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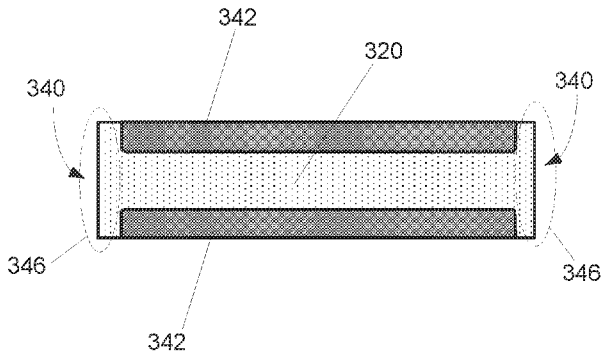


FIG. 3

(57) Abstract: Methods and apparatuses are described that provide tungsten deposition with low roughness. In some embodiments, the methods involve co-flowing nitrogen with hydrogen during an atomic layer deposition process of depositing tungsten that uses hydrogen as a reducing agent. In some embodiments, the methods involve depositing a cap layer, such as tungsten oxide or amorphous tungsten layer, on a sidewall surface of a 3D NAND structure. The disclosed embodiments have a wide variety of applications including depositing tungsten into 3D NAND structures.

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ATOMIC LAYER DEPOSITION ON 3D NAND STRUCTURES

INCORPORATION BY REFERENCE

[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 its entirety and for all purposes.

BACKGROUND

[0002] Deposition of tungsten-containing materials is an integral part of many semiconductor fabrication processes. These materials may be used for horizontal interconnects, vias between adjacent metal layers, and contacts between metal layers and devices. However, as devices shrink and more complex patterning schemes are utilized in the industry, deposition of thin tungsten films becomes a challenge. Deposition in complex high aspect ratio structures such as 3D NAND structures is particularly challenging.

[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

[0004] One aspect of the disclosure relates to a method including providing a structure to be filled with a tungsten-containing material and exposing the structure to multiple deposition cycles, where each deposition cycle includes sequentially delivering a dose of hydrogen (H_2) co-flowed with nitrogen (N_2) and a dose of a tungsten precursor to a chamber housing the structure.

[0005] In some embodiments, the structure is a partially fabricated three-dimension (3-D) NAND structure including sidewalls and a plurality of openings in the sidewalls leading to a plurality of features having a plurality of interior regions fluidically accessible through the openings. In some embodiments, the dose of the tungsten precursor is delivered at a pressure

of at least 300 Torr. In some embodiments, the dose of the tungsten precursor is delivered without nitrogen. In some embodiments, the N_2 is between 10–30% (vol.) of the total $N_2 + H_2$ flow. In some embodiments, the substrate temperature is no more than 350°C during the dose of H_2 co-flowed with N_2. In some embodiments, the N_2 is greater than 30% (vol) of the total $N_2 + H_2$ flow and the substrate temperature is at least 375°C during the dose of H_2 co-flowed with N_2. In some embodiments, the tungsten precursor is tungsten hexafluoride. In some embodiments, the tungsten precursor is a chlorine-containing tungsten precursor. In some embodiments, the dose of the tungsten precursor is delivered at a higher pressure than the dose of the H_2 co-flowed with N_2.

[0006] Another aspect of the disclosure relates to a method including: providing a structure having gaps to be filled with a tungsten-containing material; exposing the structure to multiple deposition cycles, where each deposition cycle includes sequentially delivering a dose of hydrogen (H_2) and a dose of a tungsten precursor to deposit a bulk tungsten film in the gaps; and forming a cap layer on the bulk layer.

[0007] In some embodiments, the structure is a partially fabricated three-dimension (3-D) NAND structure including sidewalls and a plurality of openings in the sidewalls leading to the gaps to be filled with tungsten. In some embodiments, the cap layer is a tungsten oxide layer. In some embodiments, the cap layer is an amorphous tungsten layer. In some embodiments, the structure is provided to a multi-station deposition chamber and where the multiple deposition cycles are performed in one or more first stations of the multi-station deposition chamber and the cap layer is formed in one or more second station of the multi-station deposition chamber. In some embodiments, the cap layer is deposited on the sidewalls.

[0008] A further aspect of the disclosure relates to a method including: (a) depositing a tungsten nucleation layer in a feature on a substrate by alternating pulses of a tungsten precursor and a boron-containing reducing agent; (b) depositing a tungsten template layer on the tungsten nucleation layer by alternating pulses of a tungsten precursor and hydrogen (H_2) at a substrate temperature between 250°C and 350°C; (c) after (b), raising the substrate temperature by at least 50°C, and (d) after (c), depositing a tungsten bulk layer by alternating pulses of a tungsten precursor and hydrogen (H2) at a substrate temperature of at least 350°C. In some embodiments, the tungsten nucleation layer is deposited to a thickness of no more than 30 Angstroms.

[0009] Yet another aspect of the disclosure relates to an apparatus including: a process

chamber having one or more stations each configured to hold a substrate; one or more process gas inlets for coupling to a hydrogen (H_2) gas source, a nitrogen (N_2) gas source, and a tungsten precursor gas source; and a controller for controlling operations in the apparatus, including machine-readable instructions for sequentially delivering a dose of hydrogen (H_2) co-flowed with a nitrogen (N_2) and a dose of a tungsten precursor to the process chamber.

[0010] These and other aspects are described further below with reference to the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1A presents a cross-sectional side-view of a 3-D NAND structure that may be filled with tungsten according to the embodiments described herein.

[0012] Figure 1B presents a cross-sectional top-down view of the -D NAND in Figure 1A.

[0013] Figures 2A and 2B are process flow diagrams depicting operations for methods in accordance with certain disclosed embodiments.

[0014] Figure 2C is a timing sequence diagram showing example cycles in methods for depositing films in accordance with certain disclosed embodiments.

[0015] Figure 3 presents a cross-sectional side-view of a filled wordline feature of a 3D-NAND structure.

[0016] Figure 4 is a timing sequence diagram showing example cycles in methods for depositing films in accordance with certain disclosed embodiments.

[0017] Figures 5A-5D are process flow diagrams depicting operations for methods in accordance with certain disclosed embodiments.

[0018] Figure 6 is a schematic diagram of an example process tool for performing certain disclosed embodiments.

[0019] Figure 7 is a schematic diagram of an example station for performing certain disclosed embodiments.

[0020] Figure 8 is a schematic diagram showing basic features of a manifold system that may be used in accordance with certain embodiments.

DETAILED DESCRIPTION

[0021] 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 with the specific embodiments, it will be understood that it is not intended to limit the disclosed embodiments.

[0022] Tungsten (W) fill of features is often used in semiconductor device fabrication to form electrical contacts. In conventional methods of depositing tungsten films, a nucleation tungsten layer is first deposited into a via or contact. In general, a nucleation layer is a thin conformal layer that serves to facilitate the subsequent formation of a bulk material thereon. The tungsten nucleation layer may be deposited to conformally coat the sidewalls and bottom of the feature. Conforming to the underlying feature bottom and sidewalls can be critical to support high quality deposition. Nucleation layers are often deposited using atomic layer deposition (ALD) or pulsed nucleation layer (PNL) methods.

[0023] In an ALD or PNL technique, pulses of reactant are sequentially injected and purged from the reaction chamber, typically by a pulse of a purge gas between reactants. A first reactant can be adsorbed onto the substrate, available to react with the next reactant. The process is repeated in a cyclical fashion until the desired thickness is achieved. In the context of the disclosed embodiments, chemical vapor deposition (CVD) embodies processes in which reactants are together introduced to a reactor for a vapor-phase or surface reaction. PNL and ALD processes are distinct from CVD processes and vice versa.

[0024] After the tungsten nucleation layer is deposited, bulk tungsten may be deposited by a CVD process by reducing tungsten hexafluoride (WF_6) using a reducing agent such as hydrogen (H_2). Bulk tungsten is different from a tungsten nucleation layer. Bulk tungsten as used herein refers to tungsten used to fill most or all of a feature, such as at least about 50% of the feature. Unlike a nucleation layer, which is a thin conformal film that serves to facilitate the subsequent formation of a bulk material thereon, bulk tungsten is used to carry current. It may be characterized by larger grain size and lower resistivity as compared to a nucleation film. In various embodiments, bulk tungsten is tungsten deposited to a thickness of at least 50Å.

[0025] There are various challenges in tungsten fill as devices scale to smaller technology

nodes and more complex patterning structures are used. One challenge is conformal deposition in these structures such that there is an even distribution of material throughout the structure. Distribution of a material within a feature or structure may be characterized by its step coverage. For the purposes of this description, "step coverage" is defined as a ratio of two thicknesses. For example, step coverage can be the thickness of the material inside the feature divided by the thickness of the material near the opening. For purposes of this document, the term "inside the feature" represents a middle portion of the feature located about the middle point of the feature along the feature's axis, e.g., an area between about 25% and 75% of the distance or, in certain embodiments, between about 40% and 60% of the distance along the feature's depth measured from the feature's opening, or an end portion of the feature located between about 75% and 95% of the distance along the feature's axis as measured from the opening. The term "near the opening of the feature" or "near the feature's opening" represents a top portion of the feature located within 25% or, more specifically, within 10% of the opening's edge or other element representative of the opening's edge. Step coverage of over 100% can be achieved, for example, by filling a feature wider in the middle or near the bottom of the feature than at the feature opening.

[0026] Another challenge is reducing the fluorine concentration or content in the deposited tungsten film. As compared to larger features, a smaller feature having the same fluorine concentration in the tungsten film as a larger feature affects the performance of the device more substantially. For example, the smaller the feature, the thinner the films are deposited. As a result, fluorine in the deposited tungsten film is more likely to diffuse through the thinner films, thereby potentially causing device failure. For structures such as 3D NAND structures, sidewall roughness is also a challenge.

[0027] The methods and apparatuses provided herein may have one or more of the following advantages. In some implementations, they provide tungsten deposition having reduced roughness. They may do so by providing smoother growth and without an intervening etch operation. Low fluorine tungsten may be deposited. Further, the methods may provide good step coverage. The disclosed embodiments have a wide variety of applications including depositing tungsten into 3D NAND structures.

[0028] 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, 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. The methods are not limit to semiconductor substrates, and may be performed to fill any feature

with metal such as tungsten.

[0029] Figure 1A presents a cross-sectional side-view of a 3-D NAND (also referred to as vertical NAND or VNAND) structure 110 (formed on a semiconductor substrate 103) having VNAND stacks (left 125 and right 126), central vertical structure 130, and a plurality of stacked horizontal features 120 with openings 122 on opposite sidewalls 140 of central vertical structure 130. Note that Figure 1F displays two stacks 125 and 126 of the exhibited 3-D NAND structure 110, which together form the trench-like central vertical structure 130, however, in certain embodiments, there may be more than two stacks arranged in sequence and running spatially parallel to one another, the gap between each adjacent pair of stacks forming a central vertical structure 130, like that explicitly illustrated in Figure 1A. In the example of Figure 1A, the horizontal features 120 are 3-D memory wordline features that are fluidically accessible from the central vertical structure 130 through the openings 122. Although not explicitly indicated in the figure, the horizontal features 120 present in both the 3-D NAND stacks 125 and 126 shown in Figure 1A (i.e., the left 3-D NAND stack 125 and the right 3-D NAND stack 126) 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). In other words, each 3-D NAND stack 125, 126 contains a stack of wordline features that are fluidically accessible from both sides of the 3-D NAND stack through a central vertical structure 130.

