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Yang et al.

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(54) **RADICAL-ACTIVATED ETCHING OF METAL OXIDES**

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H01J 37/32 (2006.01)
H01L 21/311 (2006.01)
H01L 21/3213 (2006.01)

(52) **U.S. Cl.**
CPC .. **H01L 21/68757** (2013.01); **H01J 37/32018** (2013.01); **H01J 37/32422** (2013.01); **H01J 37/3244** (2013.01); **H01L 21/31116** (2013.01); **H01L 21/32136** (2013.01); **H01J 2237/3341** (2013.01)

(58) **Field of Classification Search**

None

See application file for complete search history.

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Primary Examiner — Stephanie P Duclair

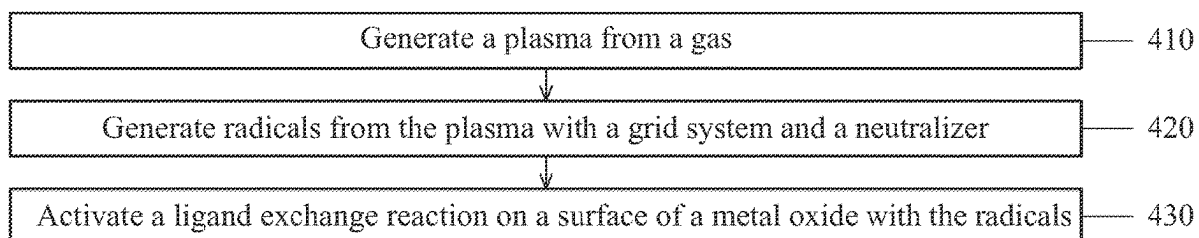
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(57) **ABSTRACT**

The present disclosure describes methods and systems for radical-activated etching of a metal oxide. The system includes a chamber, a wafer holder configured to hold a wafer with a metal oxide disposed thereon, a first gas line fluidly connected to the chamber and configured to deliver a gas to the chamber, a plasma generator configured to generate a plasma from the gas, a grid system between the plasma generator and the wafer holder and configured to increase a kinetic energy of ions from the plasma, a neutralizer between the grid system and the wafer holder and configured to generate electrons and neutralize the ions to generate radicals, and a second gas line fluidly connected to the chamber and configured to deliver a precursor across the wafer. The radicals facilitate etching of the metal oxide by the precursor.

20 Claims, 16 Drawing Sheets

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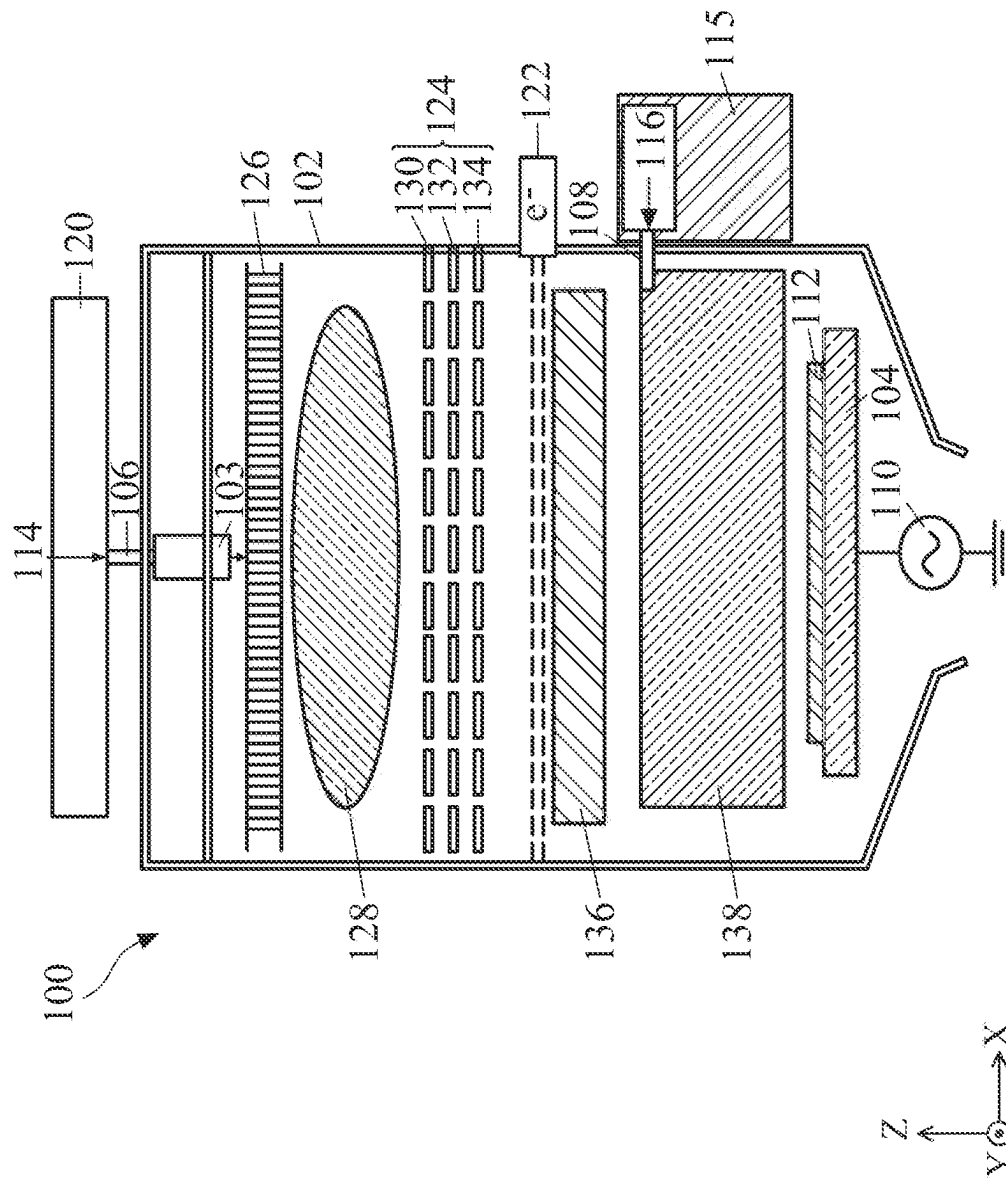
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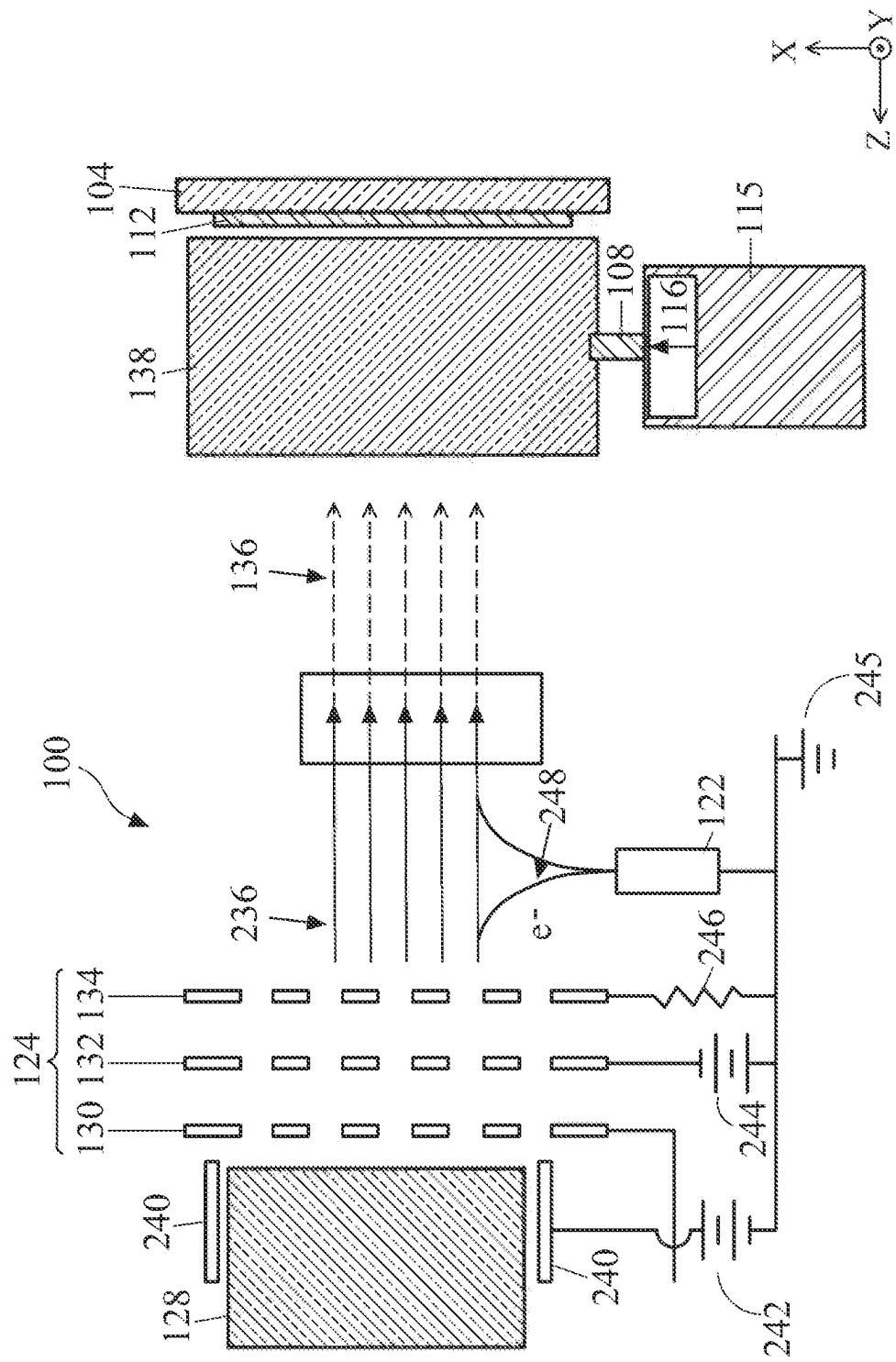


FIG. 2

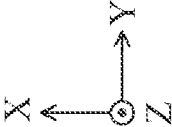
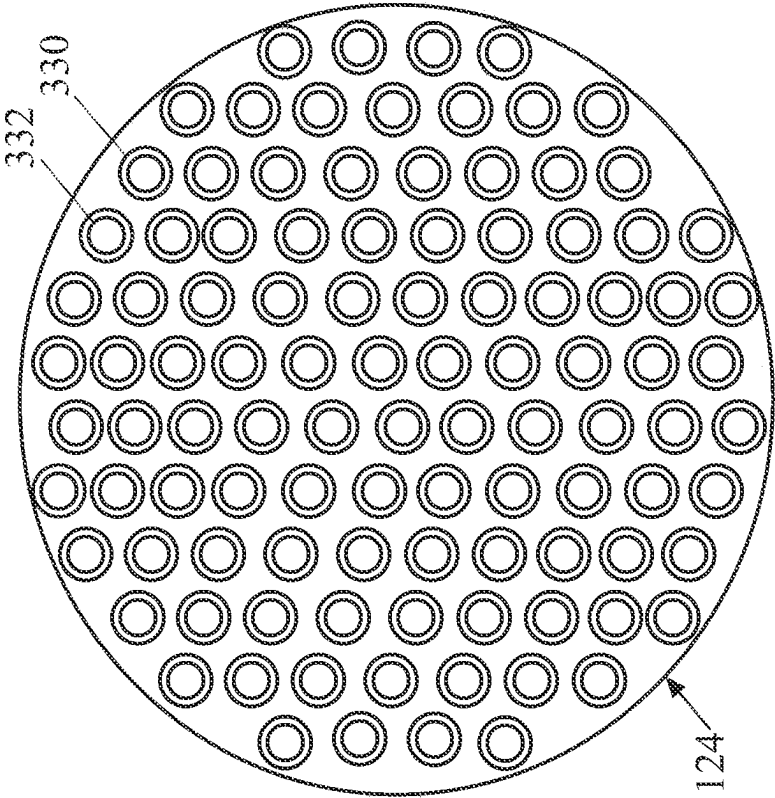


FIG. 3A

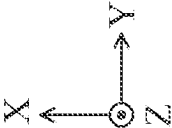
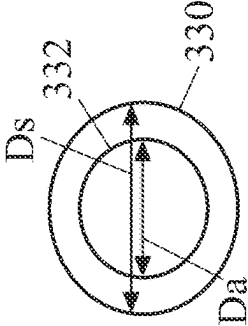


