. Deposition cycle 710B includes four phases – first phase 720B, first purge phase 740B, second phase 750B, and second purge phase 780B. First phase 720B may be the same as or may be different from first phase 720A. In this example, first phase 720B is the same as first phase

720A. During first phase 720B, the first hydrogen source gas is still on, the second hydrogen gas source is turned on, the argon source is turned off, and the molybdenum precursor gas source is turned off. During this operation only hydrogen-containing gas sources may be flowed.

5 [0129] During first purge phase 740B, the first hydrogen source gas may continue to be on (and may continue to be flowed at the same flow rate), the second hydrogen gas source may be turned off or turned down (e.g., lowered flow rate), argon gas source may be turned on, and molybdenum precursor gas source is still turned off.

10 [0130] During second phase 750B, the first hydrogen source gas may continue to be on (and may continue to be flowed at the same flow rate), the second hydrogen gas source may continue to be off (or on the lower flow rate), argon gas source may be turned off (or have reduced flow rate), and molybdenum precursor gas source is turned on.

15 [0131] During second purge phase 780B, the first hydrogen source gas may continue to be on (and may continue to be flowed at the same flow rate), the second hydrogen gas source may be still turned off or turned down (e.g., lowered flow rate), argon gas source may be turned on, and molybdenum precursor gas source is turned off.

[0132] Figure 8 shows an alternative deposition cycle scheme that may be used in some embodiments. Figure 8 shows a timing schematic illustration that shows various operations that may be performed in accordance with certain disclosed embodiments. Process 800
20 includes two deposition cycles 810A and 810B but it will be understood that only one cycle or more than two cycles may be performed in accordance with certain disclosed embodiments. In this example, deposition cycles 810A and 810B include the same operations repeated in each cycle but it will be understood that in some embodiments, various operations, or a variety of operations such as those described with respect to Figures
25 7 and 9 may be combined with cycles described here with respect to Figure 8.

[0133] Figure 8 shows various process conditions during each phase – three process conditions are depicted here but it will be understood that other gases, plasma, temperature, pressure, or other conditions may also be present and may vary or be the same across different phases and across different cycles. The process conditions shown in this example
30 include a molybdenum-containing precursor gas, a hydrogen-containing gas source (which may be a source of hydrogen gas (H₂), and argon (which may act as a purge gas, carrier gas, inert gas, or any combination thereof). In this example, the molybdenum precursor gas source may be continuously flowed.

[0134] In this example, deposition cycle 810A includes four phases – first phase 820A,

first purge phase 840A, second phase 850A, and second purge phase 880A. During first phase 820A, the molybdenum precursor gas is turned on, the hydrogen gas source is turned on, and the argon source is turned off.

5 [0135] During first purge phase 840A, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas may be turned off (or have reduced flow rate), and the argon gas is turned on.

[0136] During second phase 850A, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas may be turned on, and the argon gas is turned off (or have reduced flow rate).

10 [0137] During second purge phase 880A, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas may be turned off (or have reduced flow rate), and the argon gas is turned on.

[0138] While this process flow shows the hydrogen source turned on followed by argon gas turned on, it will be understood that the alternate may be used instead (e.g., purge, then 15 hydrogen source on, then purge, then hydrogen source on).

[0139] Deposition cycle 810A is then repeated in deposition cycle 810B. Deposition cycle 810B includes four phases – first phase 820B, first purge phase 840B, second phase 850B, and second purge phase 880B. First phase 820B may be the same as or may be different from first phase 820A. In this example, first phase 820B is the same as first phase 20 820A. During first phase 820B, the molybdenum precursor gas is turned on, the hydrogen gas source is turned on, and the argon source is turned off.

[0140] During first purge phase 840B, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas may be turned off (or have reduced flow rate), and the argon gas is turned on.

25 [0141] During second phase 850B, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas may be turned on, and the argon gas is turned off (or have reduced flow rate).

[0142] During second purge phase 880B, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas may be 30 turned off (or have reduced flow rate), and the argon gas is turned on.

[0143] Figure 9 shows yet another alternative deposition cycle scheme that may be used in some embodiments. Figure 9 shows a timing schematic illustration that shows various operations that may be performed in accordance with certain disclosed embodiments. Process 900 includes two deposition cycles 910A and 910B but it will be understood that

only one cycle or more than two cycles may be performed in accordance with certain disclosed embodiments. In this example, deposition cycles 910A and 910B include the same operations repeated in each cycle but it will be understood that in some embodiments, various operations, or a variety of operations such as those described with respect to Figures 7 and 8 may be combined with cycles described here with respect to Figure 9.

[0144] Figure 9 shows various process conditions during each phase – three process conditions are depicted here but it will be understood that other gases, plasma, temperature, pressure, or other conditions may also be present and may vary or be the same across different phases and across different cycles. The process conditions shown in this example include a hydrogen-containing gas source (which may be a source of hydrogen gas (H₂), a molybdenum-containing precursor gas, and argon (which may act as a purge gas, carrier gas, inert gas, or any combination thereof). In this example, the molybdenum precursor gas source may be continuously flowed. In this example, the hydrogen-containing gas source may be continuously flowed.

[0145] In this example, deposition cycle 910A includes four phases – first phase 920A, first purge phase 940A, second phase 950A, and second purge phase 980A. During first phase 920A, the molybdenum precursor gas is turned on, the hydrogen gas source is turned on, and the argon source is turned off.

[0146] During first purge phase 940A, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas is still on (and may continue to be flowed at the same flow rate), and the argon gas is turned on.

[0147] During second phase 950A, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas is still on (and may continue to be flowed at the same flow rate), and the argon gas is turned off (or have reduced flow rate).

[0148] During second purge phase 940A, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas is still on (and may continue to be flowed at the same flow rate), and the argon gas is turned on.

[0149] Deposition cycle 910A is then repeated in deposition cycle 910B. Deposition cycle 910B includes four phases – first phase 920B, first purge phase 940B, second phase 950B, and second purge phase 980B. First phase 920B may be the same as or may be different from first phase 920A. In this example, first phase 920B is the same as first phase 920A. During first phase 920B, the molybdenum precursor gas is turned on, the hydrogen gas source is turned on, and the argon source is turned off.

[0150] During first purge phase 940B, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas is still on (and may continue to be flowed at the same flow rate), and the argon gas is turned on.

5 [0151] During second phase 950B, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas is still on (and may continue to be flowed at the same flow rate), and the argon gas is turned off (or have reduced flow rate).

10 [0152] During second purge phase 940B, the molybdenum precursor gas source is still on (and may continue to be flowed at the same flow rate), the hydrogen source gas is still on (and may continue to be flowed at the same flow rate), and the argon gas is turned on.

[0153] The molybdenum-containing precursor used to deposit the molybdenum may be any suitable precursor, such as those listed below in the Precursors section. Examples also include m molybdenum halides, and/or organometallic molybdenum-containing precursors. One or more precursors may be used.

15 [0154] The first and/or second hydrogen-containing source gas in various embodiments may be hydrogen gas. Hydrogen gas may continue to flow so as to prevent damage to the substrate when the substrate is exposed to the molybdenum-containing precursor.

[0155] Although argon is described with respect to Figures 7–9, it will be understood that other inert gases may be used instead of argon, including and not limited to helium.

20 [0156] Plasma-enhanced CVD may be used in which a plasma is ignited during the deposition. In a pulsed CVD process, a plasma may be ignited during deposition cycle or during, e.g., pulses of the hydrogen reactant. In some embodiments, a remote plasma may be used. The plasma may be remotely-generated or direct. Further it may be generated by any appropriate plasma generator including a capacitively-coupled plasma generator or an
25 inductively-coupled plasma generators. A microwave plasma generator may be used.

[0157] Figure 10A shows an example of molybdenum deposition by an atomic layer deposition (ALD) process. In the example of Figure 10A, a substrate is exposed to a process gas including a molybdenum-containing precursor in an operation 1001. A purge operation is then performed in an operation 1003. An adsorbed layer of molybdenum-containing
30 precursor remains, with the gas phase precursor removed. The substrate is then exposed to a reactant in an operation 1005. This is typically a reducing agent, e.g., hydrogen. In plasma processes using a direct plasma, the plasma is ignited during this operation. In plasma processes using a direct plasma, reactant includes plasma species (e.g., hydrogen radicals) generated remotely. The reactant reacts with the adsorbed precursor to form a layer of

molybdenum. A purge operation is then performed in an operation 1007. Operations 1001–1007 may then be repeated until the molybdenum film is at a target thickness in an operation 1009.

[0158] Modifications of the process described in Figure 10A can include exposure to the reactant as the first operation in each cycle, followed by a purge, exposure to the molybdenum-containing compound, and purge. Further modifications can include each cycle forming less than a monolayer. This can be performed by limiting the amount of one or both reactants. In some embodiments, the ALD process may not be strictly self-limiting. For example, one or both of the purge operations may be omitted or shortened such that some gas-phase reactant remains and reacts in the gas phase. This can increase deposition rate. Further modifications can include repeating operation 1001 (with or without an intervening purge) prior to performing operation 1005 within a cycle. In some embodiments, operation 1005 is repeated one or more times within a cycle. Such modifications facilitate diffusion through a feature. Still further, in some embodiments, the reactant may be, e.g., nitrogen-containing such that a molybdenum nitride or molybdenum oxynitride layer is formed.

Selective deposition

[0159] Molybdenum may be selectively deposited into a feature using the methods described herein. Selective deposition refers to preferential deposition on a first material with respect to a second material. Molybdenum deposition and growth may be easier on a metal material relative to molybdenum deposition and growth on a dielectric material. For example, a feature may have a sidewall surface of SiO₂ and a TiN plug in a bottom portion of the feature. In selective deposition, molybdenum is deposited into the feature and may grow on the TiN plug but not grow (or grow to a lesser extent) on the SiO₂ sidewall surfaces.

