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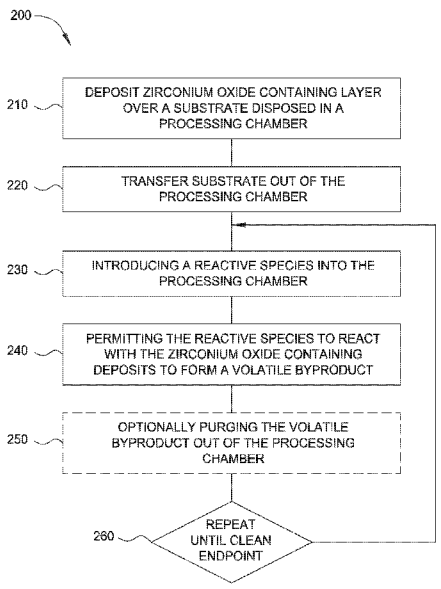


FIG. 2

(57) Abstract: Implementations described herein generally relate to methods and apparatus for in-situ removal of unwanted deposition buildup from one or more interior surfaces of a substrate-processing chamber. In one implementation, a method for cleaning a processing chamber is provided. The method comprises introducing a reactive species into a processing chamber having a residual ZrO_2 containing film formed on one or more interior surfaces of the processing chamber. The reactive species is formed from BCl_3 and the one or more interior surfaces includes at least one exposed Al_2O_3 surface The method further comprises reacting the residual ZrO_2 containing film with the reactive species to form a volatile product. The method further comprises removing the volatile product from the processing chamber, wherein a removal rate of the residual ZrO_2 containing film is greater than a removal rate of Al_2O_3.

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SELECTIVE IN-SITU CLEANING HIGH-K FILMS FROM OF PROCESSING CHAMBER USING REACTIVE GAS PRECURSOR

BACKGROUND

Field

[0001] Implementations described herein generally relate to methods and apparatus for in-situ removal of unwanted deposition buildup from one or more interior surfaces of a substrate-processing chamber.

Description of the Related Art

[0002] Display devices have been widely used for a range of electronic applications, such as TVs, monitors, mobile phones, MP3 players, e-book readers, personal digital assistants (PDAs) and the like. The display device is generally designed for producing an image by applying an electric field to a liquid crystal that fills a gap between two substrates (e.g., a pixel electrode and a common electrode) and has anisotropic dielectric constant that controls the intensity of the dielectric field. By adjusting the amount of light transmitted through the substrates, the light and image intensity, quality and power consumption may be efficiently controlled.

[0003] A variety of different display devices, such as active matrix liquid crystal display (AMLCD) or an active matrix organic light emitting diodes (AMOLED), may be employed as light sources for display. In the manufacturing of display devices, an electronic device with high electron mobility, low leakage current and high breakdown voltage, would allow more pixel area for light transmission and integration of circuitry, resulting in a brighter display, higher overall electrical efficiency, faster response time and higher resolution displays. Low film qualities of the material layers, such as dielectric layer with impurities or low film densities, formed in the device often result in poor device electrical performance and short service life of the devices. Thus, a stable and reliable method for forming and integrating film layers within TFT and OLED devices becomes crucial to provide a device structure with low film leakage, and high breakdown voltage, for use in

manufacturing electronic devices with lower threshold voltage shift and improved overall performance of the electronic device are preferred.

[0004] In particular, the interface management between a metal electrode layer and the nearby insulating materials becomes critical as improper material selection of the interface between the metal electrode layer and the nearby insulating material may adversely result in undesired elements diffusing into the adjacent materials, which may eventually lead to current short, current leakage or device failure. Furthermore, the insulating materials with different higher dielectric constant often provide different electrical performance, such as providing different capacitance in the device structures. Selection of the material of the insulating materials not only affects the electrical performance of the device, incompatibility of the material of the insulating materials to the electrodes may also result in film structure peeling, poor interface adhesion, or interface material diffusion, which may eventually lead to device failure and low product yield.

[0005] In some devices, capacitors, e.g., a dielectric layer placed between two electrodes, are often utilized and formed to store electric charges when the display devices are in operation. The capacitor as formed is required to have high capacitance for display devices. The capacitance may be adjusted by changing of the dielectric material and dimension of the dielectric layer formed between the electrodes and/or thickness of the dielectric layer. For example, when the dielectric layer is replaced with a material having a higher dielectric constant (e.g., zirconium oxide), the capacitance of the capacitor will increase as well.

[0006] As the resolution requirement for display devices becomes increasingly challenging, e.g., display resolution greater than 2,000 pixels per inch (PPI), display devices have a limited area for forming capacitors to increase electrical performance. Thus, maintaining the capacitor formed in the display devices in a confined location with a relatively small area has become crucial. Higher dielectric constant materials such as zirconium oxide have been found to enable higher resolution display devices. However, deposition of zirconium oxide is not limited to the substrate and often forms a residual film throughout the interior of the processing

chamber. Such unwanted residual deposition may create particles and flakes within the chamber, resulting in the drift of process conditions, which affects the process reproducibility and uniformity.

[0007] In order to achieve high chamber availability while reducing the cost of ownership for production and maintaining film quality, a chamber clean is performed to remove residual film residue from the interior surfaces of the processing chamber including the process kits, e.g., showerhead, etc. Unfortunately, most known cleaning techniques such as fluorine-containing plasmas are either unable to remove zirconium oxide or are so harsh that they damage chamber components. Thus, viable in-situ cleaning techniques for zirconium oxide are currently unavailable. Currently, zirconium oxide is removed from processing chambers using ex-situ cleaning processes where production is stopped, the processing chamber is opened, and the chamber parts are removed for cleaning and cleaned using wet-clean processes.

[0008] Therefore, a need exists for methods for in-situ removal of unwanted zirconium oxide deposits from substrate-processing chambers.

SUMMARY

[0009] Implementations described herein generally relate to methods and apparatus for in-situ removal of unwanted deposition buildup from one or more interior surfaces of a substrate-processing chamber. In one implementation, a method for cleaning a processing chamber is provided. The method comprises introducing a reactive species into a processing chamber having a residual ZrO_2 containing film formed on one or more interior surfaces of the processing chamber. The reactive species is formed from BCl_3 and the one or more interior surfaces includes at least one exposed Al_2O_3 surface The method further comprises reacting the residual ZrO_2 containing film with the reactive species to form a volatile product. The method further comprises removing the volatile product from the processing chamber, wherein a removal rate of the residual ZrO_2 containing film is greater than a removal rate of Al_2O_3.