FIG. 3B

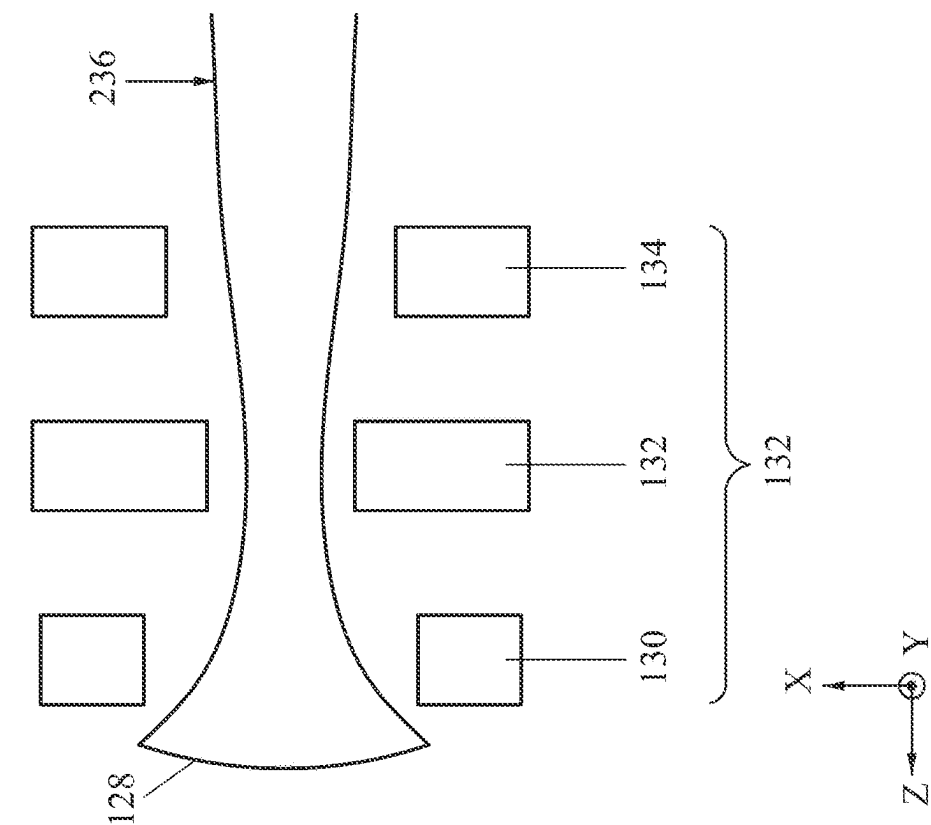


FIG. 3D

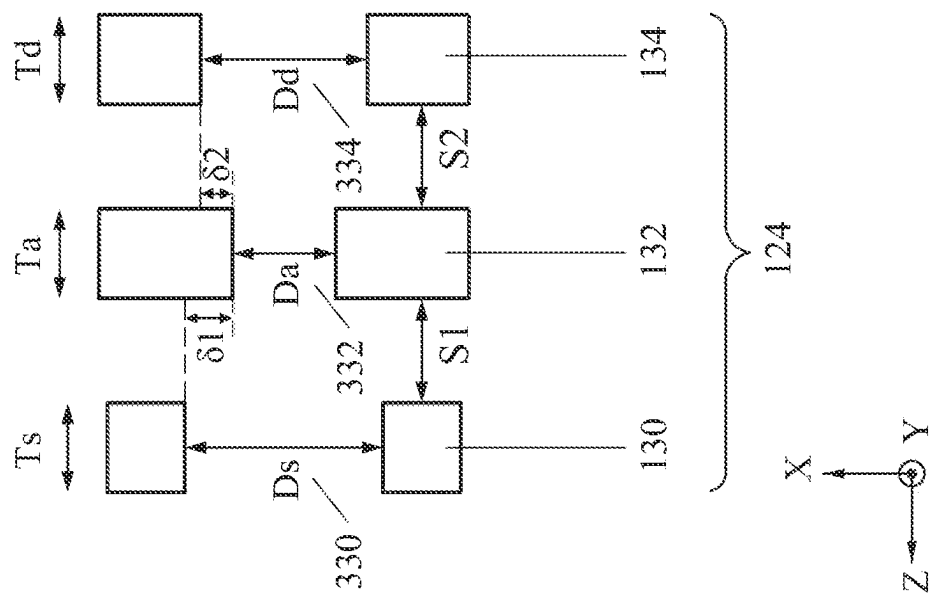


FIG. 3C

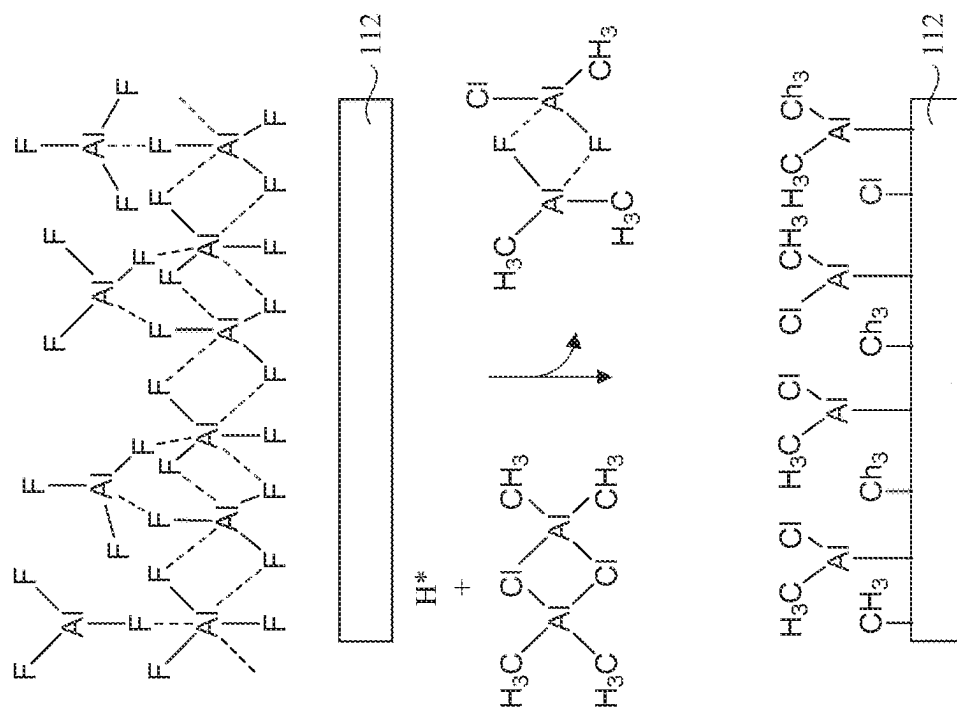


FIG. 3F

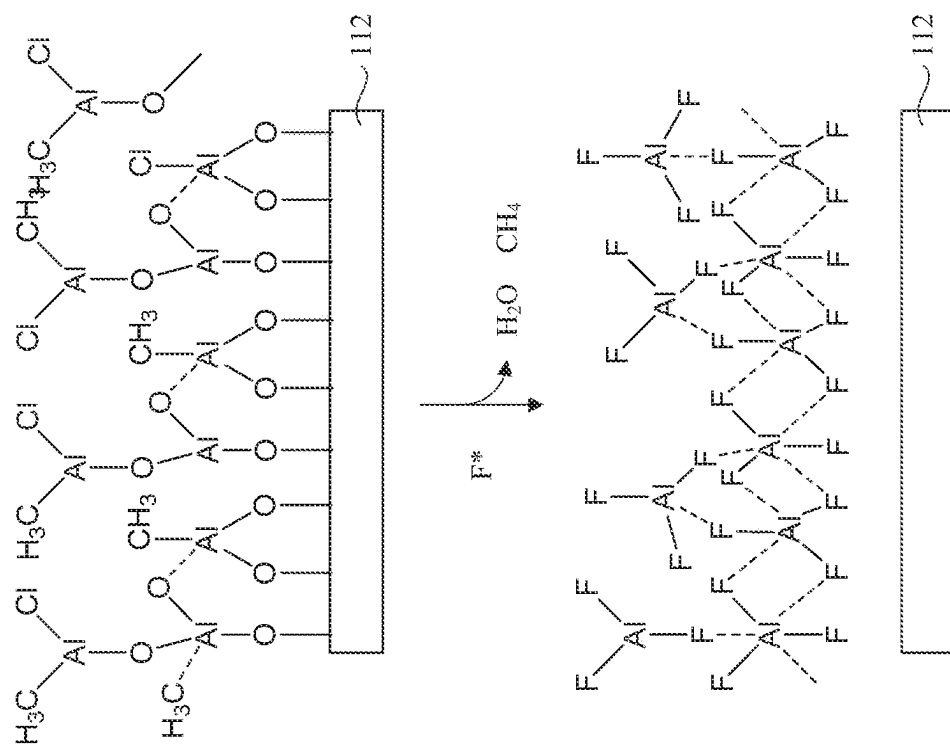


FIG. 3E

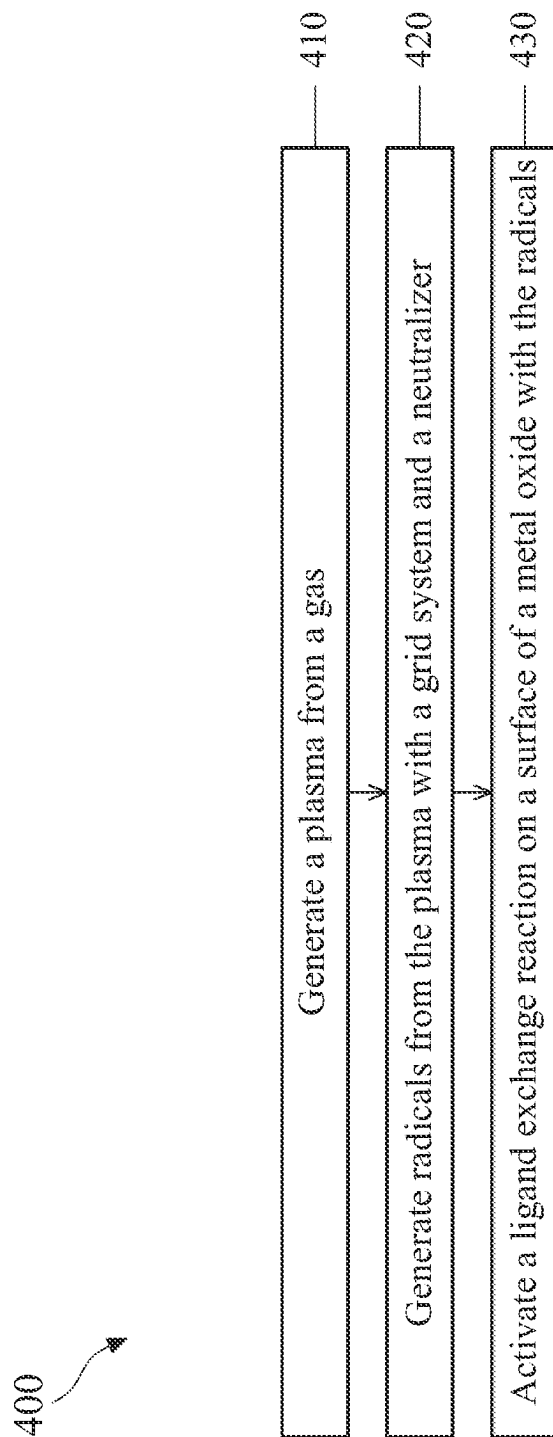


FIG. 4

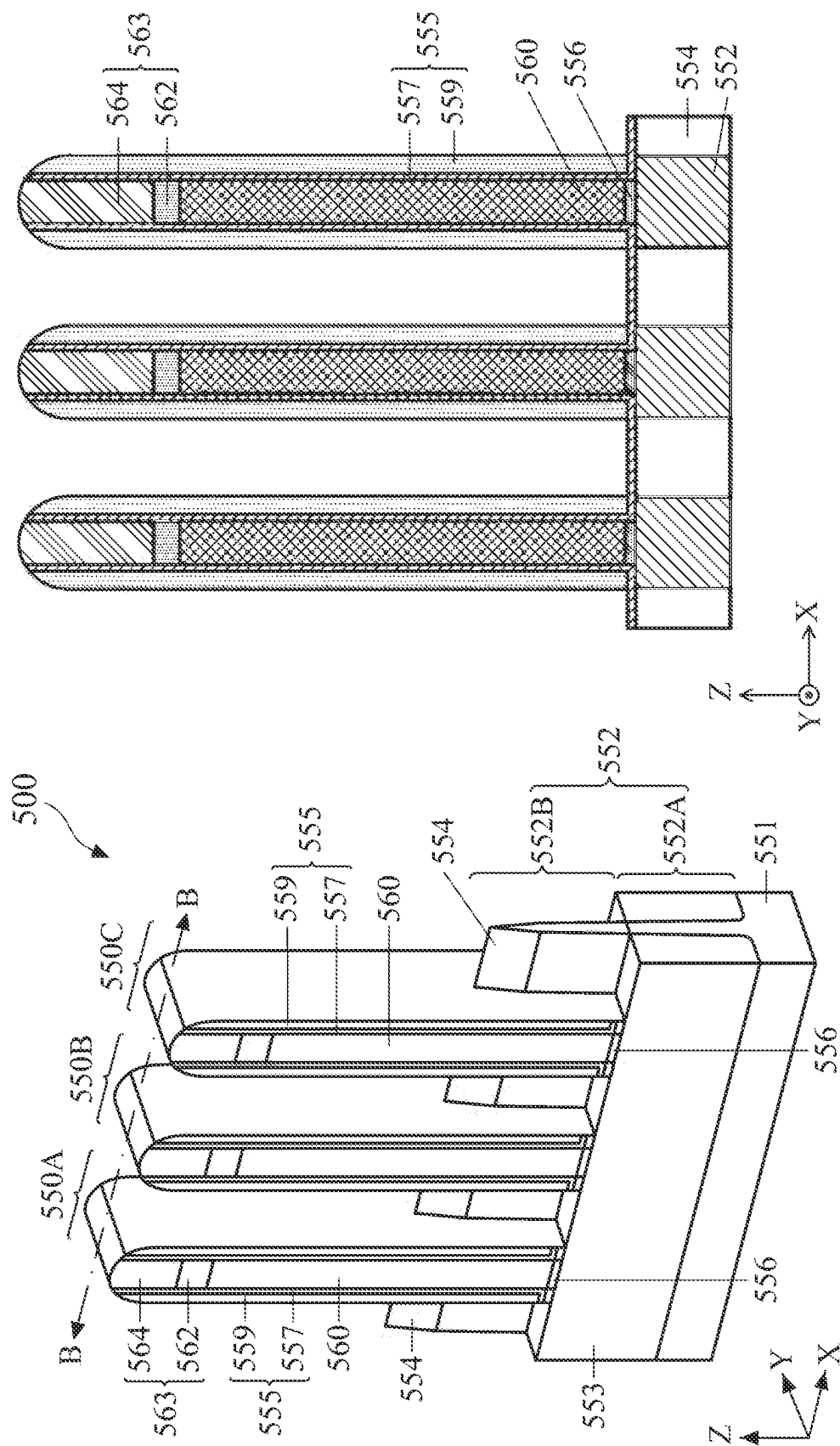


FIG. 5A

FIG. 5B

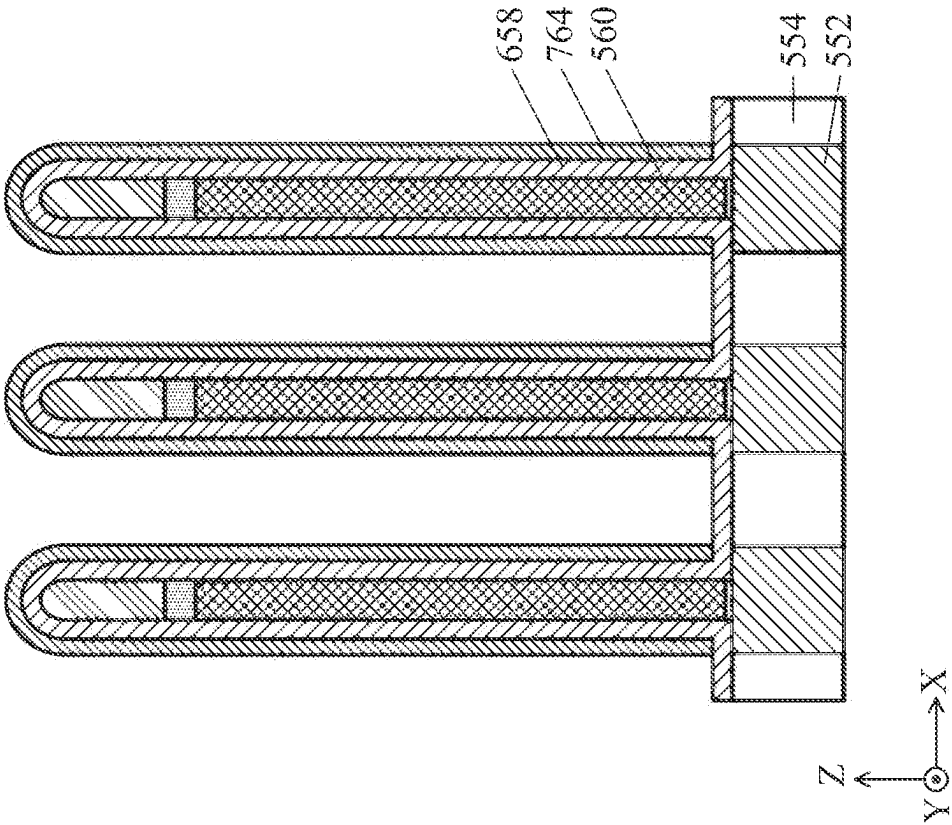


