(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 June 2014 (26.06.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/099260 A1

(51) International Patent Classification:
H01L 21/3065 (2006.01)

(21) International Application Number:
PCT/US2013/071417

(22) International Filing Date:
22 November 2013 (22.11.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/740,587 21 December 2012 (21.12.2012) US
13/791,125 8 March 2013 (08.03.2013) US

(71) Applicant: **APPLIED MATERIALS, INC.** [US/US]; 3050 Bowers Avenue, Santa Clara, California 95054 (US).

(72) Inventors: **LIU, Jie**; 888 Tamarack Lane #68, Sunnyvale, California 94086 (US). **ZHANG, Jingchun**; 1515 Four Oaks Circle, San Jose, California 95131 (US). **WANG, Anchuan**; 6556 Bollinger Road, San Jose, California 95129 (US). **INGLE, Nitin K.**; 1435 Graywood Drive, San Jose, California 95129 (US). **PARK, Seung**; 6678 Dorene Place, San Jose, California 95120 (US). **CHEN, Zhijun**; 1515 Four Oaks Circle, San Jose, California 95131 (US). **HSU, Ching-Mei**; 25 Olmsted Road #105, Stanford, California 94305 (US).

(74) Agents: **BERNARD, Eugene J.** et al.; Two Embarcadero Center, Eighth Floor, San Francisco, California 94111 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,

[Continued on next page]

(54) Title: SELECTIVE TITANIUM NITRIDE ETCHING

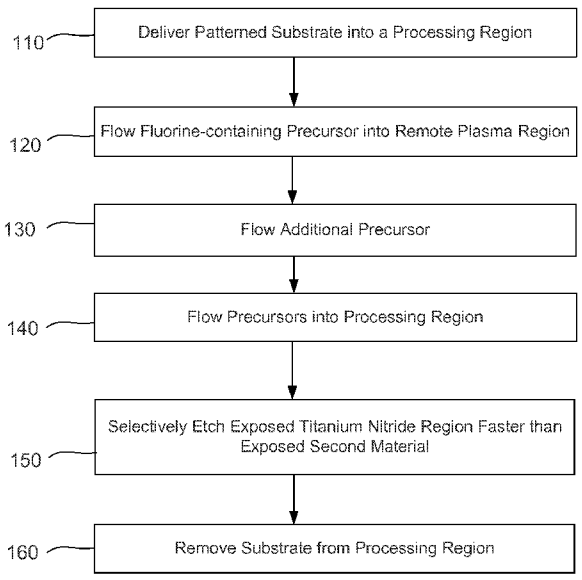

FIG. 1

(57) Abstract: Methods of etching exposed titanium nitride with respect to other materials on patterned heterogeneous structures are described, and may include a remote plasma etch formed from a fluorine-containing precursor. Precursor combinations including plasma effluents from the remote plasma are flowed into a substrate processing region to etch the patterned structures with high titanium nitride selectivity under a variety of operating conditions. The methods may be used to remove titanium nitride at faster rates than a variety of metal, nitride, and oxide compounds.

WO 2014/099260 A1

TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

SELECTIVE TITANIUM NITRIDE ETCHING

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Patent Application No. 13/791,125, filed March 8, 2013, which claims the benefit of U.S. Provisional Application No. 61/740,587, filed December 21, 2012, both entitled "Selective Titanium Nitride Etching." The entire disclosures of both are incorporated herein by reference for all purposes.

TECHNICAL FIELD

[0002] The present technology relates to semiconductor processes and equipment. More specifically, the present technology relates to selective etching of materials on semiconductor substrates.

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, 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.

[0004] A wet HF etch preferentially removes silicon oxide over other dielectrics and semiconductors. However, wet processes are unable to penetrate some constrained trenches and sometimes deform the remaining material. Dry etches produced in local plasmas formed within the substrate processing region can penetrate more constrained trenches and exhibit less deformation of delicate remaining structures. However, local plasmas can damage the substrate through the production of electric arcs as they discharge.

[0005] Thus, there is a need for improved methods and systems for selectively etching materials and structures on semiconductor substrates. These and other needs are addressed by the present technology.

SUMMARY

[0006] Methods of etching exposed titanium nitride with respect to other materials on patterned heterogeneous structures are described, and may include a remote plasma etch formed from a fluorine-containing precursor. Precursor combinations including plasma effluents from the remote plasma are flowed into a substrate processing region to etch the patterned structures with high titanium nitride selectivity under a variety of operating conditions. The methods may be used to remove titanium nitride at faster rates than a variety of metal, nitride, and oxide compounds.