[0010] In another implementation, a method for cleaning a processing chamber is provided. The method comprises depositing a ZrO_2 containing film on one or more interior surface of a processing chamber and a substrate disposed in the substrate-processing chamber. The method further comprises transferring the substrate out of the substrate-processing chamber. The method further comprises introducing a reactive species into the processing chamber having the residual ZrO_2 containing film formed on one or more interior surfaces of the processing chamber. The reactive species is formed from BCl_3 and the one or more interior surfaces include at least one exposed Al_2O_3 surface. The method further comprises reacting the residual ZrO_2 containing film with the reactive species to form a volatile product. The method further comprises removing the volatile product from the processing chamber, wherein a removal rate of the residual ZrO_2 containing film is greater than a removal rate of Al_2O_3.

[0011] In yet another implementation, a method for cleaning a processing chamber is provided. The method comprises flowing a boron trichloride (BCl_3) containing cleaning gas mixture into a remote plasma source fluidly coupled with a processing chamber. The method further comprises forming reactive species from the BCl_3 containing cleaning gas mixture. The method further comprises transporting the reactive species into the processing chamber. The processing chamber has a residual ZrO_2 containing film formed on one or more interior surfaces of the processing chamber and the one or more interior surfaces includes at least one exposed Al_2O_3 surface. The method further comprises permitting the reactive species to react with the residual ZrO_2 containing film to form zirconium chloride in a gaseous state. The method further comprises purging the zirconium chloride in a gaseous state out of the processing chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] So that the manner in which the above-recited features of the present disclosure can be understood in detail, a more particular description of the implementations, briefly summarized above, may be had by reference to implementations, some of which are illustrated in the appended drawings. It is to be

noted, however, that the appended drawings illustrate only typical implementations of this disclosure and are therefore not to be considered limiting of its scope, for the disclosure may admit to other equally effective implementations.

[0100] FIG. 1A depicts a sectional view of a processing chamber that may benefit from the cleaning processes in accordance with one or more implementations of the present disclosure;

[0101] FIG. 1B depicts a sectional view of the processing chamber of FIG. 1A having a residual film formed on one or more interior surfaces that may be removed using one or more implementations of the present disclosure; and

[0013] FIG. 2 depicts a process flow diagram of one implementation of a method that may be used to remove high-k materials from a processing chamber.

[0014] To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. It is contemplated that elements and features of one implementation may be beneficially incorporated in other implementations without further recitation.

DETAILED DESCRIPTION

[0015] The following disclosure describes techniques for in-situ removal of zirconium oxide from a substrate-processing chamber. Certain details are set forth in the following description and figures to provide a thorough understanding of various implementations of the disclosure. Other details describing well-known structures and systems often associated with plasma cleaning are not set forth in the following disclosure to avoid unnecessarily obscuring the description of the various implementations.

[0016] Many of the details, dimensions, angles and other features shown in the Figures are merely illustrative of particular implementations. Accordingly, other implementations can have other details, components, dimensions, angles and features without departing from the spirit or scope of the present disclosure. In

addition, further implementations of the disclosure can be practiced without several of the details described below.

[0017] Implementations described herein will be described below in reference to a high-k dielectric deposition process that can be carried out using any suitable thin film deposition system. One example of such a system is an AKT-90K PECVD system, suitable for substrate size 3000 mm x 3000 mm or larger size substrates, which is commercially available from Applied Materials, Inc., of Santa Clara, California. Other tools capable of performing high-k dielectric deposition processes may also be adapted to benefit from the implementations described herein. In addition, any system enabling high-k dielectric deposition processes described herein can be used to advantage. The apparatus description described herein is illustrative and should not be construed or interpreted as limiting the scope of the implementations described herein.

[0018] Implementations of the present disclosure generally relate to in-situ removal of high-k materials such as ZrO_2 from processing chambers. The processing chamber include but are not limited to PECVD, ALD or other processing chambers, which are utilized in the fabrication of high-resolution display back-plane TFT circuits. ZrO_2 is a high dielectric constant material currently used in the semiconductor industry and potentially in flat panel display industry to enable high-resolution display devices, such as Virtual Reality (VR) devices. High-k materials like ZrO_2 are critical to enable high-resolution display devices (e.g., PPI >2000). Currently, the area of the storage capacitor needs to be reduced in the pixel circuit as the whole pixel area shrinks to increase resolution. To achieve the same capacitance, current dielectric layers (e.g., SiN, K~7) used in storage capacitors are being replaced with high-K materials, such as ZrO_2 which has a K>20. One factor for enabling ZrO_2 in display applications is the efficient removal of residual ZrO_2 films from the processing chamber to reduce particles and to improve the yield.

[0019] Typically, deposition of ZrO_2 films is not limited to the substrate and forms a residual film throughout the chamber. This residual film can cause particle formation, uniformity degradation and gas inlet clogging, thus leading to yield loss

and increased cost of ownership. One way to remove the unwanted residual film on the chamber wall or other chamber components is to dissemble the chamber and remove the films with solution or solvent periodically after several deposition cycles. Dissembling the chamber, cleaning the components and re-assembling the chamber take significant time and significantly affect the uptime of the tool. Another approach is to apply plasma to promote excitation and/or dissociation of reactive gases by the application of radio frequency (RF) energy. The plasma includes highly reactive species that reacts with and etches the unwanted residual material. For example, NF_3 plasma is widely used in the display industry to remove SiO_x and SiN_x films from processing chambers. However, NF_3 plasma is unable to etch ZrO_2 residual film.

[0020] Implementations of the present disclosure include both a chamber cleaning process and modification of current hardware materials. Some implementations of the present disclosure effectively remove ZrO_2 residual films from the processing chamber by introducing a reactive species formed from BCl_3 into the processing chamber to react with the residual ZrO_2 containing film. The reactive species may be generated as in-situ plasma or ex-situ plasma. The generation of plasma can be (but not limited to) inductive-coupled plasma (ICP), capacitive-coupled plasma (CCP) or microwave plasma. In some implementations of the present disclosure, residual ZrO_2 containing films are removed by flowing BCl_3 gas into the processing chamber and then exciting and/or dissociating the BCl_3 gas to form plasma in the processing chamber. The excited free radicals from BCl_3 etch the residual ZrO_2 containing films from the chamber body. The plasma of BCl_3 etches ZrO_2 and aluminum, but does not etch Al_2O_3 if no external direct current (DC) bias is applied. Therefore, in some implementations of the present disclosure, aluminum chamber components are protected by a thin Al_2O_3 coating during the cleaning process. In some implementations, the Al_2O_3 coating is applied by a surface anodization process. If it is necessary to remove Al_2O_3, DC bias can be applied to BCl_3 plasma during the process to facilitate etching of Al_2O_3. Thus, BCl_3 can be used to selectively remove ZrO_2 relative to Al_2O_3 or remove both ZrO_2 and Al_2O_3 depending on the plasma conditions.

