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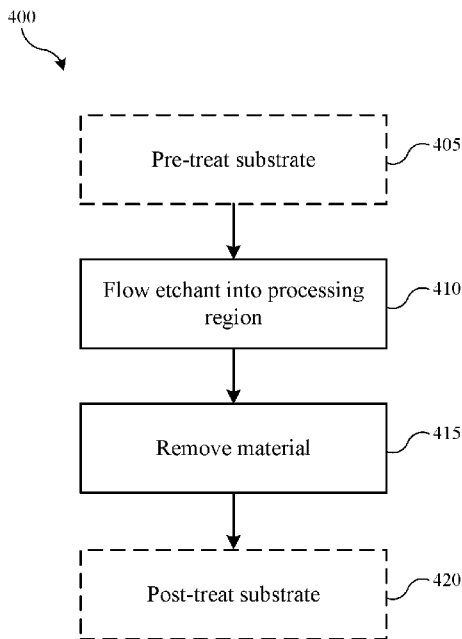


FIG. 4

(57) Abstract: Exemplary semiconductor processing methods may include flowing an etchant precursor into a processing region of a semiconductor processing chamber. A substrate may be housed within the processing region. The substrate may define an exposed region of a titanium-containing material. The methods may include contacting the substrate with the etchant precursor. The methods may include removing at least a portion of the titanium-containing material.

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SYSTEMS AND METHODS FOR TITANIUM-CONTAINING FILM REMOVAL

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] This application claims the benefit and priority of U.S. Patent Application No. 18/101,932, filed January 26, 2023, entitled “SYSTEMS AND METHODS FOR TITANIUM-CONTAINING FILM REMOVAL”, which is hereby incorporated by reference in its entirety.

10 TECHNICAL FIELD

[0002] The present technology relates to semiconductor processes and equipment. More specifically, the present technology relates to selectively etching titanium-containing structures.

15 BACKGROUND

[0003] Integrated circuits are made possible by processes which produce intricately patterned material layers on substrate surfaces. Producing patterned material on a substrate requires controlled methods for removal of exposed material. Chemical etching is used for a variety of purposes including transferring a pattern in photoresist into underlying layers, 20 thinning layers, or thinning lateral dimensions of features already present on the surface. Often it is desirable to have an etch process that etches one material faster than another facilitating, for example, a pattern transfer process. Such an etch process is said to be selective to the first material. As a result of the diversity of materials, circuits, and processes, etch processes have been developed with a selectivity towards a variety of materials.

25 [0004] Etch processes may be termed wet or dry based on the materials used in the process. For example, a wet etch may preferentially remove some oxide dielectrics over other dielectrics and materials. However, wet processes may have difficulty penetrating some constrained trenches and also may sometimes deform the remaining material. Dry etches produced in local plasmas formed within the substrate processing region can penetrate more 30 constrained trenches and exhibit less deformation of delicate remaining structures. However,

local plasmas may damage the substrate through the production of electric arcs as they discharge.

[0005] Thus, there is a need for improved systems and methods that can be used to produce high quality devices and structures. These and other needs are addressed by the present
5 technology.

SUMMARY

[0006] Exemplary semiconductor processing methods may include flowing an etchant precursor into a processing region of a semiconductor processing chamber. A substrate may be housed within the processing region. The substrate may define an exposed region of a
10 titanium-containing material. The methods may include contacting the substrate with the etchant precursor. The methods may include removing at least a portion of the titanium-containing material.

[0007] In some embodiments, the etchant precursor may be or include a halogen-containing precursor. The etchant precursor may be or include a chlorine-containing precursor. The
15 chlorine-containing precursor may be or include thionyl chloride (SOCl_2). Removing the portion of the titanium-containing material may be performed plasma-free. Removing the portion of the titanium-containing material may be performed at a temperature less than or about 450°C . Removing the portion of the titanium-containing material may be performed at a pressure greater than or about 0.1 Torr. Removing the portion of the titanium-containing
20 material may be performed at a pressure less than or about 50 Torr. The methods may include a pre-treatment performed prior to flowing the etchant precursor. The pre-treatment may include contacting the substrate with a plasma comprising one or more of oxygen, hydrogen, or nitrogen. The methods may include a post-treatment performed subsequent removing the portion of the titanium-containing material. The post-treatment may include
25 contacting the substrate with a plasma comprising one or more of oxygen, hydrogen, or nitrogen.

[0008] Some embodiments of the present technology may encompass semiconductor processing methods. The methods may include forming a plasma of a treatment precursor comprising one or more of oxygen, hydrogen, or nitrogen to produce treatment plasma
30 effluents. The methods may include flowing the treatment plasma effluents into a processing region of a semiconductor processing chamber. A substrate may be housed within the processing region. The substrate may define an exposed region of a titanium-containing

material. The methods may include contacting the substrate with the treatment plasma effluents. The treatment plasma effluents may be configured to remove a residue from a surface of the titanium-containing material. The methods may include flowing an etchant precursor into the processing region of the semiconductor processing chamber. The methods
5 may include contacting the substrate with the etchant precursor. The methods may include removing at least a portion of the titanium-containing material.

[0009] In some embodiments, the methods may include halting formation of the plasma of the treatment precursor prior to flowing the etchant precursor. The etchant precursor may be or include thionyl chloride (SOCl_2). Removing the portion of the titanium-containing
10 material may be performed at a temperature less than or about $400\text{ }^\circ\text{C}$. Removing the portion of the titanium-containing material may be performed at a pressure less than or about 30 Torr. The methods may include a post-treatment performed subsequent removing the portion of the titanium-containing material. The post-treatment may include contacting the substrate with a plasma comprising one or more of oxygen, hydrogen, or nitrogen.

[0010] Some embodiments of the present technology may include semiconductor processing methods. The methods may include flowing an etchant precursor into a processing region of a semiconductor processing chamber. A substrate may be housed within the processing region. The substrate may define an exposed region of a titanium-containing material. The methods may include contacting the substrate with the etchant precursor. The
15 methods may include removing at least a portion of the titanium-containing material. The methods may include forming a plasma of a treatment precursor comprising one or more of oxygen, hydrogen, or nitrogen to produce treatment plasma effluents. The methods may include contacting the substrate with the treatment plasma effluents.

[0011] In some embodiments, the etchant precursor may include chlorine. The treatment
25 plasma effluents may be configured to remove residual chlorine from one or more of the substrate or the semiconductor processing chamber. Removing the portion of the titanium-containing material may be performed at a temperature less than or about $380\text{ }^\circ\text{C}$ and at a pressure less than or about 30 Torr.

[0012] Such technology may provide numerous benefits over conventional systems and
30 techniques. For example, the processes may allow dry etching to be performed that may protect features of the substrate. Additionally, the processes may selectively remove titanium-containing films relative to other exposed materials on the substrate. These and

other embodiments, along with many of their advantages and features, are described in more detail in conjunction with the below description and attached figures.

BRIEF DESCRIPTION OF THE DRAWINGS

- 5 [0013] A further understanding of the nature and advantages of the disclosed technology may be realized by reference to the remaining portions of the specification and the drawings.
- [0014] FIG. 1 shows a top plan view of one embodiment of an exemplary processing system according to some embodiments of the present technology.
- [0015] FIG. 2A shows a schematic cross-sectional view of an exemplary processing
10 chamber according to some embodiments of the present technology.
- [0016] FIG. 2B shows a detailed view of a portion of the processing chamber illustrated in FIG. 2A according to some embodiments of the present technology.
- [0017] FIG. 3 shows a bottom plan view of an exemplary showerhead according to some embodiments of the present technology.
- 15 [0018] FIG. 4 shows exemplary operations in a method according to some embodiments of the present technology.
- [0019] FIGS. 5A-5B show schematic cross-sectional views of materials etched according to some embodiments of the present technology.
- [0020] Several of the figures are included as schematics. It is to be understood that the
20 figures are for illustrative purposes, and are not to be considered of scale unless specifically stated to be of scale. Additionally, as schematics, the figures are provided to aid comprehension and may not include all aspects or information compared to realistic representations, and may include additional or exaggerated material for illustrative purposes.
- [0021] In the appended figures, similar components and/or features may have the same
25 reference label. Further, various components of the same type may be distinguished by following the reference label by a letter that distinguishes among the similar components. If only the first reference label is used in the specification, the description is applicable to any one of the similar components having the same first reference label irrespective of the letter.