[0030] The wordline features in a 3-D NAND stack are typically formed by depositing an alternating stack of silicon oxide and silicon nitride layers, and then selectively removing the nitride layers leaving a stack of oxide layers 142 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 256 horizontal wordline features, or 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 end points).

[0031] Figure 1B presents a cross-sectional top-down view of the same 3-D NAND structure 110 shown in side-view in Figure 1A with the cross-section taken through the horizontal section 160 as indicated by the dashed horizontal line in Figure 1A. The cross-section of Figure 1G illustrates several rows of pillars 155, which are shown in Figure 1A to run vertically from the base of semiconductor substrate 103 to the top of 3-D NAND stack

110. In some embodiments, these pillars 155 are formed from a polysilicon material and are structurally and functionally significant to the 3-D NAND structure 110. In some embodiments, such polysilicon pillars may serve as gate electrodes for stacked memory cells formed within the pillars. The top-view of Figure 1B illustrates that the pillars 155 form constrictions in the openings 122 to wordline features 120 - i.e. fluidic accessibility of wordline features 120 from the central vertical structure 130 via openings 122 (as indicated by the arrows in Figure 1G) is inhibited by pillars 155. 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 120 with tungsten material.

[0032] Figures 2A–2C describe methods that may be performed to fill a 3D NAND structure with low-fluorine and low resistivity tungsten. Turning first to Figure 2A, operations 202-210 of Figure 2A are performed to deposit a tungsten nucleation layer by ALD. In various embodiments described herein, operations 202-210 are performed at lower pressure than the subsequent bulk deposition in operation 280. For example, operations 202–210 may be performed at a low pressure less than about 10 Torr. In some examples, operations 202–210 are performed at a pressure of about 10 Torr, or a pressure of about 3 Torr.

[0033] In some implementations, performing operations 202-210 at a low pressure reduces fluorine concentration in the deposited tungsten film due to a lower partial pressure of a fluorine-containing precursor in the chamber when the film is deposited, such that less fluorine is incorporated into the film.

[0034] In operation 202, the substrate is exposed to a tungsten-containing precursor such as WF_6. For purposes of the description herein, although WF_6 is used as an example of a tungsten-containing precursor, it should be understood that other tungsten-containing precursors may be suitable for performing disclosed embodiments. For example, a metal-organic tungsten-containing precursor may be used. Organo-metallic precursors and precursors that are free of fluorine, such as MDNOW (methylcyclopentadienyl-dicarbonylnitrosyl-tungsten) and EDNOW (ethylcyclopentadienyl-dicarbonylnitrosyl-tungsten) may also be used. Tungsten chlorides (WCl_x) and tungsten hexacarbonyl $W(CO)_6$ The tungsten-containing precursor may include a combination of these compounds. In some embodiments, a carrier gas, such as nitrogen (N_2), argon (Ar), helium (He), or other inert gases, may be flowed during operation 202.

[0035] Operation 202 may be performed for any suitable duration and at any suitable temperature. In some examples, operation 202 may be performed for a duration between about 0.25 seconds and about 30 seconds, about 0.25 seconds to about 5 seconds, or about 0.5 seconds to about 3 seconds. This operation may be performed in some embodiments for a duration sufficient to saturate the active sites on the surface of the substrate.

[0036] In operation 204, the chamber is optionally purged to remove excess WF_6 that did not adsorb to the surface of the substrate. A purge may be conducted by flowing an inert gas at a fixed pressure thereby reducing the pressure of the chamber and re-pressurizing the chamber before initiating another gas exposure.

[0037] In operation 206, the substrate is exposed to a reducing agent to deposit a tungsten nucleation layer. The reducing agent may be a borane, silane, or germane. Example boranes include borane (BH_3), diborane (B_2H_6), triborane, alkyl boranes, aminoboranes, carboboranes, and haloborane. Example silanes include silane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8), alkyl silanes, aminosilanes, carbosilanes, and halosilane. Germanes include Ge_nH_{n+4}, Ge_nH_{n+6}, Ge_nH_{n+8}, and Ge_nH_m, where n is an integer from 1 to 10, and n is a different integer than m. Other germanes may also be used, e.g., alkyl germanes, aminogermanes, carbogermanes, and halogermanes. In general, halogermanes may not have significant reducing potential but there may be process conditions and tungsten-containing precursors suitable for film formation using halogermanes.

[0038] Operation 206 may be performed for any suitable duration. In some examples, Example durations include between about 0.25 seconds and about 30 seconds, about 0.25 seconds to about 5 seconds, or about 0.5 seconds to about 3 seconds. In some embodiments, this operation may be sufficient to react with the adsorbed layer of WF_6 on the surface of the substrate. Operation 206 may be performed for a duration outside of these example ranges. In some embodiments, a carrier gas may be used, such as, for example, argon (Ar), helium (He), or nitrogen (N_2).

[0039] After operation 208, there may be an optional purge step to purge excess reducing agent still in gas phase that did not react with WF_6 on the surface of the feature. A purge may be conducted by flowing an inert gas at a fixed pressure thereby reducing the pressure of the chamber and re-pressurizing the chamber before initiating another gas exposure.

[0040] In operation 210, it is determined whether the tungsten nucleation layer has been deposited to an adequate thickness. If not, operations 202-208 are repeated until a desired thickness of a tungsten nucleation layer is deposited on the surface of the feature. Each

repetition of operations 202-208 may be referred to as an ALD "cycle." In some embodiments, the order of operations 202 and 206 may be reversed, such that reducing agent is introduced first.

[0041] After the tungsten nucleation layer is deposited to an adequate thickness, in operation 280, bulk tungsten is deposited as described below. In various embodiments, operation 280 may be performed at a pressure greater than the pressure during operations 202-210. For example, operation 280 may be performed at a pressure greater than or equal to about 10 Torr, for example about 10 Torr, or about 40 Torr. In some embodiments, the pressure during both the nucleation layer and bulk layer deposition may be about 5–20 Torr, or 10 Torr.

[0042] Figure 2B provides a process flow diagram for operations that may be performed during operation 280. Note that operations of Figure 2B may be performed without performing operations of Figure 2A. Figure 2C provides a timing sequence diagram depicting examples cycles of ALD in a process 200.

[0043] In Figure 2B, in operation 282, the substrate is exposed to a reducing agent, such as H_2. This operation may be referred to as a "pulse" or a "dose," which may be used interchangeably herein. H_2 is pulsed without flowing another reactant. In some embodiments, a carrier gas may be flowed. The carrier gas may be any of those described above with respect to operation 204 in Figure 2A. Operation 282 may be performed for any suitable duration. In some examples, Example durations include between about 0.25 seconds and about 30 seconds, about 0.25 seconds to about 5 seconds, or about 0.5 seconds to about 3 seconds.

[0044] Figure 2C shows H_2 dose 220A in deposition cycle 211A which may correspond with operation 282 of Figure 2B. During a H_2 dose 220A, a carrier gas is flowed, the reducing agent is pulsed, and WF_6 flow is turned off.

[0045] Returning to Figure 2B, in operation 284, the chamber is purged. This purge operation may remove excess H_2 that remained in gas phase. A purge is conducted by flowing an inert gas at a fixed pressure thereby reducing the pressure of the chamber and re-pressurizing the chamber before initiating another gas exposure. The chamber may be purged for any suitable duration, for example, for a duration between about 0.1 seconds and about 3 seconds. Operation 284 of Figure 2B may correspond to purge phase 240A of Figure 2C. As shown in Figure 2C, during purge phase 240A, the carrier gas is flowed but H_2 flow and WF_6 flow are turned off.

[0046] Returning to Figure 2B, in operation 286, the substrate is exposed to a tungsten-containing precursor (e.g., WF_6) to form a sub-monolayer or monolayer of film on the substrate. In various embodiments, WF_6 is flowed to the chamber during this operation for a duration between about 0.1 seconds and about 3 seconds, or about 0.5 seconds. In some embodiments, WF_6 may be diverted to fill the gas line and line change before dosing. In some embodiments, WF_6 is flowed to the chamber but does not fully react with all H_2 molecules on the surface of the substrate. Operation 286 may correspond to WF_6 dose 260A in Figure 2C. As shown in Figure 2C, during the WF_6 dose 260A, the carrier gas is flowed, the H_2 flow is turned off, and the WF_6 flow is turned on.

[0047] In operation 288 of Figure 2B, the chamber is purged to remove reacted byproducts and WF_6 in gas phase from the chamber. In some embodiments, the purge duration is between about 0.1 seconds and about 2 seconds and may prevent removing all of the WF_6 from the substrate surface due to the low adsorption rate of WF_6 to a surface of tungsten. In some embodiments, purge duration is between about 0.1 seconds and about 15 seconds, such as about 7 seconds. For example, for fabrication of a 3D NAND structure, the chamber may be purged for about 7 seconds during operation 288. The purge duration depends on the substrate and stress.

[0048] Operation 288 of Figure 2B may correspond to purge phase 270A of Figure 2C. As shown in Figure 2C, purge phase 270A concludes deposition cycle 211A. In some embodiments, operations 286 and 282 may be reversed such that operation 286 is performed before 282. In some embodiments, operation 282 may be performed before operation 286.

[0049] In operation 290 of Figure 2B, it is determined whether bulk tungsten has been deposited to an adequate thickness. If not, operations 282-288 are repeated until a desired thickness is deposited. In some embodiments, operations 282-288 are repeated until a feature is filled. In Figure 2C, it is determined that bulk tungsten has not been deposited to an adequate thickness, so operations 282-288 of Figure 2B are repeated in deposition cycle 211B, such that an H_2 dose 220B is performed, followed by a purge phase 240B. A WF_6 dose 260B is performed, followed by another purge phase 270B.

[0050] Disclosed embodiments may have various applications in tungsten deposition processes. For example, in some embodiments, a feature may be filled by depositing a tungsten nucleation layer by ALD cycles of alternating pulses of a reducing agent (e.g., a borane, a silane, or a germane) and WF_6, followed by bulk tungsten deposition by using ALD cycles of alternating pulses of H_2 and WF_6. In some embodiments, a tungsten nucleation

layer may be omitted with bulk deposition as described above with reference to Figures 2B and 2C performed directly on an underlying feature or layer. Tungsten films deposited using disclosed embodiments have low fluorine concentrations, low stress, good step coverage, and low resistivity.