[0021] FIG. 1A depicts a sectional view of a substrate-processing chamber 100 that may benefit from the cleaning processes in accordance with one or more implementations of the present disclosure. FIG. 1B depicts a sectional view of the substrate-processing chamber 100 of FIG. 1A having a residual film formed on one or more interior surfaces that may be removed using one or more implementations of the present disclosure. The substrate-processing chamber 100 may be used to perform CVD, plasma enhanced-CVD (PE-CVD), pulsed-CVD, ALD, PE-ALD, or combinations thereof. In some implementations, the substrate-processing chamber may be configured to deposit a high-k dielectric layer, such as ZrO_2. In some implementations, the substrate-processing chamber 100 is configured to process a large area substrate 102 (hereafter substrate 102) using plasma in forming structures and devices on the substrate 102 for use in the fabrication of liquid crystal displays (LCD's), flat panel displays, organic light emitting diodes (OLED's), or photovoltaic cells for solar cell arrays.

[0022] The substrate-processing chamber 100 generally includes sidewalls 142, a bottom wall 104 and a lid assembly 112, which define a process volume 106. The lid assembly 112 is generally comprised of aluminum. The lid assembly 112 may be anodized to form a layer of Al_2O_3 on the surface of the lid assembly 112. The sidewalls 142 and the bottom wall 104 may be fabricated from a unitary block of aluminum or other material compatible for plasma processing. The sidewalls 142 and the bottom wall 104 may be anodized to form a layer of Al_2O_3 on the surface of the lid assembly 112. The sidewalls 142 and the bottom wall 104 may be electrically grounded.

[0023] A gas distribution plate 110 and a substrate support assembly 130 are disposed within the process volume 106. The process volume 106 is accessed through a slit valve opening 108 formed through the sidewalls 142 such that the substrate 102 may be transferred into and out of the substrate-processing chamber 100.

[0024] The substrate support assembly 130 includes a substrate-receiving surface 132 for supporting the substrate 102 thereon. The substrate support

assembly 130 generally comprises an electrically conductive body supported by a stem 134 that extends through the bottom wall 104. The stem 134 couples the substrate support assembly 130 to a lift system 136, which raises and lowers the substrate support assembly 130 between substrate transfer and processing positions. A shadow frame 133 may be placed over a periphery of the substrate 102 during processing to prevent deposition on the edge of the substrate 102. Lift pins 138 are moveably disposed through the substrate support assembly 130 and are adapted to space the substrate 102 from the substrate-receiving surface 132. The substrate support assembly 130 may also include heating and/or cooling elements 139 utilized to maintain the substrate support assembly 130 at a chosen temperature. The substrate support assembly 130 may also include grounding straps 131 to provide an RF return path around the periphery of the substrate support assembly 130.

[0025] The gas distribution plate 110 is coupled at its periphery to the lid assembly 112 or sidewalls 142 of the substrate-processing chamber 100 by a suspension 114. In one particular implementation, the gas distribution plate 110 is fabricated from aluminum. The surface of the gas distribution plate may be anodized to form a layer of Al_2O_3 on the surface of the gas distribution plate 110. The gas distribution plate 110 may also be coupled to the lid assembly 112 by one or more center supports 116 to help prevent sag and/or control the straightness/curvature of the gas distribution plate 110. The gas distribution plate 110 may have different configurations with different dimensions. In an exemplary implementation, the gas distribution plate 110 has a quadrilateral plan shape. The gas distribution plate 110 has a downstream surface 150 having a plurality of apertures 111 formed through the gas distribution plate 110 and facing an upper surface 118 of the substrate 102 disposed on the substrate support assembly 130. The apertures 111 may have different shapes, number, densities, dimensions, and distributions across the gas distribution plate 110. In one implementation, a diameter of the apertures 111 may be selected between about 0.01 inch and about 1 inch.

[0026] A gas source 120 is coupled to the lid assembly 112 to provide gas through the lid assembly 112 and then through the apertures 111 formed in the gas distribution plate 110 to the process volume 106. A vacuum pump 109 is coupled to the substrate-processing chamber 100 to maintain the gas in the process volume 106 at a chosen pressure.

[0027] A first source of electric power 122 is coupled with the lid assembly 112 and/or to the gas distribution plate 110 to provide power that creates an electric field between the gas distribution plate 110 and the substrate support assembly 130 so that a plasma may be generated from the gases present between the gas distribution plate 110 and the substrate support assembly 130. The lid assembly 112 and/or the gas distribution plate 110 electrode may be coupled to the first source of electric power 122 through an optional filter, which may be an impedance matching circuit. The first source of electric power 122 may be DC power, pulsed DC power, RF bias power, pulsed RF source or bias power, or a combination thereof. In one implementation, the first source of electric power 122 is a RF bias power.

[0028] In one implementation, the first source of electric power 122 is an RF power source. In one implementation, the first source of electric power 122 may be operated to provide RF power at a frequency between 0.3 MHz and about 14 MHz, such as about 13.56 MHz. The first source of electric power 122 may generate RF power at about 10 Watts to about 20,000 Watts, (e.g., between about 10 Watts to about 5000 Watts; between about 300 Watts to about 1500 Watts; or between about 500 Watts and about 1000 Watts).

[0029] The substrate support assembly 130 may be grounded such that RF power supplied by the first source of electric power 122 to the gas distribution plate 110 may excite the gases disposed in the process volume 106 between the substrate support assembly 130 and the gas distribution plate 110. The substrate support assembly 130 may be fabricated from metals or other comparable electrically conductive materials. In one implementation, at least a portion of the substrate support assembly 130 may be covered with an electrically insulative

coating. The coating may be a dielectric material such as oxides, silicon nitride, silicon dioxide, aluminum dioxide, tantalum pentoxide, silicon carbide, polyimide, among others. Alternatively, the substrate-receiving surface 132 of the substrate support assembly 130 may be free of coating or anodizing.

[0030] An electrode (not shown), which may be a bias electrode and/or an electrostatic chucking electrode, may be coupled to the substrate support assembly 130. In one implementation, the electrode is positioned in the body of the substrate support assembly 130. The electrode may be coupled to a second source of electric power 160 through an optional filter, which may be an impedance matching circuit. The second source of electric power 160 may be DC power, pulsed DC power, RF bias power, pulsed RF source or bias power, or a combination thereof.

[0031] In one implementation, the second source of electric power 160 is a DC bias source. The DC bias power may be supplied at between about 10 Watts and about 3000 Watts (e.g., between about 10 Watts and about 1000 Watts; or between about 10 Watts and about 100 Watts) at a frequency of 300 kHz. In one implementation, the DC bias power may be pulsed with a duty cycle between about 10 to about 95 percent at an RF frequency between about 500 Hz and about 10 kHz. Not to be bound by theory but it is believed that the DC bias establishes a bias between the plasma and substrate support, so that the ions in the plasma bombard the substrate support, enhancing the etching effect.