[0160] Process conditions such as the precursor gas, the reducing agent, process temperature, process pressure, and exposure time may affect the selectivity of the molybdenum film being deposited. Process temperatures for selective deposition of the molybdenum film may be between 200°C to 800°C, e.g., 250°C to 550°C, or 300°C to 500°C. At these temperatures, the molybdenum film is selectively deposited on conductive metal or metal compound surfaces, such as a TiN surface, in a feature relative to dielectric surfaces.

[0161] Different precursor gases may have different process windows in which molybdenum film may be selectively deposited. Generally speaking, MoCl₅ gas has a large

process window, i.e., large temperature and pressure range, where the precursor gas retains its selectivity. For example, MoCl_5 may be selectively deposited on a metal material with respect to a dielectric material where the process temperature is 200°C to 800°C , e.g., 250°C to 550°C , or 300°C to 500°C . Generally speaking, higher process temperatures and higher
5 process pressures reduce the selectivity of the deposited gas. MoCl_5 deposits selectively on metals, titanium nitride (TiN) and other conductive materials relative to dielectric materials at a wide range of temperatures.

[0162] MoCl_5 may be reacted with different reactant to deposit a molybdenum film. Described below are examples of deposition of molybdenum film within a feature using a
10 MoCl_5 precursor and different process controls. In a first example, the MoCl_5 precursor is reacted with a hydrogen (H_2) reactant using the deposition methods described above. In the description herein, the metal precursors are reacted with H_2 as a co-reactant (also referred to as a hydrogen reactant or H_2 reactant). Other reactants may be used instead of hydrogen including other hydrogen-containing reactants such SiH_4 , B_2H_6 , NH_3 , as appropriate.
15 Reactants such as B_2H_6 and/or SiH_4 are stronger reducing agents and generally show reduced selectivity. They can also result in higher resistivity. Thus, in some embodiments, using H_2 as described herein is advantageous. As noted above, process temperatures for selective deposition of the molybdenum film from MoCl_5 may be between 200°C to 800°C , e.g., 250°C to 550°C , or 300°C to 500°C . At these temperatures, the molybdenum film is
20 selectively deposited on conductive metal or metal compound surfaces, such as a TiN surface, in a feature relative to dielectric surfaces. The molybdenum film grows from the locations where the conductive surfaces are located in a feature. If the conductive surface is a TiN plug at the bottom of the feature, the molybdenum film may be deposited and grown from the bottom of the feature. In a second example, the molybdenum film may be
25 deposited using the MoCl_5 precursor and the H_2 reactant, but at higher temperatures, i.e., above 800°C . This process window may have the molybdenum film deposited on both the dielectric and conductive surfaces within the feature. The deposition of the molybdenum film on the dielectric surface may be used to create a barrierless molybdenum layer in the feature.

30 [0163] In some embodiments, selective deposition is performed using a MoF_x precursor. Molybdenum fluoride precursors are given by the formula MoF_x as described above. As indicated above, MoF_6 can be advantageous for ease of delivery. Deposition of molybdenum from MoF_6 at the low concentrations disclosed above results in high (at least 100:1) selectivity of one elemental metal surfaces (e.g., W, Mo, Cu) relative to oxides and nitrides

such as silicon oxide and titanium nitride. MoF₆ also deposits selectively on metals with respect to dielectric materials, though is less selective than MoCl₅. An example of selectivity of MoF₆ is shown in Figure 10B. As can be seen, after a delay, MoF₆ deposits on thermal oxide. Selectivity of molybdenum halides can also be affected by operating at
5 conditions (e.g., concentration, temperature, etc.) at which the molybdenum halide also etches.

[0164] Selective deposition using a molybdenum oxyhalide precursor is much more difficult than using a molybdenum halide precursor. However, the surface treatments described above significantly improve selectivity of Mo deposition from MoO₂Cl₂. As
10 indicated above, examples of MoO_yX_z precursors include MoO₂Cl₂, MoOCl₄, MoOF₄, MoO₂Br₂, MoO₂I, and Mo₄O₁₁I. The feature may be filled using ALD, plasma enhanced ALD, chemical vapor deposition (CVD), or plasma enhanced CVD. For ALD or CVD, H₂ may be the reducing agent. Molybdenum deposits more quickly using a molybdenum oxyhalide precursor than the MoCl_x precursor used in the surface treatment. For example,
15 a MoO_yX_z precursor may deposit molybdenum at a deposition rate at least twice as fast as a MoCl_x precursor for a non-plasma process.

Non-selective Deposition

[0165] The selectivity described above may be reduced or eliminated using plasma deposition in some embodiments, such that the molybdenum is deposited on different
20 materials. This may be referred to as non-selective deposition. When ALD processes are used, the non-selective deposition may be conformal to the contours of surface. The plasma is generally an in-situ or direct plasma for non-selective deposition.

[0166] Examples of plasma processes include plasma-enhanced ALD (PEALD) or plasma enhanced CVD (PECVD) processes using a molybdenum halide precursor. In some
25 embodiments, the molybdenum halide precursor is MoCl₅ or MoF₆. A molybdenum oxyhalide may also be used, with examples including MoO₂Cl₂ or MoOCl₄. Hydrogen (H₂) or other reducing agent may be used for the PEALD or PECVD deposition.

[0167] For PECVD deposition, the molybdenum precursor can be co-flowed with the reducing agent. For MoF₆, the concentration of the MoF₆ is as described above, with the
30 mixture flowed into a plasma generator. Remote or direct plasmas may be used. In some embodiments, a capacitively-coupled direct plasma that is generated in the chamber is employed.

[0168] Non-selective deposition may also be a thermal process using molybdenum

oxyhalides. For example, thermal MoO_2Cl_2 and H_2 may be used to deposit a molybdenum layer non-selectively. Temperatures at or above 450°C may be used in for thermal deposition from MoO_2Cl_2 and H_2 .

- [0169] To reduce selectivity, an ALD process may be performed to deposit a Mo-containing nucleation layer. For nucleation layer deposition, a stronger reducing agent than hydrogen is employed. This can allow the film to grow on surfaces that face nucleation delay with hydrogen as reducing agent. As described further below, such a reducing agent can be a silicon-containing or boron-containing reducing agent such as silane (SiH_4) or diborane (B_2H_6). Germanium-containing reducing agents (e.g., GeH_4) may be used. These may be used to deposit an elemental molybdenum film. In other embodiments, a reducing agent such as ammonia (NH_3) may be used. In such cases, the molybdenum layer may be a molybdenum nitride or molybdenum oxynitride layer, depending on the presence of oxygen in the molybdenum precursor. This oxynitride layer or nitride layer may be converted into an elemental molybdenum layer in the subsequent process.
- [0170] When using MoF_6 , the concentration of MoF_6 in the MoF_6 dose may be as described above, i.e., 0.01% or less, 0.008% or less, 0.005% or less, or 0.004% or less of the total gas flowed into the chamber. Alternatively, because a stronger reducing agent than hydrogen is used in the subsequent operation, a higher concentration (e.g., up to 0.1% molar) may be used during the MoF_6 . Some amount of a reducing agent may be present to suppress etching. As described above, this can be between 0.5% and 10% or between 1% and 9% H_2 . Another reducing agent may be included instead of or in addition to hydrogen. The balance is wholly or predominately argon or other inert gas. During the reducing agent dose, the dose is wholly or predominately the reducing agent, with some amount (e.g., up to 10%, or between 1% and 9%) being argon in some embodiments, and the remainder the reducing agent. After deposition of the nucleation layer, a bulk molybdenum layer can be deposited using H_2 as a reducing agent by any of the methods described above, including thermal or plasma-enhanced ALD or CVD.

Nucleation Layer

- [0171] In some embodiments, filling a feature can involve depositing a nucleation layer. A nucleation layer is a thin layer that supports bulk deposition. It may be conformal to the feature. In many embodiments, a nucleation layer is deposited by an ALD process. In some embodiments, a Mo nucleation layer is deposited using one or more of a boron-containing reducing agent (e.g., B_2H_6) or a silicon-containing reducing agent (e.g., SiH_4) as a co-

reactant. For example, one or more S/Mo cycles or Mo/S cycles may be used to deposit a Mo nucleation layer. In another example, one or more B/Mo cycles or Mo/B cycles may be used to deposit a Mo nucleation layer on which a bulk Mo layer is deposited. B refers to a pulse of diborane or other boron-containing reducing agent and S to a pulse of silane or other silicon-containing reducing agent, such that S/Mo refers to a pulse of silane followed by a pulse of a Mo-containing precursor. B/Mo and S/Mo cycles (or Mo/B and/or Mo/S) may both be used to deposit a Mo nucleation layer, e.g., $x(\text{B/Mo}) + y(\text{S/Mo})$, with x and y being integers. Examples of boron-containing reactants include diborane (B_2H_6), alkyl boranes, alkyl boron, aminoboranes $(\text{CH}_3)_2\text{NB}(\text{CH}_2)_2$, carboranes such as $\text{C}_2\text{B}_n\text{H}_{n+2}$, and other boranes. Examples of boranes include B_nH_{n+4} , B_nH_{n+6} , B_nH_{n+8} , B_nH_m , where n is an integer from 1 to 10, and m is a different integer than n . Examples of silicon-containing reducing agents including silane (SiH_4) and other silanes such as disilane (Si_2H_6).