FIG. 6

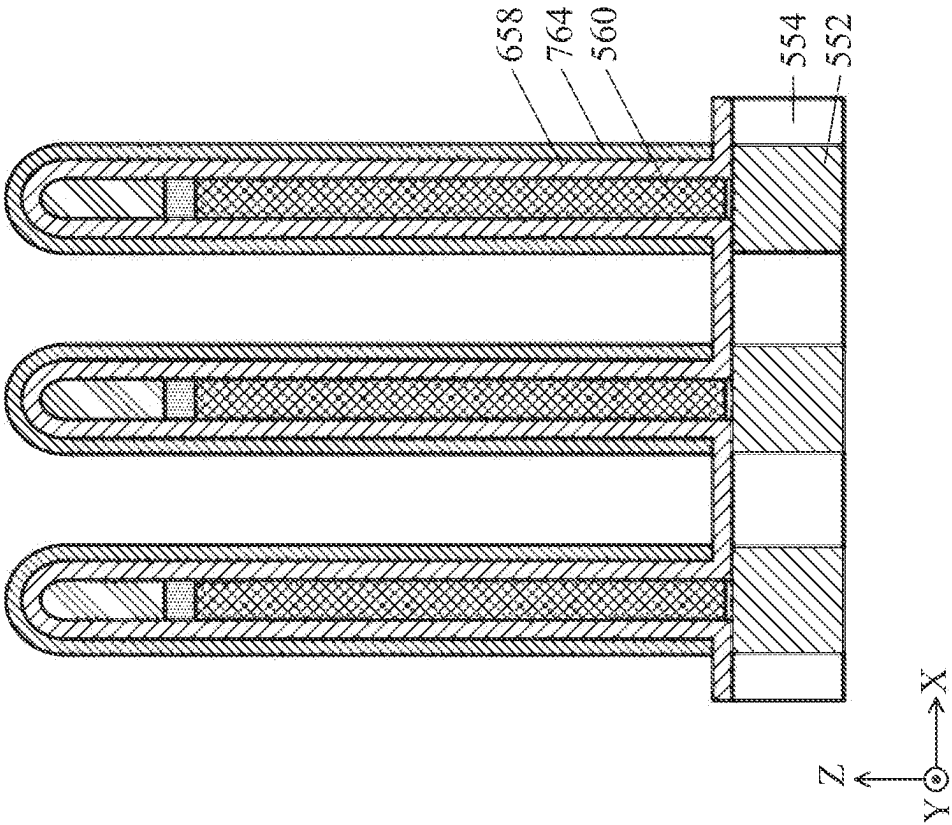


FIG. 7

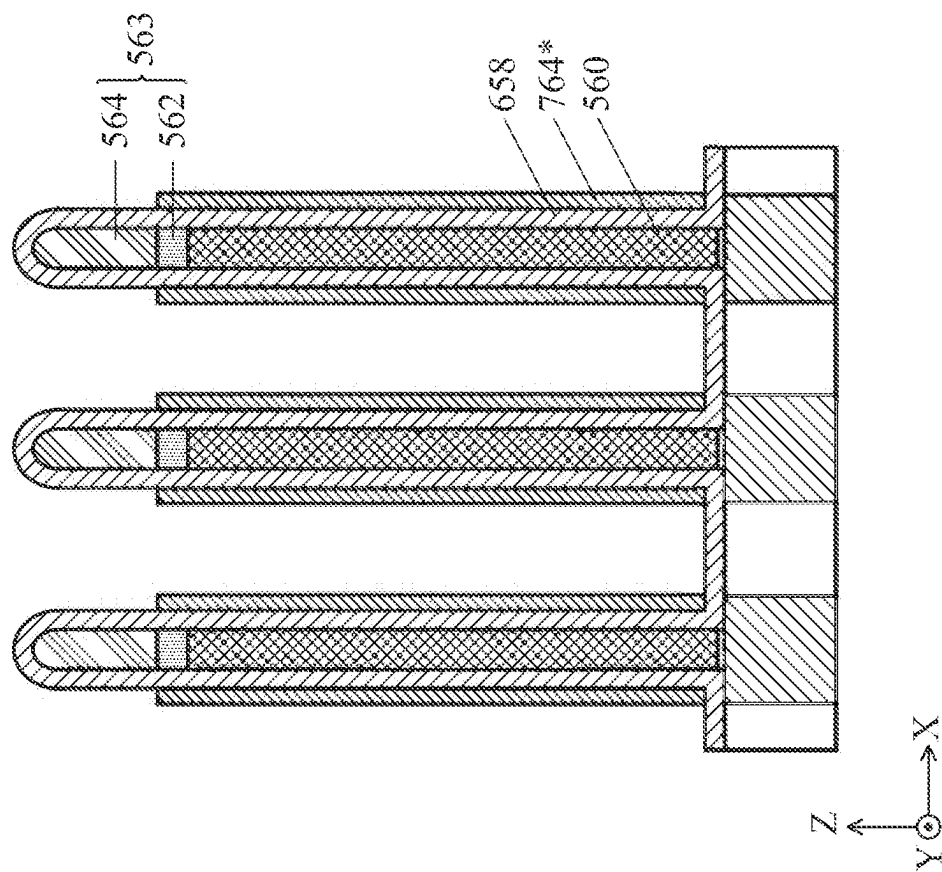


FIG. 8

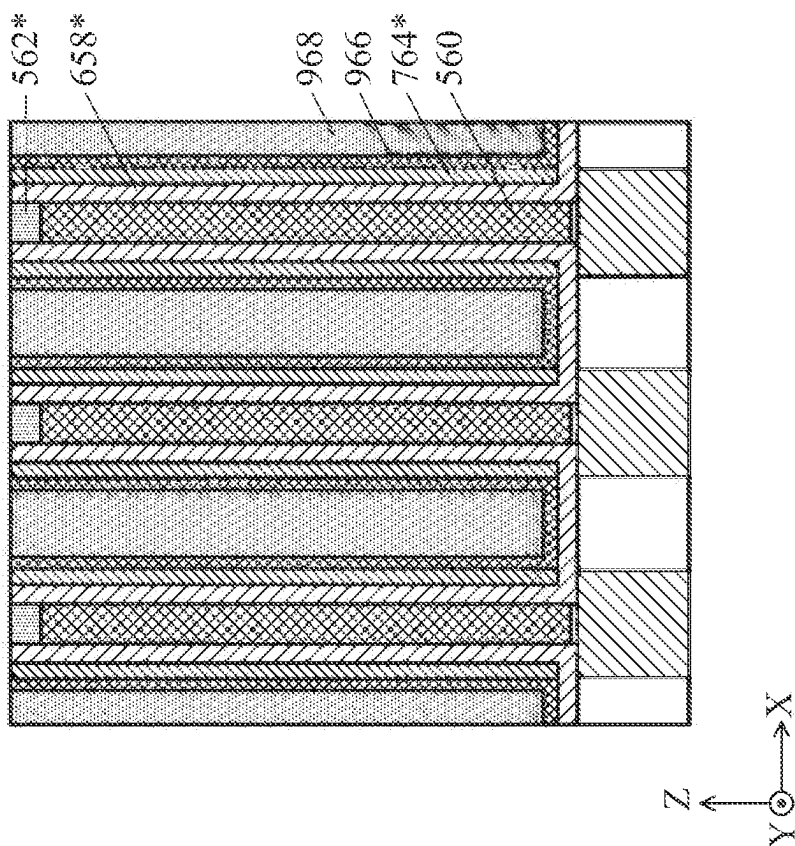


FIG. 9

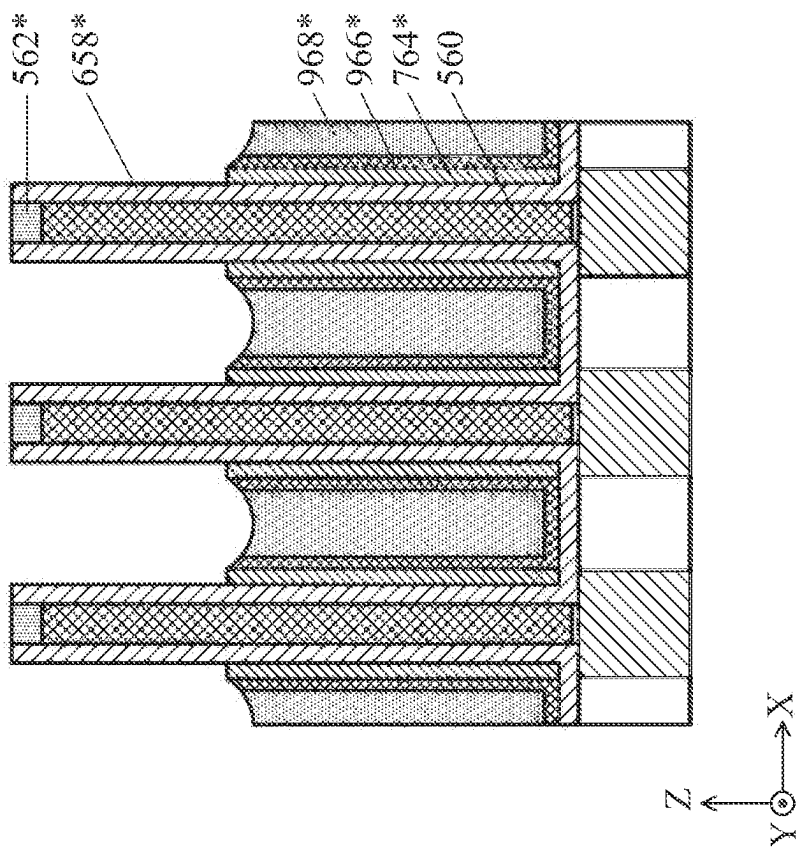


FIG. 10

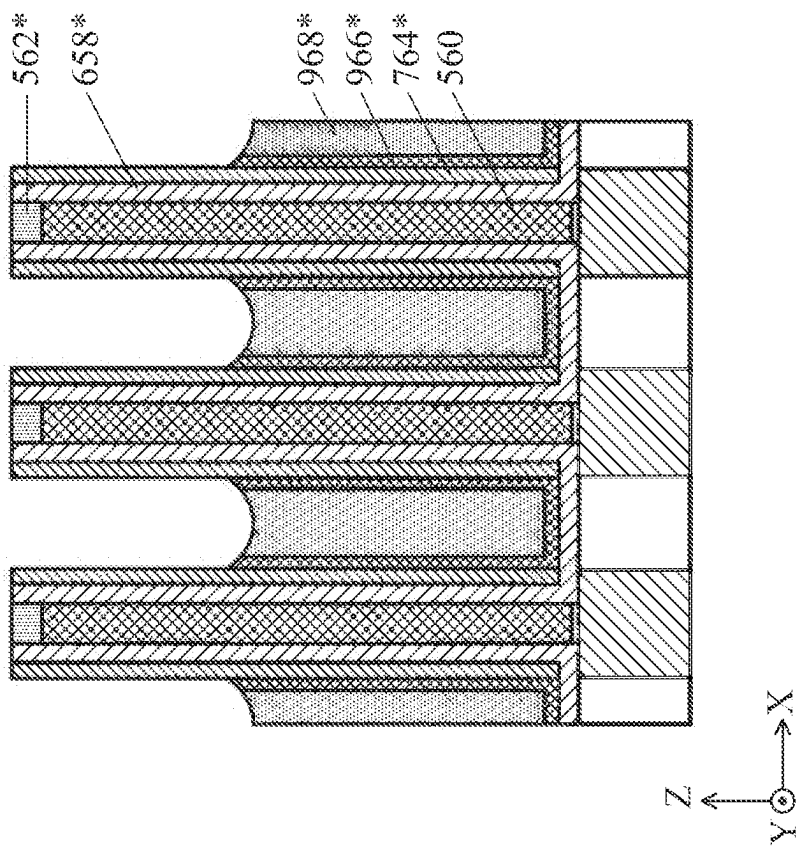


FIG. 11

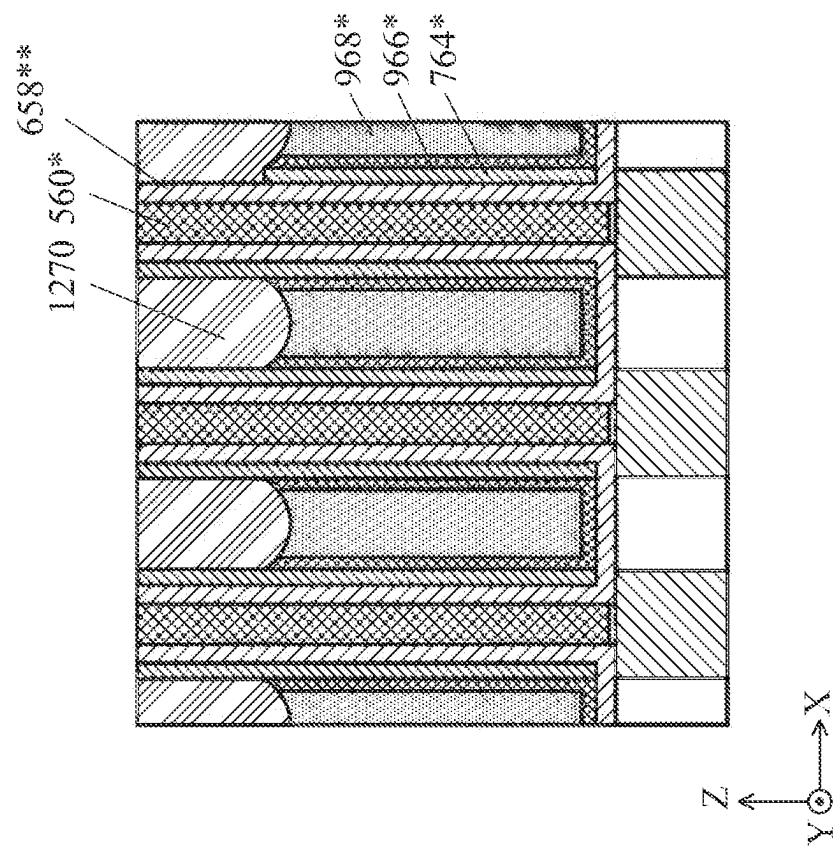


FIG. 12

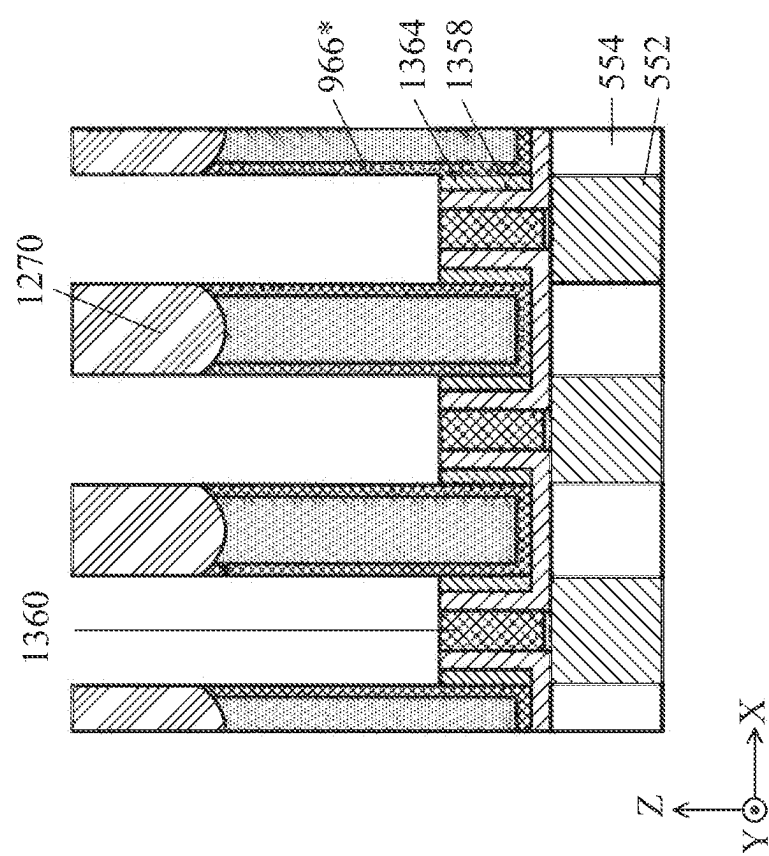