DETAILED DESCRIPTION

[0022] Diluted acids may be used in many different semiconductor processes for cleaning substrates and removing materials from those substrates. For example, diluted hydrofluoric acid (“DHF”) can be an effective etchant for silicon oxide, aluminum oxide, titanium oxide, and other materials, and may be used to remove these materials from substrate surfaces. After the etching or cleaning operation is complete, the acid may be dried from the wafer or substrate surface. Using DHF may be termed a “wet” etch where the diluent is often water. Additional etching processes may be used that utilize precursors delivered to the substrate. For example, plasma enhanced processes may also selectively etch materials by enhancing precursors through the plasma to perform a dry etch.

[0023] Although wet etchants using aqueous solutions or water-based processes may operate effectively for certain substrate structures, the water may pose challenges in a variety of conditions. For example, utilizing water during etch processes may cause issues when disposed on substrates including metal materials. For example, certain later fabrication processes, such as recessing gaps, removing oxide dielectric, or other processes to remove oxygen-containing materials, may be performed after an amount of metallization has been formed on a substrate. If water is utilized in some fashion during the etching, an electrolyte may be produced, which when contacting the metal material, may cause galvanic corrosion to occur between dissimilar metals, and the metal may be corroded or displaced in various processes. In addition, because of the surface tension of the water diluent, pattern deformation and collapse may occur with minute structures. The water-based material may also be incapable of penetrating some high aspect ratio features due to surface tension effects. Plasma etching may overcome the issues associated with water-based etching, although additional issues may occur. For example, a reactive ion etch process may expose the metal to ion activity, which through bombardment can damage the structure, and affect electrical characteristics.

[0024] The present technology overcomes these issues by performing a dry etch process that may passivate a number of materials relative to a material to be etched, and in some embodiments a process may be plasma free during the etching. By utilizing particular precursors that may facilitate halogen dissociation to provide etchant materials, an etch process may be performed that may protect the surrounding structures. Additionally, the materials and conditions used may allow improved etching relative to conventional techniques.

[0025] Although the remaining disclosure will routinely identify specific etching processes utilizing the disclosed technology, it will be readily understood that the systems and methods are equally applicable to deposition and cleaning processes as may occur in the described chambers, as well as other etching technology and other etching that may be performed with a variety of exposed materials that may be maintained or substantially maintained. Accordingly, the technology should not be considered to be so limited as for use with the exemplary etching processes or chambers alone. Moreover, although an exemplary chamber is described to provide foundation for the present technology, it is to be understood that the present technology can be applied to virtually any semiconductor processing chamber that may allow the operations described.

[0026] FIG. 1 shows a top plan view of one embodiment of a processing system 100 of deposition, etching, baking, and curing chambers according to embodiments. In the figure, a pair of front opening unified pods (FOUPs) 102 supply substrates of a variety of sizes that are received by robotic arms 104 and placed into a low pressure holding area 106 before being placed into one of the substrate processing chambers 108a-f, positioned in tandem sections 109a-c. A second robotic arm 110 may be used to transport the substrate wafers from the holding area 106 to the substrate processing chambers 108a-f and back. Each substrate processing chamber 108a-f, can be outfitted to perform a number of substrate processing operations including the dry etch processes described herein in addition to cyclical layer deposition (CLD), atomic layer deposition (ALD), chemical vapor deposition (CVD), physical vapor deposition (PVD), etch, pre-clean, degas, orientation, and other substrate processes.

[0027] The substrate processing chambers 108a-f may include one or more system components for depositing, annealing, curing and/or etching a dielectric film on the substrate wafer. In one configuration, two pairs of the processing chambers, e.g., 108c-d and 108e-f, may be used to deposit dielectric material on the substrate, and the third pair of processing chambers, e.g., 108a-b, may be used to etch the deposited dielectric. In another configuration, all three pairs of chambers, e.g., 108a-f, may be configured to etch a dielectric film on the substrate. Any one or more of the processes described may be carried out in chamber(s) separated from the fabrication system shown in different embodiments. It will be appreciated that additional configurations of deposition, etching, annealing, and curing chambers for dielectric films are contemplated by system 100.

[0028] FIG. 2A shows a cross-sectional view of an exemplary process chamber system 200 with partitioned plasma generation regions within the processing chamber. During film etching, e.g., titanium nitride, tantalum nitride, tungsten, silicon, polysilicon, silicon oxide, silicon nitride, silicon oxynitride, silicon oxycarbide, etc., a process gas may be flowed into the first plasma region 215 through a gas inlet assembly 205. A remote plasma system (RPS) 201 may optionally be included in the system, and may process a first gas which then travels through gas inlet assembly 205. The inlet assembly 205 may include two or more distinct gas supply channels where the second channel (not shown) may bypass the RPS 201, if included.

[0029] A cooling plate 203, faceplate 217, ion suppressor 223, showerhead 225, and a pedestal 265 or substrate support, having a substrate 255 disposed thereon, are shown and may each be included according to embodiments. The pedestal 265 may have a heat exchange channel through which a heat exchange fluid flows to control the temperature of the substrate, which may be operated to heat and/or cool the substrate or wafer during processing operations. The wafer support platter of the pedestal 265, which may include aluminum, ceramic, or a combination thereof, may also be resistively heated in order to achieve relatively high temperatures, such as from up to or about 100° C to above or about 1100° C, using an embedded resistive heater element.

[0030] The faceplate 217 may be pyramidal, conical, or of another similar structure with a narrow top portion expanding to a wide bottom portion. The faceplate 217 may additionally be flat as shown and include a plurality of through-channels used to distribute process gases. Plasma generating gases and/or plasma excited species, depending on use of the RPS 201, may pass through a plurality of holes, shown in FIG. 2B, in faceplate 217 for a more uniform delivery into the first plasma region 215.

[0031] Exemplary configurations may include having the gas inlet assembly 205 open into a gas supply region 258 partitioned from the first plasma region 215 by faceplate 217 so that the gases/species flow through the holes in the faceplate 217 into the first plasma region 215. Structural and operational features may be selected to prevent significant backflow of plasma from the first plasma region 215 back into the supply region 258, gas inlet assembly 205, and fluid supply system 210. The faceplate 217, or a conductive top portion of the chamber, and showerhead 225 are shown with an insulating ring 220 located between the features, which allows an AC potential to be applied to the faceplate 217 relative to showerhead 225 and/or ion suppressor 223. The insulating ring 220 may be positioned between the faceplate 217 and

the showerhead 225 and/or ion suppressor 223 enabling a capacitively coupled plasma (CCP) to be formed in the first plasma region. A baffle (not shown) may additionally be located in the first plasma region 215, or otherwise coupled with gas inlet assembly 205, to affect the flow of fluid into the region through gas inlet assembly 205.

5 [0032] The ion suppressor 223 may comprise a plate or other geometry that defines a plurality of apertures throughout the structure that are configured to suppress the migration of ionically-charged species out of the first plasma region 215 while allowing uncharged neutral or radical species to pass through the ion suppressor 223 into an activated gas delivery region between the suppressor and the showerhead. In embodiments, the ion suppressor 223 may
10 comprise a perforated plate with a variety of aperture configurations. These uncharged species may include highly reactive species that are transported with less reactive carrier gas through the apertures. As noted above, the migration of ionic species through the holes may be reduced, and in some instances completely suppressed. Controlling the amount of ionic species passing through the ion suppressor 223 may advantageously provide increased
15 control over the gas mixture brought into contact with the underlying wafer substrate, which in turn may increase control of the deposition and/or etch characteristics of the gas mixture. For example, adjustments in the ion concentration of the gas mixture can significantly alter its etch selectivity. In alternative embodiments in which deposition is performed, it can also shift the balance of conformal-to-flowable style depositions for dielectric materials.

20 [0033] The plurality of apertures in the ion suppressor 223 may be configured to control the passage of the activated gas, i.e., the ionic, radical, and/or neutral species, through the ion suppressor 223. For example, the aspect ratio of the holes, or the hole diameter to length, and/or the geometry of the holes may be controlled so that the flow of ionically-charged species in the activated gas passing through the ion suppressor 223 is reduced. The holes in
25 the ion suppressor 223 may include a tapered portion that faces the plasma excitation region 215, and a cylindrical portion that faces the showerhead 225. The cylindrical portion may be shaped and dimensioned to control the flow of ionic species passing to the showerhead 225. An adjustable electrical bias may also be applied to the ion suppressor 223 as an additional means to control the flow of ionic species through the suppressor.