[0007] The at least one additional precursor may include one or more precursors selected from the group consisting of helium, argon, and molecular hydrogen (H_2). The fluorine-containing precursor may include one or more precursors selected from the group consisting of atomic fluorine, diatomic fluorine, nitrogen trifluoride, carbon tetrafluoride, hydrogen fluoride, and xenon difluoride. The methods may be performed such that the processing region in which the semiconductor substrate resides is plasma-free during the etching process.

[0008] The methods may include having the additional precursor consist of one or both of helium and argon. The precursor combination delivered into the processing region may be substantially devoid of hydrogen. The exposed second material may include silicon oxide and/or silicon nitride, and the selectivity of the etching operation (exposed titanium nitride region: exposed silicon oxide region) may be greater than or about 5:1, and in disclosed embodiments may be greater than or about 10:1. The substrate temperature may be maintained below or about 50°C during the etch process, and in disclosed embodiments may be maintained at or below about 10°C during the etch process.

[0009] The methods can include that the at least one additional precursor comprises hydrogen, and may additionally include one or more carrier gases including helium or argon. The exposed second material may include tungsten, and the selectivity of the etching operation (exposed titanium nitride region: exposed tungsten region) may be greater than or about 50:1, and in disclosed embodiments may be greater than or about 100:1. The patterned substrate may further include additional exposed regions or materials, and in disclosed embodiments the substrate further comprises an exposed silicon nitride region. The selectivity of the etching operation (exposed titanium nitride region: exposed silicon nitride region) may be greater than or about 10:1. The patterned substrate may further include an exposed silicon oxide region, and the selectivity of the etching operation (exposed titanium

nitride region: exposed silicon oxide region) may be greater than or about 5:1. The patterned substrate may further include an exposed tantalum nitride region, and the selectivity of the etching operation (exposed titanium nitride region: exposed tantalum nitride region) may be greater than or about 10:1. The substrate temperature may be maintained at or above about 50°C during the etch process, and in disclosed embodiments may be maintained at or above about 200°C during the etch process. The method may include flowing the hydrogen into the substrate processing region without its being excited by any remote plasma prior to entering the processing region. The plasma utilized in the methods in the remote plasma region may be a capacitively-coupled plasma.

[0010] Such technology may provide numerous benefits over conventional techniques. For example, process throughput may be increased based on the improved selectivity. Additionally, less protection of exposed materials may be required with the improved selective etching with respect to multiple materials. 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

[0011] 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.

[0012] FIG. 1 shows a flow chart of a titanium nitride selective etch process according to disclosed embodiments.

[0013] FIG. 2A shows a schematic cross-sectional view of a substrate processing chamber according to the disclosed technology.

[0014] FIG. 2B shows a schematic cross-sectional view of a portion of a substrate processing chamber according to the disclosed technology.

[0015] FIG. 2C shows a bottom plan view of a showerhead according to the disclosed technology.

[0016] FIG. 3 shows a top plan view of an exemplary substrate processing system according to the disclosed technology.

[0017] In the appended figures, similar components and/or features may have the same numerical 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 and/or features. If only the first numerical reference label is used in the specification, the description is applicable to any one of the similar components and/or features having the same first numerical reference label irrespective of the letter suffix.

DETAILED DESCRIPTION

[0018] The present technology includes improved processes and chemistry profiles for removing titanium nitride on patterned semiconductor substrates with respect to other materials. While conventional processes may remove titanium nitride at slower or equal rates than other materials, the presently described technology allows for improved rates of titanium nitride removal. In so doing, substrate throughput may be improved in a variety of ways. For example, the rate at which compositions are etched may be increased. Additionally, less material may be required as initially deposited or located in, on, or as part of the patterned substrate with respect to the titanium nitride to be removed. If additional material located on the substrate with titanium nitride is to be maintained, but etches at the same rate as titanium nitride, for example, additional material would generally need to be initially deposited or located beyond what is to be maintained that is proportional to the etch rate with respect to the amount of titanium nitride to be removed. Accordingly, process times may increase. However, if the selectivity to titanium nitride can be increased, less of the second material will be removed, and less additional material would need to have been initially deposited or located on the substrate. Accordingly, process times can be reduced.

