

(19) World Intellectual Property Organization
International Bureau



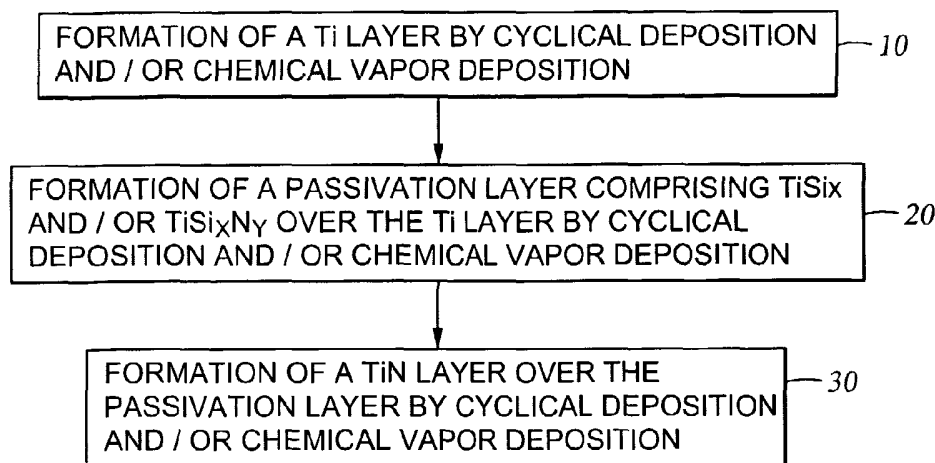
(43) International Publication Date
7 August 2003 (07.08.2003)

PCT

(10) International Publication Number
WO 03/064059 A2

- (51) International Patent Classification⁷: **B05D** (72) Inventors: **YANG, Michael, X.**; 793 Cereza Drive, Palo Alto, CA 94306 (US). **ITO, Toshio**; 2291 Princeton Street, Palo Alto, CA 94306 (US). **XI, Michael**; 138 Beaumere Way, Milpitas, CA 95035 (US).
- (21) International Application Number: PCT/US03/02217
- (22) International Filing Date: 24 January 2003 (24.01.2003) (74) Agents: **PATTERSON, Todd, B.** et al.; Moser, Patterson & Sheridan, LLP, 3040 Post Oak Blvd., Suite 1500, Houston, TX 77056 (US).
- (25) Filing Language: English
- (26) Publication Language: English (81) Designated States (national): JP, KR.
- (30) Priority Data:
60/352,191 26 January 2002 (26.01.2002) US
10/118,664 8 April 2002 (08.04.2002) US
- Published:
— without international search report and to be republished upon receipt of that report
- (71) Applicant: **APPLIED MATERIALS, INC.** [US/US]; 3050 Bowers Avenue, Santa Clara, CA 95054 (US).
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: INTEGRATION OF TITANIUM AND TITANIUM NITRIDE LAYERS



(57) Abstract: Embodiments of the present invention generally relate to an apparatus and method of integration of titanium and titanium nitride layers. One embodiment includes providing one or more cycles of a first set of compounds, providing one or more cycles of a second set of compounds, and providing one or more cycles of a third set of compounds. One cycle of the first set of compounds includes introducing a titanium precursor and a reductant. One cycle of the second set of compounds includes introducing the titanium precursor and a silicon precursor. One cycle of the third set of compounds includes introducing the titanium precursor and a nitrogen precursor. Another embodiment includes depositing a titanium layer utilizing titanium halide. Then, a passivation layer is deposited over the titanium layer utilizing titanium halide. The passivation layer may comprise titanium silicide, titanium silicon nitride, and combinations thereof. Then, a titanium nitride layer is deposited over the passivation layer utilizing titanium halide. Still another embodiment comprises depositing a titanium layer over a surface of a substrate. Then, the titanium layer is treated with a soak with a silicon precursor at a substrate temperature of about 550°C or less to form a treated titanium layer. Then, a titanium nitride layer is deposited over the treated titanium layer.



WO 03/064059 A2

Integration of Titanium and Titanium Nitride Layers

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] Embodiments of the present invention generally relate to an apparatus and method of integration of titanium and titanium nitride layers.

Description of the Related Art

[0002] Reliably producing sub-micron and smaller features is one of the key technologies for the next generation of very large scale integration (VLSI) and ultra large scale integration (ULSI) of semiconductor devices. However, as the fringes of circuit technology are pressed, the shrinking dimensions of interconnects in VLSI and ULSI technology have placed additional demands on the processing capabilities. The multilevel interconnects that lie at the heart of this technology require precise processing of high aspect ratio features, such as vias and other interconnects. Reliable formation of these interconnects is very important to VLSI and ULSI success and to the continued effort to increase circuit density and quality of individual substrates.

[0003] As circuit densities increase, the widths of interconnects, such as vias, trenches, contacts, and other features, as well as the dielectric materials between them, decrease to sub-micron dimensions (e.g., less than 0.20 micrometers or less), whereas the thickness of the dielectric layers remains substantially constant, with the result that the aspect ratios for the features, *i.e.*, their height divided by width, increase. Many traditional deposition processes have difficulty filling sub-micron structures where the aspect ratio exceeds 4:1. Therefore, there is a great amount of ongoing effort being directed at the formation of substantially void-free and seam-free sub-micron features having high aspect ratios.

[0004] In the manufacture of integrated circuits, a titanium/titanium nitride (Ti/TiN) film stack, a titanium nitride layer over a titanium layer, is often used as a

barrier layer to inhibit the diffusion of metals into regions underlying the barrier layer. These underlying regions include transistor gates, capacitor dielectric, semiconductor substrates, metal lines, and many other structures that appear in integrated circuits.

[0005] A Ti layer and a TiN layer may be formed by chemical vapor deposition and/or physical vapor deposition techniques. One example of forming a Ti Layer by chemical vapor deposition includes reacting titanium tetrachloride (TiCl_4) with a hydrogen plasma. One example of forming a TiN layer by chemical vapor deposition includes reacting TiCl_4 with a nitrogen reactant, such as a nitrogen plasma or ammonia (NH_3). One problem with the use of TiCl_4 -based chemistry used to form a TiN layer over a Ti layer is that reliability problems can occur. In particular, the TiN layer may have poor adhesion over the Ti layer resulting in peeling of the TiN layer off the Ti layer.

[0006] Therefore, there is a need for an improved apparatus and method of integration of titanium and titanium nitride layers.

SUMMARY OF THE INVENTION

[0007] Embodiments of the present invention generally relate to an apparatus and method of integration of titanium and titanium nitride layers. One embodiment includes providing one or more cycles of a first set of compounds, providing one or more cycles of a second set of compounds, and providing one or more cycles of a third set of compounds. One cycle of the first set of compounds includes introducing a titanium precursor and a reductant. One cycle of the second set of compounds includes introducing the titanium precursor and a silicon precursor. One cycle of the third set of compounds includes introducing the titanium precursor and a nitrogen precursor. Another embodiment includes depositing a titanium layer utilizing titanium halide. Then, a passivation layer is deposited over the titanium layer utilizing titanium halide. The passivation layer may comprise titanium silicide, titanium silicon nitride, and combinations thereof. Then, a titanium nitride layer is deposited over the passivation layer utilizing titanium halide. Still another embodiment comprises depositing a titanium layer over a surface of a substrate. Then, the titanium layer is treated with a soak with a silicon precursor at a substrate

temperature of about 550°C or less to form a treated titanium layer. Then, a titanium nitride layer is deposited over the treated titanium layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] So that the manner in which the above recited features of the present invention are attained and can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to the embodiments thereof which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0009] Figure 1 is a flow chart illustrating one embodiment of a process of integrating a titanium layer and a titanium nitride layer by forming a titanium silicide layer and/or a titanium silicon nitride layer between the titanium layer and the titanium nitride layer.

[0010] Figure 2A is a graph of the control signals of an exemplary process for cyclical deposition of a material.

[0011] Figure 2B is a graph of the control signals of one exemplary process for chemical vapor deposition of a material.

[0012] Figure 2C is a graph of one exemplary process of the control signals for a combined mode of cyclical deposition and chemical vapor deposition.

[0013] Figure 3A is a flow chart illustrating one embodiment of a process utilizing a continuous flow of a purge gas to deposit a Ti layer, a TiSi_x layer, and a TiN layer by cyclical deposition in the same chamber.

[0014] Figure 3B is a flow chart illustrating one embodiment of a process utilizing pulses of a purge gas to deposit a Ti layer, a TiSi_x layer, and a TiN layer by cyclical deposition in the same chamber.

[0015] Figure 3C is a flow chart illustrating one embodiment of a process utilizing a continuous flow of a purge gas to deposit a Ti layer, a TiSi_xN_y layer, and a TiN layer by cyclical deposition in the same chamber.

[0016] Figure 3D is a flow chart illustrating one embodiment of a process utilizing pulses of a purge gas to deposit a Ti layer, a TiSi_xN_y layer, and a TiN layer by cyclical deposition in the same chamber.

[0017] Figures 4 and 4A are drawings of an exemplary processing chamber that may be used to perform cyclical deposition, chemical vapor deposition, or a combined mode of cyclical deposition and chemical vapor deposition.

[0018] Figure 5 is a flow chart illustrating another embodiment of a process of integrating a Ti layer and a TiN layer by soaking a Ti layer with a flow of a silicon precursor prior to deposition of a TiN layer thereover.

[0019] Figure 6 is a schematic cross-sectional view of one embodiment of an exemplary application of an integrated Ti/TiN film stack.

[0020] Figure 7 is a schematic cross-sectional view of another embodiment of an exemplary application of an integrated Ti/TiN film stack.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Formation of a TiSi_x and/or a TiSi_xN_y film

[0021] Figure 1 is a flow chart illustrating one embodiment of a process of integrating a titanium (Ti) layer and a titanium nitride (TiN) layer by forming a titanium silicide (TiSi_x) layer and/or a titanium silicon nitride (TiSi_xN_y) layer between the Ti layer and the TiN layer. In step 10, a Ti layer may be formed over a substrate structure by cyclical deposition, chemical vapor deposition, or a combined mode of cyclical deposition and chemical vapor deposition. In step 20, a passivation layer comprising titanium silicide and/or titanium silicon nitride may be formed over the Ti layer by cyclical deposition, chemical vapor deposition, or a combined mode of cyclical deposition and chemical vapor deposition. In step 30, a TiN layer may be formed over the passivation layer by cyclical deposition, chemical vapor deposition, or a combined mode of cyclical deposition and chemical vapor deposition.

[0022] Not wishing to be bound by theory, it is believed that the TiSi_x layer or TiSi_xN_y helps protect the interface between the Ti layer and a subsequently deposited TiN layer resulting in improved adhesion of the TiN layer thereover. In the embodiment in which TiN is deposited utilizing a titanium halide, it is believed that the TiSi_x layer or TiSi_xN_y reduces the attack of the halide from the titanium halide used during deposition of TiN and thus provides a Ti/TiN film stack with improved adhesion.