[0172] In some embodiments, deposition of a Mo nucleation layer may involve using a non-oxygen-containing precursor, e.g., molybdenum hexafluoride (MoF_6) or molybdenum pentachloride (MoCl_5). Oxygen in oxygen-containing precursors may react with a silicon- or boron-containing reducing agent to form MoSi_xO_y or MoB_xO_y , which are impure, high resistivity films. In some embodiments, oxygen-containing precursors may be used for nucleation layer deposition with oxygen incorporation minimized. Oxygen incorporation can be minimized by high reducing agent flows (e.g., greater than 100:1 volumetric flow rate of reducing agent to oxygen-containing Mo precursor).

[0173] In some embodiments, H_2 may be used as a reducing gas for Mo nucleation layer deposition instead of a boron-containing or silicon-containing reducing gas. Example thicknesses for deposition of a Mo nucleation layer range from 5 Å to 30 Å. Films at the lower end of this range may not be continuous; however, as long as they can help initiate continuous bulk Mo growth, the thickness may be sufficient.

[0174] In some embodiments, the reducing agent pulses during deposition of a nucleation or bulk Mo layer may be done at lower substrate temperatures than the Mo precursor pulses. For example, for B_2H_6 or a SiH_4 (or other boron- or silicon-containing reducing agent) pulse may be performed at a temperature below 300°C, with the Mo pulse at temperatures greater than 300°C.

[0175] In some embodiments, the reducing agent is NH_3 or other nitrogen-containing reducing agents such as hydrazine (N_2H_4). NH_3 chemisorption on dielectrics is more favorable than that of H_2 . In some embodiments, the reducing agent and precursor are selected such that they react without reducing agent dissociation. NH_3 reacts with metal

oxychlorides and metal chlorides without dissociation. This is in contrast to, for example, ALD from metal oxychlorides that use H_2 as a reducing agent; H_2 dissociates on the surface to form adsorbed atomic hydrogen, which results in very low concentrations of reactive species and low surface coverage during initial nucleation of metal on the dielectric surface.

- 5 By using NH_3 and metal oxychloride or metal chloride precursors, nucleation delay is reduced or eliminated at deposition temperatures up to hundreds of degrees lower than used by H_2 reduction of the same metal precursors.

[0176] In some embodiments, the reducing agent may be a boron-containing or silicon-containing reducing agent such as B_2H_6 or SiH_4 . These reducing agents may be used with
10 metal chloride precursors, with metal oxychlorides; however, the B_2H_6 and SiH_4 may react with water formed as a byproduct during the ALD process and form solid B_2O_3 and SiO_2 . These are insulating and can remain in the film, increasing resistivity. Use of NH_3 also has improved adhesion over B_2H_6 and SiH_4 ALD processes on certain surfaces including Al_2O_3 . The resulting nucleation layer is generally not a pure elemental film but a metal nitride or
15 metal oxynitride film. In some embodiments, there may be residual chlorine or fluorine from the deposition, particularly if the deposition is performed at low temperatures. In some embodiments, there may be no more than a trace amount of residual chlorine or fluorine. In some embodiments, the nucleation layer is an amorphous layer. Impurities in the film (e.g., oxygen, NH_3 , chlorine, or other halogens) facilitate the growth of an amorphous
20 microstructure. In some embodiments, the nucleation layer as deposited is an amorphous molybdenum oxynitride layer or an amorphous molybdenum nitride layer. The amorphous character templates large grain growth in the subsequently deposited conductor. The surface energy of nitride or oxynitride relative to an oxide surface is much more favorable than that of a metal on an oxide surface, facilitating formation of a continuous and smooth film on
25 the dielectric. This allows formation of thin, continuous layers. Example thicknesses of the nucleation layer range from 5–30 Å as deposited. Depending on the temperature, this may be about 5–50 ALD cycles, for example.

Integration processes including etch and/or inhibition

[0177] Etch operations may be used in the methods for filling features with Mo films.
30 Etch operations remove materials such as metals and nitrides from the feature. For example, an etch process may partially or completely remove a liner (e.g., a TiN) layer from a feature. In another example, the etch process may be used to reduce the thickness of a liner layer. Etch processes may be performed as part of a pre-treatment process as described elsewhere

in the disclosure and/or as part of a deposition-etch-deposition process in which molybdenum is etched.

[0178] An etchant is any compound used to remove a material such as a layer, byproduct or contaminant from a surface. In some embodiments, the etchant is a halogen-containing etchant such as chlorine (Cl₂), fluorine (F₂), bromine (Br₂), iodine (I₂), hydrogen chloride (HCl), hydrogen fluoride (HF), hydrogen iodide (HI), chlorine trifluoride (ClF₃), ferric chloride (FeCl₃), trifluoromethane (CHF₃), fluoromethane (CH₃F), octafluorocyclobutane (C₄F₈), hexafluorobutadiene (C₄F₆), hexafluorocyclopentadiene (C₅F₆), carbon tetrafluoride (CF₄), carbon tetrafluoride (CCl₄), nitrogen trifluoride (NF₃), boron trichloride (BCl₃), boron trifluoride (BF₃), hydrogen iodide (HI), hydrogen bromide (HBr), sulfur tetrafluoride (SF₄), sulfur hexafluoride (SF₆), thionyl chloride (SOCl₂), phosphorus pentafluoride (PF₅), phosphorus trifluoride (PF₃), silicon tetrabromide (SiBr₄), or a combination thereof. In some embodiments, a single etchant may be sufficiently effective. In some embodiments a combination including more than one etchant may be utilized. Examples of combinations include oxygen (O₂) with one of the above halogen-containing etchants such as chlorine and oxygen; or fluorine and oxygen. Alternatively, carbon dioxide (CO₂) may be combined with one of the above halogen-containing etchants. If a combination of etchants is utilized, they may be flowed through delivery lines together (concomitantly), or sequentially (one following the other). The etchant may be co-flowed with an inert gas, such as argon. In some embodiments, etchants are combined. For example, the halogen-containing etchant may be co-flowed with a non-halogen containing etchant.

[0179] In some embodiments, the etchant is MoCl₅, MoF₆, WF₆, WCl₅, or any of the other metal halides described above. For example, an etch operation, in some embodiments, may involve soaking the feature soaked in a Mo halide. In some embodiments, an etch operation involves soaking the feature with a MoCl_x such as MoCl₅. In some embodiments, the soak may be done continuously with the Mo halide gas. In some embodiments, the soak may be pulsed, cycling the Mo halide with a purge gas, such as argon (Ar).

[0180] A molybdenum halide precursor may be used for both deposition and etch operations. For example, in certain process windows, a MoCl₅ precursor may concurrently grow a Mo film and etch away a metal or metal compound film in the feature. The process is considered a net etch operation if the rate of material removed is greater than the material deposited by the precursor. The speed at which the precursor deposits material and etches material may be controlled by a variety of process conditions, including the type of reactant

used and the process temperature. Generally speaking, the lower the temperature, the higher the ratio of etching away material is relative to deposition of material. At higher temperatures, the same precursor and reactant may be used as a net deposition operation, i.e., the amount of material deposited is greater than the material removed. For example,

5 MoCl₅ precursor and H₂ reactant may be used in an etch operation when the process temperature is below 400°C. The same precursor of MoCl₅ and H₂ reactant may be used in a deposition operation when the process temperature is above 550°C.

[0181] In some embodiments, the MoCl_x precursor at high temperatures, e.g., above 550°C, may continue to etch material at a faster rate than depositing material. For example,

10 MoCl₅ may be used to etch a feature by a soak without a reactant. In this example, the temperature may be as high as 700°C and will continue to etch away material from the feature. In operations where the feature is soaked in a MoCl₅ without a reactant, the increased temperature may increase the rate at which material is etched from the feature.

[0182] In some embodiments, deposition by ALD or CVD may result in deposition at the

15 bottom of the feature and net etch at the top of the feature due to concentration differences within the feature. For example, in Figure 11, an otherwise unfilled feature having a conformal liner layer 1112 is shown being exposed to a molybdenum precursor flow. The molybdenum precursor concentration decreases with feature depth, transitioning from an etch regime at the top to a deposition regime at the bottom. For example, for MoF₆,

20 concentration at the top may be greater than 0.01% and at the bottom, less than 0.004%. The result is net etch at the field area of the feature and net deposition at the feature bottom. For deep features (e.g., for features having aspect ratios of 10:1 or higher), the concentration gradient may occur by diffusion limits within the feature. In some embodiments, multiple operations may be performed with different precursor concentrations.

[0183] A feature may have surface oxide or contaminants on it. For example, the surface of an underlying TiN, WN, or W layer may be oxidized. If left, the oxidized surface can result in higher resistivity. Clean operations are used to remove such oxides and contaminants. In some embodiments, the clean operation may have the feature soaked in a Mo precursor gas, typically a Mo halide. Similar to the etch operations described above,

25 the precursor gas may be a MoCl_x precursor. In some embodiments, the soak may be done continuously. In some embodiments, the soak may be pulsed, cycling MoCl_x and a purge gas, such as argon (Ar). The precursor may be a non-oxygen Cl-containing Mo compound able to remove oxidation from the feature's surfaces. Examples of MoCl_x compounds are given above. A Cl-containing precursor may be used where traditional cleaning with

30

thermal or plasma H₂ does not work, such as where the oxidized surface is stable on the surface material. A Cl-containing precursor is less likely to over-etch a feature's liner layer or attack a feature's surfaces than a F-containing compound.

5 [0184] An etch may be thermal or plasma-enhanced. In some embodiments in which material in lateral features is etched, a thermal etch to allow the etchant chemistry to diffuse into the feature.

[0185] Inhibition operations may be used in the methods for filling features with Mo films. Inhibition operations inhibit molybdenum nucleation on a surface. As an example, an inhibition operation may be used to inhibit nucleation on only part of a feature, extending
10 from the feature opening to some depth within the feature. In some embodiments, an incoming structure may be treated to inhibit molybdenum nucleation. For example, feature having dielectric sidewalls and a conductive bottom surface may be treated such that nucleation is inhibited on the upper portion of the sidewalls, facilitating selective deposition. The inhibition treatment may be repeated during the subsequent deposition to maintain its
15 effectiveness.