30 [0034] The ion suppressor 223 may function to reduce or eliminate the amount of ionically charged species traveling from the plasma generation region to the substrate. Uncharged neutral and radical species may still pass through the openings in the ion suppressor to react

with the substrate. It should be noted that the complete elimination of ionically charged species in the reaction region surrounding the substrate may not be performed in embodiments. In certain instances, ionic species are intended to reach the substrate in order to perform the etch and/or deposition process. In these instances, the ion suppressor may
5 help to control the concentration of ionic species in the reaction region at a level that assists the process.

[0035] Showerhead 225 in combination with ion suppressor 223 may allow a plasma present in first plasma region 215 to avoid directly exciting gases in substrate processing region 233, while still allowing excited species to travel from chamber plasma region 215
10 into substrate processing region 233. In this way, the chamber may be configured to prevent the plasma from contacting a substrate 255 being etched. This may advantageously protect a variety of intricate structures and films patterned on the substrate, which may be damaged, dislocated, or otherwise warped if directly contacted by a generated plasma. Additionally, when plasma is allowed to contact the substrate or approach the substrate level, the rate at
15 which oxide species etch may increase. Accordingly, if an exposed region of material is oxide, this material may be further protected by maintaining the plasma remotely from the substrate.

[0036] The processing system may further include a power supply 240 electrically coupled with the processing chamber to provide electric power to the faceplate 217, ion suppressor
20 223, showerhead 225, and/or pedestal 265 to generate a plasma in the first plasma region 215 or processing region 233. The power supply may be configured to deliver an adjustable amount of power to the chamber depending on the process performed. Such a configuration may allow for a tunable plasma to be used in the processes being performed. Unlike a remote plasma unit, which is often presented with on or off functionality, a tunable plasma may be
25 configured to deliver a specific amount of power to the plasma region 215. This in turn may allow development of particular plasma characteristics such that precursors may be dissociated in specific ways to enhance the etching profiles produced by these precursors.

[0037] A plasma may be ignited either in chamber plasma region 215 above showerhead 225 or substrate processing region 233 below showerhead 225. Plasma may be present in
30 chamber plasma region 215 to produce the radical precursors from an inflow of, for example, a fluorine-containing precursor or other precursor. An AC voltage typically in the radio frequency (RF) range may be applied between the conductive top portion of the processing

chamber, such as faceplate 217, and showerhead 225 and/or ion suppressor 223 to ignite a plasma in chamber plasma region 215 during deposition. An RF power supply may generate a high RF frequency of 13.56 MHz but may also generate other frequencies alone or in combination with the 13.56 MHz frequency.

5 **[0038]** **FIG. 2B** shows a detailed view 253 of the features affecting the processing gas distribution through faceplate 217. As shown in FIGS. 2A and 2B, faceplate 217, cooling plate 203, and gas inlet assembly 205 intersect to define a gas supply region 258 into which process gases may be delivered from gas inlet 205. The gases may fill the gas supply region 258 and flow to first plasma region 215 through apertures 259 in faceplate 217. The
10 apertures 259 may be configured to direct flow in a substantially unidirectional manner such that process gases may flow into processing region 233, but may be partially or fully prevented from backflow into the gas supply region 258 after traversing the faceplate 217.

[0039] The gas distribution assemblies such as showerhead 225 for use in the processing chamber section 200 may be referred to as dual channel showerheads (DCSH) and are
15 additionally detailed in the embodiments described in FIG. 3. The dual channel showerhead may provide for etching processes that allow for separation of etchants outside of the processing region 233 to provide limited interaction with chamber components and each other prior to being delivered into the processing region.

[0040] The showerhead 225 may comprise an upper plate 214 and a lower plate 216. The
20 plates may be coupled with one another to define a volume 218 between the plates. The coupling of the plates may be so as to provide first fluid channels 219 through the upper and lower plates, and second fluid channels 221 through the lower plate 216. The formed channels may be configured to provide fluid access from the volume 218 through the lower plate 216 via second fluid channels 221 alone, and the first fluid channels 219 may be fluidly
25 isolated from the volume 218 between the plates and the second fluid channels 221. The volume 218 may be fluidly accessible through a side of the showerhead 225.

[0041] **FIG. 3** is a bottom view of a showerhead 325 for use with a processing chamber according to embodiments. Showerhead 325 may correspond with the showerhead 225 shown in FIG. 2A. Through-holes 365, which show a view of first fluid channels 219, may
30 have a plurality of shapes and configurations in order to control and affect the flow of precursors through the showerhead 225. Small holes 375, which show a view of second fluid channels 221, may be distributed substantially evenly over the surface of the showerhead,

even amongst the through-holes 365, and may help to provide more even mixing of the precursors as they exit the showerhead than other configurations.

[0042] The chamber discussed previously may be used in performing exemplary methods including etching methods. Turning to **FIG. 4** is shown exemplary operations in a method 5 400 according to embodiments of the present technology. Method 400 may include one or more operations prior to the initiation of the method, including front end processing, deposition, gate formation, etching, polishing, cleaning, or any other operations that may be performed prior to the described operations. The method may include a number of optional operations, which may or may not be specifically associated with some embodiments of 10 methods according to the present technology. For example, many of the operations are described in order to provide a broader scope of the processes performed, but are not critical to the technology, or may be performed by alternative methodology as will be discussed further below. Method 400 may describe operations shown schematically in **FIGS. 5A-5B**, the illustrations of which will be described in conjunction with the operations of method 400. 15 It is to be understood that the figures illustrate only partial schematic views, and a substrate may contain any number of additional materials and features having a variety of characteristics and aspects as illustrated in the figures.

[0043] Method 400 may or may not involve optional operations to develop the semiconductor structure to a particular fabrication operation. It is to be understood that 20 method 400 may be performed on any number of semiconductor structures or substrates 505, as illustrated in **FIG. 5A**, including exemplary structures on which a nitride removal operation may be performed. Exemplary semiconductor structures may include a trench, via, or other recessed features that may include one or more exposed materials. For example, an exemplary substrate may contain silicon or some other semiconductor substrate material as 25 well as interlayer dielectric materials through which a recess, trench, via, or isolation structure may be formed. Exposed materials at any time during the etch process may be or include metal materials such as for a gate, a dielectric material, a contact material, a transistor material, or any other material that may be used in semiconductor processes. In some embodiments, exemplary structures 500 may include a metal-containing region 510, such as a 30 tungsten-containing material, extending into the substrate 505. An aluminum-containing material 515 may overly portions of the substrate 505. Low dielectric constant material 520, such as silicon oxide, may extend from the aluminum-containing material 515. A titanium-containing material 525, such as titanium nitride, may overly the low dielectric constant

material 520. As shown in FIG. 5A, the titanium-containing material 525 may be exposed relative to one or more other materials including metal-containing materials, dielectric materials including silicon oxide, or any number of other semiconductor materials relative to which the titanium-containing material is to be removed, such as an oxide of aluminum and any other materials.

[0044] It is to be understood that the noted structure is not intended to be limiting, and any of a variety of other semiconductor structures including titanium-containing materials are similarly encompassed. Other exemplary structures may include two-dimensional and three-dimensional structures common in semiconductor manufacturing, and within which a titanium-containing material such as titanium nitride is to be removed relative to one or more other materials, as the present technology may selectively remove titanium-containing materials relative to other exposed materials, such as silicon-containing materials, metal-containing materials, oxides, and other nitrides, as well as any of the other materials discussed elsewhere. Additionally, although a high-aspect-ratio structure may benefit from the present technology, the technology may be equally applicable to lower aspect ratios and any other structures.

[0045] For example, layers of material according to the present technology may be characterized by any aspect ratios or the height-to-width ratio of the structure, although in some embodiments the materials may be characterized by larger aspect ratios, which may not allow sufficient etching utilizing conventional technology or methodology. For example, in some embodiments the aspect ratio of any layer of an exemplary structure may be greater than or about 10:1, greater than or about 20:1, greater than or about 30:1, greater than or about 40:1, greater than or about 50:1, or greater. Additionally, each layer may be characterized by a reduced width or thickness less than or about 100 nm, less than or about 80 nm, less than or about 60 nm, less than or about 50 nm, less than or about 40 nm, less than or about 30 nm, less than or about 20 nm, less than or about 10 nm, less than or about 5 nm, less than or about 1 nm, or less, including any fraction of any of the stated numbers, such as 20.5 nm, 1.5 nm, etc. This combination of high aspect ratios and minimal thicknesses may frustrate many conventional etching operations, or require substantially longer etch times to remove a layer, along a vertical or horizontal distance through a confined width. Moreover, damage to or removal of other exposed layers may occur with conventional technologies as well.