FIG. 13

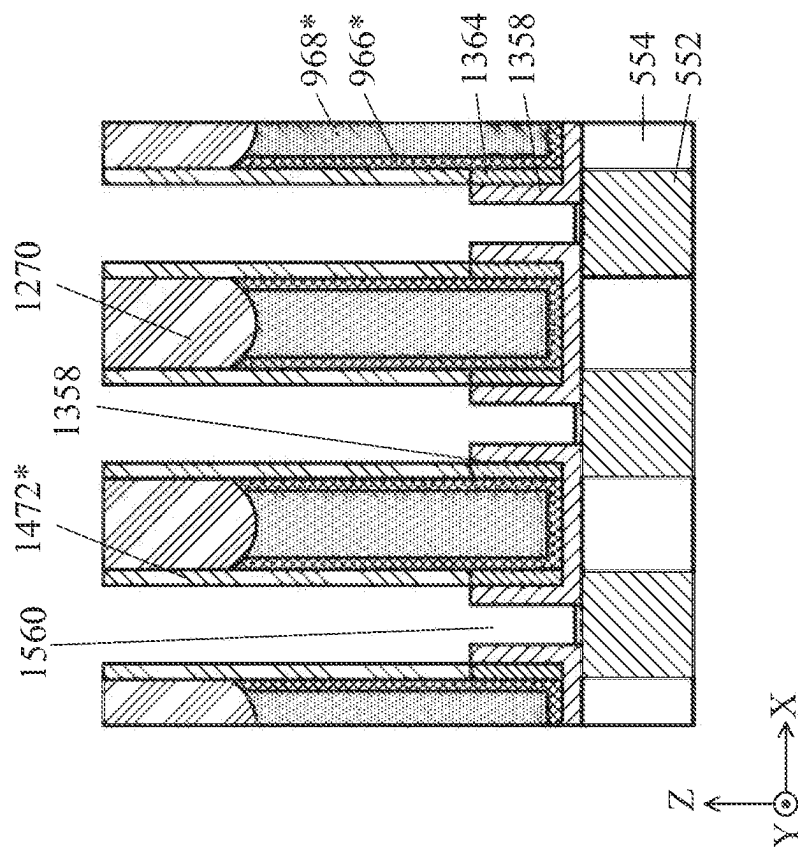


FIG. 14

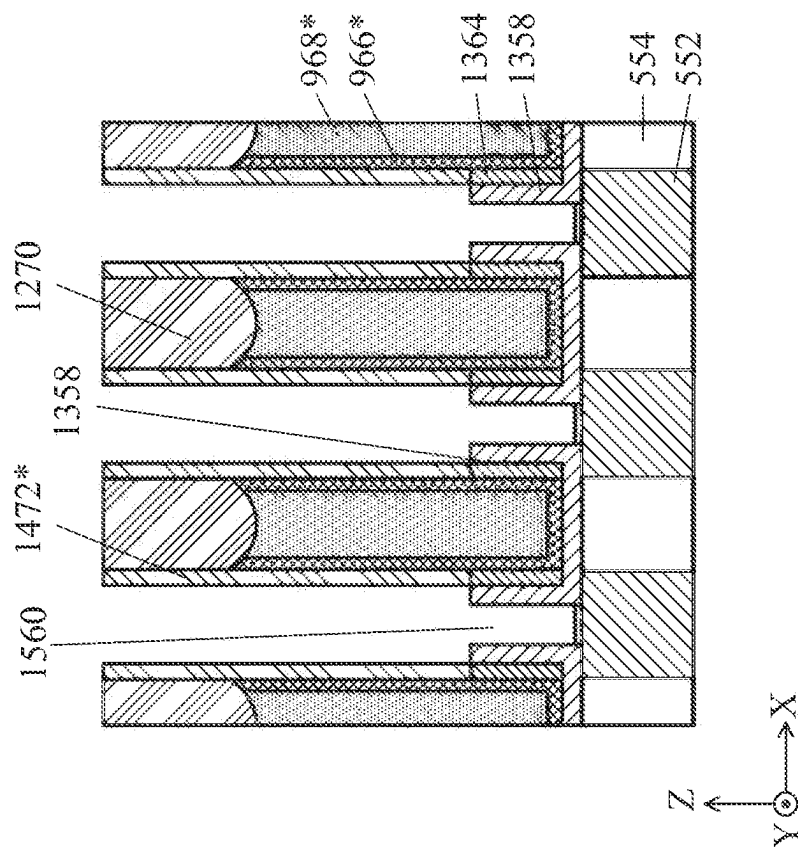


FIG. 15

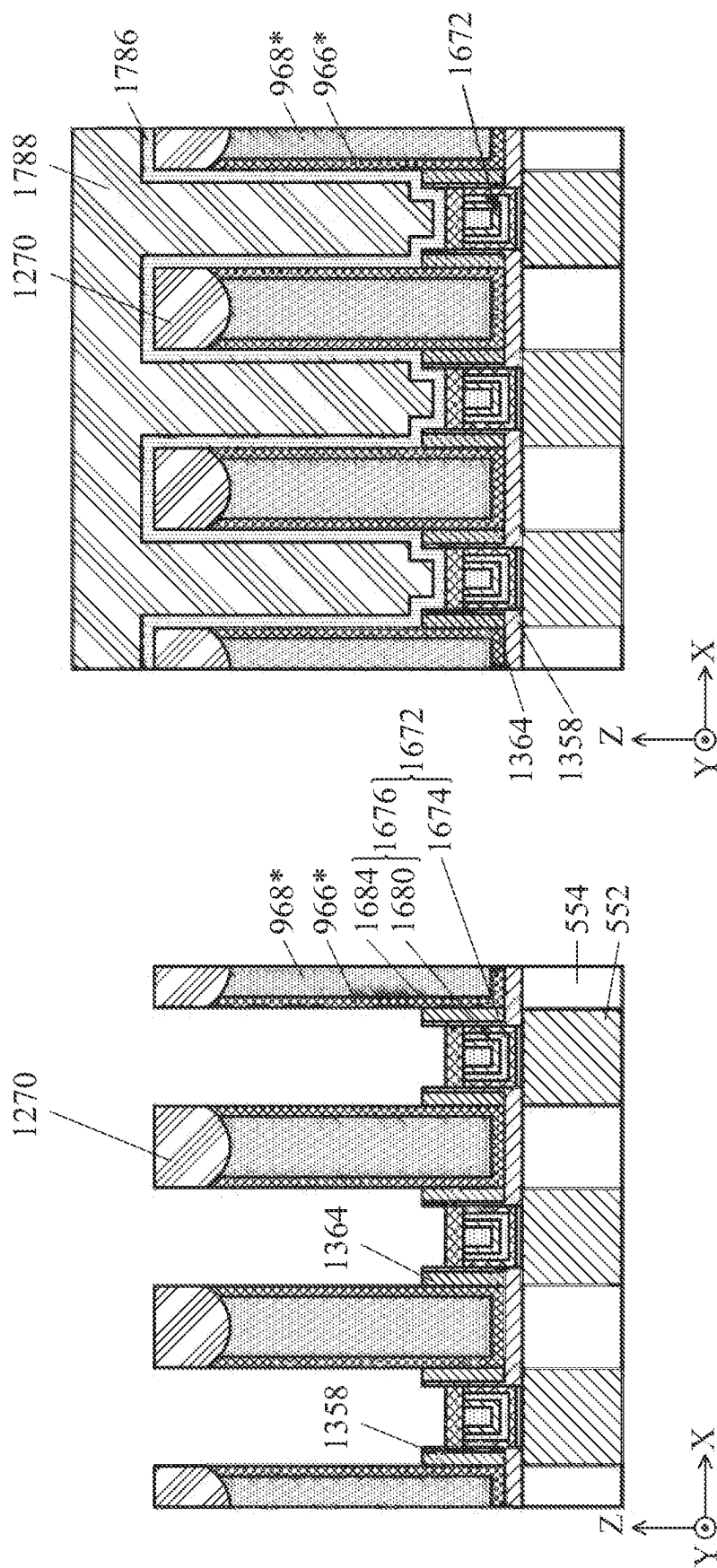


FIG. 16

FIG. 17

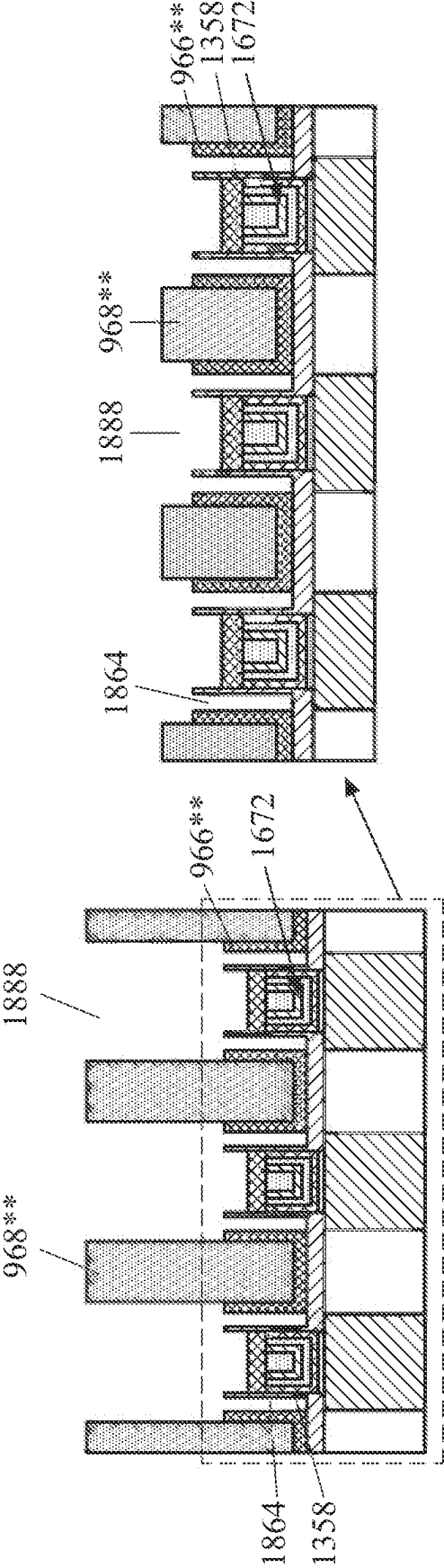


FIG. 18A

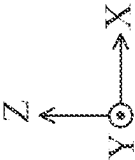


FIG. 18B

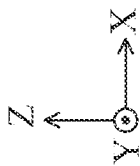
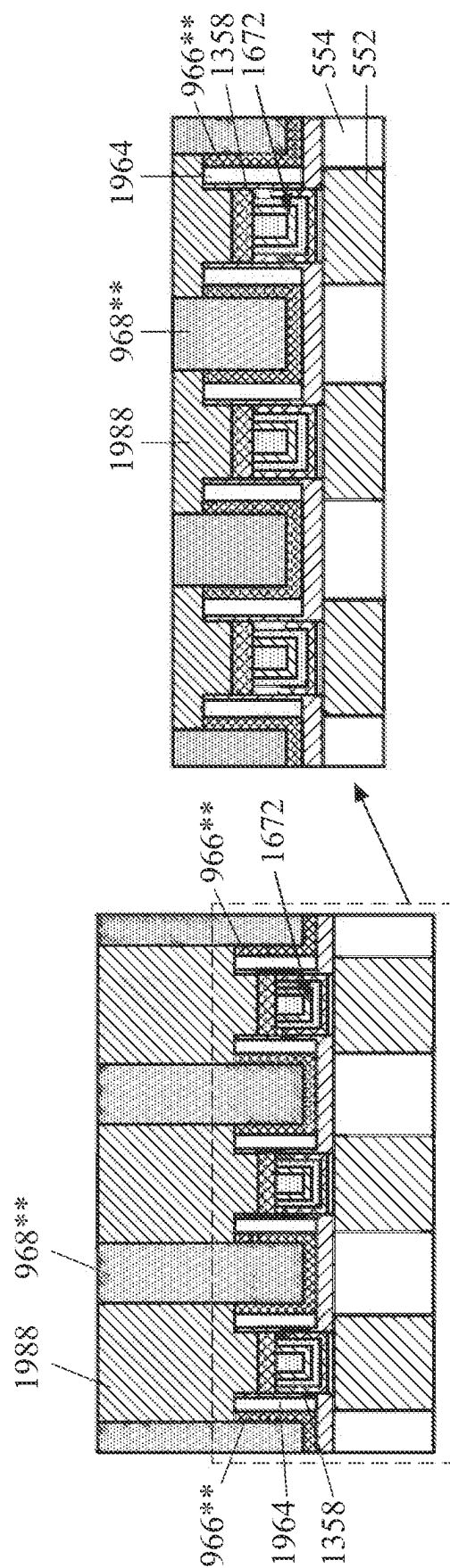