[0186] A dielectric material may be treated with a halogen-containing chemistry to inhibit molybdenum nucleation. Examples include F₂, NF₃, BCl₃, MoCl₅, and Cl₂. Each of these chlorinates or fluorinates oxides inhibiting further nucleation.

[0187] Inhibition operations may also be performed as part of deposition-inhibition-deposition (DID) techniques. In some embodiments, a portion of a molybdenum film is
20 treated to inhibit subsequent deposition. Examples of inhibition chemistries include nitrogen-containing chemistries including N₂, and NH₃, and well as halide-containing chemistries such as alkyl halides. An inhibitor such as N₂ may be co-flowed with a molybdenum precursor and/or H₂, for example. The inhibition may be a plasma or thermal
25 operation. If plasma, a remote or direct plasmas may be used. Other examples of inhibition operations can include exposure to oxygen-containing, carbon-containing, and phosphorous-containing thermal or plasma chemistries. In some embodiments in which material in lateral features is etched, a thermal inhibition to allow the inhibition chemistry to diffuse into the feature.

30 [0188] As noted above, alkyl halides may be used to inhibit nucleation on molybdenum-containing surfaces for DID operations as well as to modify other surfaces including metal nitrides such as TiN. In some embodiments, the halogen-containing compound is an alkyl halide (e.g., a tertiary alkyl halide, such as t-butyl chloride or t-butyl iodide). In some embodiments, the halogen-containing compound is an iodine-containing compound. Further

examples of inhibitors include trimethylsilylchloride $[(\text{CH}_3)_3\text{SiCl}]$ and trimethylsilyl-dimethylamide $[(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2]$. Chlorine (Cl_2) is an etchant and can also inhibit growth on molybdenum. Inhibition is observed at substrate temperatures of about 450°C to 600°C for non-plasma exposure to Cl_2 .

5 [0189] De-inhibition operations may be used to reduce the effect of inhibition, either before or after the subsequent deposition. This can be used to further tailor the fill profile. Examples of de-inhibition operations include H_2 soak, NH_3 soak, and H_2 plasma exposure. Soak operations may be continuous flow or pulsed.

[0190] Also provided herein are deposition-etch-deposition (DED) techniques and
10 deposition-inhibition-deposition (DID). These may be used to tailor deposition into features during interconnect metallization, as described above, and for memory applications. Figure 12 shows examples of DED and DID processes on a vertically-oriented features, e.g., for a logic application. For the DED process, deposited Mo film near the feature top or field region is preferentially etched. This results in a tapered profile. Subsequent deposition is
15 performed without closing off the feature. For the DID process, the field region and the top of the feature is preferentially inhibited, allowing molybdenum to be deposited at the bottom of the feature.

[0191] The DED operations described herein may be used for logic applications such as interconnects as well as memory applications. Filling a 3D NAND structure using a DED
20 techniques is described further below. In some embodiments, multiple DED operations are used to fill a feature. The same or different chemistries may be used for each deposition. The molybdenum precursor may be a molybdenum halide or molybdenum oxyhalide as described above or a molybdenum organometallic precursor. The same or different chemistries may be used for each etch operation.

25 [0192] During the etch, a high flow short dose time may be employed to achieve an anisotropic etch. As indicated above, a pre-treatment may be used to increase etch rate as well as tailor etch profile. For example, etch may be preceded by an anisotropic oxidation or nitridation. This can help etch only in the top of the feature (for vertical features) or outer part of the feature (e.g., outer wordlines in a 3D NAND structure). Examples of oxidation
30 operations include exposure to O_2 or O_3 or oxygen-containing plasmas. Examples of nitridation operations include exposure to NH_3 or N_2 or nitrogen-containing plasmas. Post-treatments can be used to remove impurities after etch. For example, exposure to a halosilane may be used to remove fluorine or chlorine. Exposure to H_2 can be used to remove impurities. According to various embodiments, a post-treatment may be performed

after every dose of the etchant or less frequently, for example, at the end of multiple cycles that include etching.

[0193] In some embodiments, the DED sequences may include one or more inhibition operations. An inhibition operation is an operation to inhibit nucleation or formation of molybdenum film in a subsequent deposition. It may be used to tune a deposition profile. Examples of inhibition chemistries include nitrogen-containing chemistries including NF_3 , N_2 , and NH_3 , and well as halide-containing chemistries such as alkyl halides, B_2H_6 , and Cl_2 . An inhibitor such as N_2 may be co-flowed with a molybdenum precursor and/or H_2 , for example. The inhibition may be a plasma or thermal operation.

[0194] De-inhibition operations may be used to reduce the effect of inhibition, either before or after the subsequent deposition. This can be used to further tailor the fill profile. Examples of de-inhibition operations include H_2 soak, NH_3 soak, and H_2 plasma exposure. Soak operations may be continuous flow or pulsed. Prolonged precursor and/or reactant dose time after an inhibition treatment may also be used to reduce or eliminate inhibition effects.

[0195] A process may use various permutations of Dep1, Dep2, Etch, Inhibition and de-Inhibition operations to tailor fill. Examples of process sequences are:

Dep – Etch – Dep

Dep – Inhibition – Dep

Dep – Etch(x) – Inhibition(y) – Dep

Dep – Etch(x) – Inhibition(y) – Dep – de-Inhibition - Dep

Dep – Inhibition – Etch - Dep

Dep – Etch – Dep – Inhibition – Dep

Dep – Etch – Dep – Inhibition – Dep – de-Inhibition – Dep

Dep – Inhibition – Dep – Etch – Dep

Dep – Oxidation – Etch – Dep

Dep – Nitridation – Etch – Dep

In some embodiments, the dep-etch-dep operations disclosed herein may be integrated into single chamber metallization processes as described above.

[0196] In some embodiments, a simultaneous DED process may be performed. This may also be referred to as a blended DED process. Figure 13 is a flow chart that depicts a method

blended deposition and etch in accordance with certain disclosed embodiments. The method may be described as a blended deposition and etch because the reducing agent and etchant are introduced into the process chamber contemporaneously. In some embodiments, the contemporaneous supply of these two reagents may be fully contemporaneous, when the

5 reducing agent and etchant are flowed into the process chamber for the same length of time. As used herein, “simultaneously” or “contemporaneously” mean a time interval or duration of delivery or flow of reagent at the same time. “Fully contemporaneous” refers to a delivery of one reagent for a first duration of time and delivery of another reagent for a second duration of time, where the overlap of the two durations of time is from 95 – 100%.

10 “Partially contemporaneous” refers to a delivery of one reagent for a first duration of time and delivery of a second reagent for a second duration of time, where the second duration of time is during the first duration of time, but shorter than the first duration of time. In Figure 13, operation 1302 is an introduction of the molybdenum-containing precursor into the processing chamber which houses a semiconductor substrate. Operation 1304 is an

15 optional purge step. Purging the chamber may involve flowing a purge gas or a sweep gas, which may be a carrier gas used in other operations or may be a different gas. In some embodiments, purging may involve evacuating the chamber. Examples of purge gases include argon (Ar), nitrogen (N₂), hydrogen (H₂), helium (He), oxygen (O₂), krypton (Kr), xenon (Xe), neon (Ne), and combinations thereof. In various embodiments, the purge gas

20 is an inert gas. The purge gas may include one or more gases. In some embodiments, operation 1304 may include one or more evacuation subphases for evacuating the process chamber. Alternatively, it will be appreciated that purges may be omitted in some embodiments. In some embodiments, increasing a flow rate of one or more purge gases may decrease the duration of a purge. For example, a purge gas flow rate may be adjusted

25 according to various reactant thermodynamic characteristics and/or geometric characteristics of the process chamber and/or process chamber plumbing for modifying the duration of the purge. In one non-limiting example, the duration of a purge phase may be adjusted by modulating purge gas flow rate. This may reduce deposition cycle time, which may improve substrate throughput. In operation 1306, at least one etchant and at least one

30 reducing agent are introduced into the process chamber. As used herein, “simultaneously” or “contemporaneously” mean a time interval or duration of delivery or flow of reagent at the same time. As shown in operation 1306, the etchant delivery and the time interval or duration of the reducing agent delivery are the same in some embodiments. While the etchant and reducing agent are delivered at the same time, they each may be delivered at

different flow rates. In other embodiments, the reducing agent may be flowed into the process chamber either before, after, or before and after etchant is introduced. The flow of reducing agent is thus partially contemporaneous with the flow of the etchant. Alternatively, the reducing agent may be introduced in pulses during etchant delivery. Furthermore, the concentration of etchant may be either held constant or varied (*i.e.*, increased gradually or tapered off) throughout the duration of its delivery. The ratio of reducing agent to etchant may be tuned in to achieve a desired outcome or property of the deposited film. These include, but are not limited to, deposition rate, uniformity, resistivity, thickness and step coverage of the film in the feature. The tuning can also be used to modulate the full-wafer uniformity of these properties. In some embodiments, the ratio of reducing agent to etchant is from about 10,000:1 to about 10:1. The flow rates, concentrations and ratios of etchant and flow rate may be the same in every cycle or may be independently adjusted from cycle to cycle.

[0197] The reducing agent is typically a reducing gas. Suitable examples of reducing agents include H_2 , SiH_4 , NH_3 , or B_2H_6 . In some embodiments, the reducing agent may be in plasma form, such as a hydrogen plasma. In some embodiments, the reducing agent is hydrogen, ammonia, hydrazine, silane, disilane, trisilane, germane, digermane, diborane or a combination thereof.