[0019] Methods of etching exposed titanium nitride with respect to other materials on patterned heterogeneous structures are described, and may include a remote plasma etch formed from a fluorine-containing precursor. Precursor combinations including plasma effluents from the remote plasma are flowed into a substrate processing region to etch the patterned structures with high titanium nitride selectivity under a variety of operating conditions. The methods may be used to remove titanium nitride at faster rates than a variety of metal, nitride, and oxide compounds.

[0020] Selective dry etch processes may be used to remove one material with respect to another material on patterned semiconductor substrates. However, depending on the exposed materials, process gases and process conditions may not provide adequate etch rates of one material without damaging exposed features of another material. The presence of certain precursor chemicals may directly affect the etch rates and selectivities of a variety of materials. The inventors have advantageously determined that the selectivity of titanium nitride over a variety of materials can be enhanced by exciting a fluorine-containing

precursor in a remote plasma, and limiting the additional precursors that are used in conjunction with the fluorine-containing precursor based on the material that is to be maintained.

[0021] In order to better understand and appreciate the invention, reference is now made to **FIG. 1**, which shows a flow chart of a titanium nitride selective etch process according to disclosed embodiments. Prior to the first operation, the substrate may be patterned leaving exposed regions of titanium nitride and exposed regions of a second material that may include one or more of tantalum nitride, tungsten, silicon nitride, silicon oxide, etc. Various front end processing may have been performed including the formation of gates, vias, and other structures. The patterned substrate may then be delivered to a substrate processing region at operation 110. In disclosed embodiments, the substrate may already be located in the processing region if a previous operation was performed in the same chamber in which the etch process is to occur. Nitrogen trifluoride (NF_3) may be flowed into a plasma region that is separate from, but fluidly coupled with, the processing region at operation 120. Other sources of fluorine may be used in conjunction with or as replacements for the nitrogen trifluoride. In general, a fluorine-containing precursor is flowed into the plasma region and the fluorine-containing precursor comprises at least one precursor selected from the group consisting of atomic fluorine, diatomic fluorine, nitrogen trifluoride, carbon tetrafluoride, hydrogen fluoride, and xenon difluoride.

[0022] The separate plasma region may be referred to as a remote plasma region herein and may be within a distinct module from the processing chamber, or as a compartment within the processing chamber. A plasma may be formed within the remote plasma region thereby generating plasma effluents from the fluorine-containing precursor. At operation 130, one or more additional precursors may be flowed that are either additionally flowed into the plasma region, or directed to bypass the plasma region to flow unexcited into the processing region. The additional precursors may include carrier gases, such as for example helium or argon, and may additionally include a hydrogen source, including molecular hydrogen (H_2) in disclosed embodiments. The combination of precursors including the plasma effluents is directed to flow into the processing region at operation 140. As previously stated, the precursors may have been pre-mixed in the remote plasma region, or the precursors may be fluidly isolated from one another until they are separately delivered into the processing region.

[0023] The patterned substrate may be selectively etched with the precursor combination including plasma effluents at operation 150, such that the exposed titanium nitride region is removed at a higher rate than the exposed second material on the patterned substrate. The reactive chemical species may be removed from the substrate processing region, and then the substrate may be removed from the processing region at operation 160. Using the gas phase dry etch processes described herein, the inventors have established that etch selectivities of over 5:1 with regard to the titanium nitride etch rate as compared to the etch rate of other materials are possible. Achievable selectivities using the methods described herein are additionally capable of etching titanium nitride at rates faster than a second material that typically etches faster than titanium nitride, such as tungsten, as will be described in greater detail below. The titanium nitride etch rate may exceed the exposed second material etch rate by a multiplicative factor of up to or about 5 or more, about 10 or more, about 15 or more, about 20 or more, about 50 or more, about 75 or more, about 100 or more, etc. or greater in embodiments of the technology.

[0024] Depending on the additional precursor or precursors used in the exemplary processes, the rates of titanium nitride etching with respect to the exposed second material may by affected. For example, in disclosed embodiments the additional precursor may be one or more precursors selected from the group consisting of helium, argon, and molecular hydrogen (H_2). In other embodiments, other hydrogen-containing precursors may be used including ammonia, for example. Depending on what additional materials are exposed, these gases may be used in combination to adjust etch characteristics.