[0051] In some aspects, the methods described herein provide smooth films having low roughness. In a 3D NAND structure, for example, the sidewalls 140 of the 3D NAND stacks 125, 126 will have tungsten at the opening of each tungsten wordline deposited at each horizontal feature 120. This is shown at 346 for a single wordline 320 in Figure 3. The tungsten at 346 lines the sidewalls 340 of the stack that includes the wordline 320 and oxide layers 342 and is etched back in subsequent processing. However, sidewall roughness can lead to an uneven profile after etch-back and can eventually lead to etch chemical diffusing into wordline and device failure.

[0052] While CVD techniques can result in smooth sidewall coverage, the step coverage and conformality within the feature can be lacking. Provided herein are ALD methods that result in low roughness that may be implemented with the processes described above with reference to Figures 2A-2C. The ALD methods described herein can reduce the surface diffusion of W adatoms that leads to faceting and roughness outside of gaps, such in 3D-NAND central trenches.

[0053] In some embodiments, the methods involve co-flowing nitrogen (N_2) with the reducing agent in operation 282 of Figure 2B. Figure 4 provides a timing sequence diagram depicting examples cycles of ALD in a process 400. The timing sequence diagram is similar to that in Figure 2B, with the addition of co-flowing N_2 during the H dose. In particular, Figure 4 shows H_2 + N_2 dose 420A in deposition cycle 411A which may correspond with operation 282 of Figure 2B. During a H_2 dose 420A, a carrier gas is flowed, H_2 and N_2 are pulsed is pulsed, and WF_6 flow is turned off. The deposition cycle 411A further includes a WF_6 dose 460A and a purge phase 470A as described above with reference to Figure 2C. These operations are repeated as shown at 420B, 440B, 460B, and 470B, in the subsequent deposition cycle. Sidewall roughness is significantly reduced using the timing sequence shown in Figure 4 as compared to one without nitrogen flow during the H_2 operation. In particular, it was found to reduce sidewall roughness by about half. This may be due to N_2 addition on the surface inhibiting the W adsorbed atom (adatom) diffusion and suppressing tungsten growth at the feature corners. Notably, flowing N_2 during the reducing agent dose was found to reduce roughness more than if flowed during the tungsten precursor pulse.

[0054] According to various embodiments, N_2 may represent about 10-30% (vol.) of the total N_2+H_2 flow. Higher N_2 flows may be used, which can lead to a further decrease in roughness but an increase in film resistivity and/or stress. Stress increase can be prevented or avoided by using a relatively high temperature, e.g., 375°C or above such as 400°C.

[0055] In some embodiments, roughness is improved by using a chamber pressure of at least 20 Torr, or 25 Torr the ALD process of Figure 2B. For example, deposition cycles 200 and 400 as shown in Figures 2C and 4, respectively, may be performed at about 25 Torr. This shows improvement over 10 Torr, which may be due to reducing W adatom diffusion length. Chamber pressure may be between 20 and 40 Torr for reduced roughness. At pressures higher than 40 Torr, step coverage can be compromised as the process becomes too CVD-like and purging can be difficult.

[0056] In some embodiments, the tungsten precursor is delivered with a high dose pressure during operation 286. As described below, the gas lines may be charged to deliver each reactant. Delivering the tungsten precursor at a high charge pressure, e.g., at least 300 Torr or about 400 Torr, results in lower roughness. This may be due to higher adsorption on the surface, which limits the adatom diffusion. In some embodiments, the tungsten precursor is delivered at pressures between 400 Torr and 700 Torr.

[0057] Table 1, below, shows the reduction in roughness achieved for different process conditions within the scope of the disclosure. Tungsten was deposited in a 3-D NAND structure to fill wordline features and sidewall roughness was measured

Process	**A – baseline**	**B**	**C**	**D**
Tungsten precursor pulse	WF6	WF6	WF6	WF6
Reducing agent pulse	H2	H2-N2 (N2 between 10%-30% of total H2 + N2)	H2	H2
Chamber Pressure	10 Torr	10 Torr	25 Torr	10 Torr
WF6 charge	180 Torr	180 Torr	180 Torr	400 Torr

RMS sidewall roughness	3.67 nm	1.69 nm	2.32 nm	2.61 nm

[0058] At high temperatures, the sidewall roughness can be reduced by co-flowing N_2 with WF_6. For example, at temperatures greater than 400°C, co-flowing N_2 with WF_6 (or other precursor) has been shown to reduce roughness from 7.4 nm to 3.5 nm. The N_2 may be from 10%–90% vol. of the total N_2 + WF_6 flow, with higher N_2 resulting in lower roughness without degrading film properties. At lower temperatures (e.g., 300°C), the roughness may not be improved. This is in contrast to the other methods described above in which roughness can be reduced at low temperatures such as 300°C.

[0059] Figure 5A is a process flow diagram showing another method of filling a structure having gaps with tungsten. In some embodiments, the structure is a 3D NAND structure as shown in Figure 1A. The method begins at an operation 502 with depositing a tungsten nucleation layer to conformally line the structure with tungsten. Operation 502 may be performed as described above with reference to operations 202-210 of Figure 2A. In some embodiments, silicon-containing and/or boron-containing reducing agents are employed during the tungsten nucleation layer deposition. In some embodiments, operation 502 may be omitted, as described above. Next, a bulk tungsten layer is deposited by ALD to fill gaps in the structure in an operation 504. Operation 504 may be performed as described above with reference to operations 282-290 of Figure 2A and/or timing sequence diagrams 200 and 400 in Figures 2C and 4, respectively. However, rather than allow the deposition to continue to deposit outside the feature (e.g., at 346 in the example of Figure 4), the deposition is stopped at an operation 506. At this point, the interior of the wordline feature may be completely or filled. A cap layer is then formed on the bulk tungsten in an operation 508. The cap layer is a relatively thin layer – thinner than the bulk tungsten layer – and may be deposited by CVD or ALD in some embodiments. Example thickness range from 100–200 Angstroms. Examples of cap layers include amorphous tungsten and tungsten oxide layers. The cap layer may be formed only outside of the wordline features.

[0060] In some embodiments, block 508 involves CVD deposition of a cap layer on the sidewalls of a 3D-NAND structure. CVD deposition on 3D-NAND structures has improved sidewall smoothness. This is because of its higher deposition rate, allowing less time for W adatom surface diffusion. Accordingly, transitioning from block 506 to block 508 can involve transitioning from alternating pulses of tungsten precursor and (hydrogen or other

reducing agent) to concurrent introduction of the tungsten precursor and the reducing agent into the deposition chamber.

[0061] In some embodiments, block 508 involves forming a tungsten oxide cap layer on the sidewalls of a 3D-NAND structure. This can involve depositing a relatively thin ALD layer of tungsten following the timing sequences of Figures 2C or 4, for example,, then exposing the structure to air to oxide the layer and then repeating. For example, block 508 can involve ALD deposition of about 20 Angstroms of tungsten, oxidation and repeat to form 100-200 Angstroms of tungsten oxide.

[0062] In some embodiments, block 508 can involve deposition of an ALD tungsten layer formed by a method as described above with respect to Figure 2A. While the cap layer is not a "nucleation" layer in the sense that there is typically not bulk deposition on it, it can be smoother than the bulk layer. The ALD tungsten layer deposited by a silane or boron reducing agent and a tungsten precursor may be an amorphous tungsten layer.

[0063] Table 2, below, shows the reduction in roughness achieved for different cap layers within the scope of the disclosure. Tungsten was deposited in a 3-D NAND structure to fill wordline features and sidewall roughness was measured

	F – baseline	**G**	**H**	**I**
Cap layer	None	CVD WF6/H2	Tungsten oxide	W "nucleation" layer (ALD WF6/B2H6)
RMS sidewall roughness	3.67 nm	2.06 nm	3.08 nm	1.47 nm

[0064] It should be noted that the higher resistivity of the cap layer can be tolerated as it will be removed during a subsequent etch operations.

[0065] Figure 5B is a process flow diagram showing another method of filling a structure having gaps with tungsten. In Figure 5B, operations 602 and 604 may be performed as described above with respect to Figure 5A. At 556, crystal growth of the ALD layer is stopped. This can involve stopping the ALD deposition and performing a process to interrupt the grain growth. In some embodiments, block 558 can involve a nitrogen (N_2) soak or a tungsten nucleation layer deposition as described above with respect to Figure 2A. A bulk layer deposition process is then performed as described above with respect to Figures 2C and 4, however, the grain growth begins anew, reducing roughness. In some embodiments, the

bulk layer deposition conditions may be changed from operation 504 to operation 558. For example, operation 504 may involve a timing diagram as described in Figure 2C, without nitrogen co-flow, with nitrogen added as in Figure 4 for operation 558. Similarly, the chamber pressure and/or tungsten delivery pressure may be increased in operation 558.

[0066] Figure 5C is a process flow diagram showing method of filling a 3D-NAND structure with tungsten. The method described in Figure 5C may also be applied to other structures having gaps to be filled. The method begins at an operation 562 with depositing a tungsten nucleation layer to conformally line the wordline features with tungsten. Operation 562 may be performed as described above with reference to operations 202-210 of Figure 2A. In some embodiments, silicon-containing and/or boron-containing reducing agents are employed during the tungsten nucleation layer deposition. In some embodiments, operation 502 may be omitted, as described above. Next, a bulk tungsten layer is deposited by ALD to fill the wordline features in the structure in an operation 564. Operation 564 may be performed as described above with reference to operations 282-290 of Figure 2A and/or timing sequence diagrams 200 in Figure 2C. Once the wordline features are filled, a smooth bulk tungsten layer is deposited outside of the wordline features in an operation 566. Operation 566 may use one or more of the techniques described above: adding N_2 to the H_2 pulses, increasing process pressure, increasing tungsten precursor delivery pressure, depositing a cap layer, and interrupting grain growth. In some embodiments, the transition from operation 564 to 566 is gradual; e.g., nitrogen may be gradually added to the reducing agent pulse as the wordline features near completion. It should also be noted that the wordline features may fill at different times; operation 566 may be implemented after some or all of the features are filled.

[0067] Figure 5D is a process flow diagram showing another method of filling a 3D-NAND structure with tungsten. The method described in Figure 5D may also be applied to other structures having gaps to be filled. The method begins at an operation 582 with depositing a thin tungsten nucleation layer to conformally line the wordline features with tungsten. Operation 582 may be performed as described above with reference to operations 202-210 of Figure 2A. In some embodiments, silicon-containing and/or boron-containing reducing agents are employed during the tungsten nucleation layer deposition. In the method of Figure 5D, however, the deposited nucleation layer is thinner than what otherwise be deposited. Ranges for nucleation layers in operation 582 may be between about 15Å –25Å, as opposed to 25Å–40Å that may be used in certain other embodiments. Reducing the nucleation thickness can effectively change the nucleation site density, thus modulating the grain size of

crystalline growth and reducing roughness. Tungsten nucleation layers of less than 20 Å may be used. However, one drawback of reducing grain size may be an increase in resistivity. An increase in resistivity can occur due to excess boron from the reducing agent being present in the nucleation layer if the nucleation layer is not fully converted. In some embodiments, operation 582 involves mitigating excess boron residue by increasing argon dilution and/or increasing tungsten precursor exposure time. For example, in some embodiments, a B_2H_6:Ar dilution is at least 1:5 or 1:9. This is increased from a 1:3 dilution used in certain other nucleation layer depositions. The dilution can be increased even further, though at levels such as 1:20, the step coverage may be poor. In some embodiments, the dilution level is 1:5–1:12, for example. In some embodiments, the tungsten precursor pulse is of longer duration than the reducing agent pulse, for example at least 1.5 or 2 times as long.