[0198] Flow rates of the etchant typically depend on a size of the chamber, etching rates, etching uniformity, and other parameters. They will typically be much lower than the flow rate of the reducing agent.

[0199] In some embodiments, the etchant or etchant combination is halogen-containing, and the halogen of the etchant of operation 1306 is the same as the halogen substituents on the metal halide precursor utilized in operation 1302. For example, molybdenum precursors including MoO_2Cl_2 or $MoCl_5$ may be utilized in conjunction with a chlorine-containing etchant such as HCl/Cl_2 ; or a fluorine-containing molybdenum precursor such as MoF_6 may be utilized in conjunction with a fluorine-containing etchant such as $HBr/HF/F_2$. The selection of a common halogen for both etchant and precursor may serve to enhance etching at the top surface and upper sidewalls of a feature; overcoming any formation of overhangs of a breadloaf-like structure near the opening of the feature. A breadloaf or breadloaf-like structure may also be referred to as a bottleneck. Furthermore, selection of a reducing agent such as hydrogen in conjunction with the use of halogen-containing etchants may be advantageous since the reactive species of the halogen-containing etchants may be relatively heavier in terms of atomic weight than the reactive species of the hydrogen, inducing the

reactive species of the halogen-containing etchants to remain near the opening of the feature and etch preferentially therein. When such combinations are utilized, a top heavy etch (*i.e.* – an etchant which etches more near the opening than at the bottom of the feature) as blended with deposition can result in a super-conformal deposition of metal; thus improving gapfill.

5 [0200] Operation 1308 is a second optional purge step. In process 1300, either purge 1304 or 1308 may be included; both purge 1304 and 1308 may be included; or no purge may be utilized.

[0201] In operation 1310, a determination of whether or not the metal deposited is of a desired thickness. If a thicker film is desired, operation 1312 is a process flow path
10 indicating that after operation 1306, operation 1302 can commence again, repeating n times. In process flow path 1312, n is the number of cycles which may be from 1 to 50 or from 20 to 40. The cycle of operations 1302 and 1306 with optional purge 1304 can be repeated as many times as necessary. As used herein, the term “cycle” refers to a particular set of sequential operations. Adequate thickness can result in the feature being completely or
15 partially filled.

Deposition-Etch-Deposition for 3D NAND Wordline Fill

[0202] As described above, the methods described herein may be used to fill 3D NAND structures. Figure 14 is a process diagram show operations in a DED method of filling wordline features of a 3D NAND structure. Figure 15A illustrates certain operations of the
20 process of Figure 14. The method of Figure 14 begins with providing a 3D NAND structure having unfilled wordline features in an operation 1401. Examples of such structures are described above with respect to Figures 2F–2J. Figure 15A shows a top-down view of pillars of an example of part of a 3D NAND structure. The outer pillars are adjacent to the slit from which the wordline feature are fluidically accessible. In the depicted example, 3
25 rows of staggered pillars are shown. According to various embodiments, the number of rows may be, e.g., 20 or more. As described above with reference to Figure 2F, there are slits on either side such that reaching the innermost wordlines of 20 rows of pillars involves diffusion through 10 rows of pillars from a slit. Referring back to Figure 2F, the critical dimension of the central vertical structure 230 may be on the order of hundreds of
30 nanometers, with the depth more than 1 micron. The critical dimension of the wordline features prior to molybdenum deposition may be, e.g., 10–20 nm, or 12–16 nm. As described, it can be challenging to fill such features uniformly and void-free. A substrate that includes the 3D NAND structure may be provided to a semiconductor processing tool. As provided, the pillars may include a dielectric layer, e.g., an Al_2O_3 layer as shown in

Figure 15A.

- [0203] Returning to Figure 14, the method includes depositing a conformal liner and thin film in the wordline features of the 3D NAND structure in an operation 1403. An example of a conformal liner + film is shown in left panel of Figure 15A. As shown, Mo is deposited
- 5 conformally around each of the features, evenly from the exterior (slit side) to the interior (non-slit side). This partial fill deposition may be referred to as the Dep1 operation. In some embodiments, the conformal liner and thin film deposition may be a single film that is the result of multiple cycles of a single ALD process used to deposit a conformal film of about 4 to 6 nm. However, in some embodiments, a nucleation layer is deposited. This may
- 10 be referred to as a liner layer. For example, molybdenum does not nucleation well on Al_2O_3 or other oxide surfaces. The nucleation layer may be deposited as described above. In some embodiments, ammonia is used as a reducing agent to deposit a molybdenum nitride or molybdenum oxynitride liner layer of less than 2 nm. This allows a subsequent process using hydrogen as the reducing agent to deposit on the liner layer to increase the total
- 15 thickness, e.g., to about 4 to 6 nm. The molybdenum nitride or molybdenum oxide nitride layer is converted to molybdenum during the Mo-containing precursor/ H_2 ALD process. The thicknesses of the liner layer and liner + thin film layer may be modified depending on the dimensions of the structure. The ALD process in Figure 14 is typically a thermal ALD process. This is because achieving lateral fill throughout the wordline feature is easier with
- 20 a thermal process. Conformal fill throughout the complex structure is also facilitated by use of a molybdenum oxyhalide precursor such as MoO_2Cl_2 rather than a molybdenum halide such as MoCl_5 . This because molybdenum halides are stronger etchants. With a large and complex structure, a molybdenum halide may etch at the top of the structure while the precursor diffuses through the structure.
- 25 [0204] In some embodiments, a thermal ALD process using MoO_2Cl_2 and NH_3 is used to deposit a conformal liner at 350°C to 550°C. In some embodiments, a thermal ALD process using MoO_2Cl_2 and H_2 is used to deposit a conformal thin film on the liner at a higher temperature, e.g., 550°C to 615°C. To achieve top to bottom as well as lateral uniformity, charge volumes may be used for the precursor and/or reducing agent doses.
- 30 [0205] An optional etch pre-treatment may be performed in an operation 1405. The pre-etch treatment makes it easier to etch in the subsequent operation. If performed, the pre-etch treatment may be conformal or non-conformal. In some embodiments, it is non-conformal, being preferentially applied to the outer wordlines relative to the inner wordlines. The pre-etch treatment may be an oxidation or nitridation of the molybdenum. The pre-etch

treatment may be a plasma or thermal treatment. In some embodiments, a thermal pre-etch treatment may be easier to control the diffusion into the structure and extent of treatment.

[0206] For oxidation, the structure may be exposed to ozone. And, because relatively high temperatures (e.g., 450° to over 600°C), exposure to oxygen gas (O₂) or water vapor may be used. For nitridation, ammonia may be used, or another nitrogen-containing gas or plasma. Operation 1405 has top to bottom uniformity. As in operation 1403, charge volumes may be used to achieve this.

[0207] After the optional pre-etch treatment, an etch that is preferential to the molybdenum in the outer wordlines is performed in an operation 1407. In the exterior portion of the wordline feature the oxide of the feature may be exposed. The interior portion of the wordline may be etched less such that molybdenum may remain on the interior features. This is illustrated in the middle panel of Figure 15A, with the molybdenum on the outermost pillars removed, the molybdenum in the second row of pillars mostly removed, and the molybdenum on the third row of pillars intact. In some embodiments, the molybdenum is thinned but not completely removed from any portion of the wordline features.

[0208] The extent of etching may be determined based on how many pillars there are, the geometry of the structure, etc. For example, a first etch may be targeted such that molybdenum is removed from all but the innermost pillars, with a subsequent etch leaving molybdenum on the next innermost row, etc. The pre-etch treatment can be used to tune the etch profile. In addition or instead of the pre-etch treatment, concentration of the etchant and/or dose time can be used to control the diffusion into the structure and the extent of etching. Chamber pressure and pedestal temperature are the other parameters that can be varied to tune the etch profile. Chamber pressure is used to control chemical diffusion and temperature is used to control the reactivity of the chemical with the Mo surface.

[0209] Higher concentration (and thus higher partial pressure) of the etchant can be used to reach further into the structure. Similarly, a continuous dose or longer pulsed doses will facilitate diffusion. Lower partial pressures and/or shorter doses of etchant can be used to keep the etchant from extending further into the structure. Charge volumes may be used for top to bottom uniformity. Examples of etch processes regimes include pressure ranging from 100mT to 100T, temperature ranging from room temperature to 750°C, gas flows ranging from 50sccm to 50slm, dose times ranging from 10ms to 60s, and etchant concentrations ranging from 0.001% to 100%.