FIG. 19B

FIG. 19A

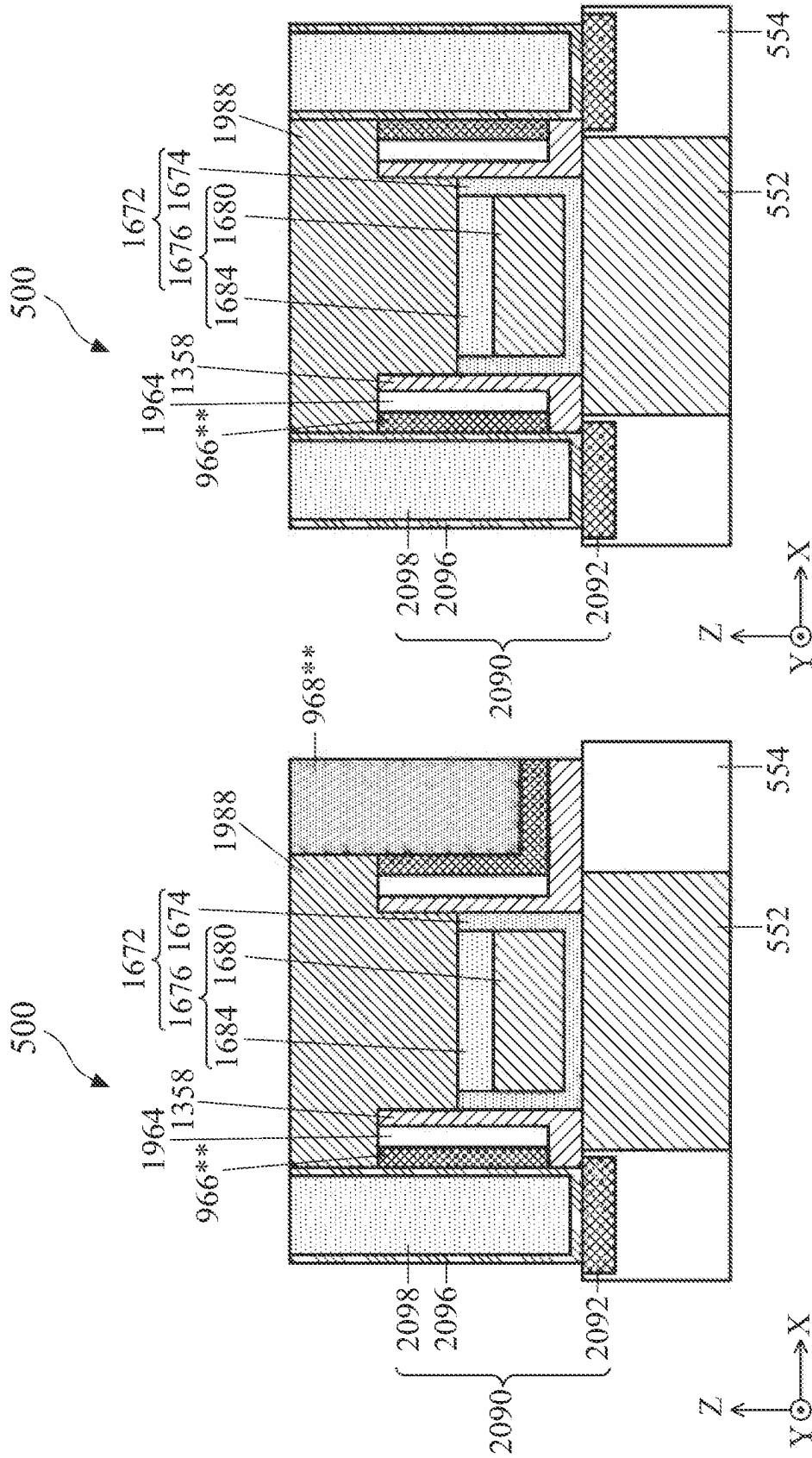


FIG. 20B

FIG. 20A

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RADICAL-ACTIVATED ETCHING OF METAL OXIDES

CROSS-REFERENCE TO RELATED APPLICATION

This application is a divisional application of U.S. patent application Ser. No. 17/081,709, filed on Oct. 27, 2020, titled "Radical-Activated Etching of Metal Oxides," the entire content of which is incorporated herein by reference.

BACKGROUND

Dry etching is a semiconductor manufacturing process that removes a masked pattern of material by exposing the material to a bombardment of ions. Before etching, a wafer can be coated with photoresist or a hard mask (e.g., oxide or nitride) and exposed to a circuit pattern during a photolithography operation. The etching process can remove material from the pattern traces. This sequence of patterning and etching can be repeated multiple times during the semiconductor manufacturing process.

BRIEF DESCRIPTION OF THE DRAWINGS

Aspects of the present disclosure are best understood from the following detailed description when read with the accompanying figures.

FIG. 1 illustrates a cross-sectional view of a radical-activated thermal atomic layer etching (ALE) system, in accordance with some embodiments.

FIG. 2 illustrates a cross-sectional view of a grid system and a neutralizer of a radical-activated thermal ALE system, in accordance with some embodiments.

FIGS. 3A-3D illustrate top-down and side views of a grid system of a radical-activated thermal ALE system, in accordance with some embodiments.

FIGS. 3E and 3F illustrate a surface modification cycle and a material removal cycle, respectively, of an exemplary radical-activated thermal ALE process, in accordance with some embodiments.

FIG. 4 illustrates a method of radical-activated thermal ALE of a metal oxide, in accordance with some embodiments.

FIGS. 5A, 5B, 6-17, 18A, 18B, 19A, 19B, 20A, and 20B illustrate cross-sectional and isometric views of a semiconductor device having an air gap at various stages of its fabrication process using a radical-activated thermal ALE process, in accordance with some embodiments.

Illustrative embodiments will now be described with reference to the accompanying drawings. In the drawings, like reference numerals generally indicate identical, functionally similar, and/or structurally similar elements.

DETAILED DESCRIPTION

The following disclosure provides many different embodiments, or examples, for implementing different features of the provided subject matter. Specific examples of components and arrangements are described below to simplify the present disclosure. These are, of course, merely examples and are not intended to be limiting. For example, the formation of a first feature over a second feature in the description that follows may include embodiments in which the first and second features are formed in direct contact, and may also include embodiments in which additional features may be formed between the first and second features, such

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that the first and second features may not be in direct contact. As used herein, the formation of a first feature on a second feature means the first feature is formed in direct contact with the second feature. In addition, the present disclosure may repeat reference numerals and/or letters in the various examples. This repetition does not in itself dictate a relationship between the various embodiments and/or configurations discussed.

Further, spatially relative terms, such as "beneath," "below," "lower," "above," "upper," and the like, may be used herein for ease of description to describe one element or feature's relationship to another element(s) or feature(s) as illustrated in the figures. The spatially relative terms are intended to encompass different orientations of the device in use or operation in addition to the orientation depicted in the figures. The apparatus may be otherwise oriented (rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein may likewise be interpreted accordingly.

It is noted that references in the specification to "one embodiment," "an embodiment," "an example embodiment," "exemplary," etc., indicate that the embodiment described may include a particular feature, structure, or characteristic, but every embodiment may not necessarily include the particular feature, structure, or characteristic. Moreover, such phrases do not necessarily refer to the same embodiment. Further, when a particular feature, structure or characteristic is described in connection with an embodiment, it would be within the knowledge of one skilled in the art to effect such feature, structure or characteristic in connection with other embodiments whether or not explicitly described.

It is to be understood that the phraseology or terminology herein is for the purpose of description and not of limitation, such that the terminology or phraseology of the present specification is to be interpreted by those skilled in relevant art(s) in light of the teachings herein.

In some embodiments, the terms "about" and "substantially" can indicate a value of a given quantity that varies within 5% of the value (e.g., $\pm 1\%$, $\pm 2\%$, $\pm 3\%$, $\pm 4\%$, $\pm 5\%$ of the value). These values are merely examples and are not intended to be limiting. The terms "about" and "substantially" can refer to a percentage of the values as interpreted by those skilled in relevant art(s) in light of the teachings herein.

Dry etching is a process used in semiconductor manufacturing. Before etching, a wafer can be coated with a photoresist or a hard mask (e.g., oxide or nitride) and a circuit pattern can be transferred on the photoresist or the hard mask using photolithographic processes (e.g., photo exposure, post exposure bake, develop, hard bake, etc.). An etching process can be subsequently used to remove material from the surface of the wafer that is not covered by the patterned photoresist or hard mask. This sequence of patterning and etching can be repeated multiple times during the semiconductor manufacturing process.

Plasma etching is performed by applying electromagnetic energy (e.g., radio frequency (RF)) to a gas that contains a chemically-reactive element, such as nitrogen trifluoride and hydrogen, to form a plasma. The plasma releases positively-charged ions that can bombard the surface of a wafer to remove, or etch, material. At the same time, chemically-reactive radicals (e.g., atoms or groups of atoms with unpaired electrons) can react with the surface of the wafer to modify surface properties. To improve etch throughput, higher etch rates (e.g., several Å/min or nm/min) are desirable.

Process chemistries can differ depending on the types of films to be etched. For example, etch chemistries used in dielectric etch applications can be fluorine-based. Silicon and metal etch applications can use chlorine-based chemistries. An etch operation can include etching one or more film layers from the surface of a wafer. When multiple layers are on the surface of the wafer, for example during the removal of a metal oxide, the etch process is required to remove the metal oxide but preserve other layers (e.g., silicon, silicon oxide, silicon nitride, etc.), the selectivity of the etch process becomes an important parameter. Selectivity of an etch chemistry or an etch process can be defined as the ratio of two etch rates: the rate for the layer to be removed to the rate for the layer to be preserved. In an etch process, high selectivity ratios (e.g., greater than 10:1) are desirable. The ions in the plasma etching can have higher kinetic energies than the radicals. Accordingly, the ions can have a higher etch rate than the radicals. However, the ions can have a lower etch selectivity than the radicals. The term "etch selectivity" can refer to the ratio of the etch rates of two different materials under the same etching conditions. A higher etch rate with higher etch selectivity can be an objective in an etch process.

Various embodiments of the present disclosure provide an exemplary radical-activated thermal atomic layer etching (ALE) process. In some embodiments, the radical-activated thermal ALE process can activate a ligand exchange reaction on a surface of a metal oxide on a wafer using radicals with increased kinetic energies, thereby increasing an etch rate of the metal oxide and increasing the etch selectivity between the metal oxide and adjacent materials on the wafer. The metal oxide can include hafnium oxide, aluminum oxide, zirconium oxide, and other suitable metal oxide dielectric materials.

Atomic layer etching, or ALE, is a technique that can remove thin layers of material from the surface of a wafer using sequential reaction cycles (e.g., duty cycles), for example, during the removal of a metal oxide on one or more dielectric layers. The sequential reaction cycles of an ALE process can be "quasi self-limiting." In some embodiments, quasi self-limiting reactions may refer to those reactions that slow down as a function of time (e.g., asymptotically), or as a function of species dosage. A radical-activated thermal ALE process can include three sequential reaction cycles: (i) a surface modification cycle, (ii) a material removal cycle, and (iii) a surface cleaning cycle. In some embodiments, a time elapsed between sequential cycles (e.g., between the surface modification cycle and the material removal cycle) is referred to as a "transition time." During the transition time, reactants/byproducts from a current cycle are removed away from the surface of the wafer, prior to the release of new reactants. Prompt delivery of reactants into the chamber can reduce the transition time between cycles and the cycle duration (cycle time). In a radical-activated thermal ALE process, the reactants can be, for example, delivered by one or more gases, a plasma, a vapor, or other suitable sources.

The surface modification cycle can form a reactive surface layer with a defined thickness from a material on the surface of a wafer that has been exposed to radicals in the surface modification process. In some embodiments, the radical-activated thermal ALE process can modify the surface of the metal oxide layer with radicals generated from a plasma during the surface modification cycle. The modified material layer (reactive surface layer) can be subsequently removed during the next cycle (e.g., material removal cycle). Any unmodified material, which is not exposed to the surface modification chemistry during the surface modifi-

cation cycle, will not be removed. The modified material, for example, can have a gradient in chemical composition and/or physical structure.

The material removal cycle can include a ligand exchange reaction, which can be performed under a thermal condition. In some embodiments, radicals generated from ions of a plasma having increased kinetic energies can increase the ligand exchange kinetic energies and the speed of the ligand exchange reaction, thus increasing removal of the modified surface of the metal oxide layer and the etching rate of the metal oxide layer. In some embodiments, one or more plates with evenly distributed holes or openings can distribute the gases and plasmas uniformly across the wafer. In some embodiments, the radical-activated thermal ALE system can include a grid system to increase kinetic energies of ions from the plasma and a neutralizer to neutralize the ions and form radicals. The grid system can include a screen grid to screen ions having appropriate angles, an accelerator grid to increase kinetic energies of the ions, and a decelerator grid to reduce divergence of the beam of the ions and block electrons generated by the neutralizer from entering the grid system. The neutralizer can generate electrons and neutralize the ions to form radicals with increased kinetic energies. The material removal cycle can remove the modified material layer while keeping the unmodified material(s) or layers intact. The total amount of material removed can be controlled by the number of repeated cycles (e.g., surface modification cycle, material removal cycle, and surface cleaning cycle).

The surface cleaning cycle can remove surface residues and byproducts from the material removal cycle on the surface of the wafer with a flush of radicals and reset the surface to a near-pristine state for the next etching cycle. The radical flush can further increase the etching rate of the radical-activated thermal ALE process. The radical-activated thermal ALE technique can be used in a variety of etching schemes including, but not limited to, directional or isotropic etching (e.g., formation of air spacers) and selective or nonselective etching (e.g., removal of dielectric layers from an exposed surface).

FIG. 1 illustrates a cross-sectional view of an exemplary radical-activated thermal atomic layer etching (ALE) system **100**, in accordance with some embodiments. By way of example and not limitation, radical-activated thermal ALE system **100** can include a chamber **102**, a shower head **103** and a wafer holder **104** in chamber **102**, a first gas line **106** and a second gas line **108** connected to chamber **102**, and an electrical source **110** connected to wafer holder **104**. In some embodiments, an inner surface of chamber **102** can be covered with yttrium oxide (Y_2O_3) to protect chamber **102** from plasmas and etch chemistries in the radical-activated ALE process. Shower head **103** can connect to first gas line **106** and release gases from first gas line **106** into chamber **102**. A pressure in chamber **102** can range from about 3 mTorr to about 4 Torr. In the surface modification cycle, the pressure in chamber **102** can range from about 1 Torr to about 4 Torr. If the pressure is less than about 1 Torr or greater than about 4 Torr, a thickness of modified surface layer may be thinner or thicker than required, respectively. In the material removal cycle, the pressure in chamber **102** can range from about 100 mTorr to about 1000 mTorr. If the pressure is less than about 100 mTorr, the ligand exchange precursors may be decomposed. If the pressure is greater than about 1000 mTorr, the ligand exchange precursors may be condensed on chamber **102**. In the surface cleaning cycle, the pressure in chamber **102** can range from about 20 mTorr to about 200 mTorr. If the pressure is less than about 20

mTorr, metal oxide surfaces may be damaged. If the pressure is greater than about 200 mTorr, byproducts and residues may not be completely cleaned.