[0023] The term "substrate structure" as used herein is intended to include any workpiece upon which film processing is performed and may be used to denote a substrate, such as a semiconductor substrate or a glass substrate, as well as other material layers formed on the substrate, such as a dielectric layer. The term "cyclical deposition" as used herein refers to the sequential introduction of one or more compounds to deposit a thin layer over a structure and includes processing techniques such as atomic layer deposition. Compounds can be reactants, reductants, precursors, catalysts, and mixtures thereof. Sequentially providing compounds may result in the adsorption of thin layers of the compounds over a substrate structure. The sequential introduction of compounds may be repeated to deposit a plurality of thin layers forming a conformal layer to a desired thickness. The terms "adsorption" and "adsorb" as used herein are defined to include chemisorption, physisorption, or any attractive and/or bonding forces which may be at work and/or which may contribute to the bonding, reaction, adherence, or occupation of a portion of a surface of a substrate structure. The term "chemical vapor deposition" as used herein refers to deposition of materials in a primarily gas-phase and/or thermal co-reaction of compounds to form a layer. A mode of deposition combining cyclical deposition and chemical vapor deposition may also be performed.

[0024] Figure 2A is a graph of the control signals of an exemplary process for cyclical deposition of a material. One cycle 310 comprises introducing a pulse 312 of a first compound 313 into a chamber by opening and closing a valve providing the first compound. After the pulse of the first compound, a pulse 314 of a second compound 315 is introduced into the chamber by opening and closing a valve providing the second compound. The cycle 310 may be repeated to deposit a

desired thickness of the material. The pulses 312 of the first compound 313 and the pulses 314 of the second compound 315 may be delivered with or without a carrier gas. Examples of carrier gases which may be used include, but are not limited to, helium (He), argon (Ar), nitrogen (N₂), hydrogen (H₂), and mixtures thereof. In one embodiment, the pulses 312 of the first compound 313 and the pulses 314 of the second compound 315 may be dosed into a continuous flow of a purge gas. Examples of purge gases which may be used include, but are not limited to, helium (He), argon (Ar), nitrogen (N₂), hydrogen (H₂), and mixtures thereof. In other embodiments, pulses 312 of the first compound 313 and pulses 314 of the second compound 315 may be separated by pulses of a purge gas. In still other embodiments, pulses 312 of the first compound 313 and pulses 314 of a second compound 315 may be separated by pump evacuation alone. In other embodiments, cyclical deposition comprises providing pulses of more than two compounds.

[0025] Figure 2B is a graph of the control signals of one exemplary process for chemical vapor deposition of a material. Chemical vapor deposition of a material may comprise introducing a first compound 323 and a second compound 325 simultaneously to a chamber by opening a valve providing the first compound and by opening a valve providing the second compound. The first compound and the second may be delivered with or without a carrier gas. Examples of carrier gases which may be used include, but are not limited to, helium (He), argon (Ar), nitrogen (N₂), hydrogen (H₂), and mixtures thereof. In other embodiments, chemical vapor deposition comprises providing more than two compounds.

[0026] Figure 2C is a graph of one exemplary process of the control signals for a combined mode of cyclical deposition and chemical vapor deposition. One cycle 330 comprises introducing at least one pulse 332 of a first compound 333 by opening and closing a valve providing the first compound and introducing pulses 334 of a second compound 335 by opening and closing a valve providing the second compound. One or more pulses 334a of the second compound 335 at least partially overlap with one or more pulses 332 of the first compound 333 in which the valve providing the first compound and the valve providing the second compound are both open at the same time for a period of time. One or more pulses 334b, 334c

of the second compound 335 do not overlap with one or more pulses 332 of the first compound 333 in which the valve providing the first compound is closed for a period of time while the valve providing the second compound is open. The cycle 330 may be repeated to deposit a desired thickness of the material. The pulses 332 of the first compound 333 and the pulses 334 of the second compound 335 may be delivered with or without a carrier gas. Examples of carrier gases which may be used include, but are not limited to, helium (He), argon (Ar), nitrogen (N₂), hydrogen (H₂), and mixtures thereof. In one embodiment, the pulses 332 of the first compound 333 and the pulses 334 of the second compound 335 may be dosed into a continuous flow of a purge gas. Examples of purge gases which may be used include, but are not limited to, helium (He), argon (Ar), nitrogen (N₂), hydrogen (H₂), and mixtures thereof. In other embodiments, pulses 332 of the first compound 333 and pulses 334 of the second compound 335 may be separated by pulses of a purge gas. In still other embodiments, pulses 332 of the first compound 333 and pulses 334 of a second compound 335 may be separated by pump evacuation alone. In one aspect, a first compound and a second compound are delivered at separate times to the substrate to provide a deposition process similar to cyclical deposition. In another aspect, a first compound and a second compound are delivered at the same time to the substrate to provide a deposition process similar to chemical vapor deposition. In other embodiments, a combined mode of cyclical deposition comprises providing pulses of more than two compounds.

[0027] Other embodiments of a combined mode of cyclical deposition and chemical vapor deposition are possible. For example, one cycle may comprise providing one pulse of a first compound and one pulse of a second compound in which the pulse of the first compound and the pulse of the second compound only partially overlap in time by opening a valve providing the first compound, then opening a valve providing the second compound, then closing the valve providing the first compound, and then closing the valve providing the second compound.

[0028] Figures 2A and 2C show the duration of pulses of compounds provided over a relative length of time, show a specific order of pulses, and show a specific number of pulses per cycle. In other embodiments, other relative lengths of time, other order of the pulses, and other number of pulses are possible.

[0029] In certain embodiments, deposition of Ti, whether by cyclical deposition, by chemical vapor deposition, or by a combined mode of deposition, comprises utilizing a titanium precursor and a reductant. The titanium precursor preferably comprises titanium tetrachloride (TiCl_4). Examples of other titanium containing compounds include, but are not limited to, titanium iodide (TiI_4), titanium bromide (TiBr_4), other titanium halides, tetrakis(dimethylamino)titanium (TDMAT), tetrakis(diethylamino) titanium (TDEAT), other titanium organic compounds, and derivatives thereof. The reductant comprises a hydrogen plasma. The hydrogen plasma is preferably provided by utilizing a hydrogen gas (H_2). Other hydrogen containing gases which may also be used include silane (SiH_4), borane (BH_3), diborane (B_2H_6), triborane (B_3H_9), among others.

[0030] In certain embodiments, deposition of TiSi_x , whether by cyclical deposition, by chemical vapor deposition, or by a combined mode of deposition, comprises utilizing a titanium precursor and a silicon precursor. The titanium precursor preferably comprises TiCl_4 . Other titanium precursors may be used, such as the titanium precursors described above in regards to the deposition of Ti. The silicon precursor preferably comprises silane (SiH_4). Other silicon containing compounds include, but are not limited to disilane (Si_2H_6), chlorosilane (SiH_3Cl), dichlorosilane (SiH_2Cl_2), trichlorosilane (SiHCl_3), silicon tetrachloride (SiCl_4), hexachlorodisilane (Si_2Cl_6), and derivatives thereof.

[0031] In certain embodiments, deposition of TiSi_xN_y , whether by cyclical deposition, by chemical vapor deposition, or by a combined mode of deposition, comprises utilizing a titanium precursor, a silicon precursor, and a nitrogen precursor. The titanium precursor preferably comprises titanium tetrachloride (TiCl_4) and the silicon precursor preferably comprises silane (SiH_4). Other titanium precursors and silicon precursors may be used, such as the titanium precursors and silicon precursors described above in regards to the deposition of Ti and TiSi_x . The nitrogen precursor preferably comprises ammonia (NH_3). Examples of other nitrogen precursors include, but are not limited to hydrazine (N_2H_4), other N_xH_y compounds with x and y being integers, dimethyl hydrazine ($(\text{CH}_3)_2\text{N}_2\text{H}_2$), t-butylhydrazine ($\text{C}_4\text{H}_9\text{N}_2\text{H}_3$), phenylhydrazine ($\text{C}_6\text{H}_5\text{N}_2\text{H}_3$), 2,2'-azoisobutane ($(\text{CH}_3)_6\text{C}_2\text{N}_2$), ethylazide ($\text{C}_2\text{H}_5\text{N}_3$), and derivatives thereof.

[0032] In certain embodiments, deposition of TiN, whether by cyclical deposition, by chemical vapor deposition, or by a combined mode of deposition, comprises utilizing a titanium precursor and a nitrogen precursor. The titanium precursor preferably comprises titanium tetrachloride (TiCl_4). Other titanium precursors may be used, such as the titanium precursors described above in regards to the deposition of Ti. The nitrogen precursor preferably comprises a nitrogen plasma, NH_3 , or combinations thereof. Examples of other nitrogen precursors include, but are not limited to hydrazine (N_2H_4), other N_xH_y compounds with x and y being integers, dimethyl hydrazine ($(\text{CH}_3)_2\text{N}_2\text{H}_2$), t-butylhydrazine ($\text{C}_4\text{H}_9\text{N}_2\text{H}_3$), phenylhydrazine ($\text{C}_6\text{H}_5\text{N}_2\text{H}_3$), 2,2'-azoisobutane ($(\text{CH}_3)_6\text{C}_2\text{N}_2$), ethylazide ($\text{C}_2\text{H}_5\text{N}_3$), and derivatives thereof. Examples of other nitrogen containing gases which may also be used to generate a nitrogen plasma include, but are not limited to, NH_3 , N_xH_y with x and y being integers (e.g., hydrazine (N_2H_4)), a mixture of hydrogen gas (H_2) and nitrogen gas (N_2), mixtures thereof, other gases or gas mixtures containing hydrogen and nitrogen.

[0033] Referring to Figure 1, in one embodiment, step 10, step 20, and step 30 are performed in separate chambers. In another embodiment, two or more of the steps 10, 20, 30 are performed in the same chamber. In still another embodiment, all of the steps 10, 20, 30 are performed in the same chamber.