[0210] Examples of etch chemistries include halogen-containing compounds such as

- MoCl₅, F₂, NF₃, MoF₆, BCl₃, HCl, Cl₂, ClF₃, Cl₂O, SF₆, CF₄, HF, HBr, WF₆, and CCl₄. For 3D NAND structures, the etch is a thermal etch to avoid plasma damage. However, aspects of the method described in Figure 14 can be applied for logic applications for which a plasma etch may be used. An optional post-etch treatment may be performed in an operation
- 5 1409. Such a treatment can be used to remove byproducts that can hinder subsequent etching and/or are unwanted in the device. For example, any of oxygen, chlorine, or boron may be removed. The post-etch treatment can involve a reducing soak (e.g., H₂ soak) or exposure to a halosilane, for example, for ligand exchange. Other examples include exposure to argon.
- 10 [0211] Returning to Figure 14, a thin film is deposited by ALD in an operation 1411. Generally, the same precursor and process ranges as used for the conformal thin film in operation 1403 are used. Use of a different precursor or process range may be performed. This may be referred to as the Dep2 operation. In embodiments in which oxide is exposed during the etch on the outer portion of the features, the deposition may be selective to the
- 15 molybdenum film remaining in the wordline features. Thus, the film deposited in the subsequent deposition may be deposited selective to the inner portion of the wordline feature. As molybdenum starts to grow and a nucleation delay is overcome (if present), the deposition may become conformal. As shown in Figure 15A, after the subsequent deposition, the Mo film may be thicker on the inner portion of the feature compared to the
- 20 outer portion of the feature. In embodiments in which there is no nucleation delay, the Mo film may be thicker on the inner portion of the feature compared to the outer portion of the feature of the greater thickness after the etch. The right panel of Figure 15A shows the structure after the Dep2 operation. In some embodiments, a liner described above or other nucleation layer may be part of the Dep2 operation.
- 25 [0212] Operations 1405-1411 may be repeated one or more times to fill more of the structure. The pre-treatment, etch, post-treatment, and deposition operations conditions may varied or the same for any two repetitions. For example, the etch in a subsequent iteration may be tailored to extend less into the structure.
- [0213] In some embodiments, MoO₂Cl₂ is used for the Dep1 partial fill and Dep2 selective
- 30 deposition. In other embodiments, other molybdenum precursors may be used with the same or different precursor used for Dep1 and Dep2. Inhibition and de-inhibition operations as described above may be incorporated into the integration processes as described above.
- [0214] In some embodiments, the dep-etch-dep operations disclosed herein may be integrated into single chamber metallization processes as described above. Figure 15B

shows an example of possible operations. In other embodiments, any one or more of the operations may occur in different chambers. These may be connected by vacuum in some embodiments.

[0215] In Figure 15B, a conformal liner and thin film may be deposited using ALD. As described above, the liner may be a molybdenum oxynitride or molybdenum nitride layer deposited using a molybdenum oxyhalide and ammonia. A bulk molybdenum thin film may be deposited on the liner using a molybdenum oxyhalide and hydrogen. An anisotropic etch may be performed with optional thermal or plasma pre- and/or post-treatments. Similarly, an anisotropic inhibition may be performed using a thermal or plasma.

[0216] For final fill, bulk molybdenum thin film may be deposited using a molybdenum oxyhalide and hydrogen ALD process. Multiple DED (or DEID, etc.) operations may be performed for gapfill optimization. An overburden process to deposit molybdenum on the sidewalls of a central vertical structure may be performed using ALD or CVD.

Apparatus

[0217] Figure 16 depicts a schematic illustration of an embodiment of an ALD process station 1600 having a process chamber 1602 for maintaining a low-pressure environment. In some embodiments, a plurality of ALD process stations may be included in a common low-pressure process tool environment. For example, Figures 17A and 17B depict embodiments of a multi-station processing tool 1700. In some embodiments, one or more hardware parameters of ALD process station 1600, including those discussed in detail below, may be adjusted programmatically by one or more computer controllers 1750. In some other embodiments, a process chamber may be a single station chamber.

[0218] ALD process station 1600 fluidly communicates with reactant delivery system 1601a for delivering process gases to a distribution showerhead 1606. Reactant delivery system 1601a includes a mixing vessel 1604 for blending and/or conditioning process gases, such as a Mo precursor-containing gas, a hydrogen-containing gas, an argon or other carrier gas, or other reactant-containing gas, for delivery to showerhead 1606. One or more mixing vessel inlet valves 1620 may control introduction of process gases to mixing vessel 1604. In various embodiments, deposition of an initial Mo layer is performed in process station 1600 and in some embodiments, other operations such as in-situ clean or Mo gap fill may be performed in the same or another station of the multi-station processing tool 1700 as further described below with respect to Figure 17A.

[0219] As an example, the embodiment of Figure 16 includes a vaporization point 1603

for vaporizing liquid reactant to be supplied to the mixing vessel 1604. In some embodiments, vaporization point 1603 may be a heated vaporizer. In some embodiments, a liquid precursor or liquid reactant may be vaporized at a liquid injector (not shown). For example, a liquid injector may inject pulses of a liquid reactant into a carrier gas stream
5 upstream of the mixing vessel 1604. In one embodiment, a liquid injector may vaporize the reactant by flashing the liquid from a higher pressure to a lower pressure. In another example, a liquid injector may atomize the liquid into dispersed microdroplets that are subsequently vaporized in a heated delivery pipe. Smaller droplets may vaporize faster than larger droplets, reducing a delay between liquid injection and complete vaporization. Faster
10 vaporization may reduce a length of piping downstream from vaporization point 1603. In one scenario, a liquid injector may be mounted directly to mixing vessel 1604. In another scenario, a liquid injector may be mounted directly to showerhead 1606.

[0220] Reactant delivery system 1601a may also include one or more solid precursor delivery components including one or more on-board ampoules 1613 and/or bulk delivery
15 components 1615. Figure 18 below provides an example of a bulk delivery system.

[0221] In some embodiments, a liquid flow controller (LFC) upstream of vaporization point 1603 may be provided for controlling a mass flow of liquid for vaporization and delivery to process chamber 1602. For example, the LFC may include a thermal mass flow
20 meter (MFM) located downstream of the LFC. A plunger valve of the LFC may then be adjusted responsive to feedback control signals provided by a proportional-integral-derivative (PID) controller in electrical communication with the MFM. However, it may take one second or more to stabilize liquid flow using feedback control. This may extend a time for dosing a liquid reactant. Thus, in some embodiments, the LFC may be dynamically switched between a feedback control mode and a direct control mode. In some
25 embodiments, this may be performed by disabling a sense tube of the LFC and the PID controller.

[0222] Showerhead 1606 distributes process gases toward substrate 1612. In the embodiment shown in Figure 16, the substrate 1612 is located beneath showerhead 1606 and is shown resting on a pedestal 1608. Showerhead 1606 may have any suitable shape
30 and may have any suitable number and arrangement of ports for distributing process gases to substrate 1612.

[0223] In some embodiments, pedestal 1608 may be raised or lowered to expose substrate 1612 to a volume between the substrate 1612 and the showerhead 1606. In some embodiments, pedestal 1608 may be temperature controlled via heater 1610. Pedestal 1608

may be set to any suitable temperature, such as between about 250°C and about 800°C during operations for performing various disclosed embodiments. It will be appreciated that, in some embodiments, pedestal height may be adjusted programmatically by a suitable computer controller 850. At the conclusion of a process phase, pedestal 1608 may be
5 lowered during another substrate transfer phase to allow removal of substrate 1612 from pedestal 1608.

[0224] In some embodiments, a position of showerhead 1606 may be adjusted relative to pedestal 1608 to vary a volume between the substrate 1612 and the showerhead 1606. Further, it will be appreciated that a vertical position of pedestal 1608 and/or showerhead
10 1606 may be varied by any suitable mechanism within the scope of the present disclosure. In some embodiments, pedestal 1608 may include a rotational axis for rotating an orientation of substrate 1612. It will be appreciated that, in some embodiments, one or more of these example adjustments may be performed programmatically by one or more suitable computer controllers 1650. The computer controller 1650 may include any of the features described
15 below with respect to controller 1650 of Figure 16.

[0225] In some embodiments where plasma may be used as discussed above, showerhead 1606 and pedestal 1608 electrically communicate with a radio frequency (RF) power supply 1614 and matching network 1616 for powering a plasma. In some embodiments, the plasma energy may be controlled by controlling one or more of a process station pressure, a gas
20 concentration, an RF source power, an RF source frequency, and a plasma power pulse timing. For example, RF power supply 1614 and matching network 1616 may be operated at any suitable power to form a plasma having a desired composition of radical species. Likewise, RF power supply 1614 may provide RF power of any suitable frequency. In some embodiments, RF power supply 1614 may be configured to control high- and low-frequency
25 RF power sources independently of one another. Example low-frequency RF frequencies may include, but are not limited to, frequencies between 0 kHz and 900 kHz. Example high-frequency RF frequencies may include, but are not limited to, frequencies between 1.8 MHz and 2.45 GHz, or greater than about 13.56 MHz, or greater than 27 MHz, or greater than 80 MHz, or greater than 60 MHz. It will be appreciated that any suitable parameters may be
30 modulated discretely or continuously to provide plasma energy for the surface reactions.

[0226] In some embodiments, the plasma may be monitored in-situ by one or more plasma monitors. In one scenario, plasma power may be monitored by one or more voltage, current sensors (e.g., VI probes). In another scenario, plasma density and/or process gas concentration may be measured by one or more optical emission spectroscopy sensors

(OES). In some embodiments, one or more plasma parameters may be programmatically adjusted based on measurements from such in-situ plasma monitors. For example, an OES sensor may be used in a feedback loop for providing programmatic control of plasma power. It will be appreciated that, in some embodiments, other monitors may be used to monitor the plasma and other process characteristics. Such monitors may include, but are not limited to, infrared (IR) monitors, acoustic monitors, and pressure transducers.

[0227] In some embodiments, instructions for a controller 1650 may be provided via input/output control (IOC) sequencing instructions. In one example, the instructions for setting conditions for a process phase may be included in a corresponding recipe phase of a process recipe. In some cases, process recipe phases may be sequentially arranged, so that all instructions for a process phase are executed concurrently with that process phase. In some embodiments, instructions for setting one or more reactor parameters may be included in a recipe phase. For example, a first recipe phase may include instructions for setting a flow rate of an inert and/or a reactant gas (e.g., a Mo precursor), instructions for setting a flow rate of a carrier gas (such as argon), and time delay instructions for the first recipe phase. A second, subsequent recipe phase may include instructions for modulating or stopping a flow rate of an inert and/or a reactant gas, and instructions for modulating a flow rate of a carrier or purge gas and time delay instructions for the second recipe phase. A third recipe phase may include instructions for modulating a flow rate of a second reactant gas such as H₂, instructions for modulating the flow rate of a carrier or purge gas, instructions for igniting a plasma, and time delay instructions for the third recipe phase. A fourth, subsequent recipe phase may include instructions for modulating or stopping a flow rate of an inert and/or a reactant gas, and instructions for modulating a flow rate of a carrier or purge gas and time delay instructions for the fourth recipe phase. It will be appreciated that these recipe phases may be further subdivided and/or iterated in any suitable way within the scope of the present disclosure.