[0032] In one implementation, the second source of electric power 160 is a RF bias power. The RF bias power may be supplied at between about 0 Watts and about 1000 Watts (e.g., between about 10 Watts and about 100 Watts) at a frequency of 300 kHz. In one implementation, the RF bias power may be pulsed with a duty cycle between about 10 to about 95 percent at a RF frequency between about 500 Hz and about 10 kHz.

[0033] In one implementation, the edges of the downstream surface 150 of the gas distribution plate 110 may be curved so that a spacing gradient is defined between the edge and corners of the gas distribution plate 110 and substrate-

receiving surface 132 and, consequently, between the gas distribution plate 110 and the upper surface 118 of the substrate 102. The shape of the downstream surface 150 may be selected to meet specific process requirements. For example, the shape of the downstream surface 150 may be convex, planar, concave or other suitable shape. Therefore, the edge to corner spacing gradient may be utilized to tune the film property uniformity across the edge of the substrate, correcting property non-uniformity in films disposed in the corner of the substrate. Additionally, the edge to center spacing may also be controlled so film property distribution uniformity may be controlled between the edge and center of the substrate. In one implementation, a concave curved edge of the gas distribution plate 110 may be used so the center portion of the edge of the gas distribution plate 110 is spaced farther from the upper surface 118 of the substrate 102 than the corners of the gas distribution plate 110. In another implementation, a convex curved edge of the gas distribution plate 110 may be used so that the corners of the gas distribution plate 110 are spaced farther than the edges of the gas distribution plate 110 from the upper surface 118 of the substrate 102.

[0034] A remote plasma source 124, such as an inductively coupled remote plasma source, may also be coupled between the gas source and the gas distribution plate 110. Between processing substrates, a cleaning gas may be energized in the remote plasma source 124 to remotely provide plasma utilized to clean chamber components. The cleaning gas entering the process volume 106 may be further excited by the RF power provided to the gas distribution plate 110 by the first source of electric power 122. Suitable cleaning gases include, but are not limited to, BCl_3 and optionally an inert gas

[0035] In one implementation, the substrate 102 that may be processed in the substrate-processing chamber 100 may have a surface area of 10,000 cm^2 or more, such as 25,000 cm^2 or more, for example about 55,000 cm^2 or more. It is understood that after processing the substrate may be cut to form smaller other devices.

[0036] In one implementation, the heating and/or cooling elements 139 may be set to provide a substrate support assembly temperature during cleaning of about 600 degrees Celsius or less; between about 10 degrees Celsius and about 300 degrees Celsius; between about 200 degrees Celsius and about 300 degrees Celsius; between about 10 degrees Celsius and about 50 degrees Celsius, or between about 10 degrees Celsius and 30 degrees Celsius.

[0037] The nominal spacing during cleaning between the upper surface 118 of the substrate 102 disposed on the substrate-receiving surface 132 and the gas distribution plate 110 may generally vary between 400 mils and about 1,200 mils, such as between 400 mils and about 800 mils, or other distance to obtain sought after deposition results. In one exemplary implementation, where the gas distribution plate 110 has a concave downstream surface, the spacing between the center portion of the edge of the gas distribution plate 110 and the substrate-receiving surface 132 is between about 400 mils and about 1,400 mils, and the spacing between the corners of the gas distribution plate 110 and the substrate-receiving surface 132 is between about 300 mils and about 1,200 mils.

[0038] FIG. 1B depicts a sectional view of the substrate-processing chamber 100 of FIG. 1A with the substrate 102 removed. FIG. 1B provides an illustration of the substrate-processing chamber 100 suitable for performing chamber cleaning using an internal energy source such as an in-situ plasma or an external energy source, respectively. In FIG. 1B, a reactive agent 170 (e.g., BCl_3) (depicted in FIG. 1B as solid arrows) is introduced into the process volume 106, which has a residual film 180 (e.g., a high-k residual film such as the ZrO_2 depicted) to be removed during the cleaning process. As shown in FIG. 1B, the residual film 180 is deposited upon at least a portion of the exposed surface within the substrate-processing chamber 100, particularly, the gas distribution plate 110, substrate support assembly 130, shadow frame 133, etc. The reactive agent 170 is exposed to an energy source, such as the first source of electric power 122, the second source of electric power 160, or remote plasma source 124, which creates reactive species 190 such as Cl. The reactive species 190 react with the residual film 180 and form a volatile product.

The volatile product is removed from the substrate-processing chamber 100. One or more interior surfaces (e.g., the gas distribution plate 110, substrate support assembly 130, shadow frame 133, sidewalls 142, etc.) of the substrate-processing chamber 100 have at least one exposed Al_2O_3 film formed thereon.

[0039] FIG. 2 depicts a process flow diagram of one implementation of a method 200 that may be used to remove high-k materials from a substrate-processing chamber. The substrate-processing chamber may be similar to the substrate-processing chamber 100 depicted in FIG. 1A and FIG. 1B. At operation 210, a zirconium oxide (ZrO_2) containing layer is deposited over a substrate disposed in a substrate-processing chamber. During deposition of the zirconium oxide containing layer over the substrate, zirconium oxide and/or zirconium oxide containing compounds may be deposited over the interior surfaces including the chamber components (e.g., the gas distribution plate, substrate support assembly, shadow frame, sidewalls, etc.) of the substrate-processing chamber. The zirconium oxide containing layer may be an aluminum-doped zirconium oxide containing layer. The zirconium oxide containing layer may be deposited using, for example, a chemical vapor deposition (CVD) process, a plasma-enhanced chemical vapor deposition (PECVD) process, chamber, an atomic layer deposition (ALD) process, and a physical vapor deposition (PVD) process. In some implementations, at least portions of the chamber components are composed of aluminum. In some implementations, at least portions of the chamber components have an alumina (Al_2O_3) layer disposed thereon.

[0040] At operation 220, the substrate is transferred out of the substrate-processing chamber. In some implementation, the substrate remains in the substrate-processing chamber during the cleaning process.

[0041] At operation 230, a reactive species is introduced into the substrate-processing chamber. The reactive species may be generated utilizing plasma generated in-situ or the plasma may be generated ex-situ (e.g., remotely). Suitable plasma generation techniques, such as inductive-coupled plasma (ICP), capacitive-coupled plasma (CCP), or microwave plasma generation techniques may be utilized

to form the reactive species. In some implementations, the reactive species are formed in-situ via an in-situ plasma process. In some implementations, the reactive species are formed ex-situ via a remote plasma source.