[0034] Figure 3A is a flow chart illustrating one embodiment of a process utilizing a continuous flow of a purge gas to deposit a Ti layer, a TiSi_x layer, and a TiN layer by cyclical deposition in the same chamber. As shown in step 602, a substrate is provided to the process chamber. The process chamber conditions, such as for example the substrate temperature and pressure, may be adjusted. In step 604, a purge gas stream is established within the process chamber. Referring to step 606, after the purge gas stream is established within the process chamber, a pulse of a Ti precursor, such as TiCl_4 , is added or dosed into the purge gas stream. In step 608, after the pulse of the Ti precursor a pulse of a reductant, such as a hydrogen plasma, is dosed into the purge gas stream. Step 606 and step 608 are repeated until a predetermined number of cycles are performed to form a Ti layer. Referring to step 610, after a predetermined number of cycles of step 606 and step 608 are performed, another pulse of the Ti precursor is dosed into the purge gas stream. In

step 612, after the pulse of the Ti precursor, a pulse of a Si precursor, such as a SiH_4 , is dosed into the purge gas stream. Step 610 and step 612 are repeated until a predetermined number of cycles are performed to form a TiSi_x layer. Referring to step 614, after a predetermined number of cycles of step 610 and step 612 are performed, another pulse of the Ti precursor is dosed into the purge gas stream. In step 616, after the pulse of the Ti precursor, a pulse of a nitrogen precursor, such as NH_3 or a nitrogen plasma, is dosed into the purge gas stream. Step 614 and step 616 are repeated until a predetermined number of cycles are performed to form a TiN layer.

[0035] Figure 3B is a flow chart illustrating one embodiment of a process utilizing pulses of a purge gas to deposit a Ti layer, a TiSi_x layer, and a TiN layer by cyclical deposition in the same chamber. As shown in step 622, a substrate is provided to a process chamber. The process chamber conditions, such as for example the substrate temperature and pressure, may be adjusted. In step 624, a pulse of a purge gas is provided to the process chamber. Referring to step 626 after the pulse of the purge gas, a pulse of a Ti precursor, such as TiCl_4 , is provided to the process chamber. In step 628, after the pulse of the Ti precursor, another pulse of the purge gas is provided. In step 630, after the pulse of the purge gas, a pulse of a reductant, such as a hydrogen plasma, is provided. Steps 624, 626, 628, and 630 are repeated until a predetermined number of cycles are performed to form a Ti layer. Referring to step 632, after a predetermined number of cycles of steps 624, 626, 628, and 630 are performed, another pulse of the purge gas is provided to the process chamber. Referring to step 634, after the pulse of the purge gas, another pulse of the Ti precursor is provided to the process chamber. In step 636, after the pulse of the Ti precursor, another pulse of the purge gas is provided. In step 638, after the pulse of the purge gas, a pulse of a silicon precursor, such as silane (SiH_4), is provided. Steps 632, 634, 636, and 638 are repeated until a predetermined number of cycles are performed to form a TiSi_x layer. Referring to step 640, after a predetermined number of cycles of steps 632, 634, 636, and 638 are performed, another pulse of the purge gas is provided to the process chamber. Referring to step 642, after the pulse of the purge gas, another pulse of the Ti precursor is provided to the process chamber. In step 644, after the pulse of the Ti precursor, another pulse of the purge gas is provided. In step 646, after the pulse of the purge

gas, a pulse of a pulse of a nitrogen precursor, such as NH_3 or a nitrogen plasma, is provided. Steps 640, 642, 644, and 646 are repeated until a predetermined number of cycles are performed to form a TiN layer.

[0036] Figure 3C is a flow chart illustrating one embodiment of a process utilizing a continuous flow of a purge gas to deposit a Ti layer, a TiSi_xN_y layer, and a TiN layer by cyclical deposition in the same chamber. As shown in step 652, a substrate is provided to the process chamber. The process chamber conditions, such as for example the substrate temperature and pressure, may be adjusted. In step 654, a purge gas stream is established within the process chamber. Referring to step 656, after the purge gas stream is established within the process chamber, a pulse of a Ti precursor, such as TiCl_4 , is added or dosed into the purge gas stream. In step 658, after the pulse of the Ti precursor a pulse of a reductant, such as a hydrogen plasma, is dosed into the purge gas stream. Step 656 and step 658 are repeated until a predetermined number of cycles are performed to form a Ti layer. Referring to step 660, after a predetermined number of cycles of step 656 and step 658 are performed, another pulse of the Ti precursor is dosed into the purge gas stream. In step 662, after the pulse of the Ti precursor, a pulse of a Si precursor, such as SiH_4 , and a pulse of a nitrogen precursor, such as NH_3 , is dosed into the purge gas stream. The pulses of the Si precursor and the nitrogen precursor may be introduced separately or may be introduced in which the pulses at least partially overlap in time. Step 660 and step 662 are repeated until a predetermined number of cycles are performed to form a TiSi_xN_y layer. Referring to step 664, after a predetermined number of cycles of step 660 and step 662 are performed, another pulse of the Ti precursor is dosed into the purge gas stream. In step 666, after the pulse of the Ti precursor, another pulse of the nitrogen precursor is dosed into the purge gas stream. Step 664 and step 666 are repeated until a predetermined number of cycles are performed to form a TiN layer.

[0037] Figure 3D is a flow chart illustrating one embodiment of a process utilizing pulses of a purge gas to deposit a Ti layer, a TiSi_xN_y layer, and a TiN layer by cyclical deposition in the same chamber. As shown in step 672, a substrate is provided to a process chamber. The process chamber conditions, such as for example the substrate temperature and pressure, may be adjusted. In step 674, a

pulse of a purge gas is provided to the process chamber. Referring to step 676 after the pulse of the purge gas, a pulse of a Ti precursor, such as TiCl_4 , is provided to the process chamber. In step 678, after the pulse of the Ti precursor, another pulse of the purge gas is provided. In step 680 after the pulse of the purge gas, a pulse of a reductant, such as a hydrogen plasma, is provided. Steps 674, 676, 678, and 680 are repeated until a predetermined number of cycles are performed to form a Ti layer. Referring to step 682, after a predetermined number of cycles of steps 674, 676, 678, and 680 are performed, another pulse of the purge gas is provided to the process chamber. Referring to step 684, after the pulse of the purge gas, another pulse of the Ti precursor is provided to the process chamber. In step 686, after the pulse of the Ti precursor, another pulse of the purge gas is provided. In step 688, after the pulse of the purge gas, a pulse of a silicon precursor, such as silane (SiH_4), and a pulse of a nitrogen precursor, such as ammonia (NH_3), is provided. The pulses of the Si precursor and the nitrogen precursor may be introduced separately or may be introduced in which the pulses at least partially overlap in time. Steps 682, 684, 686, and 688 are repeated until a predetermined number of cycles are performed to form a TiSi_xN_y layer. Referring to step 690, after a predetermined number of cycles of steps 682, 684, 686, and 688 are performed, another pulse of the purge gas is provided to the process chamber. Referring to step 692, after the pulse of the purge gas, another pulse of the Ti precursor is provided to the process chamber. In step 694, after the pulse of the Ti precursor, another pulse of the purge gas is provided. In step 696, after the pulse of the purge gas, another pulse of a pulse of a nitrogen precursor is provided. Steps 690, 692, 694, and 696 are repeated until a predetermined number of cycles are performed to form a TiN layer.

[0038] In regards to Figures 3A-3D, the same Ti precursor is preferably used to deposit a Ti layer, a $\text{TiSi}_x/\text{TiSi}_x\text{N}_y$ layer, and a TiN layer. For example, TiCl_4 may be used to deposit a Ti layer, a $\text{TiSi}_x/\text{TiSi}_x\text{N}_y$ layer, and a TiN layer. Figures 3A-3D show the deposition of a Ti layer, a $\text{TiSi}_x/\text{TiSi}_x\text{N}_y$ layer, and a TiN layer in a single chamber. In other embodiments, deposition a Ti layer, a $\text{TiSi}_x/\text{TiSi}_x\text{N}_y$ layer, and a TiN layer may be performed in more than one chamber. For example, two or more chambers may be used to deposit a Ti layer, a $\text{TiSi}_x/\text{TiSi}_x\text{N}_y$ layer, and a TiN layer. Figures 3A-3D show deposition of a Ti layer, a $\text{TiSi}_x/\text{TiSi}_x\text{N}_y$ layer, and a TiN layer

by cyclical deposition. In other embodiments, each layer may be deposited by the same or different deposition technique selected from the group including cyclical deposition, chemical vapor deposition, and a combined mode of cyclical deposition and chemical vapor deposition.

[0039] Figures 4 and 4A are drawings of an exemplary processing chamber 100 that may be used to perform cyclical deposition, chemical vapor deposition, or a combined mode of cyclical deposition and chemical vapor deposition. Other chambers may also be used. The chamber 100 comprises a chamber body 102 including a substrate support 112 having a substrate receiving surface 111 to support a substrate 110. The chamber may be adapted to heat the substrate 110, such as by a heated substrate support or by using heat lamps. A gas distribution system 130 is disposed at an upper portion of the chamber body 102 to provide a gas to the chamber 100. The gas distribution system 130 comprises a gas box 132, a top shower plate 160 positioned below the gas box 132, and a bottom shower plate 170 positioned below the top shower plate 160.

[0040] Figure 4A is a schematic partial cross-sectional view of a portion of the gas box 132, a portion of the top shower plate 160, and a portion of the bottom shower plate 170 of Figure 4. In reference to Figures 4 and 4A, the gas box 132 comprises a central gas channel 137 and a plurality of outer gas channels 143. The central gas channel 137 provides one discrete path for the flow of one or more gases through the gas box 132 while the outer channels 143 provides another discrete path for the flow of one or more gases through the gas box 132. The central gas channel 137 is coupled to a first gas source 135 (Figure 4) through valve 136 (Figure 4). The central gas channel 137 has a first gas outlet 138 and is adapted to deliver a first gas from the first gas source 135 to a gas conduit 210. The term "gas" as used herein is intended to mean a single gas or a gas mixture. The outer gas channels 143 are coupled to a second gas source 141 (Figure 4) through valve 142 (Figure 4). The outer gas channels 143 have second gas outlets 144 and are adapted to deliver a second gas from the second gas source 141 to the top shower plate 160. Preferably, the second gas outlets 144 of the outer gas channels 143 are adapted to deliver the second gas proximate a central portion of the top shower plate. Gas sources 135, 141 may be adapted to store a gas or liquid

precursor in a cooled, heated, or ambient environment. The valves 136, 142 control delivery of the first gas and the second gas into the central gas channel 137 and the outer gas channels 143 respectively and may be electrically controlled valves, pneumatically controlled valves, piezoelectric valves, or other suitable valves. In another embodiment, a third gas source may be coupled to the outer gas channels 143 to provide a third gas to the top shower plate 160 or may be coupled to the central gas channel 137 to provide a third gas to the gas conduit 210.

[0041] Referring to Figure 4A, the top shower plate 160 has a plurality of holes 162 to accommodate a gas flow therethrough from the outer gas channels 143 of the gas box 132 to the bottom shower plate 170. Referring to Figure 4, the top shower plate 160 is separated from the bottom shower plate 170 by an insulator 164 to electrically insulate the top shower plate 160 from the bottom shower plate 170. The bottom shower plate 170 may be disposed on an upper portion of the chamber body 102, such as on a lid rim 166 disposed on the chamber body 102. The lid rim 166 comprises an insulating material to electrically insulate the bottom shower plate 170 from the chamber body 102. The gas conduit 210 is disposed through an aperture 163 in the top shower plate 160 and is disposed on the bottom shower plate 170. The gas conduit 210 is made of an insulating material to prevent electrical coupling of the top shower plate 160 and the bottom shower plate 170.

