Examples of dielectric materials include oxides, such as silicon oxide (SiO_2) and aluminum oxide (Al_2O_3); nitrides, such as silicon nitride (SiN); carbides, such as nitrogen-doped silicon carbide (NDC) and oxygen-doped silicon carbide (ODC); and low k dielectrics, such as carbon-doped SiO_2. In particular implementations an under-layer can be one or more of titanium, titanium nitride, tungsten nitride, titanium aluminide, tungsten, and molybdenum. In some embodiments, the under-layer is tungsten-free. In some embodiments, the under-layer is molybdenum-free.

[0057] 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 150) 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 under-layer, such as a barrier layer or adhesion layer. Non-limiting examples of under-layers include dielectric layers and conducting layers, e.g., silicon oxides, silicon nitrides, silicon carbides, metal oxides, metal nitrides, metal carbides, and metal layers.

[0058] 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 under-layer 213 lining the sidewall or interior surfaces of the feature hole 205. Similar to Figure 2B, the under-layer 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 under-layer 213 forms an overhang 215 such that the under-layer 213 is thicker near the opening of the vertical feature 201 than inside the vertical feature 201.

[0059] 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 overhand) at the feature opening. Such an overhang could also be a potential pinch-off point. Example (c) includes a

ranges understood to include the recited endpoints).

[0062] 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.

[0063] 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

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 thermal or plasma H_2 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 an F-containing compound.

[0084] 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 molybdenum 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/molybdenum cycles or Mo/S cycles may be used to deposit a molybdenum nucleation layer. In another example, one or more B/molybdenum cycles or Mo/B cycles may be used to deposit a molybdenum nucleation layer on which a bulk molybdenum 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/molybdenum refers to a pulse of silane followed by a pulse of a Mo-containing precursor. B/molybdenum and S/molybdenum cycles (or Mo/B and/or Mo/S) may both be used to deposit a molybdenum 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 include silane (SiH_4) and other silanes such as disilane (Si_2H_6).

[0085] In some embodiments, deposition of a molybdenum 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 molybdenum precursor).

[0086] In some embodiments, H_2 may be used as a reducing gas for molybdenum nucleation layer deposition instead of a boron-containing or silicon-containing reducing gas. Example thicknesses for deposition of a molybdenum nucleation layer range from 5 Å to 30 Å. Films

nitride feature at the bottom portion of the feature. In embodiments where the feature has a metal nitride layer, molybdenum is deposited on the metal nitride layer at the bottom portion of the sidewall surfaces in the bottom portion of the feature. In embodiments where the feature has a metal nitride plug, molybdenum is deposited on the metal nitride plug in the bottom of the feature. The initially molybdenum layer may grow upward from the metal nitride surfaces at the bottom of the feature. Molybdenum may be deposited by ALD, plasma enhanced ALD, CVD, or plasma enhanced CVD using a molybdenum halide precursor with a reactant. The molybdenum halide precursor may be a molybdenum chloride compound, such as $MoCl_5$, and the reactant may be H_2. Examples of additional precursors and reactants are listed above.

[0151] As discussed above in operation 603, for ALD, the temperature of the substrate and the pressure of a chamber may be controlled. These process parameters may be used to control selectivity such that the molybdenum initial layer is initially deposited on the metal nitride surfaces on the bottom portion of the feature. In some embodiments, the substrate may be heated between 350ºC and 700ºC, e.g., between 375ºC and 475ºC. In some embodiments, the chamber may be pressurized to at least 10 Torr, e.g., to at least 30 Torr, or to at least 50 Torr. In some embodiments, the temperature of the substrate during operation 703 is greater than the temperature of the substrate in operation 702, e.g., at least 50ºC, at least 100ºC. In some embodiments, the temperature of the substrate remains the same between operation 702 and operation 703.

[0152] After the initial molybdenum layer is deposited, the feature is filled with molybdenum in operation 705. The molybdenum fill is deposited on the initial molybdenum layer deposited in operation 703. The fill may be done using the same molybdenum halide precursor used in the previous operation or may be filled using a molybdenum oxyhalide precursor. The precursor may be deposited with a reactant such as H_2. The feature may be filled using ALD, plasma enhanced ALD, CVD, or plasma enhanced CVD.

[0153] Figures 8A–8D show schematic examples of the process of Figure 7. Figure 8A shows a feature 801 formed in a dielectric material 803. The feature 801 has a metal nitride layer 805 conformally deposited into the feature 801. In some embodiments, the metal nitride layer 805 is a TiN layer. The metal nitride layer forms the two sidewall surfaces 807. The feature 801 is a V-shaped trench and has the sidewall surfaces 807 converge at a bottom portion 813 of the feature.

[0154] Figure 8B shows the feature 801 after undergoing a clean and etch operation as described above in operation 702 of Figure 7. The feature undergoes a soak using a $MoCl_x$

after a precursor is flown into a chamber, H_2 may be used as a reactant. In some embodiments, multiple pulses of the H_2 gas may be used to react with a precursor. For example, a precursor gas is flowed into the chamber followed by two or more pulses of the H_2 reactant. In some embodiments, H_2 may be pulsed sequentially. In some embodiments, the sequence may have a H_2 gas flowed into the chamber, following a purge operation, followed by a second flow of H_2 gas into the chamber. In some embodiments, the H_2 gas flow, purge operation sequence may be continued for two or more times.