[0042] In one implementation, the reactive species may be generated by flowing a cleaning gas mixture into the process volume 106. In one implementation, the cleaning gas mixture comprises BCl_3 and optionally a diluent gas. The diluent gas may be an inert gas selected from helium, argon, or combinations thereof. The cleaning gas mixture is exposed to an RF source and/or bias power. The RF source and/or bias power energizes the cleaning gas mixture within the process volume 106 such that the plasma may be sustained. In one implementation, the first source of electric power 122 may be operated to provide RF power at a frequency between 0.3 MHz and about 14 MHz, such as about 13.56 MHz. The first source of electric power 122 may generate RF power at about 10 Watts to about 5000 Watts, (e.g., between about 300 Watts to about 1500 Watts; between about 500 Watts and about 1000 Watts).

[0043] In some implementations, in addition to the RF source power, RF bias power may also be utilized during the cleaning process to assist dissociating the cleaning gas mixture forming the plasma. The RF bias may be provided by the second source of electric power 160. In one implementation, the first source of electric power 122 may be operated to provide RF power at a frequency between 0.3 MHz and about 14 MHz, such as about 13.56 MHz. The RF bias power may be supplied at between about 0 Watts and about 1000 Watts (e.g., between about 10 Watts and about 100 Watts) at a frequency of 300 kHz. In one implementation, the RF bias power may be pulsed with a duty cycle between about 10 to about 95 percent at a RF frequency between about 500 Hz and about 10 kHz. In some implementations, where this external DC bias is applied, Al_2O_3 is removed in conjunction with the residual ZrO_2 containing film.

[0044] In some implementations, in addition to the RF source power, DC bias power may also be utilized during the cleaning process to assist dissociating the cleaning gas mixture forming the plasma. The DC bias may be provided by the

second source of electric power 160. In one implementation, the first source of electric power 122 may be operated to provide RF power at a frequency between 0.3 MHz and about 14 MHz, such as about 13.56 MHz. The second source of electric power 160 may be operated to provide DC bias power at between about 10 Watts and about 3000 Watts (e.g., between about 10 Watts and about 1000 Watts; or between about 10 Watts and about 100 Watts) at a frequency of 300 kHz. In one implementation, the DC bias power may be pulsed with a duty cycle between about 10 to about 95 percent at a frequency between about 500 Hz and about 10 kHz. Not to be bound by theory, but it is believed that the DC bias establishes an electrical potential difference between plasma and the substrate to enhance etching.

[0045] In some implementations, the plasma may be formed by capacitive or inductive means, and may be energized by coupling RF power into the cleaning gas mixture. The RF power may be a dual-frequency RF power that has a high frequency component and a low frequency component. The RF power is typically applied at a power level between about 50 W and about 2,500 W, which may be all high-frequency RF power, for example at a frequency of about 13.56 MHz, or may be a mixture of high-frequency power and low frequency power, for example at a frequency of about 300 kHz.

[0046] In some implementations, where the reactive species are formed ex-situ, the BCl_3 containing gas mixture is flowed into a remote plasma source fluidly coupled with the substrate-processing chamber. The BCl_3 containing gas mixture comprises BCl_3 and optionally an inert gas. In some implementations, the optional inert gas may function as a carrier gas. In some implementations, the optional inert gas may extend the lifetime of and increase the density of the radical species. In some implementations, the BCl_3 containing gas mixture is flowed into the remote plasma source and the other process gases are delivered to the chamber separately. The optional inert gas may be selected from the group consisting of helium, argon, or combinations thereof.

[0047] The remote plasma source may be an inductively coupled plasma source. The remote plasma source accepts the BCl_3 containing gas mixture and forms a

plasma in the BCl_3 containing gas mixture, which causes dissociation of the of the BCl_3 containing gas mixture to form reactive species. The reactive species may include chlorine radicals. The remote plasma source provides high efficiency dissociation of the BCl_3 containing gas mixture.

[0048] In some implementations, the remote plasma is initiated with an initial flow of argon or similar inert gas before introducing the BCl_3 containing gas mixture into the remote plasma chamber.

[0049] The BCl_3 containing gas mixture may be flowed into the substrate-processing chamber at a flow rate of about 100 sccm to about 10,000 sccm. In some implementations, the BCl_3 containing gas mixture is flowed into the substrate-processing chamber at a flow rate from about 500 sccm to about 4,000 sccm. In some implementations, the BCl_3 containing gas mixture is flowed into the substrate-processing chamber at a flow rate of about 1,000 sccm.

[0050] The pressure within the substrate-processing chamber may be between about 10 mTorr and about 300 Torr. The pressure within the substrate-processing chamber may be between 10 mTorr and about 5 Torr, for example, about 20 mTorr.

[0051] In some implementations, the remote plasma is initiated with an initial flow of argon or similar inert gas before introducing BCl_3 into the remote plasma source. Then, as BCl_3 is introduced into the remote plasma chamber the flow rate of argon is decreased. As an example, the remote plasma may be initiated with a flow of 3,000 sccm of argon which is progressively decreased to 1,000 and then to 500 sccm as BCl_3 is introduced into the remote plasma chamber at an initial flow rate of 1,000 sccm and then increased to a flow of 1,500 sccm.

[0052] In some implementations, the cleaning process is performed at room temperature. In some implementations, the substrate support pedestal is heated to a temperature of about 600 degrees Celsius or less, for example between about 10 degrees Celsius and about 200 degrees Celsius, or between about 10 degrees Celsius and about 50 degrees Celsius, such as between about 10 degrees Celsius and 30 degrees Celsius. Controlling the temperature may be used to control the

removal/etching rate of the cobalt/cobalt containing deposits. The removal rate may increase as the chamber temperature increases.

[0053] The reactive species formed from the BCl_3 gas mixture are transported to the substrate-processing chamber. The reactive species comprise chlorine radicals.

[0054] At operation 240, the reactive species react with the zirconium oxide containing deposits to form a volatile product in gaseous state. The volatile product includes zirconium tetrachloride ($ZrCl_4$). In some implementations, a removal rate of the residual ZrO_2 containing film is greater than a removal rate of the Al_2O_3, which coats at least a portion of the aluminum chamber components. In some implementations, the removal rate of the residual ZrO_2 containing film is greater than 200 Å/min (e.g., from about 220 Å/min to about 400 Å/min; or from about 240 Å/min to about 300 Å/min). In some implementations, reacting the residual ZrO_2 containing film with the reactive species to form a volatile product is a bias-free process. In some implementations where no external DC bias is applied, the removal rate of Al_2O_3 is less than 50 Å/minute (e.g., from about 0 Å/min to about 50 Å/min; from about 0 Å/min to about 10 Å/min, or zero Å/min).