[0042] As shown in Figure 4A, the bottom shower plate 170 comprises a first piece 172 connected to a second piece 180. The first piece 172 has a plurality of holes 174 to provide a flow of a gas therethrough. The second piece 180 comprises a plurality of columns 182 having column holes 183 formed therethrough and a plurality of grooves 184 having groove holes 185 formed therethrough. The top surface of the columns 182 are connected to the bottom surface of the first piece 172 so that the column holes 183 align with the holes 174 of the first piece 172. Therefore, one discrete passageway is provided through the holes of the first piece 172 and through the column holes 183 of the columns 182 to deliver a gas flow from the top shower plate 160 to the substrate receiving surface 111. The aperture 175 is formed through the first piece 172 and aligns with the grooves on the second piece 180. Therefore, another discrete passageway is provided through the aperture 175 of the first piece 172 and through the grooves 184 and groove holes

185 of the second piece 180 to deliver a gas flow from the gas conduit 210 to the substrate receiving surface 111.

[0043] Referring to Figure 4, a power source 190 may be coupled to the top shower plate 160 through the gas box 132 to provide a power electrode and the bottom shower plate 170 may be grounded to provide a ground electrode. The power source 190 may be an RF or DC power source. An electric field may be established between the top shower plate 160 and the bottom shower plate 170 to generate a plasma from the gases introduced between the top shower plate 160 and the bottom shower plate 170. The power source 190 may be coupled to a matching network 194 to control delivery of power to the power source 190. The power source 190 may selectively provide power to selectively perform plasma and non-plasma processes.

[0044] In another embodiment, the bottom shower plate 170 may be optionally coupled to a power source 192 in addition to the power source 190 coupled to the top shower plate 160 and may be selectively powered or grounded. The power sources 190 and 192 are coupled to the matching network 194 to control delivery of any amount of power to the power source 190 and to control delivery of any amount of power to the power source 192. In one aspect, the matching network 194 may control the delivery of power to the power sources 190, 192 so that the top shower plate 160 and the bottom shower plate 170 are at the same or substantially the same potential. With a grounded substrate support 112, the top shower plate 160 and the bottom shower plate 170 act as one electrode and the substrate support 112 acts as another electrode of spaced apart electrodes in which an electric field is established between the bottom shower plate 170 and the substrate support 112 to generate a plasma from the gases introduced between the bottom shower plate 170 and the substrate support 112. Therefore, power may be selectively provided to power sources 190, 192 to selectively generate a plasma between the top shower plate 160 and the bottom shower plate 170 or between the bottom shower plate 170 and the substrate support 112. Thus, the power sources 190, 192 may selectively provide power to selectively perform plasma and non-plasma processes.

[0045] A vacuum system 196 is in communication with a pumping channel 197 formed in the chamber body 102 to evacuate gases from the chamber 100 and to

help maintain a desired pressure or a desired pressure range inside the chamber 100. Control unit 176 may be coupled to the chamber 100 to control processing conditions.

Soak with a Silicon Precursor

[0046] Figure 5 is a flow chart illustrating another embodiment of a process of integrating a Ti layer and a TiN layer by soaking a Ti layer with a flow of a silicon precursor prior to deposition of a TiN layer thereover. In step 502, a Ti layer is deposited over a substrate structure. The Ti layer may be deposited by such methods, with include, but are not limited to, chemical vapor deposition, cyclical deposition, physical vapor deposition, and combinations thereof. For example, the Ti layer may be deposited by chemical vapor deposition or cyclical deposition by utilizing a titanium precursor, such as titanium tetrachloride (TiCl_4), and a reducing agent, such as a hydrogen plasma. Examples of other titanium containing compounds include, but are not limited to, titanium iodide (TiI_4), titanium bromide (TiBr_4), other titanium halides, tetrakis(dimethylamino)titanium (TDMAT), tetrakis(diethylamino) titanium (TDEAT), other titanium organic compounds, and derivatives thereof. The hydrogen plasma is preferably provided by utilizing a hydrogen gas (H_2). Other hydrogen containing gases which may also be used include silane (SiH_4), borane (BH_3), diborane (B_2H_6), triborane (B_3H_9), among others.

[0047] Referring to step 504, after the Ti layer is deposited, the Ti layer is treated with a soak with a silicon precursor by flowing in the silicon precursor into a process chamber. The silicon precursor is preferably silane (SiH_4). Other silicon precursors may also be used, such as disilane (Si_2H_6). The silicon precursor may be flowed in with a carrier gas, such as a helium gas (He), an argon gas (Ar), hydrogen gas (H_2), nitrogen gas (N_2), other suitable gases, and combinations thereof. The substrate is preferably maintained at a substrate temperature of about 550°C or less, preferably about 500°C or less, and more preferably about 450°C or less. Not wishing to be bound by theory, it is believed that a soak of the Ti layer with a silicon precursor converts at least a portion of the Ti layer to titanium silicide (TiSi_x). It is believed that the TiSi_x helps protect the interface between the Ti layer and a subsequently deposited TiN layer resulting in improved adhesion of the TiN layer thereover. It is

believed that a soak with a silicon precursor performed at a heater temperature of about 550° C or less reduces the formation of polysilicon or amorphous silicon which would be undesirable due to the higher resistance of polysilicon or amorphous silicon in comparison to TiSi_x .

[0048] In step 506, after the SiH_4 soak, a TiN layer is deposited over the treated Ti layer. The TiN layer may be deposited by such methods, which include, but are not limited to, chemical vapor deposition, cyclical deposition, physical vapor deposition, and combinations thereof. For example, the Ti layer may be deposited by chemical vapor deposition or cyclical deposition by utilizing a titanium precursor, such as titanium tetrachloride (TiCl_4), and a nitrogen precursor, such as ammonia (NH_3) or a nitrogen plasma. When a titanium halide is used to form the TiN layer, it is believed that the TiSi_x formed during the soak with a silicon precursor protects the Ti layer from etching or attack from the halogen in the titanium halide, such as chlorine from TiCl_4 , used during chemical vapor deposition or cyclical deposition of the TiN layer.

[0049] Examples of other titanium containing compounds which may be used to form the TiN layer include, but are not limited to, titanium iodide (TiI_4), titanium bromide (TiBr_4), other titanium halides, tetrakis(dimethylamino)titanium (TDMAT), tetrakis(diethylamino) titanium (TDEAT), other titanium organic compounds, and derivatives thereof. Examples of other nitrogen precursors which may be used to form the TiN layer include, but are not limited to hydrazine (N_2H_4), other N_xH_y compounds with x and y being integers, dimethyl hydrazine ($(\text{CH}_3)_2\text{N}_2\text{H}_2$), t-butylhydrazine ($\text{C}_4\text{H}_9\text{N}_2\text{H}_3$), phenylhydrazine ($\text{C}_6\text{H}_5\text{N}_2\text{H}_3$), 2,2'-azoisobutane ($(\text{CH}_3)_6\text{C}_2\text{N}_2$), ethylazide ($\text{C}_2\text{H}_5\text{N}_3$), and derivatives thereof. Examples of other nitrogen containing gases which may also be used to generate a nitrogen plasma to form the TiN layer include, but are not limited to, NH_3 , N_xH_y with x and y being integers (e.g., hydrazine (N_2H_4)), a mixture of hydrogen gas (H_2) and nitrogen gas (N_2), mixtures thereof, other gases or gas mixtures containing hydrogen and nitrogen.

[0050] In one embodiment, step 502, step 504, and step 506 may each be performed in separate chambers. In another embodiment, two or more of step 502, step 504, and step 506 may be performed in the same chamber. For example, deposition of a Ti layer and a soak of the Ti layer with a silicon precursor may be

performed in the same chamber. In another example, a soak of a Ti layer with a silicon precursor and deposition of a TiN layer may be performed in the same chamber. In still another example, deposition of a Ti layer, a soak of the Ti layer with a silicon precursor, and deposition of a TiN over the treated Ti layer may be performed in the same chamber. Preferably, two or more of step 502, step 504, and step 506 are performed in the same chamber to increase throughput of processing the substrates.

[0051] Processing chambers which may be used to deposit a Ti layer, perform a soak with a silicon precursor, and/or deposit a TiN layer include the chamber as described in reference to Figures 4 and 4A. Other chambers may also be used such as the processing chamber described in U.S. Patent Application (Serial No. 10/032,293) entitled "Chamber Hardware Design For Titanium Nitride Atomic Layer Deposition," filed on December 21, 2001; the processing chamber described in U.S. Patent Application (Serial No. 10/016,300) entitled "Lid Assembly For A Processing System To Facilitate Sequential Deposition Techniques," filed on December 12, 2001, which claims priority to U.S. Provisional Application Serial No. 60/305,970 filed on July 16, 2001; and the process chamber disclosed in U.S. Patent Application (Serial No. 10/032,284) entitled "Gas Delivery Apparatus and Method For Atomic Layer Deposition," filed on December 21, 2001, which claims priority to U.S. Provisional Patent Application (Serial No. 60/346,086) entitled "Method and Apparatus for Atomic Layer Deposition," filed on October 26, 2001, which are all incorporated by reference in its entirety to the extent not inconsistent with the present disclosure.

[0052] One exemplary process of treating a Ti layer with a soak of a silicon precursor comprises flowing in silane (SiH_4) into a chamber, such as chamber 100 described in reference to Figure 4, at a flow rate between about 5 sccm and about 500 sccm, preferably about 100 sccm. Silane may be introduced with a carrier gas, such as a helium gas (He), an argon gas (Ar), hydrogen gas (H_2), nitrogen gas (N_2), other suitable gases, and combinations thereof. The chamber may be maintained at a pressure between about 0.1 torr to about 50 torr, preferably about 3 torr. The substrate is preferably maintained at a substrate temperature about 550°C or less, preferably about 500°C or less, and more preferably about 450°C or less. The SiH_4

soak is preferably carried out for a time period between about 15 seconds and about 60 seconds. In general, treatment time will depend on the flow rate of SiH_4 and the pressure of the chamber.