[0175] A third technique is to use charge volumes. Charge volumes may be used to increase the mass flow of the gas into the chamber. In some embodiments, multiple charge volumes may be used. By using multiple charge volumes, the mass flow of gas may increase as it enters into the chamber. In some embodiments, the multiple charge volumes may be used to sustain a higher mass flow rate into the chamber. In some embodiments, the charge volume may be used to flow the reactant, such as H_2 into the chamber. In some embodiments, the charge volume may be used to flow a purge gas. By using a charge volume to flow purge gas into the chamber, the chamber may be purged more quickly.

[0176] Shown in Figure 13 is an example sequence that may be used to reduce the resistivity. In the sequence shown, a molybdenum-containing precursor is first flowed into the chamber. Examples of molybdenum-containing precursor are given above. Following the flow of the molybdenum-containing precursor is a purge operation. Following the purge, the pressure within the chamber is pumped down to a lower pressure. After the chamber pressure is pumped down, hydrogen is flowed into the chamber. The hydrogen is followed up by a purge operation and then chamber pressure pump down. As described above, the chamber pressure pump down lowers the chamber pressure. The mini-cycle of flowing hydrogen, followed by a purge operation and chamber pressure pump down may be repeated multiple times. In some embodiments, the mini-cycle may be cycled two or more times. In the sequence shown in Figure 13, the mini-cycle of flowing hydrogen, followed by a purge operation and chamber pressure pump down is cycled three times.

[0177] In some embodiments, multiple charge volumes may be used for each purge operation. This is described in WO 2020/214732, incorporated by reference herein.

[0178] In some embodiments, one or more of the following techniques may be used to reduce grain boundaries. In a first technique, an inhibitor may be used on sidewalls of a feature. During deposition of molybdenum into the feature, an inhibitor may be used on the sidewalls to slow down or stop the growth of molybdenum on the sidewalls. A second technique is to

etch or remove any Mo nuclei on the sidewalls of a feature. For example, during an etch operation as described above, $MoCl_5$ may be used to etch Mo nuclei on the sidewalls of the feature. In another example, molybdenum oxytetrachloride ($MoOCl_4$) may be used to etch Mo nuclei on the sidewalls. An example process may include a deposition of molybdenum into a feature. In the initial deposition of molybdenum, molybdenum nuclei may be deposited onto sidewalls of the feature. The deposition may be followed by an etch operation. An example etch operation may use $MoCl_5$ to etch. The etch may etch part of the Mo deposited into the feature include any Mo nuclei deposited onto the sidewalls. The etch may be followed by a deposition. The deposition may include depositing Mo. The deposition may be a bottom-up fill, depositing molybdenum onto molybdenum in the feature not etched away in the previous operation

[0179] In 3D NAND structures, treatment of lateral features, such as wordlines, may be used to improve fill within the structures. Treatment may include nucleation inhibition, etching, or a combination thereof. Nucleation inhibition inhibits subsequent molybdenum nucleation at the treated surfaces. It can involve one or more of: deposition of an inhibition film, reaction of treatment species with the Mo film to form a compound film (e.g., Mo_2N), and adsorption of inhibition species. During a subsequent deposition operation, there is a nucleation delay on the inhibited portions of the underlying film relative to the non- or lesser-inhibited portions. As shown in Figure 14A, an inhibitor non-conformally treats the feature. A higher amount of the inhibitor 1403 is towards the exterior of a feature and reduces as you move toward the interior of the feature. Higher amounts of untreated Mo film 1405 are on the interior of the feature. In the example shown, the Mo film 1405 may be deposited in the interior part of the feature. In a subsequent deposition, deposited Mo may be deposited on Mo within the feature while the inhibitor reduces or delays growth of the Mo. Examples of inhibitors include ammonia (NH_3), oxygen (O_2), nitrogen (N_2), H_2, methane (CH_4), hydrazine (N_2H_4), nitrogen trifluoride (NF_3), SiH_4, B_2H_6 and derivatives thereof, with or without plasma

[0180] Etch removes deposited film at the treated surfaces. This can involve reacting an etchant species with the molybdenum film to form a gaseous byproduct that is then removed. Other methods of etching, including atomic layer etching, may be performed. The etch operation may be a plasma or a non-plasma operation. If a non-plasma operation, it may be purely thermal or activated by some other energy such as UV.

[0181] Nitrogen acts as inhibition species and halogen (e.g., fluorine and chlorine) species act as etchants. To perform a purely inhibition treatment, one example includes treating the feature with a nitrogen-containing chemistry that does not contain halogens. To perform a

purely etch treatment, treatment includes exposing the Mo film to a halogen-containing chemistry that does not contain nitrogen. Other inhibition chemistries (e.g., oxygen-containing chemistries) may be used in some embodiments. Exposing the film to both a nitrogen-containing and halogen-containing chemistry (e.g., nitrogen trifluoride (NF_3) or ammonia/fluorine (NH_3/F_2)) can both inhibit and etch.

[0182] Figure 14B shows a feature after a deposition, etch, deposition sequence. A conformal ALD process may be used to deposit Mo into the features. As shown, Mo is deposited conformally around each of the features, evenly from the exterior (slit side) to the interior (non-slit side). Following the deposition, an etch operation may be performed. The etch may etch non-conformally such that the etch removes more of the Mo film on the exterior part of the wordline. In the exterior portion of the wordline, the oxide of the feature may be exposed. The interior portion of the wordline may be etched less such that Mo may remain on the interior features. A second deposition operation may performed after the etch operation shown. The deposition may be selective to the Mo film remaining on the film. Thus, the film deposited in the subsequent deposition may be deposited selective to the inner portion of the wordline. As Mo starts to grow, the deposition may become conformal. As shown, after the subsequent deposition, the Mo film may be thicker on the inner portion of the feature compared to the outer portion of the feature.