[0055] Optionally, at operation 250, the volatile product, which is in a gaseous state, is purged out of the substrate-processing chamber. The substrate-processing chamber may be actively purged by flowing a purge gas into the substrate-processing chamber. Alternatively, or in addition to introducing the purge gas, the substrate-processing chamber may be depressurized in order to remove any residual cleaning gas as well as any byproducts from the substrate-processing chamber. The substrate-processing chamber may be purged by evacuating the substrate-processing chamber. The time-period of the purge process should generally be long enough to remove the volatile products from the substrate-processing chamber. The time-period of purge gas flow should be generally long enough to remove the volatile products from the interior surfaces of the chamber including the chamber components.

[0056] At operation 260, at least one of operation 230, operation 240, and operation 250 are repeated until a chosen cleaning endpoint is achieved. It should be understood that several cycles of cleaning may apply with an optional purge process performed in between cleaning cycles.

[0057] In some implementations, the method 200 further comprises removing the Al_2O_3 containing film from the substrate-processing chamber. The Al_2O_3 is removed by applying an external DC bias while forming the reactive species and/or while reacting the Al_2O_3 containing film with the reactive species to form a second volatile product. The second volatile product may be removed from the substrate-processing chamber.

[0058] **Examples:**

[0059] The following non-limiting examples are provided to further illustrate implementations described herein. However, the examples are not intended to be all-inclusive and are not intended to limit the scope of the implementations described herein. Table I depicts the results for a cleaning process performed according to one implementations of the present disclosure. As depicted in Table I, an inductively coupled plasma process performed with BCl_3 and without DC bias has a higher removal rate for ZrO_2, aluminum-doped ZrO_2 and aluminum relative to Al_2O_3. As further depicted in Table 1, when DC bias is applied, the process also removes Al_2O_3.

Process	**ICP BCl_3 without DC bias**				**BCl_3 with DC bias**
Material	ZrO_2	Al doped ZrO_2	Aluminum	Al_2O_3	Al_2O_3
Etch Rate	240 Å/min	220 Å/min	410 Å/min	0 Å	600 Å

Table I.

[0060] In summary, some benefits of the present disclosure include the ability to selectivity etch residual ZrO_2 films without etching Al_2O_3. This selectivity can be used to protect aluminum chamber components. Aluminum chamber components are typically etched during plasma cleaning processes. The inventors have found

that using Al_2O_3 anodization to protect aluminum components in the chamber allows for the preferential removal of residual ZrO_2 films without damaging aluminum components, which ensures the reliability and lifetime of hardware parts. Selectivity is central to enable the in-situ cleaning capability. Thus, during cleaning, the residual films can be removed by the cleaning agent (e.g., BCl_3), but the aluminum sidewalls and other aluminum hardware components inside the chamber remain intact. As mentioned above, implementations of the present disclosure include using BCl_3 plasma to clean residual ZrO_2 films, and using Al_2O_3 coating on aluminum hardware parts inside the chamber to protect the aluminum hardware parts. The BCl_3 plasma can effectively etch ZrO_2 and aluminum, but does not etch Al_2O_3 if no additional DC bias applied. Thus, aluminum can be used as the material of hardware parts, as long as coated with Al_2O_3, which can be done by surface anodization. When external DC bias is applied, BCl_3 plasma can also etch Al_2O_3. These features make BCl_3 plasma an ideal cleaning agent for in-situ cleaning of ZrO_2 deposition chambers.

[0061] When introducing elements of the present disclosure or exemplary aspects or implementation(s) thereof, the articles “a,” “an,” “the” and “said” are intended to mean that there are one or more of the elements.

[0062] The terms “comprising,” “including” and “having” are intended to be inclusive and mean that there may be additional elements other than the listed elements.

[0063] While the foregoing is directed to implementations of the present disclosure, other and further implementations of the present disclosure 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 for cleaning a processing chamber, comprising:

introducing a reactive species into a processing chamber having a residual ZrO_2 containing film formed on one or more interior surfaces of the processing chamber, wherein the reactive species is formed from BCl_3 and the one or more interior surfaces includes at least one exposed Al_2O_3 surface;

reacting the residual ZrO_2 containing film with the reactive species to form a volatile product; and

removing the volatile product from the processing chamber, wherein a removal rate of the residual ZrO_2 containing film is greater than a removal rate of Al_2O_3.

2. The method of claim 1, wherein the removal rate of Al_2O_3 is zero Å/minute.

3. The method of claim 1, further comprising exposing the reactive species to one or more energy sources sufficient to react the residual ZrO_2 containing film with the reactive species and form a volatile product.

4. The method of claim 3, wherein the one or more energy sources are selected from a capacitive-coupled plasma source, an inductive-coupled plasma source, and a microwave plasma source.

5. The method of claim 1, wherein a pressure of the reacting the residual ZrO_2 containing film with the reactive species to form a volatile product is between at least about 10 mTorr and about 5 Torr.

6. The method of claim 1, wherein the processing chamber is a plasma-enhanced chemical vapor deposition (PECVD) chamber, an atomic layer deposition (ALD) chamber, and a physical vapor deposition (PVD) chamber.

7. The method of claim 1, wherein the reacting the residual ZrO_2 containing film with the reactive species to form a volatile product is a bias-free process.

8. The method of claim 1, wherein no external DC bias is applied while reacting the residual ZrO_2 containing film with the reactive species to form a volatile product.

9. The method of claim 8, further comprising:

reacting the Al_2O_3 containing film with the reactive species to form a second volatile product while applying an external DC bias; and

removing the second volatile product from the processing chamber.

10. A method for cleaning a processing chamber, comprising:

depositing a ZrO_2 containing film on one or more interior surface of a processing chamber and a substrate disposed in the substrate-processing chamber;

transferring the substrate out of the substrate-processing chamber;

introducing a reactive species into the processing chamber having the residual ZrO_2 containing film formed on one or more interior surfaces of the processing chamber, wherein the reactive species is formed from BCl_3 and the one or more interior surfaces includes at least one exposed Al_2O_3 surface;

reacting the residual ZrO_2 containing film with the reactive species to form a volatile product; and

removing the volatile product from the processing chamber, wherein a removal rate of the residual ZrO_2 containing film is greater than a removal rate of Al_2O_3.

11. The method of claim 10, wherein the removal rate of Al_2O_3 is zero Å/minute.

12. The method of claim 10, further comprising exposing the reactive species to one or more energy sources sufficient to react the residual ZrO_2 containing film with the reactive species and form a volatile product.

13. The method of claim 12, wherein the one or more energy sources are selected from a capacitive-coupled plasma source, an inductive-coupled plasma source, and a microwave plasma source.

14. The method of claim 10, wherein the reacting the residual ZrO_2 containing film with the reactive species to form a volatile product is a bias-free process.

15. The method of claim 10, wherein no external DC bias is applied while reacting the residual ZrO_2 containing film with the reactive species to form a volatile product.