Applications

[0053] Figure 6 is a schematic cross-sectional view of one embodiment of an exemplary application of an integrated Ti/TiN film stack formed by the process of Figure 1 or Figure 5. As shown in Figure 6, a doped source/drain region 854 may be formed over a substrate 852. The substrate 852 may be a semiconductor substrate, such as a silicon substrate. A dielectric layer 858, such as a silicon dioxide layer or a low-k dielectric layer, may be formed over the substrate 852. One example of a low-k dielectric layer is an oxidized organosilane layer or an oxidized organosiloxane layer described in more detail in U.S. Patent No. 6,348,725, issued February 19, 2002, which is incorporated by reference herein. The dielectric layer 858 may be patterned and etched to form an aperture. A titanium layer 859 may be deposited over the aperture to form titanium silicide 856 *in situ* or in an annealing step. A passivation layer 860 comprising TiSi_x , TiSi_xN_y , or combinations thereof is deposited over the titanium layer 859 or formed by a soak of the titanium layer 859 with a silicon precursor. A TiN layer 861 is deposited over the passivation layer 860. A conductive layer 862, such as a tungsten layer, may be deposited over the TiN layer 861.

[0054] Figure 7 is a schematic cross-sectional view of another embodiment of an exemplary application of an integrated Ti/TiN film stack formed by the process of Figure 1 or Figure 5. As shown in Figure 7, the film stack 1200 includes an underlying substrate 1202, such as a semiconductor substrate, and includes a doped source/drain region 1204. A metal silicide layer 1206, such as a titanium silicide layer, nickel silicide layer, cobalt silicide layer, or tungsten silicide layer, may be formed over the region 1204. A dielectric layer 1208, such as a silicon dioxide layer or a low-k dielectric layer, may be formed over the metal silicide layer 1206. One example of a low-k dielectric layer is an oxidized organosilane layer or an oxidized organosiloxane layer described in more detail in U.S. Patent No. 6,348,725, issued February 19, 2002, which is incorporated by reference herein. The dielectric layer 1208 may be patterned and etched to form an aperture exposing

the metal silicide layer 1206. A titanium layer 1212 may be formed over the aperture. A passivation layer 1214 comprising TiSi_x , TiSi_xN_y , or combinations thereof is deposited over the titanium layer 1212 or formed by a soak of the titanium layer 1212 with a silicon precursor. A titanium nitride layer 1216 may be formed over the passivation layer 1214. A conductive layer 1222 comprising a conductive material, such as tungsten, copper, aluminum, and combinations thereof, may be deposited over the titanium nitride layer 1216. Other applications of the integrated Ti/TiN film stack are possible.

[0055] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

Claims:

1. A method of processing a substrate, comprising:
 - (a) providing one or more cycles of a first set of compounds, comprising introducing a titanium precursor and a reductant;
 - (b) providing one or more cycles of a second set of compounds, comprising introducing the titanium precursor and a silicon precursor; and
 - (c) providing one or more cycles of a third set of compounds, comprising introducing the titanium precursor and a nitrogen precursor.
2. The method of claim 1, wherein providing one or more cycles of the second set of compounds further comprises introducing the nitrogen precursor.
3. The method of claim 1, wherein providing one or more cycles of the first set of compounds comprises delivering one or more pulses of the titanium precursor and one or more pulses of the reductant.
4. The method of claim 3, wherein the pulses of the titanium precursor and the pulses of the reductant of the first set of compounds are dosed into a continuous flow of a purge gas.
5. The method of claim 3, wherein the pulses of the titanium precursor and the pulses of the reductant of the first set of compounds are separated by pulses of a purge gas.
6. The method of claim 3, wherein at least one of the pulses of the titanium precursor and at least one of the pulses of the reductant of the first set of compounds at least partially overlap in time.
7. The method of claim 1, wherein providing one or more cycles of the second set of compounds comprises delivering one or more pulses of the titanium precursor and one or more pulses of the silicon precursor.

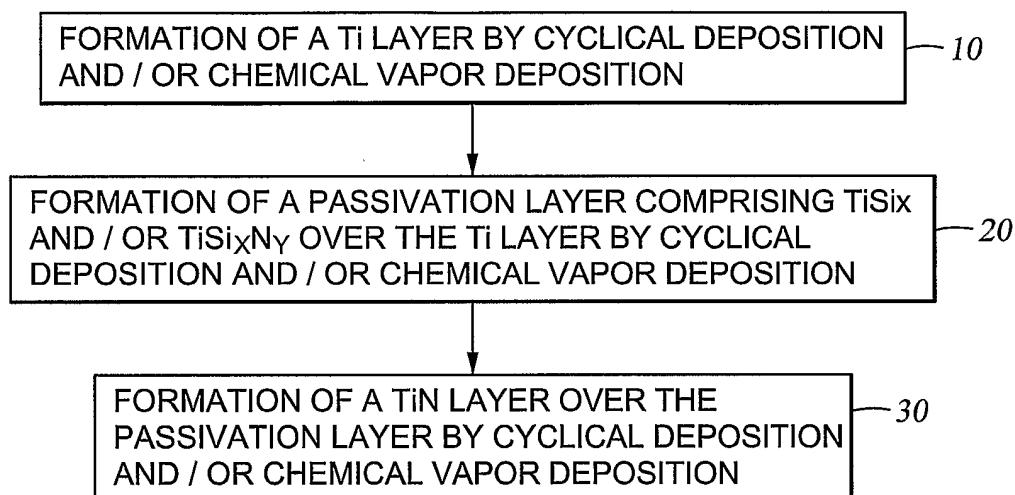
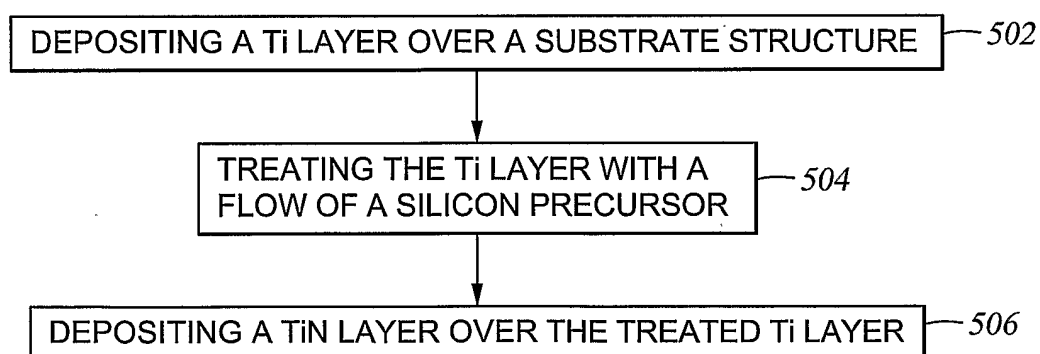
- 8, The method of claim 7, wherein the pulses of the titanium precursor and the pulses of the silicon precursor of the second set of compounds are dosed into a continuous flow of a purge gas.
9. The method of claim 7, wherein the pulses of the titanium precursor and the pulses of the silicon precursor of the second set of compounds are separated by pulses of a purge gas.
10. The method of claim 7, wherein at least one of the pulses of the titanium precursor and at least one of the pulses of the silicon precursor of the second set of compounds at least partially overlap in time.
11. The method of claim 1, wherein providing one or more cycles of the third set of compounds comprises delivering one or more pulses of the titanium precursor and one or more pulses of the nitrogen precursor.
- 12, The method of claim 11, wherein the pulses of the titanium precursor and the pulses of the nitrogen precursor of the third set of compounds are dosed into a continuous flow of a purge gas.
13. The method of claim 11, wherein the pulses of the titanium precursor and the pulses of the nitrogen precursor of the third set of compounds are separated by pulses of a purge gas.
14. The method of claim 11, wherein at least one of the pulses of the titanium precursor and at least one of the pulses of the nitrogen precursor of the third set of compounds at least partially overlap in time.
15. The method of claim 1, wherein steps (a) through (c) are performed in separate process chambers.
16. The method of claim 1, wherein steps (a) through (c) are performed in a single process chamber.

17. The method of claim 1, wherein steps (a) and (b) are performed in a single process chamber.
18. The method of claim 1, wherein steps (b) and (c) are performed in a single process chamber.
19. The method of claim 1, wherein steps (a) and (c) are performed in a single process chamber.
20. The method of claim 1, wherein the titanium precursor comprises a titanium halide.
21. The method of claim 20, wherein the titanium precursor comprises titanium tetrachloride.
22. The method of claim 2, wherein the nitrogen precursor comprises ammonia.
23. A method of processing a substrate, comprising:
 - (a) depositing a titanium layer utilizing titanium halide;
 - (b) depositing a passivation layer utilizing titanium halide over the titanium layer, comprising a material selected from the group including titanium silicide, titanium silicon nitride, and combinations thereof; and
 - (c) depositing a titanium nitride layer over the passivation layer utilizing titanium halide.
24. The method of claim 23, wherein the titanium layer is deposited by a technique selected from the group including cyclical deposition, chemical vapor deposition, and combinations thereof.
25. The method of claim 23, wherein the passivation layer is deposited by a technique selected from the group including cyclical deposition, chemical vapor deposition, and combinations thereof.

26. The method of claim 23, wherein the titanium nitride layer is deposited by a technique selected from the group including cyclical deposition, chemical vapor deposition, and combinations thereof.
27. The method of claim 23, wherein steps (a) through (c) are performed in separate process chambers.
28. The method of claim 23, wherein two or more of steps (a) through (c) are performed in a single process chamber.
29. The method of claim 23, wherein titanium halide comprises titanium tetrachloride.
30. A method of processing a substrate, comprising:
depositing a titanium layer over a surface of a substrate;
treating the titanium layer with a soak with a silicon precursor at a substrate temperature of about 550°C or less to form a treated titanium layer; and
depositing a titanium nitride layer over the treated titanium layer.
31. The method of claim 30, wherein treating the titanium layer is performed at a substrate temperature of about 500°C or less.
32. The method of claim 31, wherein treating the titanium layer is performed at a substrate temperature of about 450°C or less.
33. The method of claim 30, where the silicon precursor comprises silane.
34. The method of claim 30, wherein steps (a) through (c) are performed in separate process chambers.
35. The method of claim 30, wherein steps (a) through (c) are performed in a single process chamber.

36. The method of claim 30, wherein two or more steps (a) through (b) are performed in a single process chamber.
37. The method of claim 30, wherein depositing a titanium layer is performed by a deposition technique selected from the group consisting of chemical vapor deposition, cyclical deposition, physical vapor deposition and combinations thereof.
38. The method of claim 30, wherein depositing a titanium layer is performed by utilizing a titanium halide and a hydrogen plasma.
39. The method of claim 30, wherein depositing a titanium nitride layer is performed by a deposition technique selected from the group consisting of chemical vapor deposition, cyclical deposition, physical vapor deposition, and combinations thereof.
40. The method of claim 30, wherein depositing a titanium nitride layer is performed utilizing a titanium halide and a nitrogen precursor.

