[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, after non-conformally etching the conformal thin 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.

silicon carbide (ODC); and low k dielectrics, such as carbon-doped SiO_2. 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.

[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 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 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 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 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 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.

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.

[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 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 is in the feature without deposition on the sidewalls above the layer.

[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 400ºC, thermal ALD may be used to deposit a conformal layer using MoO_2Cl_2. 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 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 description of possible fill techniques of re-entrant features is described below. Figure 6A shows the structure after the fill, with bulk Mo film 612 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-

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 618 and a metal silicide layer (MSix) 617 connected to a semiconductor layer 616, 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 601 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 $MoCl_5$ 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 601 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 605 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

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), $MoCl_5$ may be used as a precursor and H_2 as a reducing agent. Doses of $MoCl_5$ and H_2 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 200ºC and 800ºC, e.g., between 250ºC and 550ºC or between 300ºC and 500ºC between 350ºC and 450ºC. 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 fluoride precursors are given by the formula MoF_x, where x is 4, 5, or 6, and include molybdenum tetrafluoride (MoF_4), molybdenum pentafluoride (MoF_5), and molybdenum hexafluoride (MoF_6).

[0117] MoF_6 can be advantageous as it has a boiling point of 34ºC. Being a gas at standard pressure and 35ºC allows MoF_6 to be delivered through a mass flow controller (MFC) at room temperature, without heating and without condensing and forming particles. However MoF_6 is an aggressive etchant and exposure to MoF_6 during a process can result in etching instead of or in addition to Mo deposition. In some embodiments, deposition using MoF_6 involves providing a flow of MoF_6 in a process gas with the MoF_6 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 MoF_6 molecules per 1 million gas particles (atoms, molecules)) or less, 80 ppm or less, or 40 ppm or less. At temperatures between 200ºC and 650ºC, for example, a molar concentration at or below 0.004% results in CVD deposition when flowed with H_2 and argon. Higher temperatures may be used to favor the deposition reaction and allow higher concentrations of MoF_6, e.g., up to 0.01%. In some embodiments, concentrations may be 0.0039% or .0035% or less. In some embodiments, the MoF_6 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 MoF_6 with H_2 as reducing agent occurs only at unusually low concentration. As an example, for 0.5 sccm of MoF_6, a total flow rate of 13,500 sccm may

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 (H_2), 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 980A, 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.

[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).

[0152] During second purge phase 980B, 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 other molybdenum halides, and/or organometallic molybdenum-containing precursors. One or more precursors may be used.

[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.

[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 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 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

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(B/Mo) + y(S/Mo), with x and y being integers. Examples of boron-containing reactants include diborane (B_2H_6), alkyl boranes, alkyl boron, aminoboranes $(CH_3)_2NB(CH_2)_2$, carboranes such as $C_2B_nH_{n+2}$, 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, or 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

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 (Cl_2), fluorine (F_2), bromine (Br_2), iodine (I_2), hydrogen chloride (HCl), hydrogen fluoride (HF), hydrogen iodide (HI), chlorine trifluoride (ClF_3), ferric chloride ($FeCl_3$), trifluoromethane (CHF_3), fluoromethane (CH_3F), octafluorocyclobutane (C_4F_8), hexafluorobutadiene (C_4F_6), hexafluorocyclopentadiene (C_5F_6), carbon tetrafluoride (CF_4), carbon tetrachloride (CCl_4), nitrogen trifluoride (NF_3), boron trichloride (BCl_3), boron trifluoride (BF_3), hydrogen iodide (HI), hydrogen bromide (HBr), sulfur tetrafluoride (SF_4), sulfur hexafluoride (SF_6), thionyl chloride ($SOCl_2$), phosphorus pentafluoride (PF_5), phosphorus trifluoride (PF_3), silicon tetrabromide ($SiBr_4$), 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 (O_2) with one of the above halogen-containing etchants such as chlorine and oxygen; or fluorine and oxygen. Alternatively, carbon dioxide (CO_2) 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 $MoCl_5$, MoF_6, WF_6, WCl_5, 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 $MoCl_5$. 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 $MoCl_5$ 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

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 reducing agent and etchant 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

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 850. 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

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 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 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 850. The computer controller 850 may include any of the features described below with respect to controller 850 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 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 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 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 850 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 H_2, 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 an 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 deposition of bulk Mo is performed in station 1715. 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 17A.

[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

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 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 "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 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 processing tools and/or modules, e.g., the fab floor. The system 1800 of Figure 18 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 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 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.

Claims

1. A method for deposition of a molybdenum in a feature, the method comprising:
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.

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 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.

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.

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.

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 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.

12. An apparatus for deposition of a molybdenum in a feature, the 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
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.