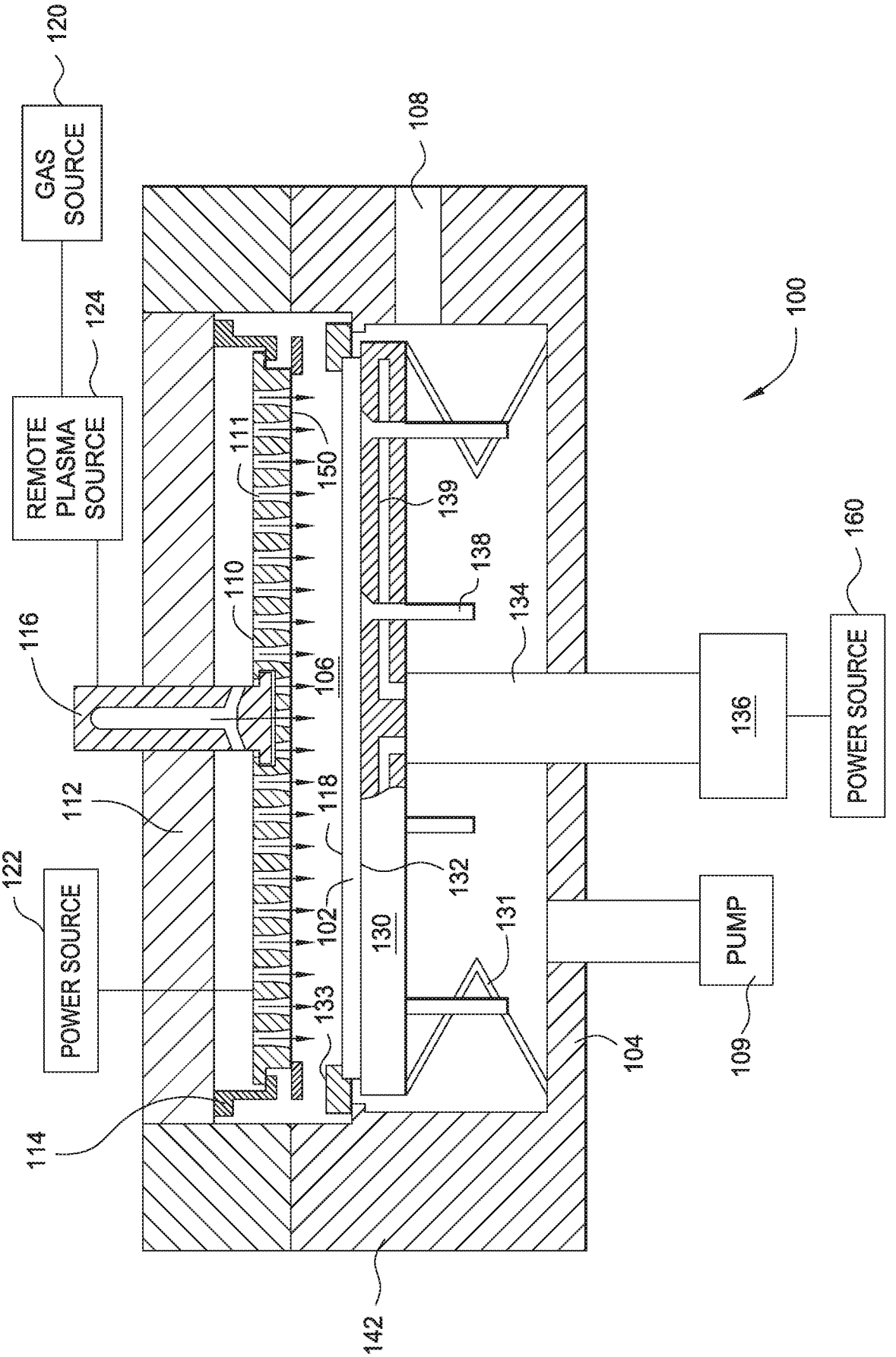

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FIG. 1A

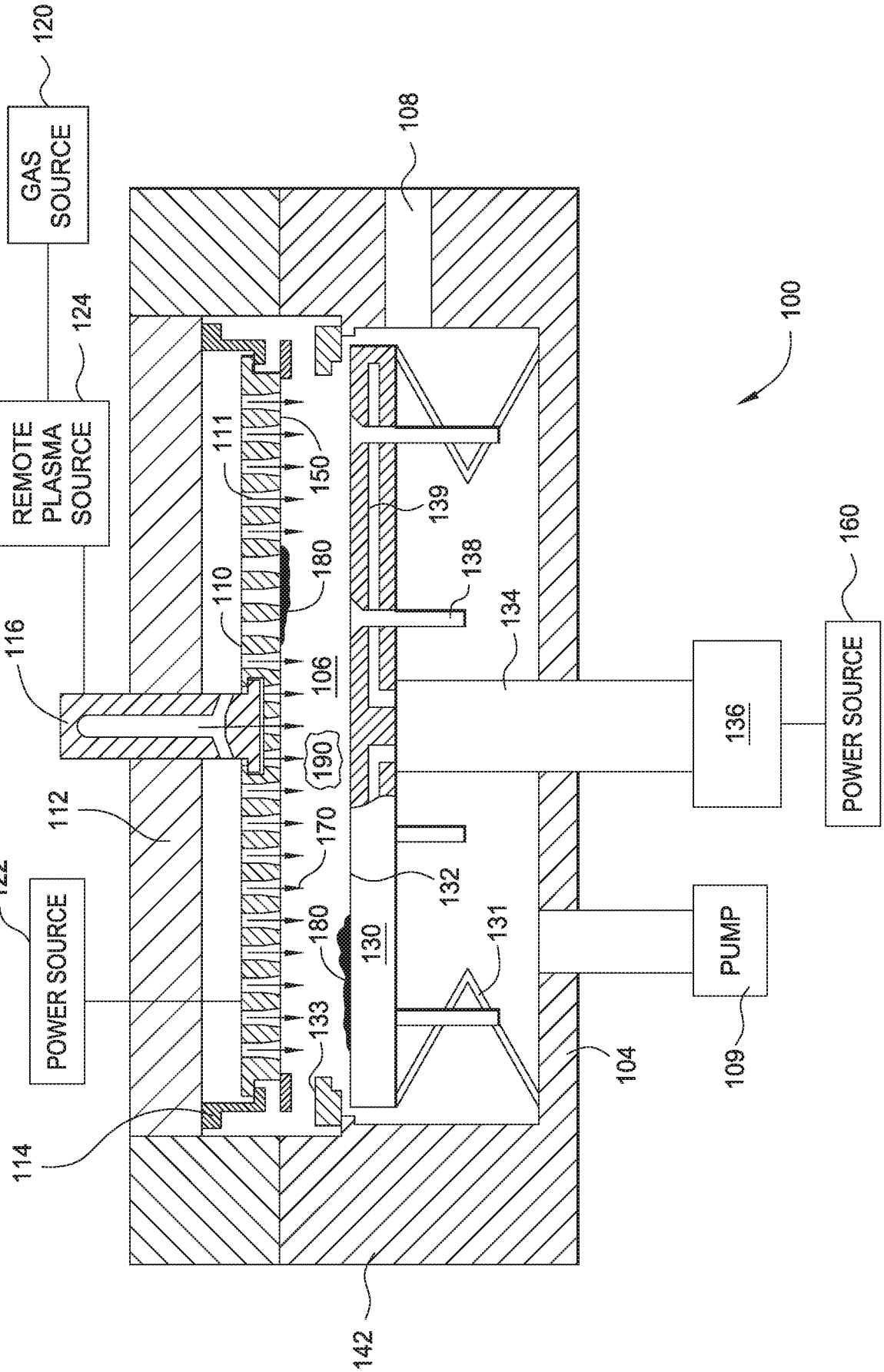

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FIG. 1B

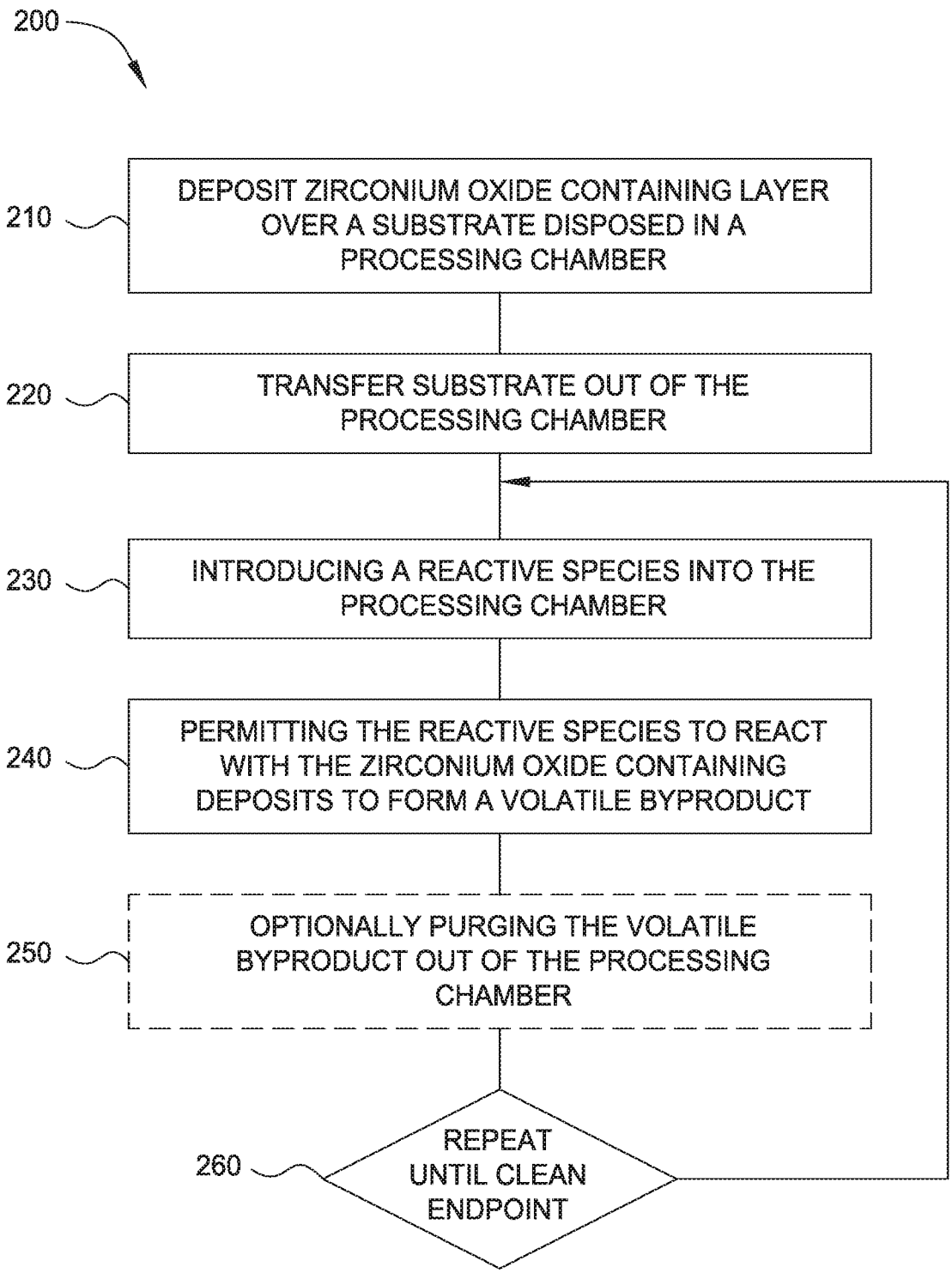

200
210
DEPOSIT ZIRCONIUM OXIDE CONTAINING LAYER OVER A SUBSTRATE DISPOSED IN A PROCESSING CHAMBER
220
TRANSFER SUBSTRATE OUT OF THE PROCESSING CHAMBER
230
INTRODUCING A REACTIVE SPECIES INTO THE PROCESSING CHAMBER
240
PERMITTING THE REACTIVE SPECIES TO REACT WITH THE ZIRCONIUM OXIDE CONTAINING DEPOSITS TO FORM A VOLATILE BYPRODUCT
250
OPTIONALLY PURGING THE VOLATILE BYPRODUCT OUT OF THE PROCESSING CHAMBER
260
REPEAT UNTIL CLEAN ENDPOINT

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/030213

A. CLASSIFICATION OF SUBJECT MATTER

H01L 21/02(2006.01)i, H01L 21/67(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L 21/02; H01L 21/3213; H01L 21/205; C23F 1/00; F26B 3/00; B08B 9/00; B08B 3/12; H01L 21/67

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: chamber, cleaning, selective, removal, ZrO2, Al2O3, bias

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2005-0108892 A1 (DINGJUN WU et al.) 26 May 2005 See paragraphs 19, 41; and claims 2, 8, 10, 18.	1-15
Y	US 2004-0129671 A1 (BING JI et al.) 08 July 2004 See paragraphs 86, 94; and tables 24, 28.	1-15
A	US 2005-0028927 A1 (CEM BASCERI et al.) 10 February 2005 See the entire document.	1-15
A	US 2016-0118268 A1 (APPLIED MATERIALS, INC.) 28 April 2016 See the entire document.	1-15
A	KR 10-2004-0074681 A (SAMSUNG ELECTRONICS CO., LTD.) 26 August 2004 See the entire document.	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 August 2018 (09.08.2018)	**10 August 2018 (10.08.2018)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2018/030213

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