[0228] Further, in some embodiments, pressure control for process station 1600 may be provided by butterfly valve 1618. As shown in the embodiment of Figure 16, butterfly valve 1618 throttles a vacuum provided by a downstream vacuum pump (not shown). However, in some embodiments, pressure control of process station 1600 may also be adjusted by varying a flow rate of one or more gases introduced to the process station 1600.

[0229] Figure 17A and Figure 17B show examples of processing systems. Figure 17A shows an example of a processing system including multiple chambers. The system 1700 includes a transfer module 1703. The transfer module 1703 provides a clean, vacuum

environment to minimize risk of contamination of substrates being processed as they are moved between various modules. Mounted on the transfer module 1703 is a multi-station chamber 1709 capable of performing in-situ clean and/or ALD processes described above. Surface treatment and/or initial Mo layer deposition may be performed in the same or different station or chamber as the subsequent Mo gap fill.

[0230] Chamber 1709 may include multiple stations 1711, 1713, 1715, and 1717 that may sequentially perform operations in accordance with disclosed embodiments. For example, chamber 1709 may be configured such that station 1711 performs an in-situ treatment using a MoCl_x precursor. Station 1713 may be configured to selectively treat the field region and upper sidewalls and stations 1715 and 1717 may be configured to perform ALD of bulk Mo using a molybdenum oxyhalide precursor and H_2 . In another example, chamber 1709 may be configured such that station 1711 performs in-situ clean, station 1713 performs ALD of an initial Mo layer, station 1713 selectively treats the layer, and 1714 deposition of bulk Mo. In another example, the chamber 1709 may be configured to do parallel processing of substrates, with each station performing multiple processes sequentially.

[0231] Two or more stations may be included in a multi-station chamber, e.g., 2–6, with the operations appropriately distributed. For example, a two-station chamber may be configured to perform ALD of an initial Mo layer in a first station followed by ALD of bulk Mo in a second station. Stations may include a heated pedestal or substrate support, one or more gas inlets or showerhead or dispersion plate.

[0232] Also mounted on the transfer module 1703 may be one or more single or multi-station modules 1707. In some embodiments, a preclean as described above may be performed in a module 1707, after which the substrate is transferred under vacuum to another module (e.g., another module 1707 or chamber 1709) for ALD. In another example, a module for selective treatment of a film may be mounted on the transfer module. An example is shown in Figure 10.

[0233] The system 1700 also includes one or more wafer source modules 1701, where wafers are stored before and after processing. An atmospheric robot (not shown) in the atmospheric transfer chamber 1719 may first remove wafers from the source modules 1701 to loadlocks 1721. A wafer transfer device (generally a robot arm unit) in the transfer module 1703 moves the wafers from loadlocks 1721 to and among the modules mounted on the transfer module 1703.

[0234] Referring to Figures 6A and 6B, for example, in some embodiments, chamber 1709 is configured to perform pre-treatment, selective fill, conformal liner deposition, and

final fill. In one example, station 1711 is configured to perform pre-treatment, station 1713 is configured to perform selective fill, station 1713 is configured to perform conformal liner deposition, and station 1715 is configured to perform final fill. In some embodiments, etch and/or inhibition processes may be performed. For example, station 1711 is configured to perform pre-treatment, station 1713 is configured to perform selective fill, station 1713 is configured to perform inhibition, and station 1715 is configured to perform final fill. Similarly, chamber 1709 may be configured to perform all processes described in Figures 6C–6F and Figure 15B.

[0235] Chamber 1709 may have one or more of the following features to enable single chamber metallization processes:

Individually addressable plasma power generators associated with each station;

Individually addressable reactant inputs associated with each station;

Multi-plenum showerheads on each station;

Dual solid precursor delivery systems.

[0236] Solid precursor delivery systems may include bulk delivery systems and/or on-board ampoules. Figure 18 below provides an examples of a solid precursor delivery system that may be employed.

[0237] Figure 17B is an embodiment of a system 1700. The system 1700 in Figure 17B has wafer source modules 1701, a transfer module 1703, atmospheric transfer chamber 1719, and loadlocks 1721, as described above with reference to Figure 17A. The system in Figure 17B has three single station modules 1757a–1757c. The system 1700 may be configured to sequentially perform operations in accordance with disclosed embodiments. For example, the single station modules 1757a–1757c may be configured so that a first module 1757a performs a surface treatment, a second module 1757b performs ALD of an initial Mo layer using a molybdenum halide precursor, and a third module 1757c performs ALD of bulk Mo using a molybdenum oxyhalide precursor. In this example, an in-situ clean may be optionally performed in second module 1757b instead of or in addition to a preclean in first module 1757a. In another example, the single station modules 1757a–1757c may be configured so that a first module 1757a performs a deposition of an initial metal layer, a second module 1757b performs selective treatment, and a third module 1757c performs ALD of bulk Mo using a molybdenum oxyhalide precursor. In yet another example, one module may be configured for deposition, another module for selective treatment, and

another module for etch.

[0238] Stations may include a heated pedestal or substrate support, one or more gas inlets or showerhead or dispersion plate as described above with reference to Figure 16.

[0239] Returning to Figure 17A and 17B, in various embodiments, a system controller
5 1729 is employed to control process conditions during deposition. The controller 1729 will typically include one or more memory devices and one or more processors. A processor may include a CPU or computer, analog and/or digital input/output connections, stepper motor controller boards, etc. Such a system controller may be employed in control of any of the processes and apparatus described herein.

10 [0240] The controller 1729 may control all the activities of the apparatus. The system controller 1729 executes system control software, including sets of instructions for controlling the timing, mixture of gases, chamber pressure, chamber temperature, wafer temperature, radio frequency (RF) power levels, wafer chuck or pedestal position, and other parameters of a particular process. Other computer programs stored on memory devices
15 associated with the controller 1729 may be employed in some embodiments.

[0241] Typically, there will be a user interface associated with the controller 1729. The user interface may include a display screen, graphical software displays of the apparatus and/or process conditions, and user input devices such as pointing devices, keyboards, touch screens, microphones, etc.

20 [0242] System control logic may be configured in any suitable way. In general, the logic can be designed or configured in hardware and/or software. The instructions for controlling the drive circuitry may be hard coded or provided as software. The instructions may be provided by "programming." Such programming is understood to include logic of any form, including hard coded logic in digital signal processors, application-specific integrated
25 circuits, and other devices which have specific algorithms implemented as hardware. Programming is also understood to include software or firmware instructions that may be executed on a general-purpose processor. System control software may be coded in any suitable computer readable programming language.

[0243] The computer program code for controlling the Mo precursor pulses, hydrogen
30 pulses, and argon flow, and other processes in a process sequence can be written in any conventional computer readable programming language: for example, assembly language, C, C++, Pascal, Fortran, or others. Compiled object code or script is executed by the processor to perform the tasks identified in the program. Also as indicated, the program code may be hard coded.

[0244] The controller parameters relate to process conditions, such as, for example, process gas composition and flow rates, temperature, pressure, cooling gas pressure, substrate temperature, and chamber wall temperature. These parameters are provided to the user in the form of a recipe and may be entered utilizing the user interface.

- 5 [0245] Signals for monitoring the process may be provided by analog and/or digital input connections of the system controller 1729. The signals for controlling the process are output on the analog and digital output connections of the deposition apparatus.

- [0246] The system software may be designed or configured in many ways. For example, various chamber component subroutines or control objects may be written to control
10 operation of the chamber components necessary to carry out the deposition processes in accordance with the disclosed embodiments. Examples of programs or sections of programs for this purpose include substrate positioning code, process gas control code, pressure control code, and heater control code.

- [0247] In some implementations, a controller 1729 is part of a system, which may be part
15 of the above-described examples. Such systems can include semiconductor processing equipment, including a processing tool or tools, chamber or chambers, a platform or platforms for processing, and/or specific processing components (a wafer pedestal, a gas flow system, etc.). These systems may be integrated with electronics for controlling their operation before, during, and after processing of a semiconductor wafer or substrate. The
20 electronics may be referred to as the “controller,” which may control various components or subparts of the system or systems. The controller 1729, depending on the processing requirements and/or the type of system, may be programmed to control any of the processes disclosed herein, including the delivery of processing gases, temperature settings (e.g., heating and/or cooling), pressure settings, vacuum settings, power settings, radio frequency
25 (RF) generator settings in some systems, RF matching circuit settings, frequency settings, flow rate settings, fluid delivery settings, positional and operation settings, wafer transfers into and out of a tool and other transfer tools and/or load locks connected to or interfaced with a specific system.

- [0248] Broadly speaking, the controller may be defined as electronics having various
30 integrated circuits, logic, memory, and/or software that receive instructions, issue instructions, control operation, enable cleaning operations, enable endpoint measurements, and the like. The integrated circuits may include chips in the form of firmware that store program instructions, digital signal processors (DSPs), chips defined as application specific integrated circuits (ASICs), and/or one or more microprocessors, or microcontrollers that

execute program instructions (e.g., software). Program instructions may be instructions communicated to the controller in the form of various individual settings (or program files), defining operational parameters for carrying out a particular process on or for a semiconductor wafer or to a system. The operational parameters may, in some
5 embodiments, be part of a recipe defined by process engineers to accomplish one or more processing steps during the fabrication of one or more layers, materials, metals, oxides, silicon, silicon dioxide, surfaces, circuits, and/or dies of a wafer.