[0068] In some embodiments, a thin template layer of tungsten is then deposited on the nucleation layer in an operation 584. This operation may be performed in addition to or instead of limiting boron incorporation in operation 582. In some embodiments, operation 584 may be omitted if resistance increase is effectively mitigated in operation 584. If performed, operation 584 involves ALD using pulses of WF_6 (or other tungsten precursor) and H_2 reducing agent a low temperatures, of between 250°C–350°C, or in some embodiments, 250°C–325°C, or 250°C–300°C. In some embodiments, temperatures of less than 300°C may be used. Example thicknesses of the template film may be 20Å–50Å, or about 30Å. This low temperature template layer provides a better template for large grain growth in the subsequent bulk tungsten deposition. The method then continues with depositing bulk tungsten on the template layer in an operation 586. This also may be performed by an ALD WF_6/H_2 operation (or using other tungsten precursors) but at higher temperatures, e.g., 350°–450°C, or above 375°C. Examples of total tungsten deposition may be about 300Å, including the nucleation layer, template layer, and bulk layer. In some embodiments, for example, a deposition sequence may involve:

ALD deposition of a tungsten nucleation layer: WF_6/B_2H_6 pulses

ALD deposition of a template layer: WF_6/H_2 pulses at 250°C–350°C;

Raise substrate temperature, e.g., at least 50°C;

ALD deposition of bulk layer: WF_6/H_2 pulses at 350°C–450°C

[0069] The method described in Figure 5D may also be implemented in combination with any of the methods that are described above. For example, depositing a thin tungsten nucleation layer as described above, with or without a subsequent template layer, may be

performed in any of the methods described with reference to Figures 5A–5C.

Apparatus

[0070] Any suitable chamber may be used to implement the disclosed embodiments. Example deposition apparatuses include various systems, e.g., ALTUS® and ALTUS® Max, available from Lam Research Corp., of Fremont, California, or any of a variety of other commercially available processing systems. In some embodiments, atomic layer deposition (ALD) may be performed at a first station that is one of two, five, or even more deposition stations positioned within a single deposition chamber. Thus, for example, diborane (B_2H_6) and tungsten hexafluoride (WF_6) may be introduced in alternating pulses to the surface of the semiconductor substrate, at the first station, using an individual gas supply system that creates a localized atmosphere at the substrate surface. Another station may be used for tungsten bulk layer deposition. Another station may be used to deposit a cap layer by CVD. Two or more stations may be used to deposit tungsten in parallel processing. Alternatively a wafer may be indexed to have operations performed over two or more stations sequentially.

[0071] Figure 6 is a schematic of a process system suitable for conducting deposition processes in accordance with embodiments. The system 600 includes a transfer module 603. The transfer module 603 provides a clean, pressurized environment to minimize risk of contamination of substrates being processed as they are moved between various reactor modules. Mounted on the transfer module 603 is a multi-station reactor 609 capable of performing ALD and CVD according to various embodiments. Multi-station reactor 609 may include multiple stations 611, 613, 615, and 617 that may sequentially perform operations in accordance with disclosed embodiments. For example, multi-station reactor 609 may be configured such that station 611 performs a tungsten nucleation layer deposition using a chlorine-containing tungsten precursor or a fluorine-containing precursor, and station 613 performs an ALD tungsten deposition operation according to various embodiments. In some embodiments, station 615 may also form an ALD tungsten deposition operation, and station 617 may perform a CVD operation.

[0072] Stations may include a heated pedestal or substrate support, one or more gas inlets or showerhead or dispersion plate. An example of a deposition station 700 is depicted in Figure 7, including substrate support 702 and showerhead 703. A heater may be provided in pedestal portion 701.

[0073] Returning to Figure 6, also mounted on the transfer module 503 may be one or more single or multi-station modules 607 capable of performing plasma or chemical (non-plasma)

pre-cleans, other deposition operations, or etch operations. The module may also be used for various treatments to, for example, prepare a substrate for a deposition process. The system 600 also includes one or more wafer source modules 601, where wafers are stored before and after processing. An atmospheric robot (not shown) in the atmospheric transfer chamber 619 may first remove wafers from the source modules 601 to loadlocks 621. A wafer transfer device (generally a robot arm unit) in the transfer module 603 moves the wafers from loadlocks 621 to and among the modules mounted on the transfer module 603.

[0074] In various embodiments, a system controller 629 is employed to control process conditions during deposition. The controller 629 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.

[0075] The controller 629 may control all of the activities of the deposition apparatus. The system controller 629 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 associated with the controller 629 may be employed in some embodiments.

[0076] Typically there will be a user interface associated with the controller 629. 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.

[0077] 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 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.

[0078] The computer program code for controlling the germanium-containing reducing agent pulses, hydrogen flow, and tungsten-containing precursor pulses, 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.

[0079] 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.

[0080] Signals for monitoring the process may be provided by analog and/or digital input connections of the system controller 629. The signals for controlling the process are output on the analog and digital output connections of the deposition apparatus 600.

[0081] The system software may be designed or configured in many different ways. For example, various chamber component subroutines or control objects may be written to control 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.

[0082] In some implementations, a controller 629 is part of a system, which may be part 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 electronics may be referred to as the "controller," which may control various components or subparts of the system or systems. The controller 629, 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 (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.

[0083] Broadly speaking, the controller may be defined as electronics having various 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 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.

[0084] The controller 629, 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, or a combination thereof. For example, the controller 629 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 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 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. It should be understood that 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 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 chamber.

[0085] 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 physical vapor deposition (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.

[0086] 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.

[0087] The controller 629 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 and/or target. 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.

[0088] 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.

[0089] The apparatus may include a gas manifold system, which provides line charges to the various gas distribution lines as shown schematically in Figure 8. Manifold 804 has an input 802 from a source of a tungsten-containing precursor gas (not shown), manifold 811 has an input 809 from a source of hydrogen or other reducing gas (not shown) and manifold 821 has an input 819 from a source of inert purge gas (not shown). The manifolds 804, 811 and 821 provide the tungsten-containing precursor gas, reducing gas and purge gas to the

deposition chamber through valved distribution lines, 805, 813 and 825 respectively. The various valves are opened or closed to provide a line charge, i.e., to pressurize the distribution lines. For example, to pressurize distribution line 805, valve 806 is closed to vacuum and valve 808 is closed. After a suitable increment of time, valve 808 is opened and the tungsten-containing precursor gas is delivered to the chamber. Charging the tungsten precursor to a high pressure during ALD deposition of the bulk layer (e.g., to 400 Torr) can improve resistivity in some embodiments. After a suitable time for delivery of the gas, valve 808 is closed. The chamber can then be purged to a vacuum by opening of valve 806 to vacuum.

[0090] Similar processes are used to deliver the reducing gas and the purge gas. To introduce the reducing gas, for example, distribution line 813 is charged by closing valve 815 and closing valve 817 to vacuum. Opening of valve 815 allows for delivery of the reducing gas to the chamber. Similarly, to introduce the purge gas, distribution line 825 is charged by closing valve 827 and closing valve 823 to vacuum. Opening of valve 827 allows for delivery of the argon or other inert purge gas to the chamber. The amount of time allowed for line charges changes the amount and timing of the initial delivery of the gas.

[0091] Figure 8 also shows vacuum pumps in which valves 806, 817 and 823, respectively, can be opened to purge the system. The supply of gas through the various distribution lines is controlled by a controller, such as a mass flow controller which is controlled by a microprocessor, a digital signal processor or the like, that is programmed with the flow rates, duration of the flow, and the sequencing of the processes.

[0092] Note that the processes described above may require precise timing of valves and mass flow controllers (MFCs) supplying pulses of reagent to the semiconductor substrate during deposition. In one way to make this possible, valve and MFC commands are delivered to embedded digital input-output controllers (IOC) in discrete packets of information containing instructions for all time-critical commands for all or a part of a deposition sequence. The ALTUS systems of Lam Research provide at least one IOC sequence. The IOCs can be physically located at various points in the apparatus; e.g., within the process module or on a stand-alone power rack standing some distance away from the process module. There may be multiple IOCs in each module (e.g., 3 per module). With respect to the actual instructions included in a sequence, all commands for controlling valves and setting flow for MFCs (for all carrier and reactant gases) may be included in a single IOC sequence. This assures that the timing of all the devices is tightly controlled from an absolute standpoint and also relative to each other. There are typically multiple IOC sequences running at any given time. This allows for, say, ALD to run at station 1-2 with all timing

controlled for all the hardware components needed to deposit a ALD-W nucleation layer at those stations. A second sequence might be running concurrently to deposit a tungsten bulk using the timing sequence described above at other deposition stations in the same module. The relative timing of the devices controlling the delivery of reagents to stations 3-4 is important within that group of devices, but the relative timing of the ALD process at stations 1-2 can be offset from the relative timing of stations 3-4. An IOC translates the information in a packetized sequence and delivers digital or analog command signals directly to MFC or pneumatic solenoid banks controlling the valves.

[0093] A pulse of tungsten-containing gas may be generated as follows. Initially, the system diverts WF_6 to a vacuum pump for a period of time while the MFC or other flow-controlling device stabilizes. This may be done for a period of between about 0.5 to 5 seconds in one example. Next, the system pressurizes the tungsten gas delivery manifold by closing both the divert outlet 606 and the outlet 608 to the deposition chamber. This may be done for a period of between about 0.1 and 5 seconds, for example, to create an initial burst of reagent when the outlet to the deposition chamber is opened. This is accomplished by opening outlet valve 808 for between about 0.1 and 10 seconds in one example. Thereafter, the tungsten-containing gas is purged from the deposition chamber using a suitable purge gas. The pulsed flow of other reagents may be done in a similar manner.

[0094] 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.

CONCLUSION

[0095] Although the foregoing embodiments have been described in some detail for purposes of clarity of understanding, it will be apparent that certain changes and modifications may be practiced within the scope of the appended claims. It should be noted that there are many alternative ways of implementing the processes, systems, and apparatus of the present embodiments. Accordingly, the present embodiments are to be considered as illustrative and not restrictive, and the embodiments are not to be limited to the details given herein.

CLAIMS

What is claimed is:

1. A method comprising:

providing a structure to be filled with a tungsten-containing material;

exposing the structure to multiple deposition cycles, wherein each deposition cycle comprises sequentially delivering a dose of hydrogen (H_2) co-flowed with nitrogen (N_2) and a dose of a tungsten precursor to a chamber housing the structure.

2. The method of claim 1, wherein the structure is a partially fabricated three-dimension (3-D) NAND structure comprising sidewalls and a plurality of openings in the sidewalls leading to a plurality of features having a plurality of interior regions fluidically accessible through the openings.