1/9

*Fig. 1**Fig. 5*

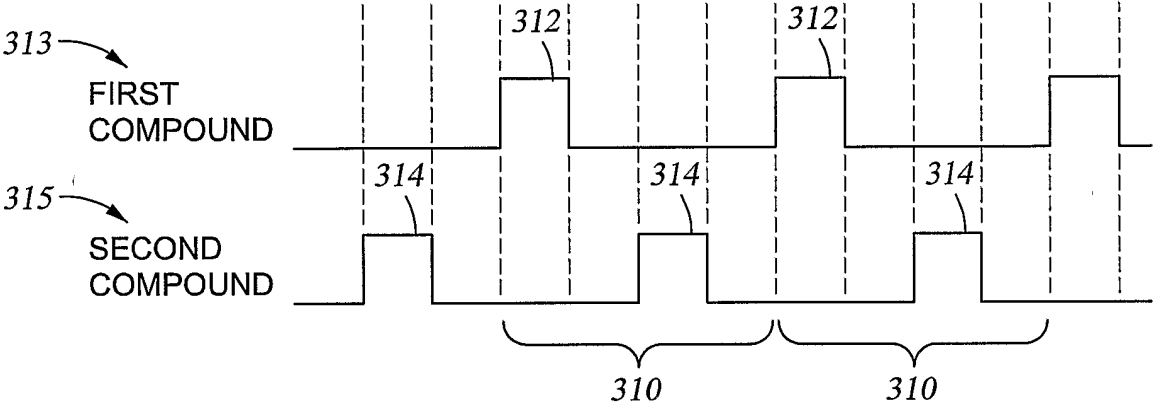


Fig. 2A

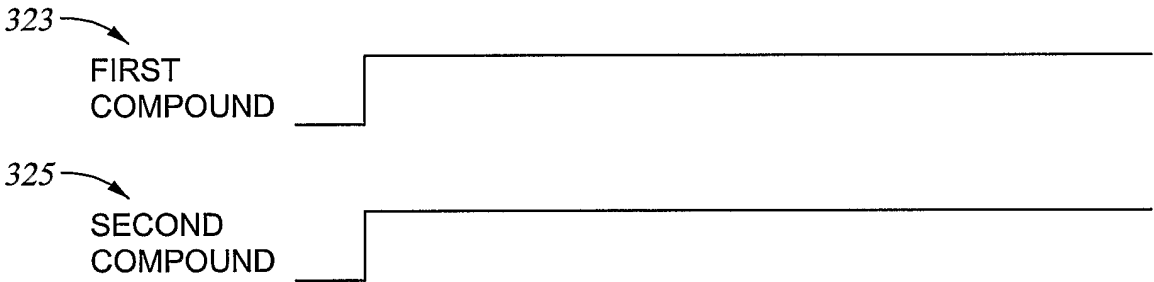


Fig. 2B

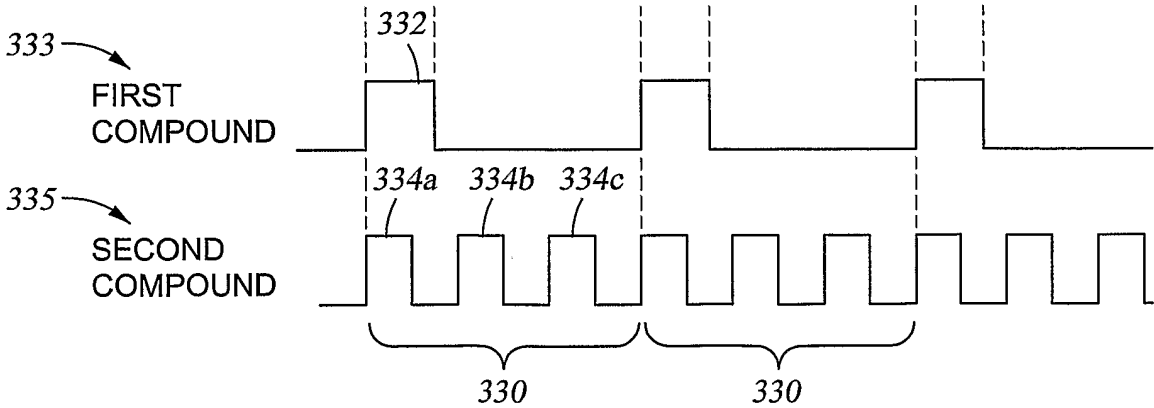


Fig. 2C

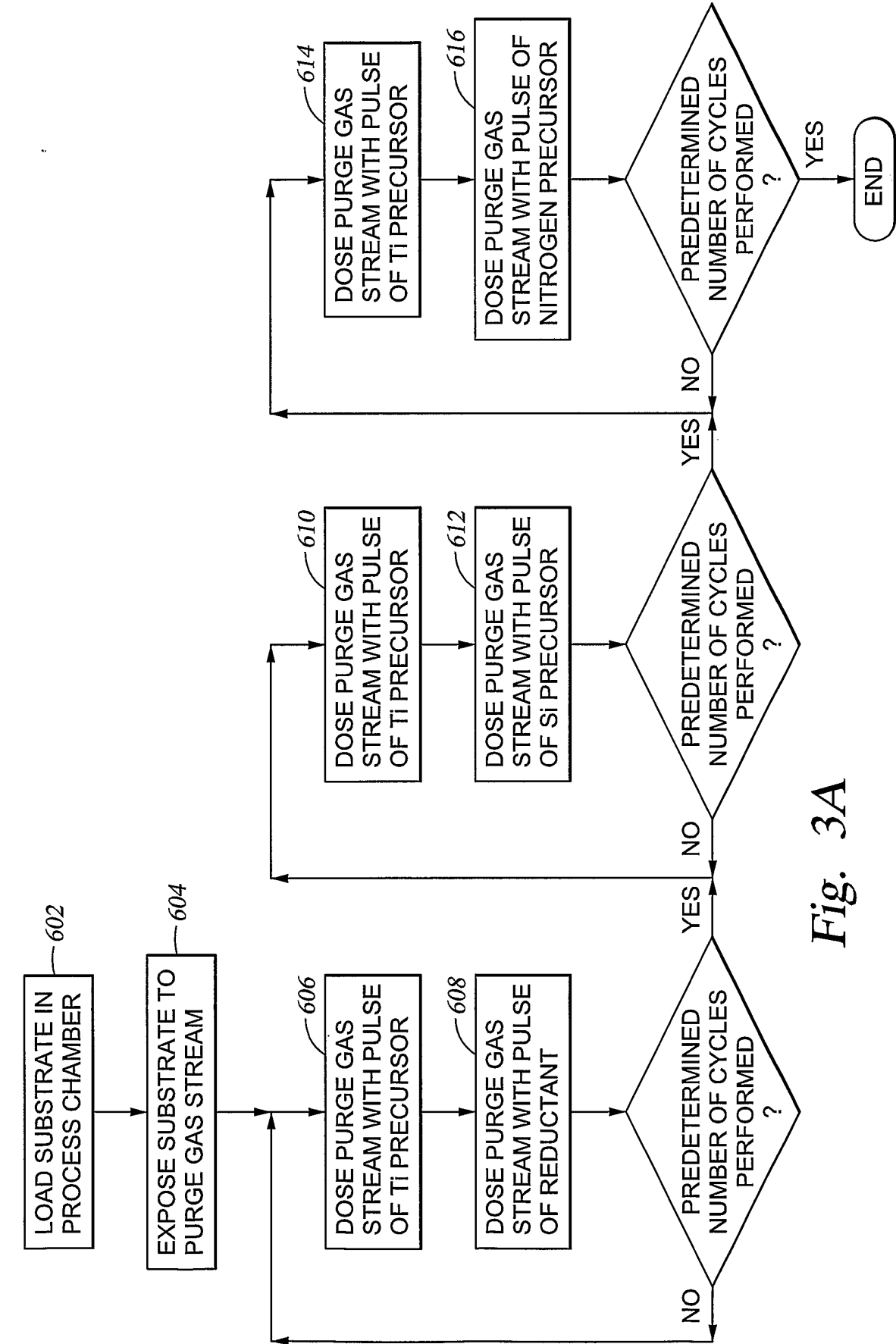