Wafer holder 104 can be an electrostatic wafer chuck and configured to hold a wafer 112. Wafer 112 can be patterned and have areas of a metal oxide layer on a surface of wafer 112 exposed for etching. In some embodiments, the metal oxide layer can include hafnium oxide, aluminum oxide, zirconium oxide, and other suitable metal oxide dielectric materials. Wafer holder 104 can include a heater (not shown) to heat wafer 112. In some embodiments, wafer 112 can be heated to a temperature ranging from about 150° C. to about 300° C. for the radical-activated thermal ALE process. If the temperature is less than about 150° C., the ligand exchange reaction may not initiate and the metal oxide layer may not be removed. If the temperature is greater than about 300° C., the radical-activated thermal ALE process may have less etch selectivity between the metal oxide layer and adjacent structures and cause surface damage to the adjacent structures. In some embodiments, wafer holder 104 can be biased by electrical source 110 to provide vertical profile control for a directional etch process. For example, in the surface modification cycle and the surface cleaning cycle, a small amount of ions (e.g., less than about 5%) in radicals 136 can provide a vertical etch profile and a faster etch rate with bias control by electrical source 110.

First gas line 106 can connect to a gas panel 120, which can provide a gas 114 to chamber 102 to generate radicals for the radical-activated thermal ALE process. In some embodiments, gas panel 120 can provide gases including fluorine (F₂), hydrogen fluoride (HF), nitrogen trifluoride (NF₃), carbon tetrafluoride (CF₄), trifluoromethane (CHF₃), hexafluorobutadiene (C₄F₆), octafluorocyclobutane (C₄F₈), sulfur hexafluoride (SF₆), hydrogen (H₂), helium (He), and argon (Ar). In some embodiments, gas 114 can include F₂, HF, NF₃, CF₄, CHF₃, C₄F₆, C₄F₈, and SF₆ to generate plasmas and fluorine radicals for modifying the surface of the metal oxide layer. In some embodiments, gas 114 can include inert gases, such as He and Ar, to generate radicals with increased kinetic energies for activating ligand exchange precursors and speeding up ligand exchange reaction. In some embodiments, gas 114 can include H₂ and He to generate radicals for cleaning the surface of the metal oxide layer after the ligand exchange reaction. In some embodiments, gas 114 can include He for a transition cycle after each cycle of the radical-activated thermal ALE process to pump and purge chamber 102, preventing intermixing of gases and plasmas of different cycles. In some embodiments, the transition cycle can last from about 30 s to about 60 s. In some embodiments, the plasma and radicals of He can be more effectively pumped and purged than H₂. In some embodiments, a plasma generator (shown in FIG. 2) can generate plasmas from gas 114 provided to shower head 103 from gas panel 120 through first gas line 106. In some embodiments, plasmas of gas 114 can be generated outside chamber 102 and first gas line 106 can direct plasmas of gas 114 to shower head 103 in chamber 102.

Second gas line 108 can connect to a vaporizer 115 and control a gas flow of a vapor 116 flowing from vaporizer 115 into chamber 102. Vaporizer 115 can convert a ligand exchange precursor from liquid to vapor 116, which can be drawn to chamber 102 by the vacuum in chamber 102. In some embodiments, a flow rate of vapor 116 can range from about 50 sccm to about 900 sccm. If the flow rate of vapor 116 is less than about 50 sccm, the modified surface may not

be fully removed. If the flow rate of vapor 116 is greater than about 900 sccm, ligand residues may form on the surface of wafer 112.

Radical-activated thermal ALE system 100 can further include a gas distribution plate 126, a grid system 124, and a neutralizer 122 in chamber 102. In some embodiments, gas distribution plate 126 can have evenly distributed openings or concentric openings to uniformly distribute gas 114 delivered into chamber 102. Plasma region 128 can be formed between gas distribution plate 126 and grid system 124 by a plasma generator shown in FIG. 2. When gas 114 is delivered to chamber 102 through first gas line 106 and shower head 103, plasma region 128 can be formed including ions and radicals of gas 114. Grid system 124 can include a screen grid 130, an accelerator grid 132, and a decelerator grid 134. Grid system 124 can increase kinetic energies of the ions from the plasmas of plasma region 128. Neutralizer 122 can neutralize the ions with increased kinetic energies and generate radicals 136 with increased kinetic energies. Radicals 136 with increased kinetic energies can transfer the kinetic energies to vapor 116 of ligand exchange precursors and generate activated gas region 138 to react with modified surface of the metal layer on wafer 112.

FIG. 2 illustrates a cross-sectional view of grid system 124 and neutralizer 122 of radical-activated thermal ALE system 100, in accordance with some embodiments. As shown in FIG. 2, plasma region 128 can be generated between plates of plasma generator 240 using a power supply 242. In some embodiments, power supply 242 can be a direct current (DC) power supply. Referring to FIG. 2, grid system 124 can have screen grid 130, accelerator grid 132, and decelerator grid 134 aligned in the path of the ions towards wafer 112. Screen grid 130 can be in contact with plasma region 128. Screen grid 130 can be biased at a positive voltage relative to a ground to separate ions from plasma region 128 having appropriate angles (e.g., about 90 degrees relative to screen grid 130). In some embodiments, screen grid 130 can be biased at a positive voltage ranging from about 500 V to about 2000 V by power supply 242. Accelerator grid 132 can be disposed between screen grid 130 and decelerator grid 134. Accelerator grid 132 can be biased at a negative voltage related to a ground to accelerate the ions screened by screen grid 130. In some embodiments, accelerator grid 132 can be biased at a negative voltage ranging from about -50 V to about -400 V by power supply 244. A voltage different between accelerator grid 132 and screen grid 130 can create an electric field to accelerate the ions, thereby increasing kinetic energies of the ions. Decelerator grid 134 can be disposed between decelerator grid 134 and neutralizer 122. Decelerator grid 134 can connect to a ground 245 (e.g., 0 V) through a resistor 246. Decelerator grid 134 can reduce divergence of a beam of the accelerated ions and form ion beam 236 with increased kinetic energies. A voltage different between decelerator grid 134 and accelerator grid 132 can create another electric field to prevent electrons generated by neutralizer from entering grid system 124.

Referring to FIG. 2, neutralizer 122 can be disposed after decelerator grid 134 on the path of the ions from plasma region 128. Neutralizer 122 can generate electrons 248 to neutralize the ions in ion beam 236. As ion beam 236 includes ions with increased kinetic energies from grid system 124, neutralizer 122 can neutralize the ions with electrons 248 and form radicals 136 with increased kinetic energies. In some embodiments, neutralizer 122 can generate electrons 248 at a rate that balances positive charges of the ions in ion beam 236.

FIGS. 3A and 3B illustrate top-down views of grid system 124 of radical-activated thermal ALE system 100, in accordance with some embodiments. FIGS. 3C and 3D illustrate side views of apertures and ion beams in grid system 124, in accordance with some embodiments. As shown in FIG. 3A, the grids in grid system 124 can have apertures evenly distributed on the grids. In some embodiments, as shown in FIGS. 3B-3D, a diameter D_s of apertures 330 on screen grid 130 can be larger than a diameter D_a of apertures 332 on accelerator grid 132. And a diameter D_d of the apertures on decelerator grid 134 can be larger than diameter D_a of apertures 332 on accelerator grid 132. As a result, apertures 332 can be seen inside apertures 330 from top-down views in FIGS. 3A and 3B while the apertures on decelerator grid 134 may not be seen from top-down views. In some embodiments, diameter D_s can range from about 4 mm to about 7 mm. Diameter D_a can range from about 2 mm to about 5 mm. Diameter D_d can range from about 3 mm to about 7 mm. For example, diameter D_s can be about 5 mm, diameter D_a can be about 3.5 mm, and diameter D_d can be about 4.5 mm. In some embodiments, a difference 61 between diameters D_s and D_a can range from about 0.5 mm to about 4 mm. In some embodiments, as shown in FIG. 3C, a difference 62 between diameters D_d and D_a can range from about 0.5 mm to about 2.5 mm. For example, difference 61 can be about 1.5 mm and difference 62 can be about 1 mm. Screen grid 130 with diameter D_s greater than diameter D_a of accelerator grid 132 can increase the number of ions in ion beam 236. Accelerator grid 132 with diameter D_a less than diameter D_s can accelerate and focus ions in ion beam 236. In some embodiments, diameter D_s can be greater than, less than, or the same as diameter D_d . In some embodiments, screen grid 130 can have a thickness T_s along a Z-axis ranging from about 0.3 mm to about 0.8 mm. In some embodiments, accelerator grid 132 can have a thickness T_a along a Z-axis ranging from about 0.4 mm to about 1 mm. In some embodiments, decelerator grid 134 can have a thickness T_d along a Z-axis ranging from about 0.4 mm to about 1.2 mm. For example, thickness T_s can be about 0.4 mm, thickness T_a can be about 0.5 mm, and thickness T_d can be about 0.7 mm. In some embodiments, as shown in FIG. 3C, a separation space S_1 between screen grid 130 and accelerator grid 132 along a Z-axis can range from about 0.4 mm to about 0.6 mm. And a separation space S_2 between accelerator grid 132 and decelerator grid 134 along a Z-axis can range from about 0.5 mm to about 0.7 mm. For example, separation space S_1 can be about 0.5 mm and separation space S_2 can be about 0.6 mm. With the configurations of screen grid 130, accelerator grid 132, and decelerator grid 134 as shown in FIGS. 3A-3D, ions in plasma 128 can be focused through these grids without direct interception and form ion beam 236. Misalignment of these grids and out of range for the diameters and thicknesses can lead to direct interception of ion beam 236 on the grids, which can cause erosion to the grids by ions in ion beam 236 with increased kinetic energies. In some embodiments, FIGS. 3E and 3F illustrate a surface modification cycle and a material removal cycle, respectively, of an exemplary radical-activated thermal ALE process, which are described in detail below.

FIG. 4 illustrates method 400 of radical-activated thermal ALE of a metal oxide, in accordance with some embodiments. Additional operations may be performed between various operations of method 400 and may be omitted merely for clarity and ease of description. Additional operations can be provided before, during, and/or after method 400; one or more of these additional processes are briefly

described herein. Therefore, method 400 may not be limited to the operations described below.

Method 400 can be performed by exemplary radical-activated thermal ALE system 100 shown in FIGS. 1, 2, and 3A-3F and other suitable radical-activated thermal ALE systems. For illustrative purposes, the operations in FIG. 4 will be described with reference to exemplary radical-activated thermal ALE system 100 shown in FIGS. 1, 2, and 3A-3F. As shown in FIGS. 1, 2, and 3A-3F, radical-activated thermal ALE system 100 can include first gas line 106 to deliver gas 114 from gas panel 120 to chamber 102 and second gas line 108 to deliver vapor 116 to chamber 102. Shower head 103 can release gases from first gas line 106 to chamber 102. Wafer holder 104 can hold and heat wafer 112 having the metal oxide layer on the surface exposed for etching. Plasma generator 240 can generate a plasma from gas 114.

Referring to FIG. 4, method 400 begins with operation 410 and the process of generating a plasma from a gas. As shown in FIGS. 1 and 2, plasma generator 240 can generate a plasma in plasma region 128 from a gas 114. Gas 114 can be delivered from gas panel 120 to shower head 103 in chamber 102 through first gas line 106. Gas 114 can include F_2 , HF , NF_3 , CF_4 , CHF_3 , C_4F_6 , C_4F_8 , SF_6 , He , Ar , H_2 , and He to generate plasmas for different cycles of the radical-activated thermal ALE process. Gas distribution plate 126 can have evenly distributed openings or concentric openings to uniformly distribute gas 114 delivered into chamber 102. Plasma generator 240 can generate a plasma from gas 114 in plasma region 128 using power supply 242.

Referring to FIG. 4, method 400 continues with operation 420 and the process of generating radicals from the plasma with a grid system and a neutralizer. The grid system can include a screen grid, an accelerator grid, and a decelerator grid. As shown in FIG. 2, grid system 124 can generate ion beam 236 with increased kinetic energies from the plasma in plasma region 128. Neutralizer 122 can generate electrons 248 to neutralize the ions in ion beam 236 and form radicals 136 with increased kinetic energies. Grid system 124 can include screen grid 130, accelerator grid 132, and decelerator grid 134. Screen grid 130 can be biased at a positive voltage relative to a ground to separate ions from plasma region 128 having appropriate angles (e.g., about 90 degrees relative to screen grid 130). Accelerator grid 132 can be biased at a negative voltage related to a ground to accelerate the ions screened by screen grid 130. After accelerator grid 132, the ions can have increased kinetic energies. Decelerator grid 134 can connect to a ground 245 through a resistor 246 to reduce divergence of a beam of the accelerated ions and form ion beam 236 having increased kinetic energies. In addition, decelerator grid 134 can prevent electrons generated by neutralizer 122 from entering grid system 124.

Referring to FIG. 4, method 400 continues with operation 430 and the process of activating a ligand exchange reaction on a surface of a metal oxide with the radicals. As shown in FIGS. 1 and 2, radicals 136 with increased kinetic energies can transfer kinetic energies to vapor 116 and activate vapor 116 of ligand exchange precursor to form activated gas region 138. The activated ligand exchange vapors in gas region 138 can remove the modified surface of the metal oxide layer on wafer 112 and speed up the ligand exchange reaction. In some embodiments, without radicals having increased kinetic energies, the ligand exchange reaction can remove the metal oxide at an etch rate ranging from about 0.1 Å per cycle to about 0.6 Å per cycle. In some embodiments, with radicals 136 having increased kinetic energies, the ligand exchange reaction can remove the metal oxide at

an etch rate ranging from about 1 Å per cycle to about 5 Å per cycle. In some embodiments, radicals **136** having increased kinetic energies can increase the etch rate of the metal oxide by about 3 to about 10 times.