[0249] The controller 1729, in some implementations, may be a part of or coupled to a computer that is integrated with, coupled to the system, otherwise networked to the system,
10 or a combination thereof. For example, the controller 1729 may be in the “cloud” or all or a part of a fab host computer system, which can allow for remote access of the wafer processing. The computer may enable remote access to the system to monitor current progress of fabrication operations, examine a history of past fabrication operations, examine trends or performance metrics from a plurality of fabrication operations, to change
15 parameters of current processing, to set processing steps to follow a current processing, or to start a new process. In some examples, a remote computer (e.g. a server) can provide process recipes to a system over a network, which may include a local network or the Internet. The remote computer may include a user interface that enables entry or programming of parameters and/or settings, which are then communicated to the system
20 from the remote computer. In some examples, the controller receives instructions in the form of data, which specify parameters for each of the processing steps to be performed during one or more operations. The parameters may be specific to the type of process to be performed and the type of tool that the controller is configured to interface with or control. Thus, as described above, the controller may be distributed, such as by including one or
25 more discrete controllers that are networked together and working towards a common purpose, such as the processes and controls described herein. An example of a distributed controller for such purposes would be one or more integrated circuits on a chamber in communication with one or more integrated circuits located remotely (such as at the platform level or as part of a remote computer) that combine to control a process on the
30 chamber.

[0250] Without limitation, example systems may include a plasma etch chamber or module, a deposition chamber or module, a spin-rinse chamber or module, a metal plating chamber or module, a clean chamber or module, a bevel edge etch chamber or module, a PVD chamber or module, a CVD chamber or module, an ALD chamber or module, an

atomic layer etch (ALE) chamber or module, an ion implantation chamber or module, a track chamber or module, and any other semiconductor processing systems that may be associated or used in the fabrication and/or manufacturing of semiconductor wafers.

[0251] As noted above, depending on the process step or steps to be performed by the tool, the controller might communicate with one or more of other tool circuits or modules, other tool components, cluster tools, other tool interfaces, adjacent tools, neighboring tools, tools located throughout a factory, a main computer, another controller, or tools used in material transport that bring containers of wafers to and from tool locations and/or load ports in a semiconductor manufacturing factory.

[0252] The controller 1729 may include various programs. A substrate positioning program may include program code for controlling chamber components that are used to load the substrate onto a pedestal or chuck and to control the spacing between the substrate and other parts of the chamber such as a gas inlet. A substrate tilt and rotation program may include for tilt and rotation. A process gas control program may include code for controlling gas composition, flow rates, pulse times, and optionally for flowing gas into the chamber prior to deposition in order to stabilize the pressure in the chamber. A pressure control program may include code for controlling the pressure in the chamber by regulating, e.g., a throttle valve in the exhaust system of the chamber. A heater control program may include code for controlling the current to a heating unit that is used to heat the substrate. Alternatively, the heater control program may control delivery of a heat transfer gas such as helium to the wafer chuck.

[0253] Examples of chamber sensors that may be monitored during deposition include mass flow controllers, pressure sensors such as manometers, and thermocouples located in the pedestal or chuck. Appropriately programmed feedback and control algorithms may be used with data from these sensors to maintain desired process conditions.

[0254] Figure 18 depicts an example precursor delivery system according to various implementations. The precursor delivery system 1800, which may also be referred to herein as the system 1800, includes an ampoule 1802 that is configured to have a precursor 1804 (shown with cross-hatching) and heat that precursor 1804 to vaporize it and create a precursor vapor in the headspace 1806 of the ampoule 1802. The ampoule includes an inlet 1808 and an outlet 1810. The inlet 1808 is configured to receive inert gas from an inert gas source 1812. The inert gas and precursor vapor in the headspace of the ampoule form a mixture that is flowed out of the outlet 1810. In some implementations, like in Figure 18, the pressure in the ampoule 1802 may be maintained or controlled by pressure flow control

which may include a controller and/or flow control valve 1814, which in some implementations may be a throttle valve. As the mixture of inert gas and precursor vapor flows out of the outlet 1810, the pressure flow control of the ampoule flows inert gas into the ampoule 1802 through the inlet 1808 to maintain the pressure in the ampoule 1802. The
5 ampoule also includes an inlet valve 1816 configured to control flow of the inert gas into the ampoule and an outlet valve 1818 configured to control flow out of the outlet 1810, as well as bypass valve 1820 through which the inert gas can flow downstream of the ampoule 1802 without flowing through the ampoule 1802.

[0255] The ampoule 1802 is located in one location of a fabrication facility, such as a
10 “sub-fab,” that is different than the location of the semiconductor processing tool, and the processing modules, to where the mixture is flowed. For example, the semiconductor processing tool may be located on a fabrication floor that is a different level in the facility than where the ampoule is located. The different locations of the ampoule and semiconductor processing tool / processing modules is exemplified by the vertical dashed
15 line.

[0256] The mixture of precursor vapor and inert gas is configured to flow out of the outlet 1810 and towards a plurality of flow paths configured to flow the mixture to a plurality of processing modules and into a process volume of each processing module. These flow paths span from the location of the ampoule, e.g., in the sub-fab, to the separate location of the
20 processing tools and/or modules, e.g., the fab floor. The system 1800 of Figure 1 includes four flow paths 1822A–D that each span from the location of the ampoule on the left side of the dashed dividing line, e.g., the sub-fab, to a corresponding processing module 1824A–D on the right side of the dashed dividing line, e.g., on the fab floor. Each flow path 1822A–D is configured to flow the mixture of precursor vapor and inert gas which includes having
25 delivery conduits and other flow elements to contain and direct the flow of mixture to the corresponding processing module 1824A–D. Each flow path is also configured to maintain the mixture at a temperature between about 100 C and 150 C which may include having heating elements that heat the delivery conduits of the flow path and/or thermal insulation around the delivery conduits. Each flow path also has a high-temperature mass flow
30 controller located at or near the corresponding processing module 1824A–D that is configured to control the flow of the mixture along the flow path. Although four flow paths and four processing modules are shown, the number of flow paths and processing modules may vary such that there are 2, 3, 4, 5, 6, 7, 8, or 10 processing modules and corresponding flow paths.

[0257] The foregoing describes implementation of disclosed embodiments in a single or multi-chamber semiconductor processing tool. The apparatus and process described herein may be used in conjunction with lithographic patterning tools or processes, for example, for the fabrication or manufacture of semiconductor devices, displays, LEDs, photovoltaic panels, and the like. Typically, though not necessarily, such tools/processes will be used or conducted together in a common fabrication facility. Lithographic patterning of a film typically includes some or all of the following steps, each step provided with a number of possible tools: (1) application of photoresist on a workpiece, i.e., substrate, using a spin-on or spray-on tool; (2) curing of photoresist using a hot plate or furnace or UV curing tool; (3) exposing the photoresist to visible or UV or x-ray light with a tool such as a wafer stepper; (4) developing the resist so as to selectively remove resist and thereby pattern it using a tool such as a wet bench; (5) transferring the resist pattern into an underlying film or workpiece by using a dry or plasma-assisted etching tool; and (6) removing the resist using a tool such as an RF or microwave plasma resist stripper.

15

Claims

1. A method comprising:
providing a feature to be filled with molybdenum, the feature including a metal-
containing bottom and dielectric sidewalls;
5 selectively depositing molybdenum on the metal-containing bottom to partially fill
the feature, leaving exposed dielectric sidewalls;
depositing a conformal molybdenum liner on the exposed sidewalls and
molybdenum; and
filling the feature with molybdenum.
10
2. The method of claim 1, wherein the operations are performed in a single chamber.
3. The method of claim 1, further comprising, prior to selectively depositing
molybdenum on the metal-containing bottom, exposing the metal-containing
15 bottom to a metal halide to remove oxide from the metal-containing bottom.
4. The method of claim 1, further comprising, prior to selectively depositing
molybdenum on the metal-containing bottom, exposing the metal-containing
bottom to a reducing plasma to remove oxide from the metal-containing bottom.
20
5. The method of claim 1, wherein selectively depositing molybdenum on the metal-
containing bottom comprises a thermal atomic layer deposition (ALD) processing
using a molybdenum halide precursor.
- 25 6. The method of claim 5, wherein depositing a conformal molybdenum liner
comprises a thermal ALD or plasma enhanced ALD process using a molybdenum
oxyhalide.
- 30 7. The method of claim 5, wherein depositing a conformal molybdenum liner
comprises a plasma enhanced ALD process using a molybdenum oxyhalide.
8. The method of claim 1, wherein the metal-containing bottom comprises titanium.

9. The method of claim 1, wherein the metal-containing bottom comprises molybdenum.
10. The method of claim 1, wherein filling the feature with molybdenum comprises an
5 integration process including etching molybdenum.
11. The method of claim 1, wherein filling the feature with molybdenum comprises an integration process including inhibiting molybdenum deposition.
- 10 12. An apparatus comprising:
a multi-station chamber, wherein each station comprises a substrate support configured to support a substrate, a showerhead configured to inlet gases to a volume above substrate support, and a plasma generator configured to generate a plasma between the substrate support and showerhead; and
15 a controller having instructions for:
inletting pulses of a molybdenum halide and a reducing agent to a first station housing a substrate to selectively deposit molybdenum in feature to be filled with molybdenum, the feature including a metal-containing bottom and dielectric sidewalls to fill the feature, leaving exposed dielectric sidewalls;
20 transferring the substrate to a second station;
inletting pulses of a molybdenum oxyhalide and a reducing agent, generating a plasma during the reducing agent pulses, to deposit a conformal liner in the feature;
transferring the substrate to a third station; and
25 inletting a molybdenum-containing precursor to continue fill of the feature.