[0046] Method 400 may be performed to remove an exposed titanium-containing material in embodiments, although any number of nitride or titanium-containing materials may be removed in any number of structures in embodiments of the present technology. The methods may include specific operations for the removal of titanium-containing materials, and may include one or more optional operations to prepare or treat the titanium-containing materials. For example, an exemplary substrate structure may have previous processing residues on a film to be removed, such as titanium nitride. For example, residual photoresist or byproducts from previous processing may reside on the titanium nitride layer. These materials may prevent access to the titanium nitride, or may interact with etchants differently than a clean titanium nitride surface, which may frustrate one or more aspects of the etching. Accordingly, in some embodiments an optional pre-treatment of the titanium-containing film or material may occur at optional operation 405. Exemplary pre-treatment operations may include a thermal treatment, wet treatment, or plasma treatment, for example, which may be performed in chamber 200 as well as any number of chambers that may be included on system 100 described above.

[0047] In one exemplary plasma treatment, a remote or local plasma may be developed from a precursor intended to interact with residues in one or more ways. For example, utilizing chambers such as chamber 200 described above, either a remote or local plasma may be produced from one or more precursors. For example, an oxygen-containing precursor, a hydrogen-containing precursor, a nitrogen-containing precursor, a helium-containing precursor, or some other precursor may be flowed into a remote plasma region or into the processing region, where a plasma may be struck. The plasma effluents may be flowed to the substrate, and may contact the residue material. The plasma process may be either physical or chemical depending on the material to be removed to expose the titanium-containing material. For example, plasma effluents may be flowed to contact and physically remove the residue, such as by a sputtering operation, or the precursors may be flowed to interact with the residues to produce volatile byproducts that may be removed from the chamber.

[0048] Exemplary precursors used in the pre-treatment may be or include hydrogen, a hydrocarbon, water vapor, an alcohol, hydrogen peroxide, or other materials that may include hydrogen as would be understood by the skilled artisan. Exemplary oxygen-containing precursors may include molecular oxygen, ozone, nitrous oxide, nitric oxide, or other oxygen-containing materials. Nitrogen gas may also be used, or a combination precursor having one or more of hydrogen, oxygen, and/or nitrogen may be utilized to remove

particular residues. Once the residue or byproducts have been removed, a clean titanium nitride surface may be exposed for etching.

5 The halogen-containing precursor may be flowed through a remote plasma region of the processing chamber, such as region 215 described above, although in some embodiments method 400 may not utilize plasma effluents during the etching operations. For example, method 400 may flow a fluorine-containing or other halogen-containing precursor to the substrate without exposing the precursor to a plasma, and may perform the removal of the titanium-containing material without production of plasma effluents. In some embodiments
10 the halogen-containing precursor may be plasma enhanced, which may occur in a remote plasma region to protect materials on the substrate from contact with plasma effluents. The halogen-containing precursor may contact a semiconductor substrate including an exposed titanium-containing material, and may produce a fluorinated material, such as titanium fluoride or an titanium halide material, which may remain on the semiconductor substrate.
15 The halogen-containing precursor may donate one or more fluorine atoms, while accepting one or more oxygen atoms in some embodiments. Some halogen-containing precursors, such as plasma enhanced precursors, may provide fluorine radicals, while other plasma radicals may accept oxygen from the film.

[0049] Method 400 may include flowing an etchant precursor into the substrate processing
20 region of a semiconductor processing chamber housing the described substrate, or some other substrate, at operation 410. The etchant precursor may be flowed through a remote plasma region of the processing chamber, such as region 215 described above, although in some embodiments method 400 may not utilize plasma effluents during the etching operations. For example, method 400 may flow the etchant precursor to the substrate without exposing the
25 precursor to a plasma, and may perform the removal of the titanium-containing material without production of plasma effluents. In some embodiments, the etchant precursor may be plasma enhanced, which may occur in a remote plasma region to protect materials on the substrate from contact with plasma effluents. The etchant precursor may contact a semiconductor substrate including an exposed region of titanium-containing material, and
30 may produce a chlorinated material, such as titanium chloride fluoride or a titanium halide material, which may remain on the semiconductor substrate or may volatilize. The halogen-containing precursor may donate one or more chlorine atoms, while accepting one or more

nitrogen atoms in some embodiments. Some halogen-containing precursors, such as plasma enhanced precursors, may provide chlorine radicals, while other plasma radicals may accept nitrogen from the film. Accordingly, the etchant precursor may etch or remove the titanium-containing material at operation 415, as shown in FIG. 5B.

5 [0050] As noted above, the present technology may be performed without plasma development during the etching operations 410-415. By utilizing particular precursors, and performing the etching within certain process conditions, a plasma-free removal may be performed, and the removal may also be a dry etch. Accordingly, techniques according to aspects of the present technology may be performed to remove titanium nitride from narrow
10 features, as well as high aspect ratio features, and thin dimensions that may otherwise be unsuitable for wet etching. An optional operation may be performed to clear the substrate or chamber of residues and may include a post-treatment at optional operation 420. The post-treatment may include similar operations as the pre-treatment, and may include any of the precursors or operations discussed above for the pre-treatment. The post-treatment may clear
15 residual etchant, such as chlorine, from the substrate or chamber in some embodiments. It is to be understood that although the pre-treatment and/or post-treatment operations may include plasma generation and plasma effluent delivery to the substrate, plasma may not be formed during the etching operations 410-415. For example, in some embodiments no plasma may be generated while the etchant precursor or precursors are being delivered into
20 the processing chamber.

[0051] The etchant precursor during the etching operations 410-415 may include halogen-containing precursors, and may include one or more of fluorine or chlorine in some embodiments. The specific precursors may be based on bonding or stability of the precursors. An exemplary etchant precursor may include thionyl chloride (SOCl_2), as well as
25 halogen-containing precursors such as other chlorine-containing precursors or fluorine-containing precursors. The etchant may also be flown together with a variety of other precursors. In some embodiments, in addition to the etchant precursor, boron trichloride (BCl_3), nitrogen trifluoride (NF_3), tungsten hexafluoride (WF_6), or other halogen-containing precursors may optionally be delivered to a remote plasma region to be plasma enhanced
30 prior to being flowed to the processing region. In embodiments, the etchant precursor may be provided with a hydrogen-containing precursor, such as molecular hydrogen (H_2). The etchant precursor may also be provided with any number of carrier gases, which may include nitrogen, helium, argon, or other noble, inert, or useful precursors. The carrier gases may

serve to dilute the etchant precursor, which may control etch rate, as well as distribute the etchant precursor.

[0052] As a non-limiting example, thionyl chloride (SOCl_2) may readily donate a chlorine atom or two as well as an oxygen atom at elevated temperatures, and accept a nitrogen atom, such as from the titanium nitride, and be maintained in a gas phase. Accordingly, titanium-containing materials may be developed as reaction byproducts, which may be gas molecules and may be pumped or removed from the processing chamber. For example, chlorine from the etchant precursor may combine with the titanium nitride to form titanium tetrachloride (TiCl_4), titanium(III) chloride (TiCl_3), or titanium oxychloride (TiOCl_2). Additionally, nitrogen-containing materials may be developed as reaction byproducts, which may be gas molecules and may be pumped or removed from the processing chamber. For example, nitrogen from the titanium nitride may form stable byproducts such as diatomic nitrogen (N_2), nitrous oxide (N_2O), or nitrogen dioxide (NO_2). Further, sulfur-containing materials may be developed as reaction byproducts, which may be gas molecules and may be pumped or removed from the processing chamber. For example, remaining sulfur from the etchant precursor may exist as sulfur dioxide (SO_2), sulfur monoxide (SO), or disulfur dichloride (S_2Cl_2). Accordingly, the process may remove titanium nitride under processing conditions configured to exchange chlorine and nitrogen between the etchant precursor and the exposed region of titanium nitride, which may produce volatile byproducts. Because of the controlled delivery and processing, chlorine-containing materials may not etch or may minimally interact with other exposed surfaces, while readily removing titanium nitride, which may produce enhanced selectivity over conventional techniques.