In some embodiments, radicals with increased kinetic energies can be generated in each cycle of the radical-activated thermal ALE process. In the surface modification cycle, the surface of the metal oxide layer on wafer **112** can be fluorinated by fluorine radicals, as shown in FIG. 3E. The fluorine radicals can be generated from the plasma of gas **114** through grid system **124** and neutralizer **122**, as shown in FIGS. 1 and 2. In some embodiments, the metal oxide layer on wafer **112** can include aluminum oxide and gas **114** can include NF_3 , F_2 , HF , CF_4 , CHF_3 , C_4F_6 , C_4F_8 , or SF_6 for the surface modification cycle. In some embodiments, NF_3 plasma can be generated at a pressure ranging from about 1 Torr to about 4 Torr with a power ranging from about 400 W to about 700 W. NF_3 gas flow rate can range from about 100 sccm to about 500 sccm. A gas flow rate of H_2 or He can range from about 1000 sccm to about 3000 sccm. A temperature of wafer holder **104** can range from about 250° C. to about 300° C. for the surface modification cycle. In some embodiments, a plasma of F_2 , HF , CF_4 , CHF_3 , or SF_6 can be generated at a pressure ranging from about 0.1 Torr to about 2 Torr with a flow rate ranging from about 100 sccm to about 500 sccm. The plasma power can range from about 500 W to about 800 W. A gas flow rate of H_2 or He can range from about 500 sccm to about 4000 sccm. In some embodiments, a plasma of C_4F_6 or C_4F_8 can be generated at a pressure ranging from about 30 mTorr to about 200 mTorr with a flow rate ranging from about 10 sccm to about 50 sccm. The plasma power can range from about 500 W to about 900 W. A gas flow rate of H_2 or He can range from about 500 sccm to about 200 sccm.

Grid system **124** can generate ions with increased kinetic energy and neutralizer **122** can generate electrons to neutralize the ions and form radicals **136** with increased kinetic energy for the surface modification cycle. In some embodiments, screen grid **130** can be biased at about 1.2 kV. Accelerator grid **132** can be biased at a voltage ranging from about -100 V to about -400 V. Decelerator grid **134** can be connected to ground **245**. Neutralizer **122** can generate electrons with a discharge current ranging from about 0.2 amperes (A) to about 0.5 Å and a mass flow rate ranging from about 0.2 mg/s to about 0.25 mg/s to neutralize the ions and form radicals **136** with increased kinetic energies. As radicals can have higher etch selectivity than ions, radicals **136** with increased kinetic energies can increase etch selectivity between the metal oxide and adjacent structures (e.g., a mask layer) and prevent surface damage to the adjacent structures.

An etch time of the surface modification cycle can range from about 10 s to about 30 s and a depth of fluorinated metal oxide on the surface of the metal oxide layer can range from about 3 Å to about 30 Å after the surface modification cycle. If the depth of fluorinated metal oxide is less than about 3 Å, the surface of the metal oxide layer may not be fully fluorinated for the ligand exchange reaction. If the depth of fluorinated metal oxide is greater than about 30 Å, the fluorinated metal oxide may not be fully removed by the ligand exchange reaction and ligand residues and byproducts may remain on the surface after the ligand exchange reaction. In some embodiments, FIG. 3E illustrates a surface modification cycle of an exemplary radical-activated thermal ALE process using fluorine radicals to fluorinate the surface of the metal oxide layer on wafer **112**.

The surface modification cycle can be followed by the material removal cycle. The fluorinated metal oxide on the surface of the metal oxide layer can be removed by a ligand exchange reaction, as shown in FIGS. 1, 2, and 3F. In some embodiments, gas **114** can include H_2 or an inert gas, such as He and Ar, at a flow rate ranging from about 1000 sccm to about 5000 sccm. In some embodiments, a plasma of H_2 , He, or Ar can be generated at a pressure ranging from about 100 mTorr to about 1000 mTorr. The plasma can be generated by a plasma source with a pulsing power ranging from about 250 W to about 500 W and a duty cycle from about 10% to about 80%.

Grid system **124** can generate ions with increased kinetic energy from gas **114** and neutralizer **122** can generate electrons to neutralize the ions and form radicals **136** with increased kinetic energy for the ligand exchange reaction. In some embodiments, screen grid **130** can be biased at about 1.2 kV. Accelerator grid **132** can be biased at a voltage ranging from about -50 V to about -600 V. Decelerator grid **134** can be connected to ground **245**. Neutralizer **122** can generate electrons with a discharge current ranging from about 0.2 Å to about 0.5 Å and a mass flow rate ranging from about 0.2 mg/s to about 0.25 mg/s to neutralize the ions and form radicals **136** with increased kinetic energies. Radicals **136** with increased kinetic energies can transfer kinetic energies to vapor **116** of ligand exchange precursor and form activated gas region **138**, speeding up the ligand exchange reaction at the surface of the metal oxide layer.

In some embodiments, the ligand exchange reaction can be performed at a temperature ranging from about 250° C. to about 300° C. and a temperature of wafer holder **104** can range from about 250° C. to about 300° C. In some embodiments, vapor **116** can include metal precursors, such as trimethyl-aluminum chloride ($\text{Al}(\text{CH}_3)_3$ or TMA), diethyl-aluminum chloride ($\text{Al}(\text{CH}_3)_2$ or DMAC), tin (II) acetylacetonate ($\text{Sn}(\text{acac})_2$), silicon tetrachloride (SiCl_4), and boron trichloride (BCl_3). In some embodiments, vapor **116** can have a flow rate ranging from about 50 sccm to about 900 sccm. In some embodiments, a time of the ligand exchange reaction in material removal cycle can range from about 10 s to about 50 s and the ligand exchange reaction can remove the fluorinated metal oxide on the surface of the metal oxide layer with a thickness ranging from about 3 Å to about 30 Å. If the time of the ligand exchange reaction is less than about 10 s, some of the fluorinated metal oxide may not be removed. If the time of the ligand exchange reaction is greater than about 50 s, ligand residues and byproducts may be formed on the surface of the metal layer after the fluorinated metal oxide are removed. In some embodiments, FIG. 3F illustrates a material removal cycle of an exemplary radical-activated thermal ALE process using hydrogen radicals to increase kinetic energies of ligand exchange precursor.

The material removal cycle can be followed by the surface cleaning cycle. The surface cleaning cycle can remove ligand residues and byproducts on the surface of the metal oxide layer with hydrogen or helium radicals and create a fresh surface for the next etching cycle, as shown in FIGS. 1 and 2. In some embodiments, gas **114** can include H_2 or He at a flow rate ranging from about 100 sccm to about 1000 sccm. In some embodiments, a plasma of H_2 or He can be generated at a pressure ranging from about 20 mTorr to about 200 mTorr. The plasma can be generated by a plasma source with a pulsing power ranging from about 150 W to about 400 W and a duty cycle from about 10% to about 80%. In some embodiments, a temperature of wafer holder **104** can range from about 250° C. to about 300° C. for the

surface cleaning cycle. In some embodiments, a time of the surface cleaning cycle can range from about 10 s to about 30 s to remove the ligand residues and byproducts on the surface of the metal oxide layer by the hydrogen or helium radicals with increased kinetic energies. If the time of the surface cleaning cycle is less than about 10 s, the ligand residues and byproducts may remain on the surface of the metal oxide layer and they can block the next cycle of surface modification. If the time of the surface cleaning cycle is greater than about 30 s, exposed areas of other materials (e.g., silicon oxide, silicon nitride, silicon, etc.) may be damaged.

Grid system 124 can generate ions with increased kinetic energy from gas 114 and neutralizer 122 can generate electrons to neutralize the ions and form radicals 136 with increased kinetic energy for the surface cleaning cycle. In some embodiments, screen grid 130 can be biased at about 1.2 kV. Accelerator grid 132 can be biased at a voltage ranging from about -50 V to about -200 V. Decelerator grid 134 can be connected to ground 245. Neutralizer 122 can generate electrons with a discharge current ranging from about 0.2 Å to about 0.5 Å and a mass flow rate ranging from about 0.2 mg/s to about 0.25 mg/s to neutralize the ions and form radicals 136 with increased kinetic energies. As radicals can have higher etch selectivity than ions, radicals 136 with increased kinetic energies can increase etch selectivity between the metal oxide and adjacent structures (e.g., a mask layer) and prevent surface damage to the adjacent structures. As a result, radicals 136 can remove the ligand residues and byproducts on the surface of metal oxide layer and create a fresh surface without damaging the adjacent structures.

FIG. 5A illustrates an isometric view of semiconductor device 500 after the formation of epitaxial fin structures 554, in accordance with some embodiments. FIGS. 5B, 6-17, 18A, 18B, 19A, 19B, 20A, and 20B illustrate partial cross-sectional views along line B-B of semiconductor device 500 in FIG. 5A at various stages of its fabrication process to form air spacers 1964 using the radical-activated thermal ALE process described above, in accordance with some embodiments. Semiconductor device 500 can include planar metal oxide semiconductor field-effect transistors (MOSFETs) or fin field effect transistors (finFETs). As shown in FIG. 5A, semiconductor device 500 can be formed on a substrate 551 and can include finFETs 550A-550C. In some embodiments, finFETs 550A-550C can be all p-type finFETs (PFETs) or n-type finFETs (NFETs) or a combination of each type of finFETs. Though three finFETs are shown in FIGS. 5A, 5B, and subsequent figures, semiconductor device 500 can have any number of finFETs. The discussion of elements of finFETs 550A-550C with the same annotations applies to each other, unless mentioned otherwise. In addition, semiconductor device 500 can be incorporated into an integrated circuit through the use of other structural components, such as gate contact structures, conductive vias, conductive lines, dielectric layers, and passivation layers, which are not shown for the sake of clarity.

As shown in FIGS. 5A and 5B, semiconductor device 500 can further include shallow trench isolation (STI) region 553, fin structures 552, epitaxial fin structures 554, sacrificial gate structures 560, hard mask layer 563, and gate spacers 555 disposed on opposite sides of sacrificial gate structures 560. STI region 553 can be configured to provide electrical isolation between finFETs 550A-550C from each other and from neighboring finFETs with different fin structures (not shown) on substrate 551 and/or neighboring active and passive elements (not shown) integrated with or depos-

ited on substrate 551. Fin structures 552 of semiconductor device 500 can extend along an X-axis and through finFETs 550A-550C. Fin structures 552 can include fin bottom portion 552A and fin top portion 552B disposed on fin bottom portion 552A. Epitaxial fin structures 554 can be grown on portions of fin bottom portion 552A that are not underlying sacrificial gate structures 560. Sacrificial gate structures 560 can be formed on fin structures 552 over substrate 551. Gate spacers 555 can be disposed on sidewalls of sacrificial gate structures 560 to protect sacrificial gate structures 560 during the formation of epitaxial fin structures 554. In some embodiments, gate spacers 555 can include a first gate spacer 557 and a second gate spacer 559. A hard mask layer 563 can be disposed on sacrificial gate structures 560 to protect sacrificial gate structures 560 during various processing operations (e.g., during formation of gate spacers 555 and/or epitaxial fin structures 554). In some embodiments, hard mask layer 563 can include a nitride layer 562 and an oxide layer 564 for profile control of sacrificial gate structures 560. In some embodiments, protective oxide layers 556 can be disposed between fin structures 552 and sacrificial gate structures 560.

The formation of epitaxial fin structures 554 can be followed by removal of gate spacers 555 and deposition of a third gate spacer 658, as shown in FIG. 6. According to some embodiments, gate spacers 555 can be damaged (e.g., partially etched off) during the formation of epitaxial fin structures 554. As a result, gate spacers 555 can be removed after the formation of epitaxial fin structures 554 and third gate spacer 658 can be deposited on sidewalls of sacrificial gate structures 560 having improved structural integrity and few defects than damaged gate spacers 555. In some embodiments, third gate spacer 658 can have a thickness ranging from about 2 nm to about 3 nm and include dielectric materials similar to first gate spacer 557. The deposition of third gate spacer 658 can be followed by deposition of an aluminum oxide layer 764, as shown in FIG. 7. Aluminum oxide layer 764 can be deposited by atomic layer deposition (ALD), chemical vapor deposition (CVD), or other suitable deposition methods. In some embodiments, aluminum oxide layer 764 can be deposited by ALD at a temperature ranging from about 180° C. to about 300° C. using aluminum precursors, such as TMA. In some embodiments, aluminum oxide layer 764 can have a thickness ranging from about 2 nm to about 4 nm.

The deposition of aluminum oxide layer 764 can be followed by removal of a portion of aluminum oxide layer 764, as shown in FIG. 8. Referring to FIG. 8, a portion of aluminum oxide layer 764 can be removed by the radical-activated thermal ALE process discussed above using radical-activated thermal ALE system 100 shown in FIGS. 1 and 2. The radical-activated thermal ALE process can be a directional etching process and remove aluminum oxide layer 764 over hard mask layer 563 and epitaxial fin structures 554 to form aluminum oxide layer 764*. After the radical-activated thermal ALE process, aluminum oxide layer 764* can remain on sidewalls of sacrificial gate structures 560. In some embodiments, the radical-activated thermal ALE process can remove the portion of aluminum oxide layer 764 at a higher etching rate ranging from about 1 Å to about 5 Å per etching cycle. In addition, the radical-activated thermal ALE process can prevent third gate spacer 658 from surface damage during the removal of the portion of aluminum oxide layer 764.

The removal of a portion of aluminum oxide layer 764 can be followed by the formation of etch stop layer 966 and inter-layer dielectric (ILD) 968, as shown in FIG. 9. The

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formation of etch stop layer **966** and ILD **968** can include deposition of an etch stop layer and inter-layer dielectric materials followed by a chemical mechanical polishing (CMP) process to coplanarize top surfaces of etch stop layer **966**, ILD **968**, aluminum oxide layer **764***, third gate spacer **658***, and nitride layer **562***. In some embodiments, the CMP process can stop on nitride layer **562***. The formation of etch stop layer **966** and ILD **968** can be followed by removal of a portion of ILD **968** and etch stop layer **966**, as shown in FIG. **10**.

The removal of a portion of ILD **968** and etch stop layer **966** can be followed by removal of a portion of aluminum oxide layer **764*** on sidewalls of sacrificial gate structures **560**, as shown in FIG. **11**, according to some embodiments. Referring to FIG. **11**, a portion of aluminum oxide layer **764*** can be removed by the radical-activated thermal ALE process discussed above using radical-activated thermal ALE system **100** shown in FIGS. **1** and **2**. The radical-activated thermal ALE process can remove exposed aluminum oxide layer **764*** on sidewalls of sacrificial gate structures **560** to form aluminum oxide layer **764****. In some embodiments, the radical-activated thermal ALE process can remove the portion of aluminum oxide layer **764*** at a higher etching rate ranging from about 1 Å to about 5 Å per etching cycle. In addition, the radical-activated thermal ALE process may prevent etch stop layer **966***, ILD **968***, third gate spacer **658***, and nitride layer **562*** from surface damage during the removal of the portion of aluminum oxide layer **764***.