[0025] When the exposed materials include titanium nitride and certain other materials including silicon nitride or silicon oxide, the one or more additional precursors may include only carrier gases, such as helium and/or argon. In one embodiment, the additional precursors consist exclusively of helium and/or argon. Put another way, the precursor combination including plasma effluents delivered to the processing region may be completely or substantially devoid of any hydrogen or hydrogen-containing precursors. The additional precursors may be flowed with the fluorine-containing precursor into the plasma region to produce plasma effluents. When these precursor combinations including plasma effluents are delivered into the processing region, the selectivity of the etching operation of an exposed titanium nitride region to an exposed silicon oxide region may be up to, greater than, or about 2:1. The etching selectivity may also be up to, greater than, or about 5:1, 10:1, 15:1, 17:1, 20:1, etc. or more. In terms of material etched, in one minute of processing time about 100

Angstrom or more of titanium nitride may be etched while less than or about 20 Angstrom of silicon oxide may be removed. In other embodiments less than or about 15 Angstrom, 12, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, or 0 Angstrom of silicon oxide may be removed, the last case indicating that the silicon oxide is maintained during the etching of titanium nitride.

[0026] During the etching process, the substrate may be maintained at or below about 400°C, and may be maintained at or below about 300°C, 200°C, 100°C, 80°C, 75°C, 50°C, 25°C, 10°C, 0°C, or less. The processing chamber may be maintained at or below about 100 Torr during the processes, and may be maintained at or below about 50 Torr, 25 Torr, 15 Torr, 5 Torr, 1 Torr, 0.1 Torr, etc., or between about 0.1 mTorr and about 10 Torr. By maintaining the substrate temperature at lower temperatures, such as about 10°C or less, and maintaining the process chamber at a pressure below about 10 Torr, the inventors have determined that the amount of oxide removal can be further limited during the removal of titanium nitride.

[0027] Certain materials may typically etch at a faster rate than titanium nitride, including other metals such as tungsten. For example, if the above-described etch process is performed, any exposed tungsten may etch faster than the exposed titanium nitride. If a region of titanium nitride is to be removed, but an exposed region of tungsten is to be maintained, these etching processes may be difficult to control and may damage the tungsten features. To address the selectivity of tungsten to titanium nitride, the inventors have determined that by including hydrogen as one of the additional precursors, the rate at which tungsten etches may be slowed significantly such that the selectivity to titanium nitride reverses, and in disclosed embodiments the rate at which tungsten is etched can be reduced to about zero.

[0028] In embodiments, the precursors may include molecular hydrogen with the fluorine-containing radical, or alternatively a hydrogen-containing precursor. The hydrogen may be included with the fluorine-containing radical and carrier gas or gases discussed above that are delivered into the remote plasma region where the plasma effluents are developed. Alternatively, the hydrogen may be delivered separately from the fluorine-containing precursor such that it bypasses the remote plasma region. For example, when a dual-channel showerhead such as that discussed below is utilized, the hydrogen may be delivered into the volume defined by the showerhead plates. Accordingly, the hydrogen may be delivered to the processing region without being excited by any remote plasma, and it may not come into contact with the plasma effluents until it enters the processing region.

[0029] When these precursor combinations including hydrogen and containing plasma effluents are delivered into the processing region, the selectivity of the etching operation of an exposed titanium nitride region to an exposed tungsten region may be up to, greater than, or about 10:1. The etching selectivity may also be up to, greater than, or about 20:1, 50:1, 100:1, 500:1, 1000:1, etc. or more, up to the point at which the process is fully selective to titanium nitride and no tungsten is removed. In terms of material etched, in one minute of processing time up to or about 3 Angstrom or more, 6 Angstrom or more, or 10 Angstrom or more of titanium nitride may be etched while less than or about 1 Angstrom of tungsten may be removed. In other embodiments less than or about 0.5 Angstrom, 0.1, 0.05, 0.01, 0.005, 0.001, 0.0001, or 0 Angstrom of tungsten may be removed, that last case of which indicates that the exposed tungsten region is completely maintained.