3. The method of claim 1, wherein the dose of the tungsten precursor is delivered at a higher pressure than the dose of H_2 co-flowed with N_2.

4. The method of any of claims 1–3, wherein the dose of the tungsten precursor is delivered at a pressure of at least 300 Torr.

5. The method of any of claims 1–3, wherein the dose of the tungsten precursor is delivered without nitrogen.

6. The method of any of claims 1–3, wherein N_2 is between 10–30% (vol.) of the total $N_2 + H_2$ flow of the dose of H_2 co-flowed with N_2.

7. The method of claim 6, wherein the substrate temperature is no more than 350°C during the dose of H_2 co-flowed with N_2.

8. The method of any of claims 1–3, wherein the N_2 is greater than 30% (vol) of the total $N_2 + H_2$ flow and the substrate temperature is at least 375°C during the dose of H_2 co-flowed with N_2.

9. The method of any of claims 1–3, wherein the tungsten precursor is tungsten hexafluoride.

10. The method of any of claims 1–3, wherein the tungsten precursor is a chlorine-containing tungsten precursor.

11. A method comprising:

providing a structure having gaps to be filled with a tungsten-containing material;

exposing the structure to multiple deposition cycles, wherein each deposition cycle comprises sequentially delivering a dose of hydrogen (H_2) and a dose of a tungsten precursor to deposit a bulk tungsten film in the gaps;

forming a cap layer on the bulk tungsten film.

12. The method of claim 11, wherein the structure is a partially fabricated three-dimension (3-D) NAND structure comprising sidewalls and a plurality of openings in the sidewalls leading to the gaps to be filled with tungsten.

13. The method of claim 12, wherein the cap layer is deposited on the sidewalls.

14. The method of any of claims 11–13, wherein the cap layer is a tungsten oxide layer.

15. The method of any of claims 11–13, wherein the cap layer is an amorphous tungsten layer.

16. The method of any of claims 11–13, wherein the structure is provided to a multi-station deposition chamber and wherein the multiple deposition cycles are performed in one or more first stations of the multi-station deposition chamber and the cap layer is formed in one or more second station of the multi-station deposition chamber.

17. A method comprising:

(a) depositing a tungsten nucleation layer in a feature on a substrate by alternating pulses of a tungsten precursor and a boron-containing reducing agent;

(b) depositing a tungsten template layer on the tungsten nucleation layer by alternating pulses of a tungsten precursor and hydrogen (H_2) at a substrate temperature between 250°C and 350°C;

(c) after (b), raising the substrate temperature by at least 50°C; and

(d) after (c), depositing a tungsten bulk layer by alternating pulses of a tungsten precursor and hydrogen (H_2) at a substrate temperature of at least 350°C.

18. The method of claim 17, wherein the tungsten nucleation layer is deposited to a thickness of no more than 30Å.

19. An apparatus comprising:

a process chamber having one or more stations each configured to hold a substrate;

one or more process gas inlets for coupling to a hydrogen (H_2) gas source, a nitrogen (N_2) gas source, and a tungsten precursor gas source; and

a controller for controlling operations in the apparatus, comprising machine-readable instructions for sequentially delivering a dose of hydrogen (H_2) co-flowed with nitrogen (N_2) and a dose of a tungsten precursor to the process chamber.

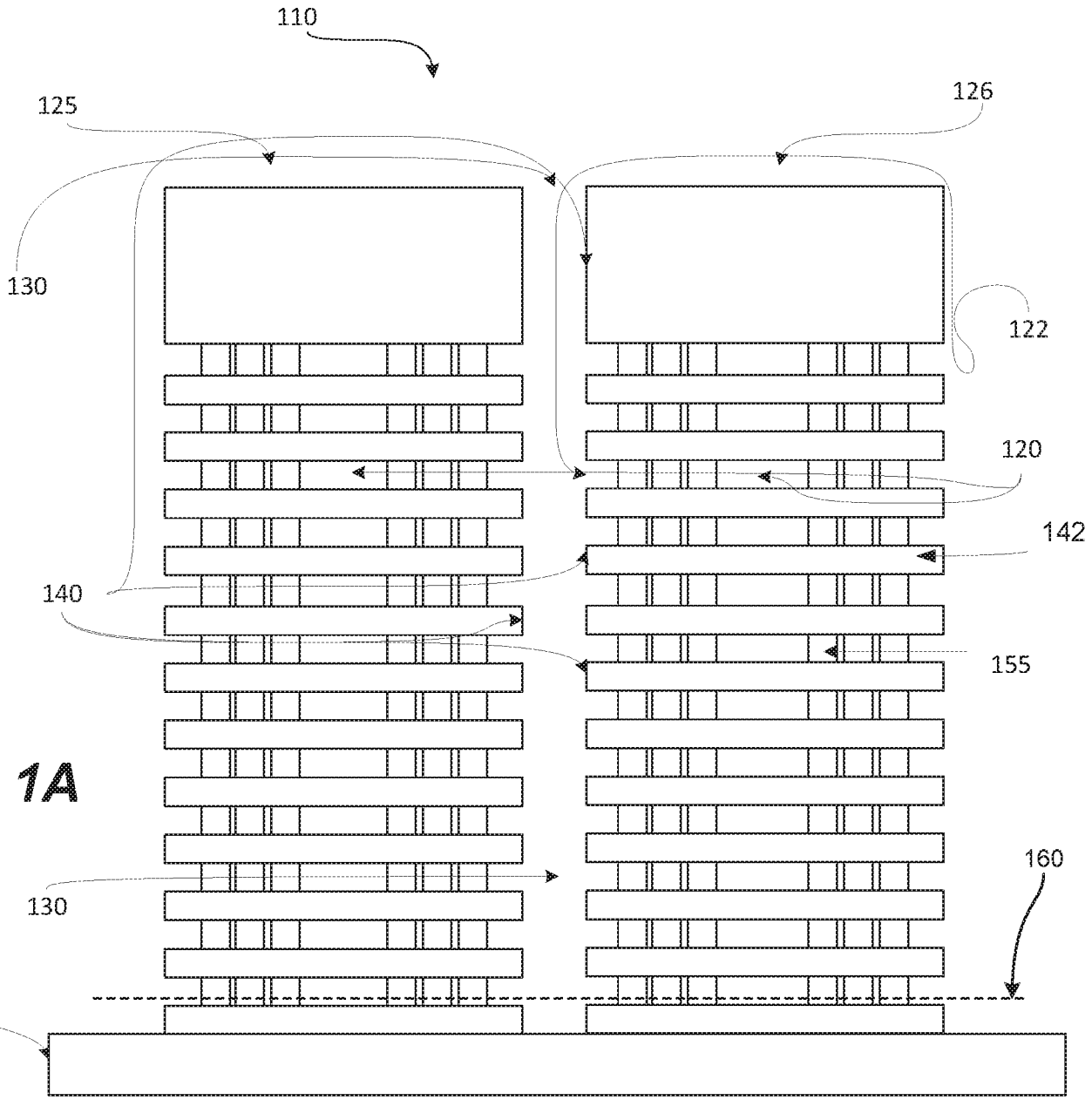


FIG. *1A*

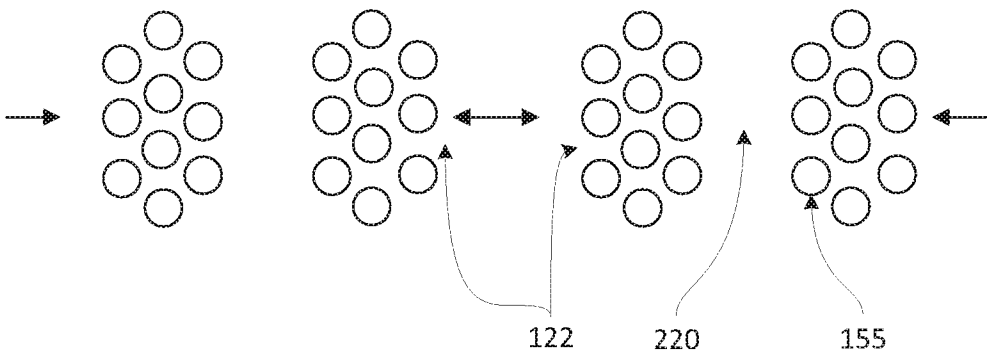


FIG. *1B*

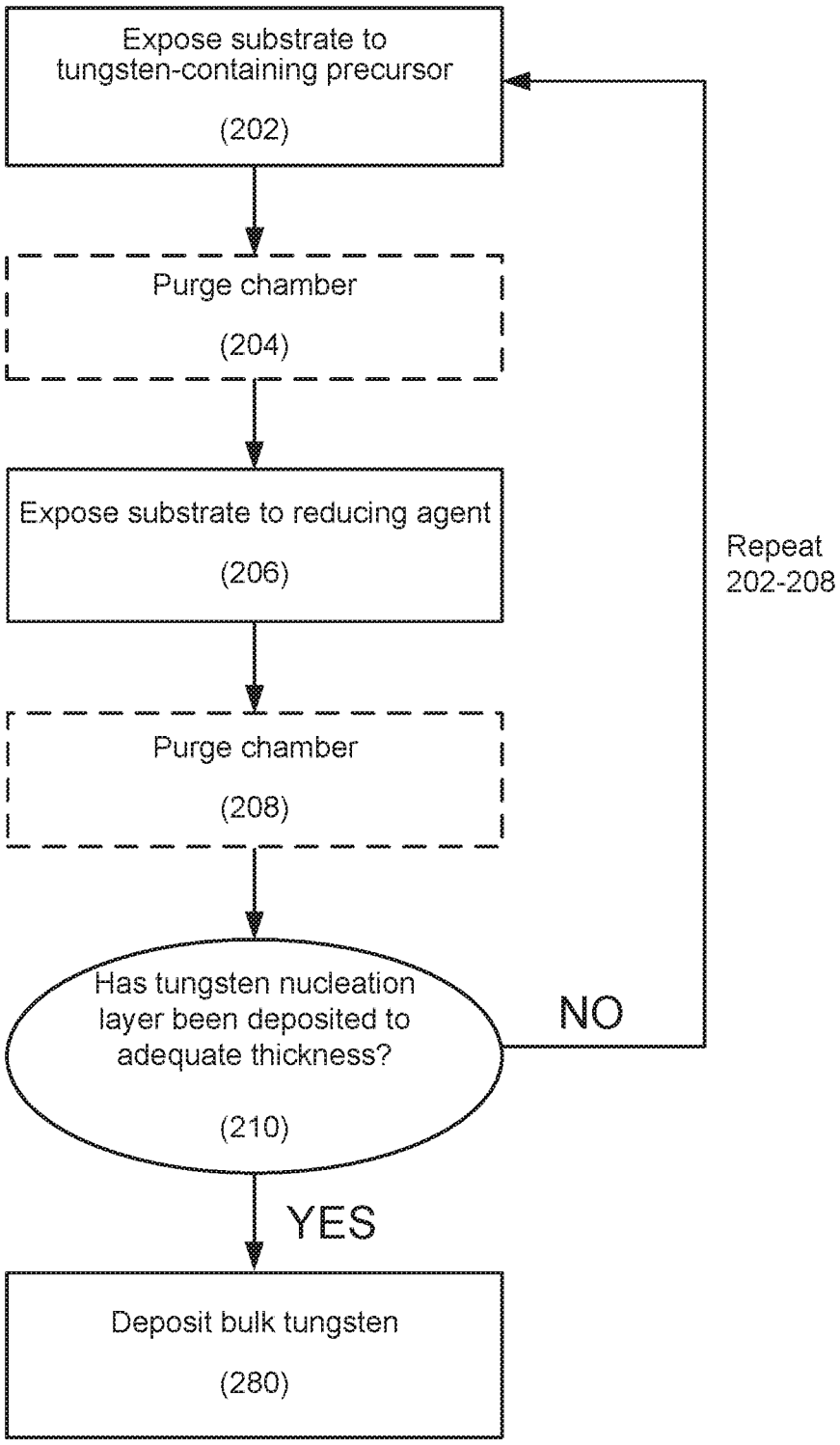

Expose substrate to tungsten-containing precursor
(202)
Purge chamber
(204)
Expose substrate to reducing agent
(206)
Purge chamber
(208)
Has tungsten nucleation layer been deposited to adequate thickness?
(210)
NO
Repeat 202-208
YES
Deposit bulk tungsten
(280)