Fig. 3A

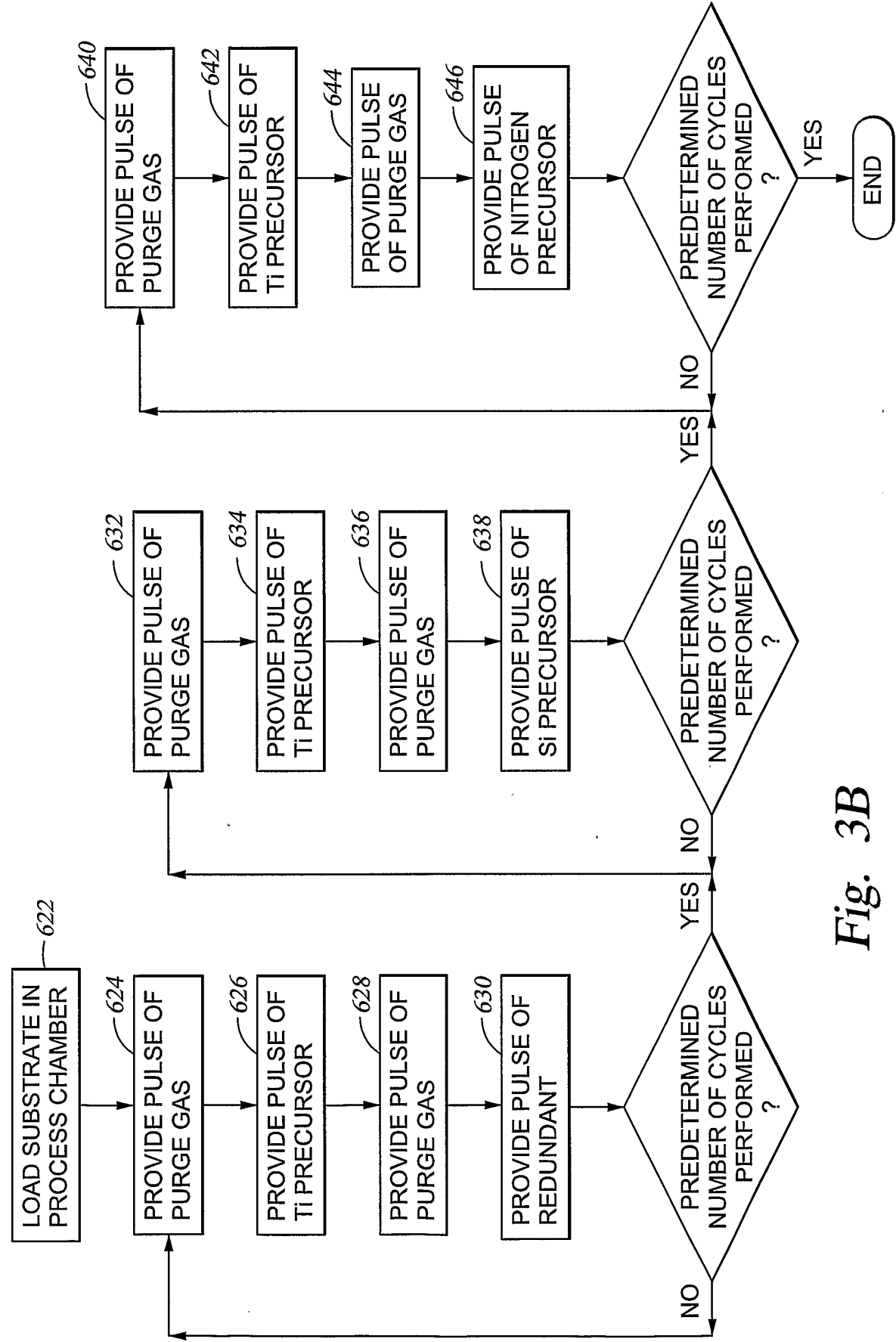


Fig. 3B

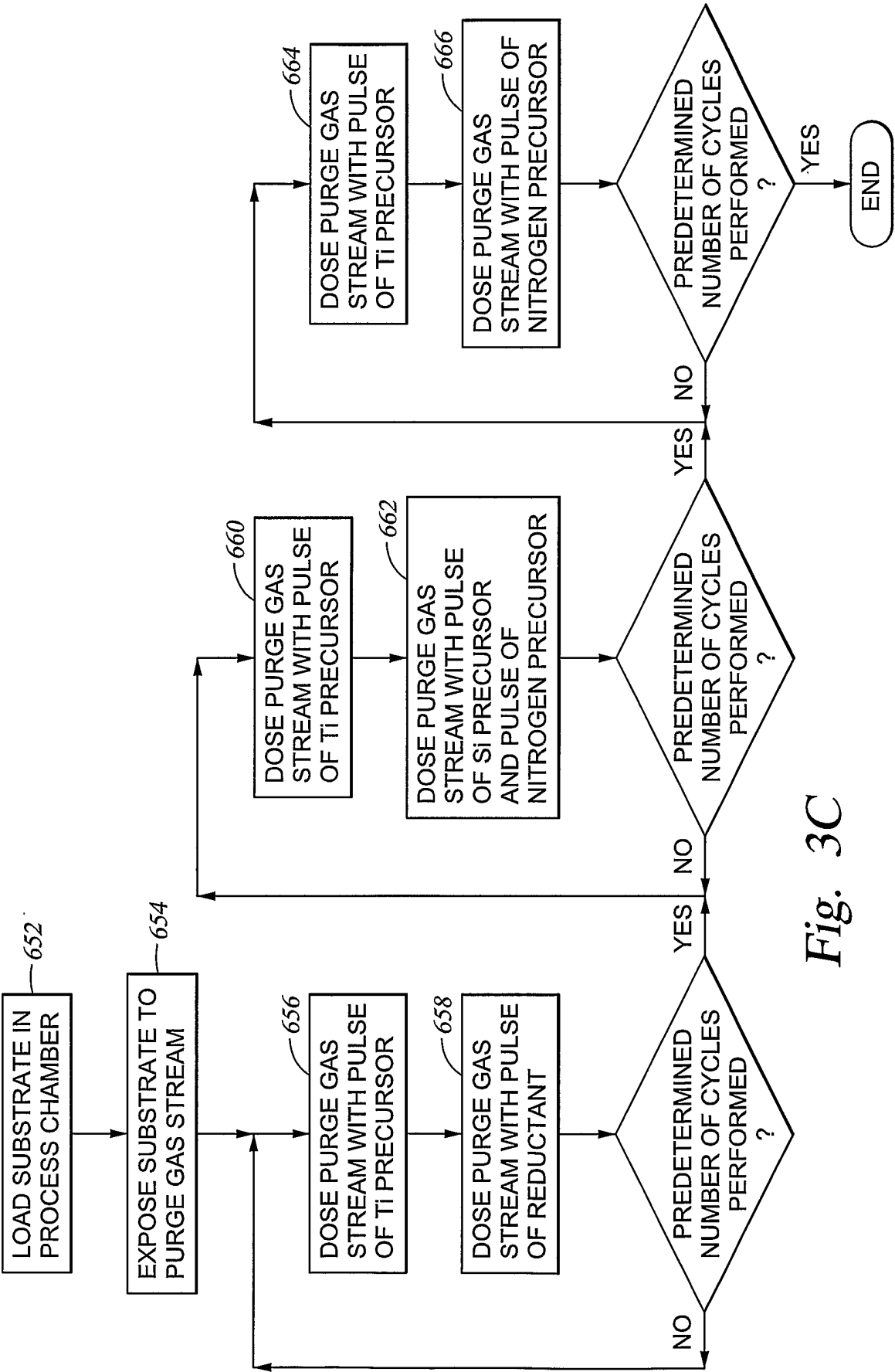


Fig. 3C

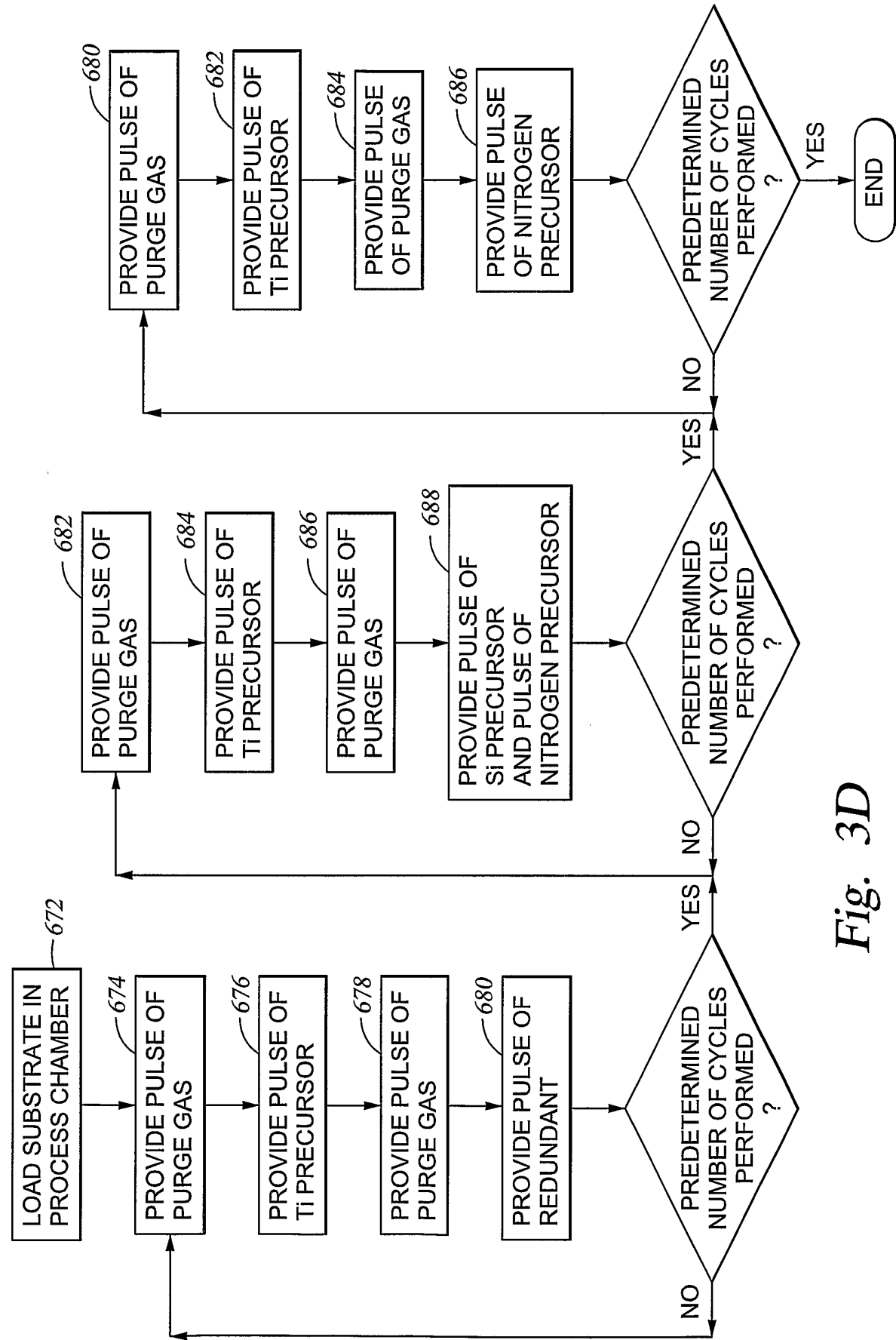
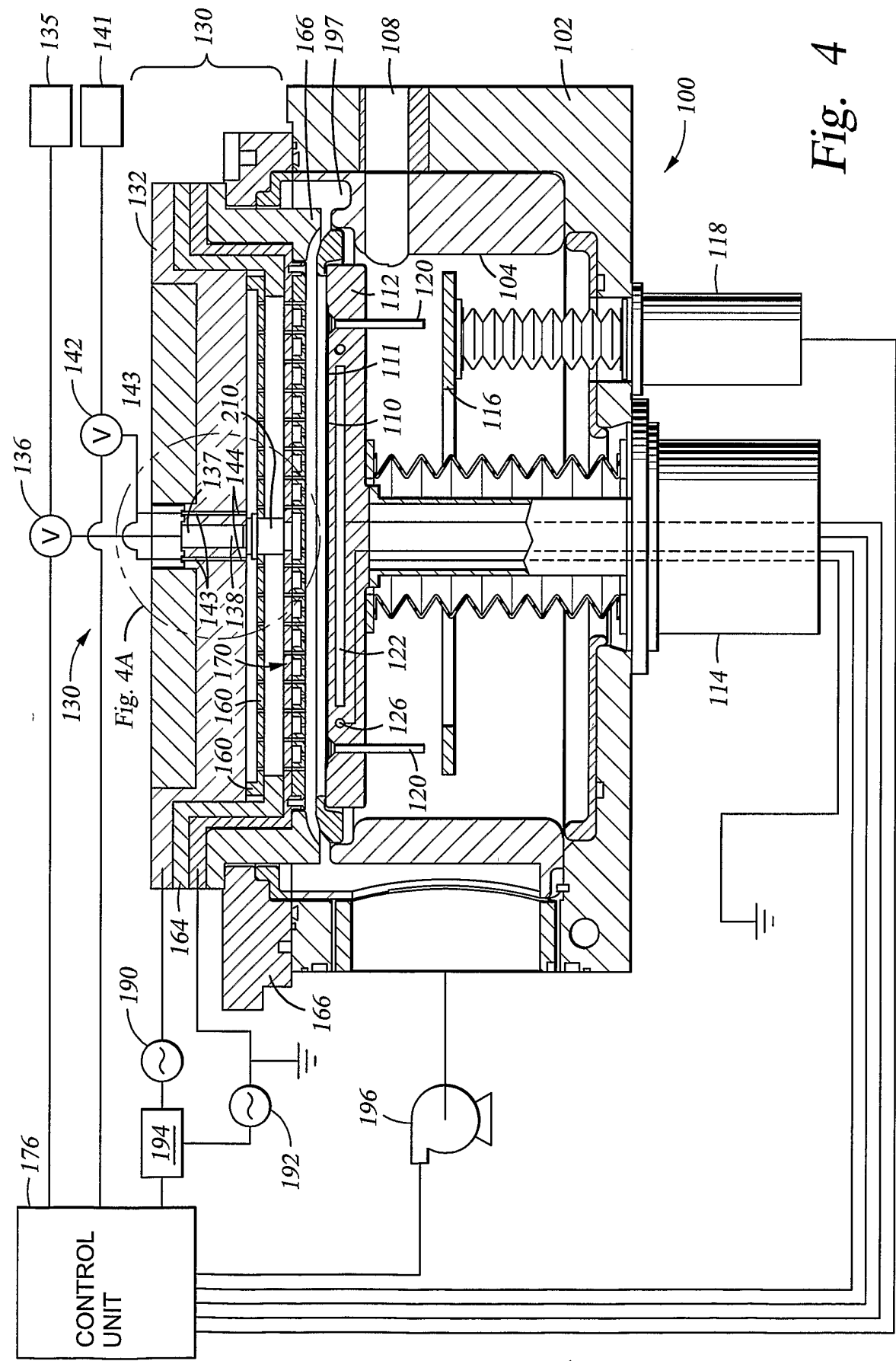