[0030] This process may additionally remove titanium nitride with respect to other materials as well. For example, when titanium nitride is used in gate applications as an interface layer, or as a hard mask for patterning low-k stacks, additionally exposed materials may include one or more materials such as metals including tungsten, and materials including silicon nitride, silicon oxide, and tantalum nitride. In many applications, these layers are to be maintained as much as possible during the titanium nitride removal. Utilizing the processes encompassed by this technology, titanium nitride may be etched with respect to all of these materials, and the selectivity to titanium nitride with respect to each material may be at least or about 5:1. In disclosed embodiments, titanium nitride may be etched with respect to silicon oxide, and the selectivity of the etching operation may be greater than or about 2:1, or greater than or about 5:1. Titanium nitride may be etched with respect to silicon nitride, and the selectivity of the etching operation may be greater than or about 5:1, or greater than or about 10:1. Titanium nitride may also be etched with respect to tantalum nitride, and the selectivity of the etching operation may be greater than or about 5:1, or greater than or about 10:1.

[0031] By utilizing the hydrogen precursor, the plasma density with respect to the fluorine-containing precursor may be reduced, which may reduce the etch rate of the materials. This in turn may reduce the substrate throughput for these processes. Etch rate may often be increased by increasing the substrate temperature, but this may also increase the rate at which materials to be maintained are etched. However, the inventors have determined that the process chemistries utilizing hydrogen described in this technology may act synergistically when the temperatures are raised, such that the rate at which titanium nitride is removed may

increase faster than the etch rate of other materials to be maintained. Accordingly, the processes may allow the substrate to be maintained at or above about 0°C or between about 0°C and about 400°C, but may also be maintained at or above about 10°C, 25°C, 50°C, 75°C, 80°C, 100°C, 200°C, 300°C, 400°C, or more. The processing chamber may be maintained at or below about 100 Torr, and may be maintained at or below about 50 Torr, 25 Torr, 15 Torr, 5 Torr, 1 Torr, 0.1 Torr, etc., or between about 0.1 mTorr and about 10 Torr.

[0032] The described processes may also be used in conjunction with one another for a variety of operations in which tungsten and titanium nitride may be both located and exposed on patterned substrates. For example, in gate structures including NAND or 3D NAND devices, both tungsten and titanium nitride may be located on the substrate as gate metal and barrier material respectively. During processing, the exposed gate metal may need to be recessed while maintaining a portion of titanium nitride, or otherwise etching the titanium nitride at a slower rate. Accordingly, the described chemistry devoid of hydrogen may be utilized at a lower substrate temperature, which may remove tungsten at a rate faster than titanium nitride.

[0033] The recessing operation may expose regions or additional regions of titanium nitride, and may additionally expose regions of tantalum nitride, silicon nitride, and silicon oxide, for example. Once the tungsten has been recessed but otherwise maintained, further etching of the titanium nitride and or other exposed materials may be needed without further etching, or with minimal further etching, of the remaining tungsten. Accordingly, the described process synergistically utilizing hydrogen as a precursor with increased temperature may be performed. For example, the substrate temperature may be increased while hydrogen is incorporated with the precursor fluids. Consequently, further etching of the tungsten may be minimized while exposed titanium nitride may be removed. In this way, by combining these etching processes, etching of titanium nitride with respect to tungsten may be modified tuned in situ. By utilizing the combined processes, tungsten may be etched faster than titanium nitride, titanium nitride may be etched faster than tungsten, or the two materials may be etched at substantially similar or directly equivalent rates by adjusting the hydrogen concentration and/or certain of the processing conditions such as temperature. As would be understood, additional modifications to chamber pressure and plasma power may be used to further tune the etching processes as may be required. Advantageously, tuning these processes may be performed without the need to break vacuum conditions or move the substrate to an additional chamber. This may reduce overall processing times and save costs

over conventional techniques. Additional examples of etch process parameters, chemistries, and components are disclosed in the course of describing an exemplary processing chamber and system below.

Exemplary Processing System

[0034] **FIG. 2A** shows a cross-sectional view of an exemplary process chamber section 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. Accordingly, in disclosed embodiments the precursor gases may be delivered to the processing chamber in an unexcited state. In another example, the first channel provided through the RPS may be used for the process gas and the second channel bypassing the RPS may be used for a treatment gas in disclosed embodiments. The process gas may be excited within the RPS 201 prior to entering the first plasma region 215. Accordingly, the fluorine-containing precursor as discussed above, for example, may pass through RPS 201 or bypass the RPS unit in disclosed embodiments. Various other examples encompassed by this arrangement will be similarly understood.