FIG. 2A

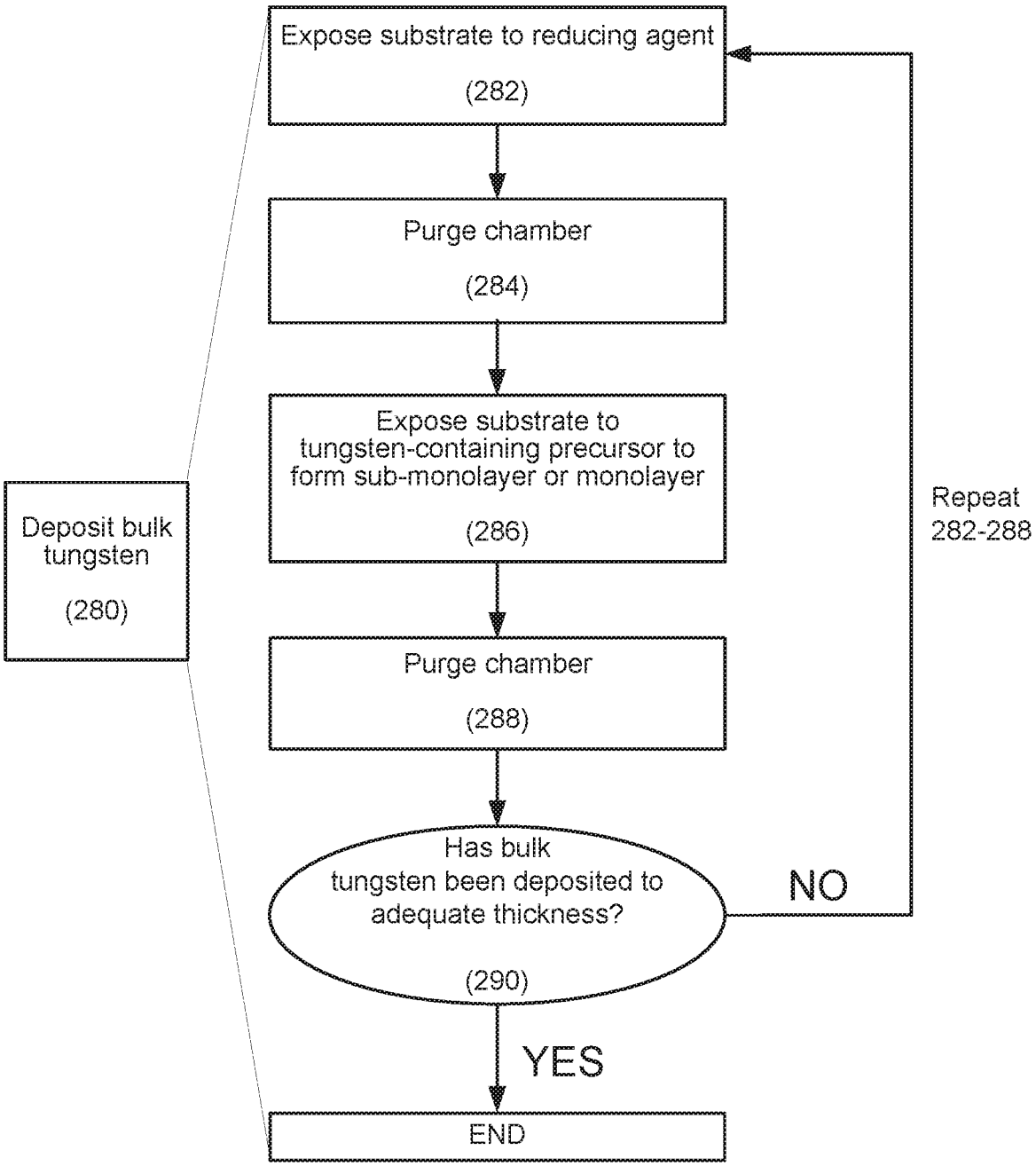

Deposit bulk tungsten
(280)
Expose substrate to reducing agent
(282)
Purge chamber
(284)
Expose substrate to tungsten-containing precursor to form sub-monolayer or monolayer
(286)
Purge chamber
(288)
Has bulk tungsten been deposited to adequate thickness?
(290)
NO
Repeat 282-288
YES
END

FIG. 2B

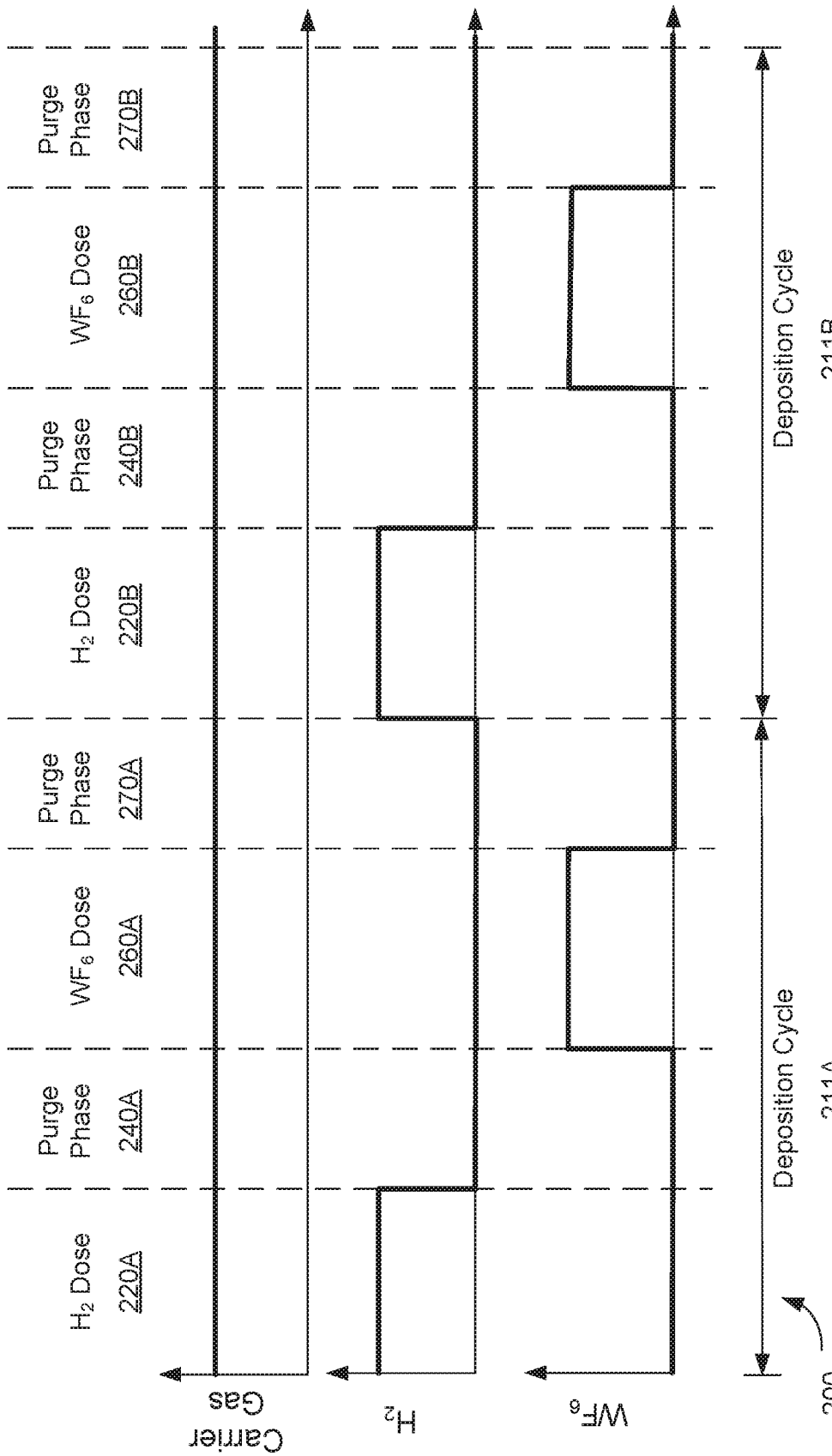

Carrier Gas
H2
WF6
200
Deposition Cycle
211A
Deposition Cycle
211B
H2 Dose
220A
Purge Phase
240A
WF6 Dose
260A
Purge Phase
270A
H2 Dose
220B
Purge Phase
240B
WF6 Dose
260B
Purge Phase
270B