[0053] Processing conditions may impact and facilitate etching according to the present technology. Because the etch reaction may proceed based on thermal dissociation of a halogen from the etchant precursor, the temperatures may be at least partially dependent on the particular halogen and/or other atoms of the etchant precursor in order to initiate dissociation. As temperature increases above or about $250\text{ }^\circ\text{C}$, for example, etching begins to occur or increase, which may indicate dissociation of the precursor, and/or activation of the reaction with titanium nitride. As temperature continues to increase, dissociation may be further facilitated as may the reaction with titanium nitride.

[0054] Accordingly, in some embodiments of the present technology, etching methods may be performed at substrate, pedestal, and/or chamber temperatures less than or about $450\text{ }^\circ\text{C}$,

and may be performed at temperatures less than or about 440 °C, less than or about 430 °C, less than or about 420 °C, less than or about 410 °C, less than or about 400 °C, less than or about 390 °C, less than or about 380 °C, less than or about 370 °C, less than or about 360 °C, less than or about 350 °C, or lower. The temperature may also be maintained at any
5 temperature within these ranges, within smaller ranges encompassed by these ranges, or between any of these ranges. In some embodiments the method may be performed on substrates that may have a number of produced features, which may produce a thermal budget. In embodiments, a greater temperature may increase etching of the titanium-containing material 425. Accordingly, in some embodiments, the methods may be performed
10 at temperatures greater than or about 300 °C, and may be performed at temperatures greater than or about 310 °C, greater than or about 320 °C, greater than or about 330 °C, greater than or about 340 °C, greater than or about 350 °C, greater than or about 360 °C, or higher.

[0055] The pressure within the chamber may also affect the operations performed as well as affect at what temperature the etchant precursor may dissociate, such as what temperature
15 the sulfur, oxygen, and chlorine may dissociate when thionyl chloride (SOCl₂) is used as the etchant precursor. Accordingly, in some embodiments the pressure may be maintained above or about 0.5 Torr, above or about 1 Torr, above or about 2 Torr, above or about 3 Torr, above or about 4 Torr, above or about 5 Torr, above or about 6 Torr, above or about 7 Torr, above or about 8 Torr, above or about 9 Torr, above or about 10 Torr, above or about 15 Torr,
20 above or about 20 Torr, above or about 25 Torr, above or about 30 Torr, or higher. Additionally, the pressure may be maintained below or about 50 Torr, below or about 40 Torr, below or about 30 Torr, below or about 25 Torr, below or about 20 Torr, below or about 15 Torr, below or about 10 Torr, below or about 9 Torr, below or about 8 Torr, below or about 7 Torr, below or about 6 Torr, below or about 5 Torr, below or about 4 Torr, below or
25 about 3 Torr, below or about 2 Torr, below or about 1 Torr, below or about 0.1 Torr, or less. The pressure may also be maintained at any pressure within these ranges, within smaller ranges encompassed by these ranges, or between any of these ranges. In some embodiments, etch amount may be facilitated and may initiate as pressure increases above about 0.5 Torr. Additionally, as pressure continues to increase, etching may improve up to a point before
30 beginning to reduce, and eventually cease as pressure continues to increase.

[0056] Without being bound to any particular theory, pressure within the chamber may affect processing with precursors described above. At low pressures, flow across a substrate may be reduced, and dissociation may similarly be reduced. As pressure increases,

interactions between the etchant precursor and the substrate may increase, which may increase reactions and etch rates. However, as pressure continues to increase, recombination of the dissociated etchant precursor atoms may increase due to the relative stability of the molecules. Thus, the precursors may effectively be pumped back out of the chamber without reacting with the substrate. Additionally, interactions with the titanium nitride surface may be suppressed as pressure continues to increase, or byproduct titanium chloride may be reintroduced to the film being etched, further limiting removal. Accordingly, in some embodiments, pressure within the processing chamber may be maintained below or about 30 Torr in some embodiments.

5 [0057] Flow rates of the etchant precursor may be tuned, including in situ, to control the etch process. For example, a flow rate of the etchant precursor may be reduced, maintained, or increased during the removal operations. By increasing the flow rate of the etchant precursor, etch rates may be increased up to a point of saturation. During any of the operations of method 400, the flow rate of the etchant precursor may be between about 5 sccm and about 1,000 sccm. Additionally, the flow rate of the etchant precursor may be maintained below or about 900 sccm, below or about 800 sccm, below or about 700 sccm, below or about 600 sccm, below or about 500 sccm, below or about 400 sccm, below or about 300 sccm, below or about 200 sccm, below or about 100 sccm, or less. The flow rate may also be between any of these stated flow rates, or within smaller ranges encompassed by any of these numbers.

15 [0058] Adding further control to the etch process, the etchant precursor may be pulsed in some embodiments, and may be delivered throughout the etch process either continually or in a series of pulses, which may be consistent or varying over time. The pulsed delivery may be characterized by a first period of time during which the etchant precursor is flowed, and a second period of time during which the etchant precursor is paused or halted. In some embodiments, during the second period of time, a purge gas may be flowed during the second period of time. The purge gas may be or include nitrogen, helium, argon, or other noble, inert, or useful purge gases. The time periods for any pulsing operation may be similar or different from one another with either time period being longer. In embodiments either period of time or a continuous flow of precursor may be performed for a time period greater than or about 1 second, and may be greater than or about 2 seconds, greater than or about 3 seconds, greater than or about 4 seconds, greater than or about 5 seconds, greater than or about 6 seconds, greater than or about 7 seconds, greater than or about 8 seconds, greater than

or about 9 seconds, greater than or about 10 seconds, greater than or about 11 seconds, greater than or about 12 seconds, greater than or about 13 seconds, greater than or about 14 seconds, greater than or about 15 seconds, greater than or about 20 seconds, greater than or about 30 seconds, greater than or about 45 seconds, greater than or about 60 seconds, or longer. The times may also be any smaller range encompassed by any of these ranges. For example, in some embodiments, either period of time or a continuous flow of precursor may be performed for a time period less than or about 60 seconds, and may be less than or about 45 seconds, less than or about 30 seconds, less than or about 20 seconds, less than or about 15 seconds, less than or about 10 seconds, less than or about 5 seconds, less than or about 4 seconds, less than or about 3 seconds, less than or about 2 seconds, less than or about 1 second, less than or about 0.5 seconds, less than or about 0.1 seconds, or less. In some embodiments as delivery of the precursor occurs for longer periods of time, etch rate may increase.

[0059] By performing operations according to embodiments of the present technology, titanium nitride or other titanium-containing materials may be etched selectively relative to other materials, including other oxides or nitrides. For example, the present technology may selectively etch titanium oxide relative to exposed regions of metals, dielectrics including silicon-containing materials including silicon oxide, or other materials. Embodiments of the present technology may etch titanium nitride relative to silicon oxide or any of the other materials at a rate of at least about 2:1, and may etch titanium nitride relative to silicon oxide or other materials noted at a selectivity greater than or about 3:1, greater than or about 4:1, greater than or about 5:1, greater than or about 6:1, greater than or about 7:1, greater than or about 8:1, greater than or about 9:1, greater than or about 10:1, greater than or about 15:1, greater than or about 20:1, greater than or about 25:1, greater than or about 30:1, greater than or about 35:1, greater than or about 40:1, greater than or about 45:1, greater than or about 50:1, or more. For example, etching performed according to some embodiments of the present technology may etch titanium nitride while substantially or essentially maintaining silicon oxide or other materials, such as nitrides or oxides of silicon, aluminum, or hafnium, metals such as tungsten or molybdenum, or materials such as polysilicon for example.

[0060] Selectivity may be based in part on precursors used and the ability to dissociate at more controlled temperature ranges. Conventional dry etchants may be incapable of producing etch selectivities of embodiments of the present technology. Similarly, because

wet etchants readily remove silicon oxide, wet etchants may also be incapable of etching selectively at rates comparable to embodiments of the present technology.

5 [0061] The previously discussed methods may allow the removal of titanium-containing materials relative to a number of other exposed materials. By utilizing etchants at operating conditions as previously described, improved etching of titanium nitride may be performed, which may both increase selectivity over conventional techniques, as well as improve etching access in small pitch features.

10 [0062] In the preceding description, for the purposes of explanation, numerous details have been set forth in order to provide an understanding of various embodiments of the present technology. It will be apparent to one skilled in the art, however, that certain embodiments may be practiced without some of these details, or with additional details.