Fig. 3D



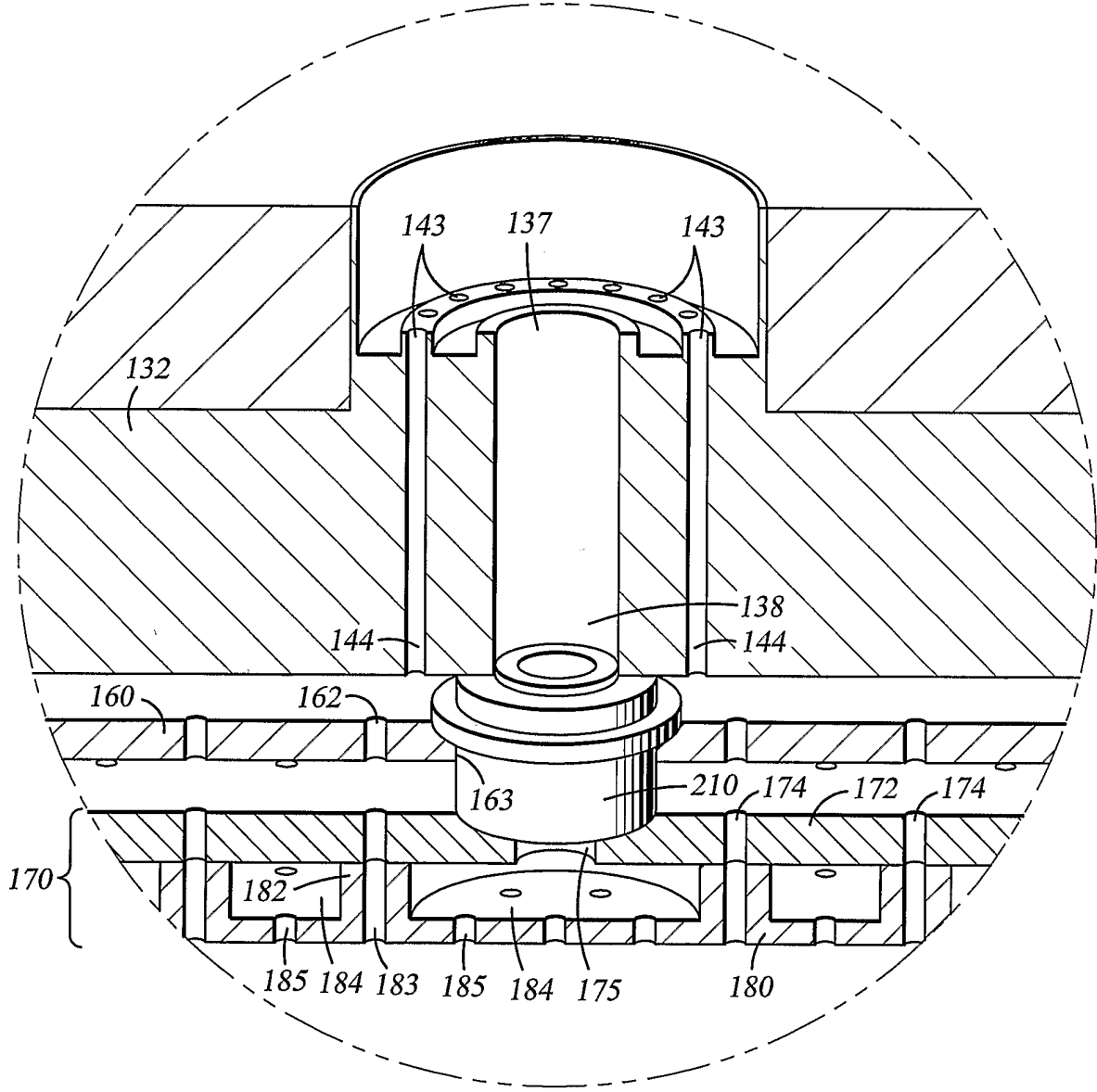


Fig. 4A

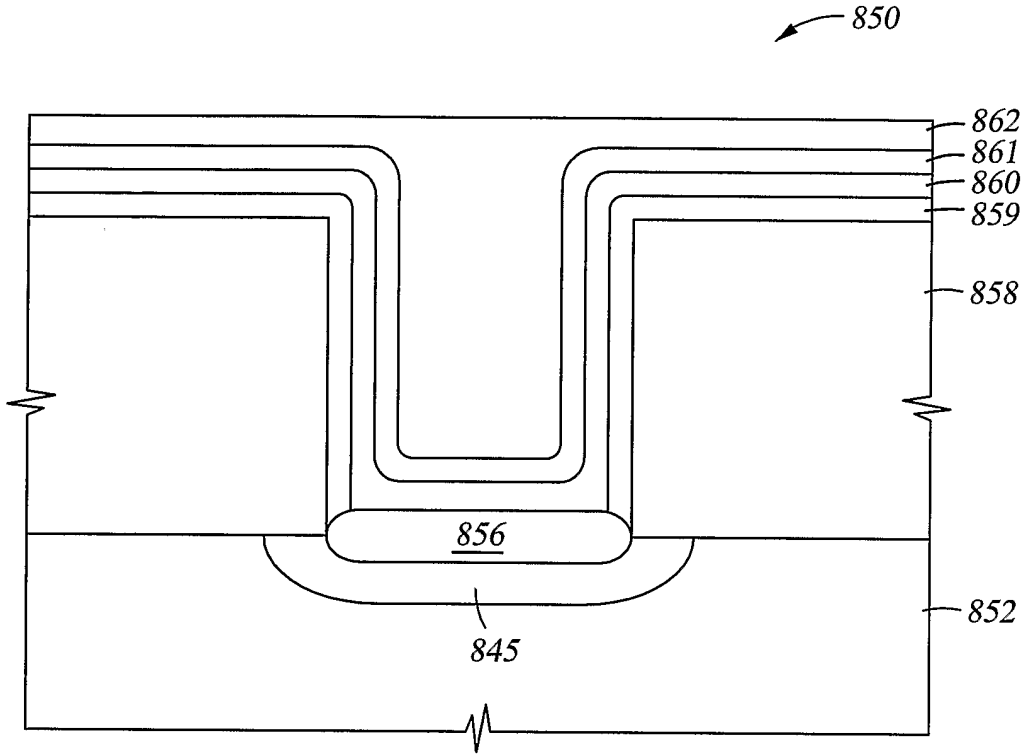


Fig. 6

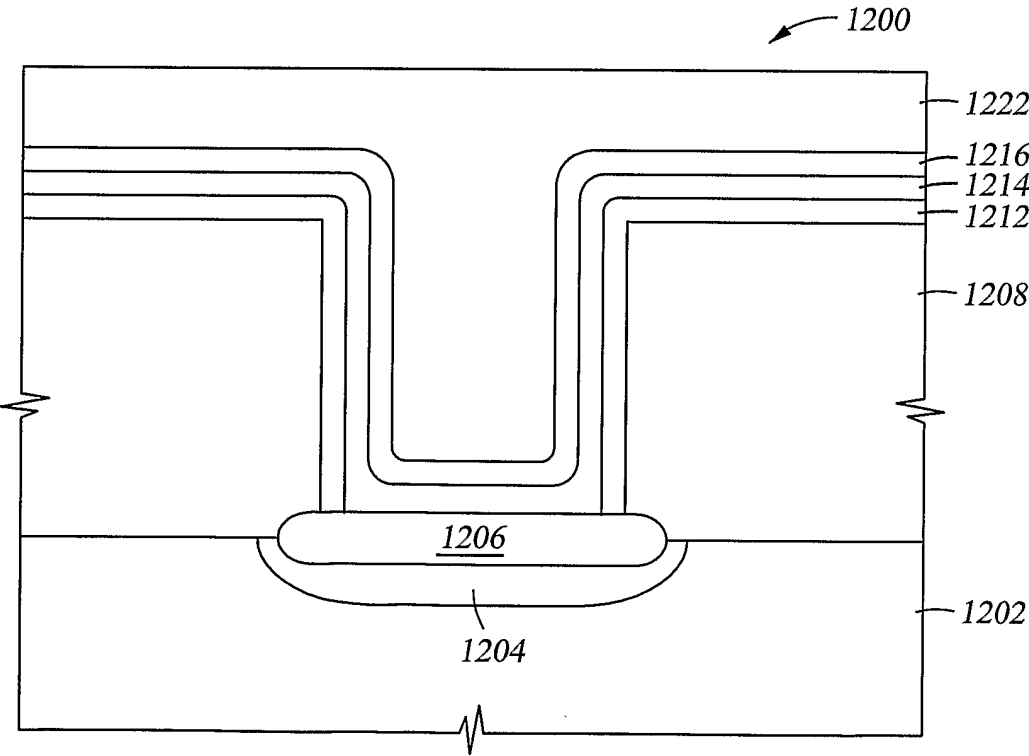


Fig. 7