FIG. 2C

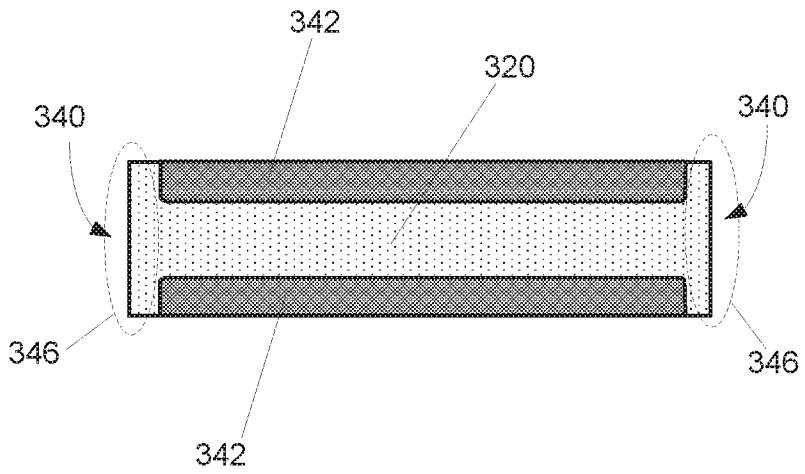


FIG. 3

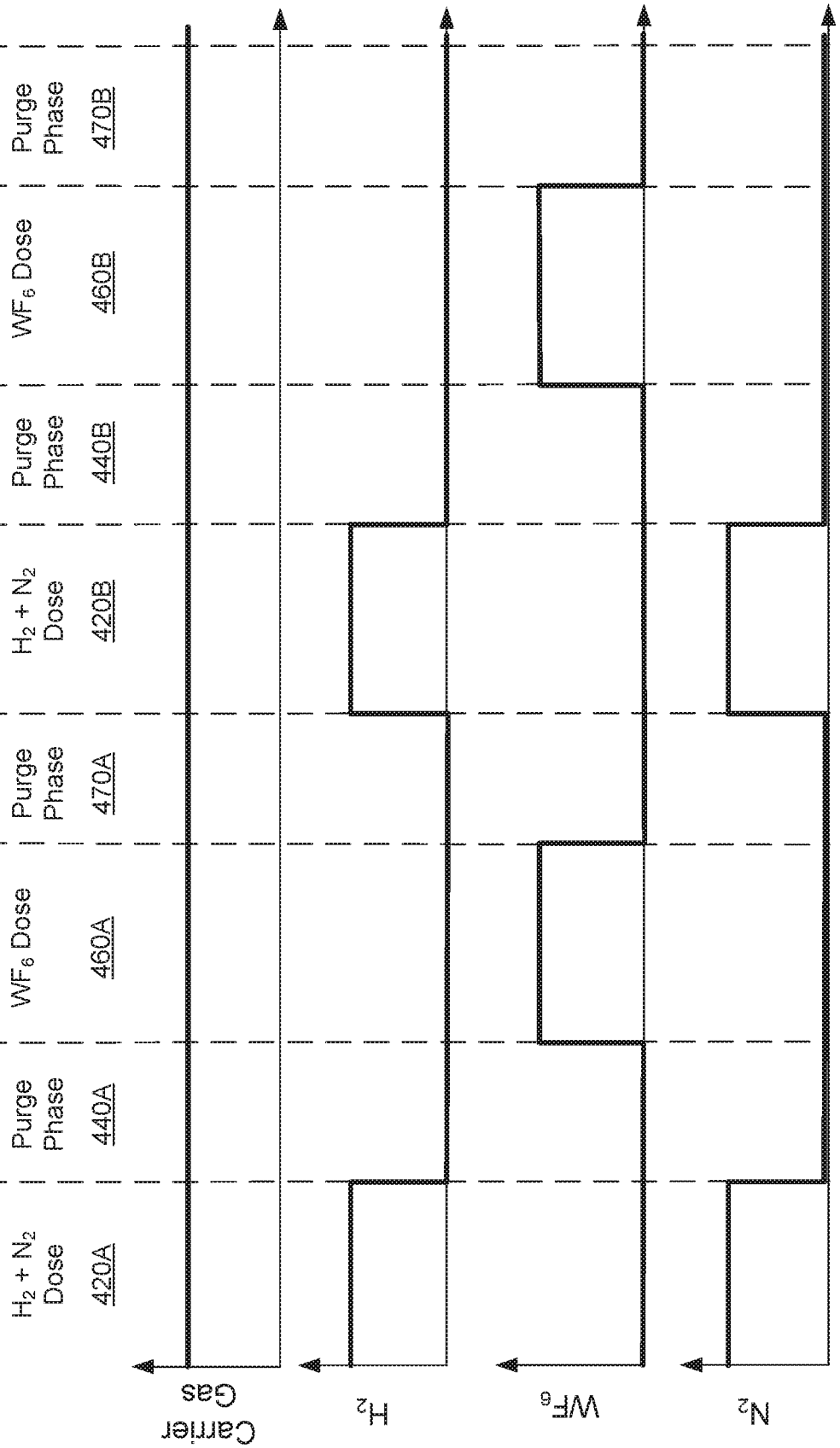

H_2 + N_2 Dose 420A
Purge Phase 440A
WF_6 Dose 460A
Purge Phase 470A
H_2 + N_2 Dose 420B
Purge Phase 440B
WF_6 Dose 460B
Purge Phase 470B
Deposition Cycle 411A
Deposition Cycle 411B
Carrier Gas
H_2
WF_6
N_2
400

FIG. 4

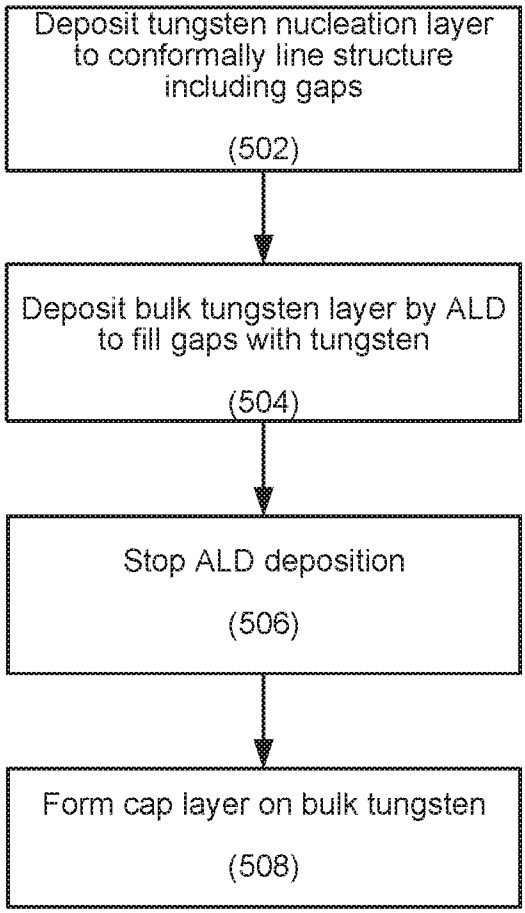

Deposit tungsten nucleation layer to conformally line structure including gaps
(502)
Deposit bulk tungsten layer by ALD to fill gaps with tungsten
(504)
Stop ALD deposition
(506)
Form cap layer on bulk tungsten
(508)

FIG. 5A

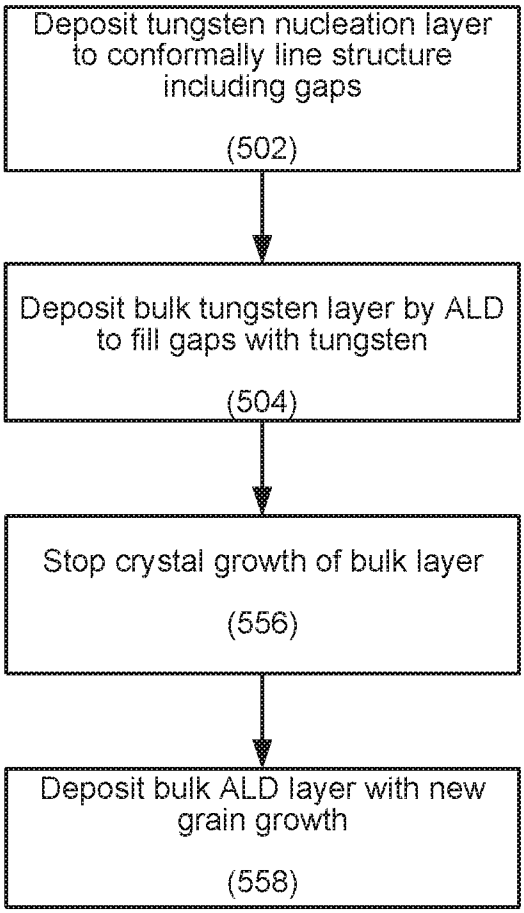

Deposit tungsten nucleation layer to conformally line structure including gaps
(502)
Deposit bulk tungsten layer by ALD to fill gaps with tungsten
(504)
Stop crystal growth of bulk layer
(556)
Deposit bulk ALD layer with new grain growth
(558)

FIG. 5B

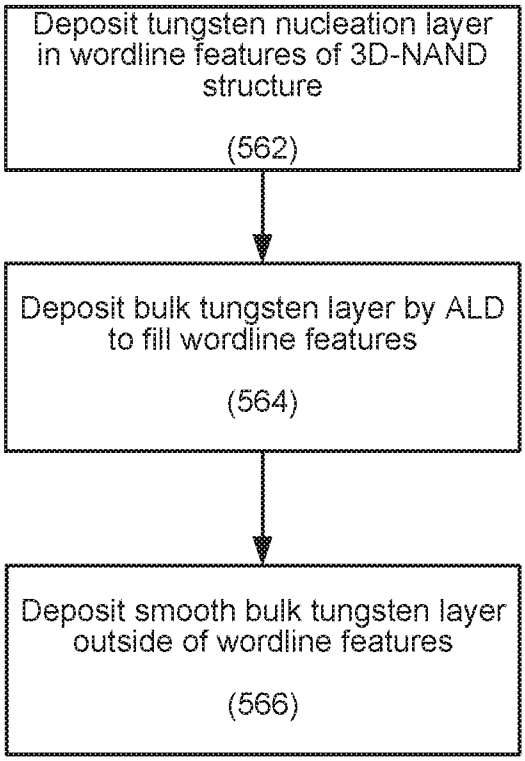

Deposit tungsten nucleation layer in wordline features of 3D-NAND structure
(562)
Deposit bulk tungsten layer by ALD to fill wordline features
(564)
Deposit smooth bulk tungsten layer outside of wordline features
(566)

FIG. 5C

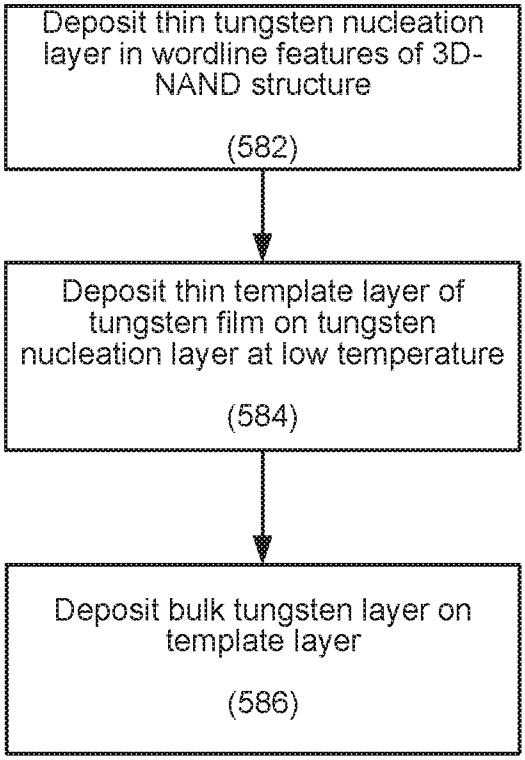

Deposit thin tungsten nucleation layer in wordline features of 3D-NAND structure
(582)
Deposit thin template layer of tungsten film on tungsten nucleation layer at low temperature
(584)
Deposit bulk tungsten layer on template layer
(586)