15 [0063] Having disclosed several embodiments, it will be recognized by those of skill in the art that various modifications, alternative constructions, and equivalents may be used without departing from the spirit of the embodiments. Additionally, a number of well-known processes and elements have not been described in order to avoid unnecessarily obscuring the present technology. Accordingly, the above description should not be taken as limiting the scope of the technology. Additionally, methods or processes may be described as sequential or in steps, but it is to be understood that the operations may be performed concurrently, or in different orders than listed.

20 [0064] Where a range of values is provided, it is understood that each intervening value, to the smallest fraction of the unit of the lower limit, unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Any narrower range between any stated values or unstated intervening values in a stated range and any other stated or intervening value in that stated range is encompassed. The upper and lower limits of those smaller ranges may independently be included or excluded in the range, and each range where either, neither, or both limits are included in the smaller ranges is also encompassed within the technology, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included.

30 [0065] As used herein and in the appended claims, the singular forms “a”, “an”, and “the” include plural references unless the context clearly dictates otherwise. Thus, for example, reference to “a precursor” includes a plurality of such precursors, and reference to “the

material” includes reference to one or more materials and equivalents thereof known to those skilled in the art, and so forth.

[0066] Also, the words “comprise(s)”, “comprising”, “contain(s)”, “containing”, “include(s)”, and “including”, when used in this specification and in the following claims, are
5 intended to specify the presence of stated features, integers, components, or operations, but they do not preclude the presence or addition of one or more other features, integers, components, operations, acts, or groups.

CLAIMS:

1. A semiconductor processing method comprising:
flowing an etchant precursor into a processing region of a semiconductor
processing chamber, wherein a substrate is housed within the processing region, and wherein
5 the substrate defines an exposed region of a titanium-containing material;
contacting the substrate with the etchant precursor; and
removing at least a portion of the titanium-containing material.
2. The semiconductor processing method of claim 1, wherein the etchant
precursor comprises a halogen-containing precursor.
- 10 3. The semiconductor processing method of claim 1, wherein the etchant
precursor comprises a chlorine-containing precursor.
4. The semiconductor processing method of claim 3, wherein the
chlorine-containing precursor comprises thionyl chloride (SOCl₂).
5. The semiconductor processing method of claim 1, wherein removing
15 the portion of the titanium-containing material is performed plasma-free.
6. The semiconductor processing method of claim 1, wherein removing
the portion of the titanium-containing material is performed at a temperature less than or
about 450 °C.
7. The semiconductor processing method of claim 1, wherein removing
20 the portion of the titanium-containing material is performed at a pressure greater than or
about 0.1 Torr.
8. The semiconductor processing method of claim 1, wherein removing
the portion of the titanium-containing material is performed at a pressure less than or about
50 Torr.
- 25 9. The semiconductor processing method of claim 1, further comprising a
pre-treatment performed prior to flowing the etchant precursor, wherein the pre-treatment
comprises contacting the substrate with a plasma comprising one or more of oxygen,
hydrogen, or nitrogen.

10. The semiconductor processing method of claim 1, further comprising a post-treatment performed subsequent removing the portion of the titanium-containing material, wherein the post-treatment comprises contacting the substrate with a plasma comprising one or more of oxygen, hydrogen, or nitrogen.
- 5 11. A semiconductor processing method comprising:
forming a plasma of a treatment precursor comprising one or more of oxygen, hydrogen, or nitrogen to produce treatment plasma effluents;
flowing the treatment plasma effluents into a processing region of a semiconductor processing chamber, wherein a substrate is housed within the processing
10 region, and wherein the substrate defines an exposed region of a titanium-containing material;
contacting the substrate with the treatment plasma effluents, wherein the treatment plasma effluents are configured to remove a residue from a surface of the titanium-containing material;
15 flowing an etchant precursor into the processing region of the semiconductor processing chamber;
contacting the substrate with the etchant precursor; and
removing at least a portion of the titanium-containing material.
12. The semiconductor processing method of claim 11, further comprising
20 halting formation of the plasma of the treatment precursor prior to flowing the etchant precursor.
13. The semiconductor processing method of claim 11, wherein the etchant precursor comprises thionyl chloride (SOCl₂).
14. The semiconductor processing method of claim 11, wherein removing
25 the portion of the titanium-containing material is performed at a temperature less than or about 400 °C.
15. The semiconductor processing method of claim 11, wherein removing the portion of the titanium-containing material is performed at a pressure less than or about 30 Torr.

16. The semiconductor processing method of claim 11, further comprising a post-treatment performed subsequent removing the portion of the titanium-containing material, wherein the post-treatment comprises contacting the substrate with a plasma comprising one or more of oxygen, hydrogen, or nitrogen.

5 17. A semiconductor processing method comprising:
flowing an etchant precursor into a processing region of a semiconductor processing chamber, wherein a substrate is housed within the processing region, and wherein the substrate defines an exposed region of a titanium-containing material;
contacting the substrate with the etchant precursor;
10 removing at least a portion of the titanium-containing material;
forming a plasma of a treatment precursor comprising one or more of oxygen, hydrogen, or nitrogen to produce treatment plasma effluents; and
contacting the substrate with the treatment plasma effluents.

15 18. The semiconductor processing method of claim 17, wherein the etchant precursor comprises chlorine.

19. The semiconductor processing method of claim 18, wherein the treatment plasma effluents are configured to remove residual chlorine from one or more of the substrate or the semiconductor processing chamber.

20 20. The semiconductor processing method of claim 17, wherein removing the portion of the titanium-containing material is performed at a temperature less than or about 380 °C and at a pressure less than or about 30 Torr.