[0035] A cooling plate 203, faceplate 217, ion suppressor 223, showerhead 225, and a substrate support 265, having a substrate 255 disposed thereon, are shown and may each be included according to disclosed embodiments. The pedestal 265 may have a heat exchange channel through which a heat exchange fluid flows to control the temperature of the substrate. This configuration may allow the substrate 255 temperature to be cooled or heated to maintain relatively low temperatures, such as between about -20°C to about 200°C, or therebetween. The heat exchange fluid may comprise ethylene glycol and/or water. The wafer support platter of the pedestal 265, which may comprise 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. The heating element may be formed within the pedestal as one or more loops, and an outer portion of the heater element may run adjacent to a perimeter of the support platter, while an inner portion runs on the path of a concentric circle

having a smaller radius. The wiring to the heater element may pass through the stem of the pedestal 265, which may be further configured to rotate.

[0036] 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.

[0037] 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 structural features may include the selection of dimensions and cross-sectional geometries of the apertures in faceplate 217 to deactivate back-streaming plasma. The operational features may include maintaining a pressure difference between the gas supply region 258 and first plasma region 215 that maintains a unidirectional flow of plasma through the showerhead 225. 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.

[0038] 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 plasma excitation 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 disclosed embodiments, the ion suppressor 223 may 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 provide increased 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, e.g., TiNx:SiOx etch ratios, TiN:W etch ratios, etc. In alternative embodiments in which deposition is performed, it can also shift the balance of conformal-to-flowable style depositions for dielectric materials.

[0039] The plurality of holes 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 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.

[0040] The ion suppression element 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 is not always the desired goal. In many instances, ionic species are required to reach the substrate in order to perform the etch and/or deposition process. In these instances, the ion suppressor may help to control the concentration of ionic species in the reaction region at a level that assists the process.

[0041] Showerhead 225 in combination with ion suppressor 223 may allow a plasma present in chamber 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 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 which oxide species etch may increase. Accordingly, if the exposed second material is oxide, this material may be further protected by maintaining the plasma remotely from the substrate.

[0042] 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 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 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.

[0043] A plasma may be ignited either in chamber plasma region 215 above showerhead 225 or substrate processing region 233 below showerhead 225. A plasma may be present in chamber plasma region 215 to produce the radical-fluorine precursors from an inflow of the fluorine-containing 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.

[0044] Plasma power can be of a variety of frequencies or a combination of multiple frequencies. In the exemplary processing system the plasma may be provided by RF power delivered to faceplate 217 relative to ion suppressor 223 and/or showerhead 225. The RF power may be between about 10 watts and about 2000 watts, between about 100 watts and about 2000 watts, between about 200 watts and about 1500 watts, or between about 200 watts and about 1000 watts in different embodiments. The RF frequency applied in the exemplary processing system may be low RF frequencies less than about 200 kHz, high RF frequencies between about 10 MHz and about 15 MHz, or microwave frequencies greater than or about

1 GHz in different embodiments. The plasma power may be capacitively-coupled (CCP) or inductively-coupled (ICP) into the remote plasma region.

[0045] The top plasma region 215 may be left at low or no power when a bottom plasma in the substrate processing region 233 is turned on to, for example, cure a film or clean the interior surfaces bordering substrate processing region 233. A plasma in substrate processing region 233 may be ignited by applying an AC voltage between showerhead 255 and the pedestal 265 or bottom of the chamber. A cleaning gas may be introduced into substrate processing region 233 while the plasma is present.

[0046] A fluid, such as a precursor, for example a fluorine-containing precursor, may be flowed into the processing region 233 by embodiments of the showerhead described herein. Excited species derived from the process gas in the plasma region 215 may travel through apertures in the ion suppressor 223, and/or showerhead 225 and react with an additional precursor flowing into the processing region 233 from a separate portion of the showerhead. Alternatively, if all precursor species are being excited in plasma region 215, no additional precursors may be flowed through the separate portion of the showerhead. Little or no plasma may be present in the processing region 233. Excited derivatives of the precursors may combine in the region above the substrate and, on occasion, on the substrate to etch structures or remove species on the substrate in disclosed applications.

[0047] Exciting the fluids in the first plasma region 215 directly, or exciting the fluids in the RPS units 201, may provide several benefits. The concentration of the excited species derived from the fluids may be increased within the processing region 233 due to the plasma in the first plasma region 215. This increase may result from the location of the plasma in the first plasma region 215. The processing region 233 may be located closer to the first plasma region 215 than the remote plasma system (RPS) 201, leaving less time for the excited species to leave excited states through collisions with other gas molecules, walls of the chamber, and surfaces of the showerhead.