The removal of the portion of aluminum oxide layer **764*** on sidewalls of sacrificial gate structures **560** can be followed by formation of a hard mask layer **1270**, as shown in FIG. **12**. The formation of hard mask layer **1270** can include blanket deposition of dielectric materials for hard mask layer **1270** followed by a CMP process. The CMP process can stop on sacrificial gate structures **560*** and coplanarize top surfaces of sacrificial gate structures **560***, third gate spacer **658****, and hard mask layer **1270**. The formation of hard mask layer **1270** can be followed by removal of a portion of sacrificial gate structures **560***, third gate spacer **658****, and aluminum oxide layer **764****. In some embodiments, a portion of sacrificial gate structures **560*** can be removed by an etching process (e.g., a Frontier etching process) and sacrificial gate structures **1360** of the remaining portion can have a height along a Z-axis ranging from about 10 nm to about 15 nm after the etching process. In some embodiments, a portion of third gate spacer **658**** and aluminum oxide layer **764**** can be removed from sidewalls and form third gate spacer **1358** and aluminum oxide layer **1364** having top surfaces aligned with sacrificial gate structures **1360**.

In some embodiments, the portion of aluminum oxide layer **764**** can be removed by the radical-activated thermal ALE process discussed above using radical-activated thermal ALE system **100** shown in FIGS. **1** and **2**. The radical-activated thermal ALE process can remove the portion of aluminum oxide layer **764**** on sidewalls to form aluminum oxide layer **1364**. After the radical-activated thermal ALE process, aluminum oxide layer **1364** can have top surfaces aligned with sacrificial gate structures **1360**. In some embodiments, the radical-activated thermal ALE process can remove the portion of aluminum oxide layer **764**** at a higher etching rate ranging from about 1 Å to about 5 Å per etching cycle. In addition, the radical-activated thermal ALE process may prevent third gate spacer **1358**, sacrificial gate

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structures **1360**, etch stop layer **966***, and hard mask layer **1270** from surface damage during the removal of aluminum oxide layer **764****.

The removal of a portion of third gate spacer **658**** and aluminum oxide layer **764**** from sidewalls can be followed by a deposition of an oxide layer **1472**, as shown in FIG. **14**. In some embodiments, oxide layer **1472** can be blanket deposited by an ALD process on top surfaces of the structures in FIG. **13**. The deposition of oxide layer **1472** can be followed by a removal of a portion of oxide layer **1472** and removal of sacrificial gate structures **1360**, as shown in FIG. **15**. In some embodiments, the removal of a portion of oxide layer **1472** can include a directional etching process and oxide layer **1472*** on sidewalls can remain after the directional etching process. Sacrificial gate structures **1360** can be exposed for subsequent removal after the directional etching process. In some embodiments, the removal of sacrificial gate structures **1360** can include an etching process (e.g., a Selis etching process) with a nitrogen-based chemistry. Openings **1560** can be formed after the removal of sacrificial gate structures **1360**.

The removal of sacrificial gate structures **1360** can be followed by the formation of gate structures **1672**, as shown in FIG. **16**. Gate structures **1672** can be formed on fin structures **552** in openings **1560**. In some embodiments, each of gate structures **1672** can include a gate dielectric layer **1674** and a gate electrode **1676**. Gate electrode **1676** can further include a work function layer **1680** and a metal fill **1684**. In some embodiments, gate dielectric layer **1674** can include an interfacial layer and a high-k dielectric layer. In some embodiments, work function layer **1680** can include a stack of work function layers. In some embodiments, the formation of gate structures **1672** can include deposition of each layer of gate structures **1672** followed by a CMP process and an etching back process.

The formation of gate structures **1672** can be followed by blanket deposition of aluminum oxide layer **1786** and amorphous silicon **1788**, as shown in FIG. **17**. A CMP process can coplanarize top surfaces of aluminum oxide layer **1786**, amorphous silicon **1788**, etch stop layer **966***, and ILD **968***. A cut process can separate gate structures **1672** as required by a design. Amorphous silicon **1788** can be removed following the cut process to form openings **1888** shown in FIGS. **18A** and **18B**. FIG. **18B** illustrates an enlarged view of region B in FIG. **18A**. The removal of amorphous silicon **1788** can be followed by removal of aluminum oxide layer **1786** and aluminum oxide layer **1364**. Air gaps **1864** can be formed after the removal of aluminum oxide layer **1364**.

In some embodiments, aluminum oxide layer **1786** and aluminum oxide layer **1364** can be removed by the radical-activated thermal ALE process discussed above using radical-activated thermal ALE system **100** shown in FIGS. **1** and **2**. The radical-activated thermal ALE process can remove aluminum oxide layer **1786** after the removal of amorphous silicon **1788**. The radical-activated thermal ALE process can further remove aluminum oxide layer **1364** between etch stop layer **966**** and third gate spacer **1358** to form air gaps **1864**. In some embodiments, the radical-activated thermal ALE process can remove aluminum oxide layer **1786** and aluminum oxide layer **1364** at a higher etching rate ranging from about 1 Å to about 5 Å per etching cycle. In addition, the radical-activated thermal ALE process may prevent third gate spacer **1358**, ILD **968****, and etch stop layer **966**** from surface damage during the removal of aluminum oxide layer **1786** and aluminum oxide layer **1364**.

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The removal of aluminum oxide layer **1786** and aluminum oxide layer **1364** can be followed by formation of capping structures **1988**, as shown in FIGS. **19A** and **19B**. FIG. **19B** illustrates an enlarged view of region B in FIG. **19A**. The formation of capping structures **1988** can include deposition of dielectric materials capping on gate structures **1672** and scaling air gaps **1864** to form air spacers **1964**. In some embodiments, air spacers **1964** can have a width along an X-axis ranging from about 2 nm to about 4 nm and a depth along a Z-axis ranging from about 16 nm to about 25 nm. An aspect ratio of the height to the width for air spacers **1964** can range from about 4 to about 12. The formation of capping structures **1988** and air spacers **1964** can be followed by formation of source/drain (S/D) contact structures **2090** in contact with epitaxial fin structures **554**, as shown in FIGS. **20A** and **20B**. Referring to FIGS. **20A** and **20B**, S/D contact structures **2090** can include a silicide layer **2092**, a metal liner **2096**, and a metal contact **2098**. In some embodiments, an epitaxial fin structures **554** of a finFET may not be connected to an S/D contact structure and ILD **968**** can remain on epitaxial fin structures **554**, as shown in FIG. **20A**. In some embodiments, ILD **968**** can be removed and epitaxial fin structures **554** of a finFET can be connected to S/D contact structures **2090**, as shown in FIG. **20B**. In some embodiments, air spacers **1964** can reduce parasitic capacitances between gate structures **1672** and S/D contact structures **2090** and improve device performance of semiconductor device **500**.

Various embodiments of the present disclosure provide an exemplary radical-activated thermal atomic layer etching (ALE) process performed in exemplary radical-activated thermal ALE system **100**. In some embodiments, the radical-activated thermal ALE process can activate a ligand exchange reaction on a surface of a metal oxide on wafer **112** using radicals **136** with increased kinetic energies, thereby increasing an etch rate of the metal oxide and increasing the etch selectivity between the metal oxide and adjacent materials on wafer **112**.

In some embodiments, the radical-activated thermal ALE process can include three sequential reaction cycles: (i) a surface modification cycle, (ii) a material removal cycle, and (iii) a surface cleaning cycle. In some embodiments, the radical-activated thermal ALE process can modify the surface of the metal oxide layer on wafer **112** with radicals from a plasma during the surface modification cycle. The material removal cycle can include a ligand exchange reaction, which can be performed under a thermal condition. In some embodiments, radicals **136** generated from ions of a plasma having increased kinetic energy can increase the ligand exchange kinetic energy and the speed of the ligand exchange reaction, thus increasing removal of the modified surface of the metal oxide and the etching rate of the metal oxide. In some embodiments, gas distribution plate **126** with evenly distributed holes or openings can distribute the gases and plasmas uniformly across wafer **112**. In some embodiments, radical-activated thermal ALE system **100** can include grid system **124** to increase a kinetic energy of ions from the plasma and neutralizer **122** to neutralize the ions. Grid system **124** can include screen grid **130** to screen ions having appropriate angles (e.g., about 90 degrees relative to screen grid **130**), accelerator grid **132** to increase kinetic energies of the ions, and decelerator grid **134** to reduce divergence of the beam of the ions and block electrons generated by neutralizer **122** from entering grid system **124**. Neutralizer **122** can generate electrons and neutralize the ions to form radicals **136** with increased kinetic energies. The material removal cycle can remove the modified mate-

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rial layer at a higher etching rate while keeping the unmodified material(s) or layers intact. In some embodiments, a flush of radicals during the surface cleaning cycle can remove surface ligand residues and byproducts and create a fresh surface for the next etching cycle. The radical flush can further increase the etching rate of the radical-activated thermal ALE process.

In some embodiments, a system includes a chamber, a wafer holder in the chamber configured to hold a wafer with a metal oxide disposed thereon, a plasma generator configured to generate a plasma from a gas, a grid system configured to increase a kinetic energy of ions from the plasma, and a neutralizer configured to generate electrons to neutralize the ions and generate radicals to facilitate etching of the metal oxide.

In some embodiments, a system includes a chamber, a wafer holder in the chamber configured to hold a wafer with a metal oxide disposed thereon, a first gas line fluidly connected to the chamber and configured to deliver a gas to the chamber, a plasma generator configured to generate a plasma from the gas, a grid system between the plasma generator and the wafer holder configured to increase a kinetic energy of ions from the plasma, a neutralizer between the grid system and the wafer holder and configured to generate electrons and neutralize the ions to generate radicals, and a second gas line fluidly connected to the chamber and configured to deliver a precursor across the wafer. The radicals facilitate etching of the metal oxide by the precursor.

In some embodiments, a method includes generating a plasma from a gas, generating with a grid system and a neutralizer radicals from the plasma, and activating a ligand exchange reaction on a surface of a metal oxide with the radicals. The grid system includes a screen grid, an accelerator grid, and a decelerator grid.

It is to be appreciated that the Detailed Description section, and not the Abstract of the Disclosure section, is intended to be used to interpret the claims. The Abstract of the Disclosure section may set forth one or more but not all possible embodiments of the present disclosure as contemplated by the inventor(s), and thus, are not intended to limit the subjoined claims in any way.

The foregoing disclosure outlines features of several embodiments so that those skilled in the art may better understand the aspects of the present disclosure. Those skilled in the art will appreciate that they may readily use the present disclosure as a basis for designing or modifying other processes and structures for carrying out the same purposes and/or achieving the same advantages of the embodiments introduced herein. Those skilled in the art will also realize that such equivalent constructions do not depart from the spirit and scope of the present disclosure, and that they may make various changes, substitutions, and alterations herein without departing from the spirit and scope of the present disclosure.

What is claimed is:

1. A method, comprising:

- treating a surface of a metal oxide on a wafer with a first plasma;
- generating a second plasma from a gas;
- generating, with a grid system and a neutralizer, radicals from the second plasma, wherein the grid system comprises a screen grid, an accelerator grid, and a decelerator grid;
- vaporizing a precursor with a vaporizer;
- delivering the vaporized precursor to a wafer having a metal oxide disposed thereon; and

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activating a ligand exchange reaction on the treated surface of the metal oxide with the radicals and the vaporized precursor.

2. The method of claim 1, wherein the generating the radicals from the second plasma comprises:

- separating ions from the second plasma with the screen grid;
- accelerating the ions from the second plasma with the accelerator grid;
- generating electrons with the neutralizer; and
- neutralizing the ions with the electrons to form the radicals.

3. The method of claim 1, wherein the activating the ligand exchange reaction comprises:

- distributing the vaporized precursor across the surface of the metal oxide;
- increasing a kinetic energy of the precursor with the radicals; and
- etching the surface of the metal oxide with the precursor via the ligand exchange reaction.

4. The method of claim 1, further comprising distributing the second plasma above the grid system with a gas distribution plate.

5. The method of claim 1, further comprising blocking, with the decelerator grid, electrons generated by the neutralizer.

6. The method of claim 1, further comprising heating the metal oxide with a heating system.

7. The method of claim 1, further comprising cleaning the surface of the metal oxide with a third plasma.

8. A method, comprising:

- delivering a first gas with a first gas line to a chamber, wherein the chamber comprises a wafer holder configured to hold a wafer with a metal oxide disposed thereon;
- distributing the first gas uniformly above the wafer;
- generating a plasma from the first gas with a plasma generator;
- generating, with a grid system and a neutralizer, radicals from the plasma, wherein the grid system is configured to increase a kinetic energy of ions in the plasma;
- delivering a second gas with a second gas line to the wafer, wherein the second gas line is adjacent to the wafer; and
- activating a ligand exchange reaction on a surface of the metal oxide with the radicals and the second gas.

9. The method of claim 8, wherein the generating the radicals from the plasma comprises:

- separating ions from the plasma with a screen grid in the grid system;
- accelerating, with an accelerator grid in the grid system, the ions from the plasma;
- generating electrons with the neutralizer; and
- neutralizing the ions with the electrons to form the radicals.

10. The method of claim 8, wherein the activating the ligand exchange reaction comprises:

- distributing the second gas across the wafer;

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increasing a kinetic energy of the second gas with the radicals; and

etching the surface of the metal oxide with the second gas via the ligand exchange reaction.

11. The method of claim 8, wherein distributing the first gas uniformly above the wafer comprises distributing the first gas above the grid system with a gas distribution plate.

12. The method of claim 8, further comprising blocking, with a decelerator grid in the grid system, electrons generated by the neutralizer.

13. The method of claim 8, further comprising heating the wafer with a heating system in the wafer holder.

14. The method of claim 8, further comprising cleaning the surface of the metal oxide with a plasma of a third gas.

15. A method, comprising:

- delivering a first gas with a first gas line to a chamber, wherein the chamber comprises a wafer holder configured to hold a wafer with a metal oxide disposed thereon;
- generating a first plasma from the first gas with a plasma generator;
- treating the metal oxide with the first plasma;
- delivering a second gas with the first gas line to the chamber;
- generating a second plasma from the second gas with the plasma generator;
- increasing a kinetic energy of ions in the second plasma with a grid system;
- neutralizing the ions into radicals with a neutralizer;
- delivering a third gas to the wafer with a second gas line; and
- activating a ligand exchange reaction on a surface of the treated metal oxide with the radicals and the third gas.

16. The method of claim 15, wherein the increasing the kinetic energy of the ions comprises:

- separating the ions from the second plasma with a screen grid in the grid system; and
- accelerating, with an accelerator grid in the grid system, the ions from the plasma.

17. The method of claim 15, wherein the activating the ligand exchange reaction comprises:

- increasing a kinetic energy of the third gas with the radicals; and
- etching the surface of the metal oxide with the third gas via the ligand exchange reaction.

18. The method of claim 15, wherein the neutralizing the ions into the radicals comprises:

- generating electrons with the neutralizer; and
- neutralizing the ions with the electrons to form the radicals.

19. The method of claim 15, further comprising distributing the first and second gases above the grid system with a gas distribution plate.

20. The method of claim 15, further comprising blocking, with a decelerator grid in the grid system, electrons generated by the neutralizer.

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