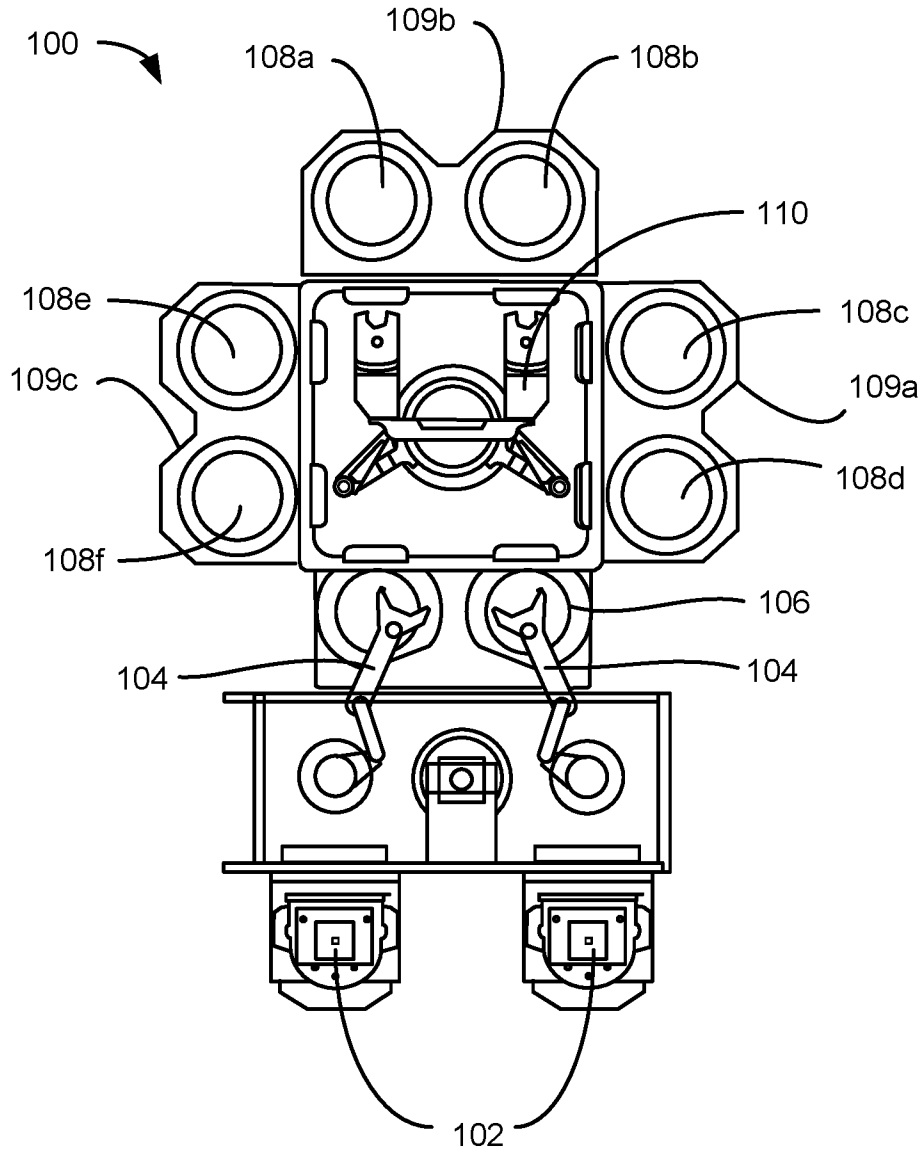


FIG. 1

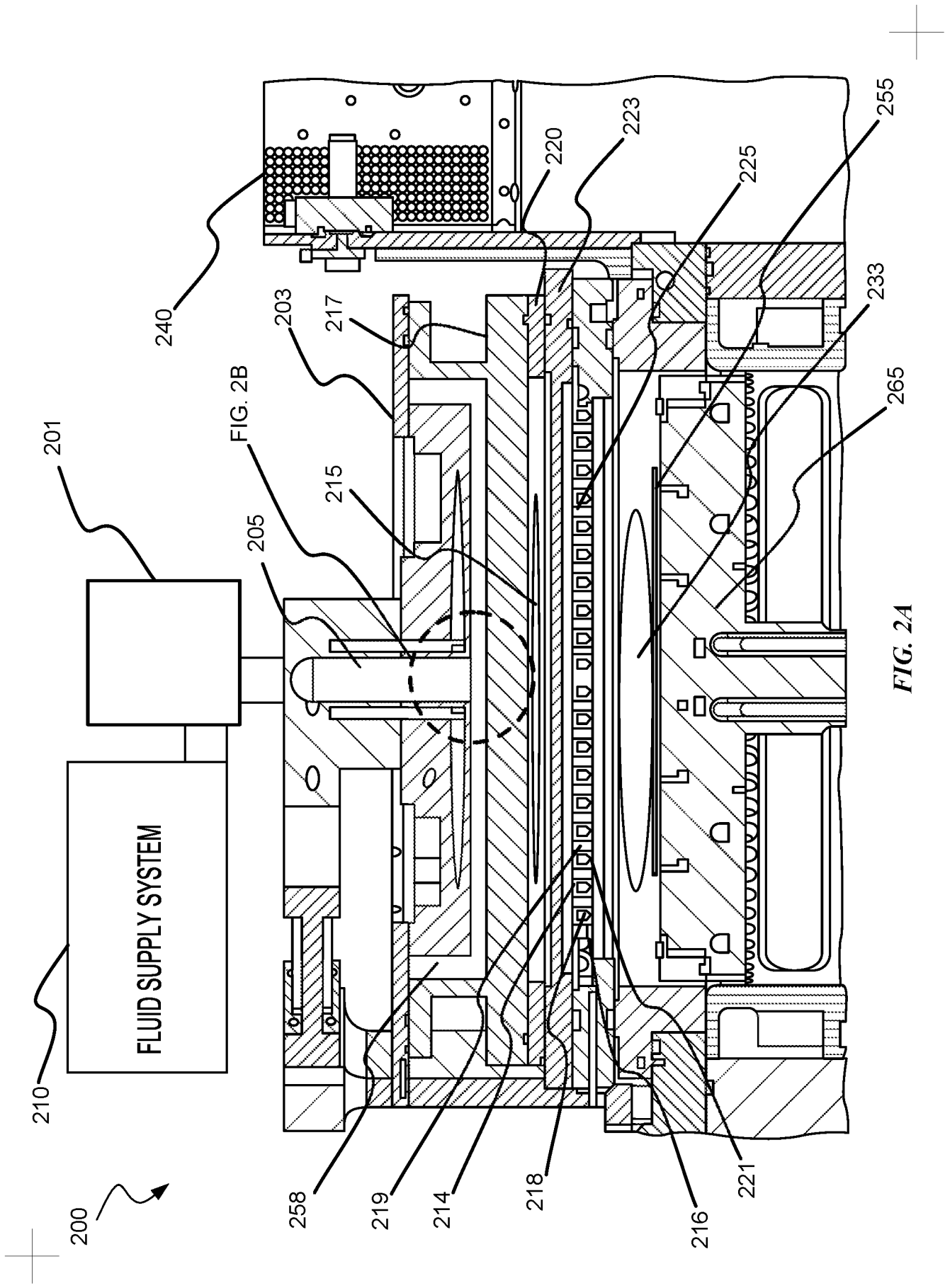


FIG. 2A

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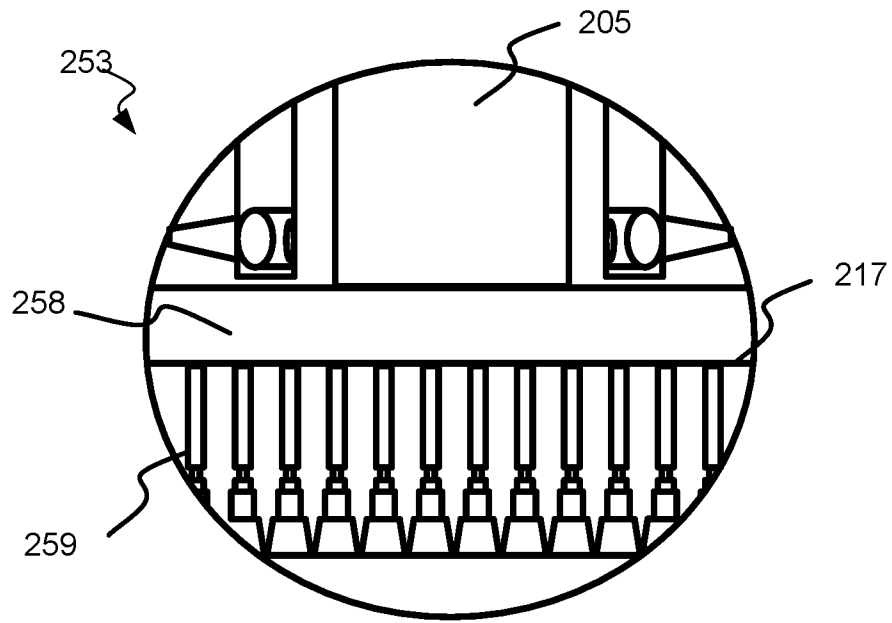