FIG. 5D

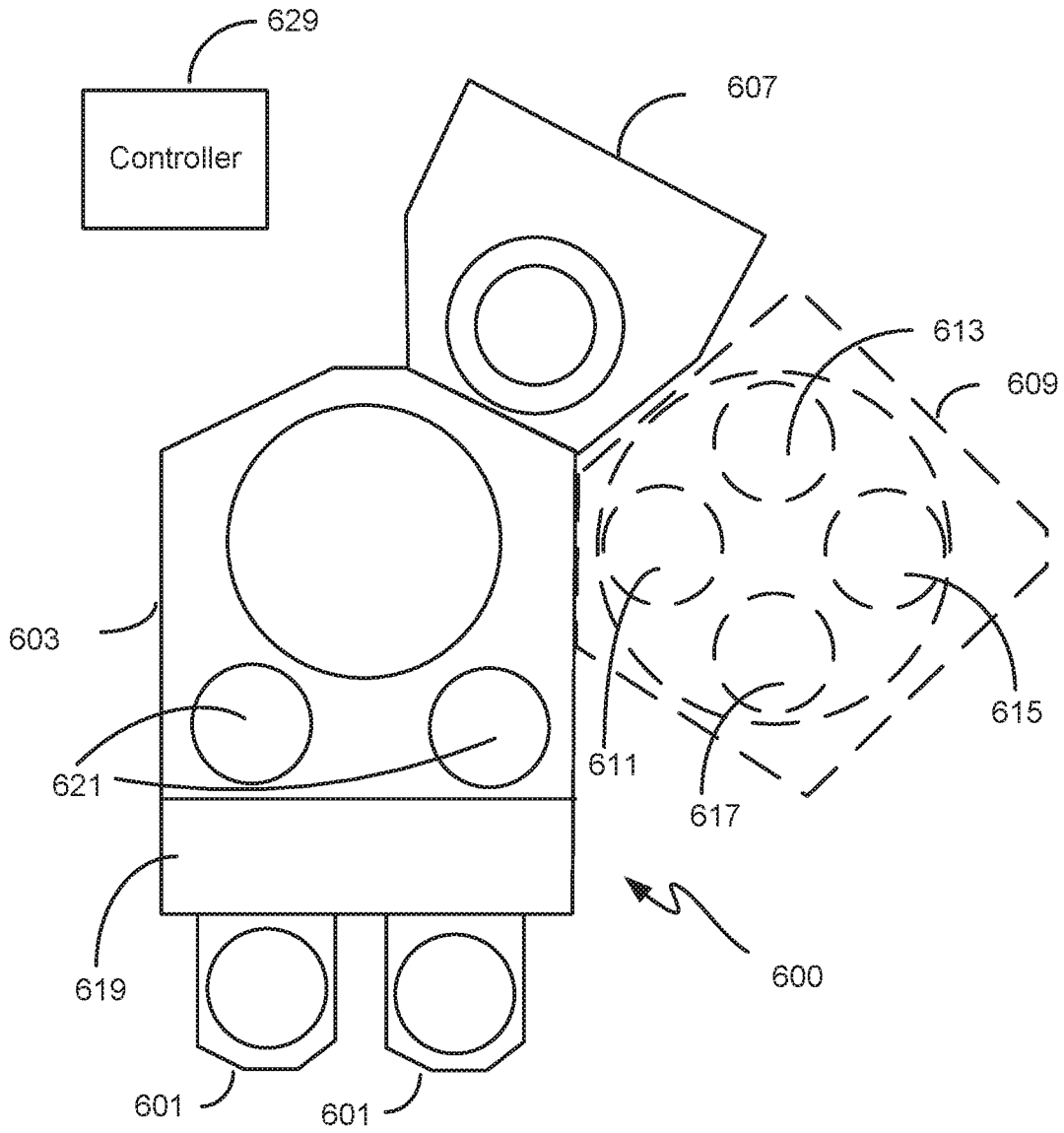


FIG. 6

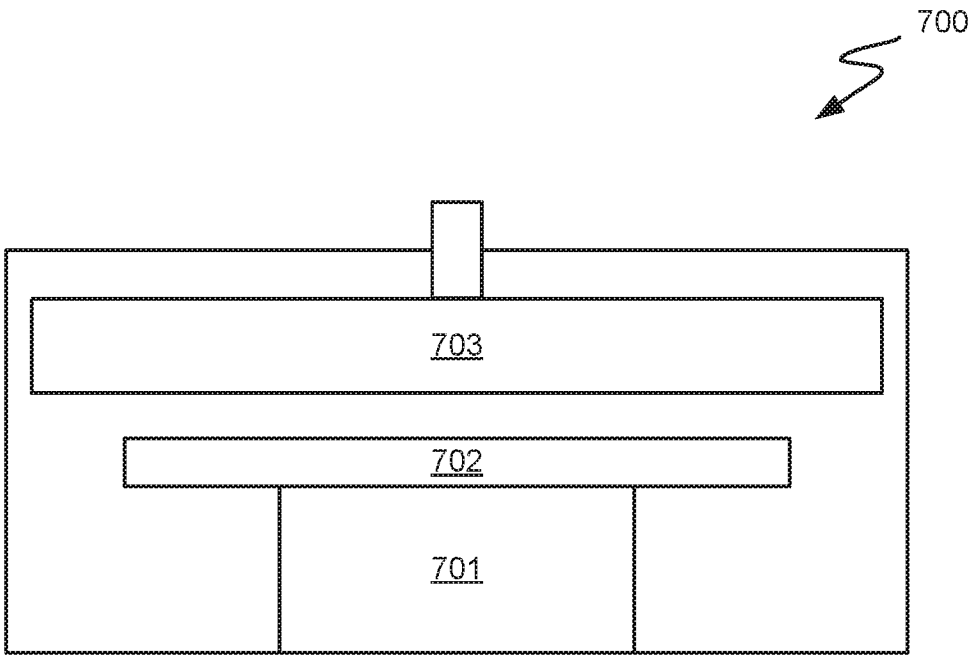


FIG. 7

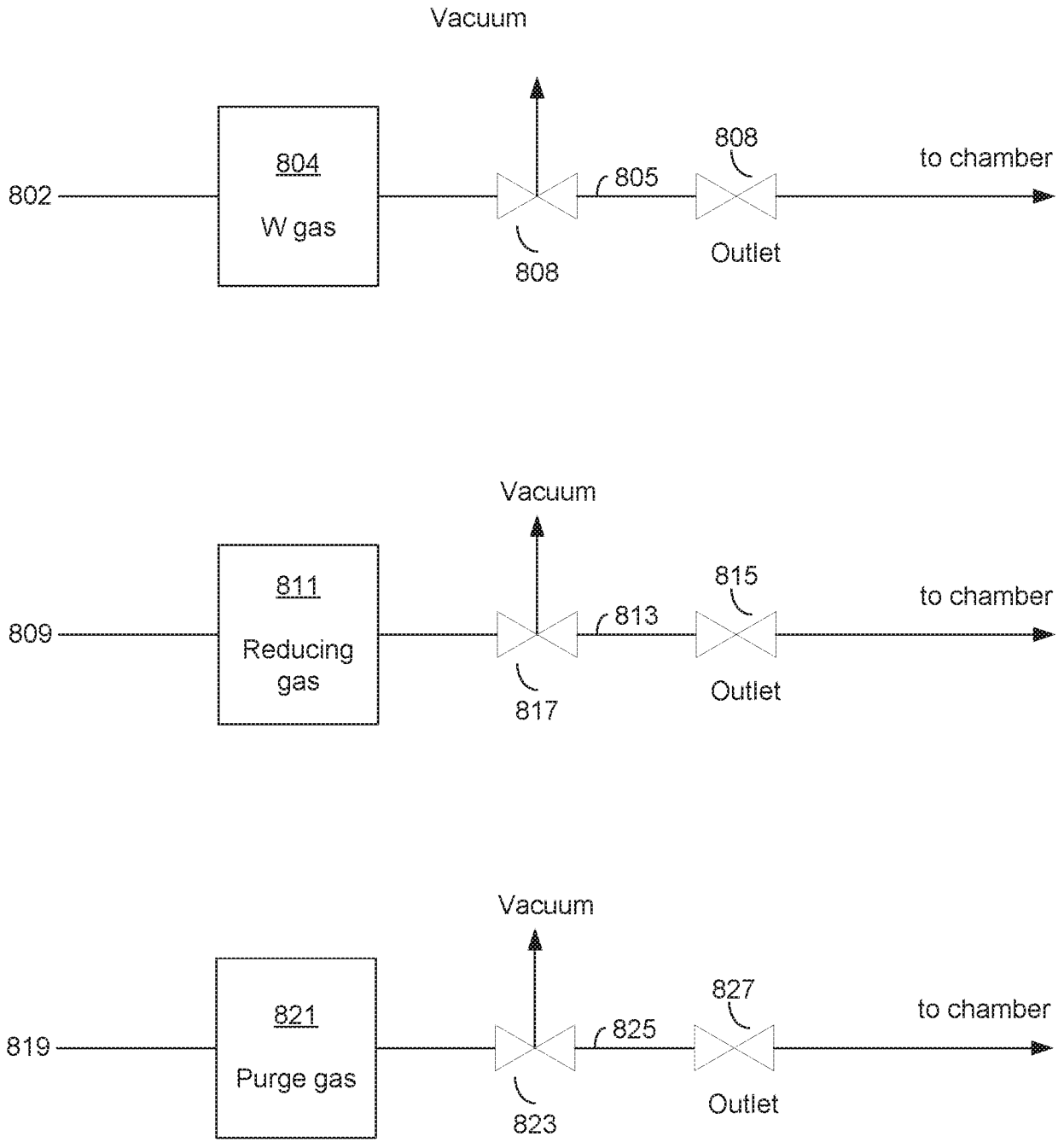

Vacuum
802
804
W gas
808
805
808
Outlet
to chamber
Vacuum
809
811
Reducing gas
817
813
815
Outlet
to chamber
Vacuum
819
821
Purge gas
823
825
827
Outlet
to chamber

FIG. 8

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

H01L 21/285(2006.01)i, H01L 27/11551(2017.01)i, H01L 27/11578(2017.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L 21/285; C23C 016/00; C23C 16/08; C23C 16/455; H01L 21/44; H01L 23/532; H01L 23/535; H01L 27/11551; H01L 27/11578

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: tungsten, nucleation, boron, hydrogen, template, bulk, nitrogen

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005-0031786 A1 (SANG-HYEOB LEE et al.) 10 February 2005 paragraphs [0006], [0013]-[0014], [0028]-[0032], [0074], [0078], [0097], claims 1-7 and figure 4C	1-16,19
A		17-18
A	US 7709385 B2 (MING XI et al.) 04 May 2010 claims 1-5 and figures 3-5	1-19
A	US 7485340 B2 (KAI-ERIK ELERS et al.) 03 February 2009 claims 1, 9-15 and figure 1	1-19
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A	US 2016-0351402 A1 (TOKYO ELECTRON LIMITED) 01 December 2016 claims 1-5 and figure 3	1-19

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
13 April 2020 (13.04.2020)	**13 April 2020 (13.04.2020)**

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