FIG. 2B

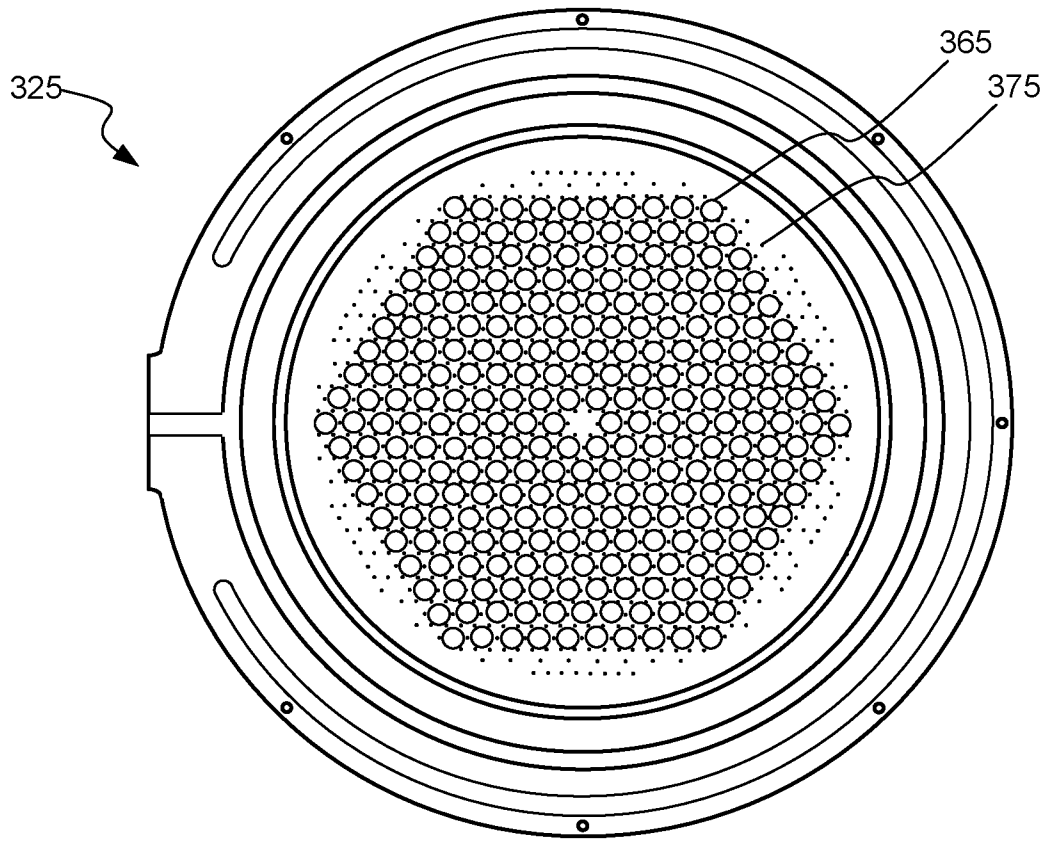


FIG. 3

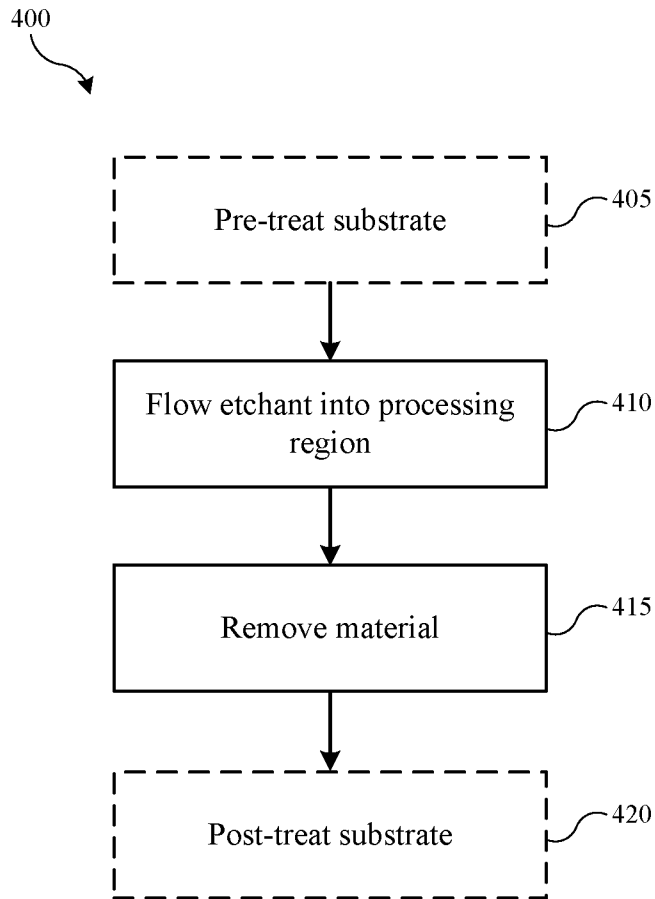


FIG. 4

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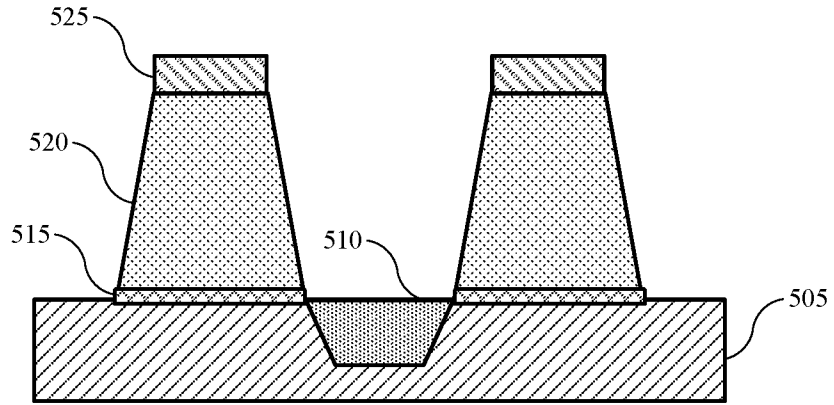


FIG. 5A

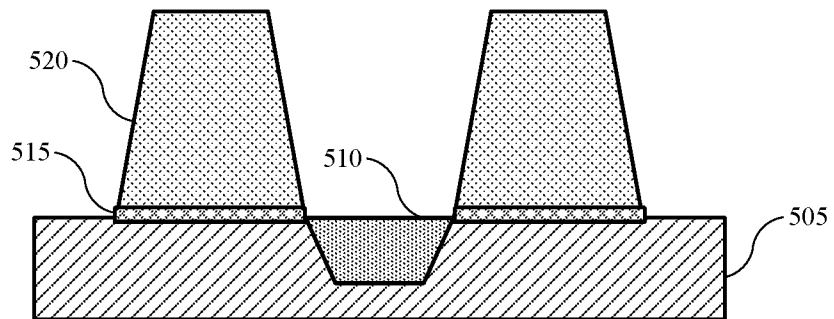


FIG. 5B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2023/086423

A. CLASSIFICATION OF SUBJECT MATTER		
H01L 21/311(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 21/311(2006.01); C23F 1/12(2006.01); H01L 21/02(2006.01); H01L 21/3065(2006.01); H01L 21/3213(2006.01); H01L 21/67(2006.01)		
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: titanium-containing material, etchant precursor, thionyl chloride (SOCl ₂), treatment precursor		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	VARUN SHARMA et al. Thermal gas-phase etching of titanium nitride (TiN) by thionyl chloride (SOCl ₂). Applied Surface Science. 28 February 2021, Vol. 540, Part 1, pages 1-8, https://doi.org/10.1016/j.apsusc.2020.148309 [retrieved on 2024-03-27]. Retrieved from <sciencedirect, https://www.sciencedirect.com/science/article/pii/S016943322033066X >. See abstract, pages 1-7 and figure 9.	1-8 9-20
Y	US 2022-0351979 A1 (APPLIED MATERIALS, INC.) 03 November 2022 (2022-11-03) See claims 11, 16-17 and figure 4.	9-20
A	US 2020-0027746 A1 (ASM IP HOLDING B.V.) 23 January 2020 (2020-01-23) See paragraphs [0048]-[0049], claims 1, 23-25 and figures 7-8C.	1-20
A	US 2015-0357205 A1 (APPLIED MATERIALS, INC.) 10 December 2015 (2015-12-10) See paragraphs [0019]-[0031] and figure 1.	1-20
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> 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 "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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 25 April 2024		Date of mailing of the international search report 26 April 2024
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon 35208, Republic of Korea Facsimile No. +82-42-481-8578		Authorized officer LEE, Kang Ha Telephone No. +82-42-481-5003

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2023/086423

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2022-055876 A1 (APPLIED MATERIALS, INC.) 17 March 2022 (2022-03-17) See paragraphs [0043]-[0065] and figures 4-5B.	1-20

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US2023/086423

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	2022-0351979	A1	03 November 2022	CN	115485819	A	16 December 2022
				JP	2023-531127	A	21 July 2023
				KR	10-2022-0154798	A	22 November 2022
				TW	202226366	A	01 July 2022
				TW	I785783	B	01 December 2022
				US	11769671	B2	26 September 2023
				US	2022-0084832	A1	17 March 2022
				WO	2022-055900	A1	17 March 2022

US	2020-0027746	A1	23 January 2020	CN	110739204	A	31 January 2020
				CN	110739204	B	29 August 2023
				KR	10-2020-0010099	A	30 January 2020
				KR	10-2550244	B1	30 June 2023
				TW	202008458	A	16 February 2020
				TW	I788584	B	01 January 2023
				US	10720337	B2	21 July 2020

US	2015-0357205	A1	10 December 2015	TW	201448041	A	16 December 2014
				TW	I618144	B	11 March 2018
				US	2014-0256131	A1	11 September 2014
				US	9040422	B2	26 May 2015
				US	9607856	B2	28 March 2017
				WO	2014-137658	A1	12 September 2014

WO	2022-055876	A1	17 March 2022	CN	115485821	A	16 December 2022
				JP	2023-529534	A	11 July 2023
				KR	10-2022-0154787	A	22 November 2022
				TW	202217959	A	01 May 2022
				TW	I781757	B	21 October 2022
				US	11062921	B1	13 July 2021