[0048] The uniformity of the concentration of the excited species derived from the process gas may also be increased within the processing region 233. This may result from the shape of the first plasma region 215, which may be more similar to the shape of the processing region 233. Excited species created in the RPS 201 may travel greater distances in order to pass through apertures near the edges of the showerhead 225 relative to species that pass through apertures near the center of the showerhead 225. The greater distance may result in a reduced excitation of the excited species and, for example, may result in a slower growth rate

near the edge of a substrate. Exciting the fluids in the first plasma region 215 may mitigate this variation for the fluid flowed through RPS 201, or alternatively bypassed around the RPS unit.

[0049] The processing gases may be excited in first plasma region 215 and may be passed through the showerhead 225 to the processing region 233 in the excited state. While a plasma may be generated in the processing region 233, a plasma may alternatively not be generated in the processing region. In one example, the only excitation of the processing gas or precursors may be from exciting the processing gases in plasma region 215 to react with one another in the processing region 233. As previously discussed, this may be to protect the structures patterned on the substrate 255.

[0050] In addition to the fluid precursors, there may be other gases introduced at varied times for varied purposes, including carrier gases to aid delivery. A treatment gas may be introduced to remove unwanted species from the chamber walls, the substrate, the deposited film and/or the film during deposition. A treatment gas may be excited in a plasma and then used to reduce or remove residual content inside the chamber. In other disclosed embodiments the treatment gas may be used without a plasma. When the treatment gas includes water vapor, the delivery may be achieved using a mass flow meter (MFM), an injection valve, or by commercially available water vapor generators. The treatment gas may be introduced to the processing region 233, either through the RPS unit or bypassing the RPS unit, and may further be excited in the first plasma region.

[0051] **FIG. 2B** shows a detailed view 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 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.

[0052] 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 additionally detailed in the embodiments described in FIG. 2A as well as FIG. 2C herein. 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.

[0053] The showerhead 225 may comprise an upper plate 214 and a lower plate 216. The 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 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 gas distribution assembly 225. Although the exemplary system of FIG. 2 includes a dual-channel showerhead, it is understood that alternative distribution assemblies may be utilized that maintain first and second precursors fluidly isolated prior to the processing region 233. For example, a perforated plate and tubes underneath the plate may be utilized, although other configurations may operate with reduced efficiency or not provide as uniform processing as the dual-channel showerhead as described.

[0054] In the embodiment shown, showerhead 225 may distribute via first fluid channels 219 process gases which contain plasma effluents upon excitation by a plasma in chamber plasma region 215. In embodiments, the process gas introduced into the RPS 201 and/or chamber plasma region 215 may contain fluorine, e.g., CF_4, NF_3 or XeF_2. The process gas may also include a carrier gas such as helium, argon, nitrogen (N_2), etc. Plasma effluents may include ionized or neutral derivatives of the process gas and may also be referred to herein as a radical-fluorine precursor referring to the atomic constituent of the process gas introduced.

[0055] **FIG. 2C** is a bottom view of a showerhead 225 for use with a processing chamber according to disclosed embodiments. Showerhead 225 corresponds with the showerhead shown in FIG. 2A. Through-holes 231, which show a view of first fluid channels 219, may have a plurality of shapes and configurations in order to control and affect the flow of precursors through the showerhead 225. Small holes 227, 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 231, which may help to provide more even mixing of the precursors as they exit the showerhead than other configurations.

[0056] An additional dual channel showerhead, as well as this processing system and chamber, are more fully described in patent application Ser. No. 13/251,714 filed on Oct. 3, 2011, which is hereby incorporated by reference for all purposes to the extent not inconsistent with the claimed features and description herein.

[0057] The chamber plasma region 215 or a region in an RPS may be referred to as a remote plasma region. In embodiments, the radical precursor, e.g., a radical-fluorine precursor, is created in the remote plasma region and travels into the substrate processing region where it may or may not combine with additional precursors. In embodiments, the additional precursors are excited only by the radical-fluorine precursor. Plasma power may essentially be applied only to the remote plasma region in embodiments to ensure that the radical-fluorine precursor provides the dominant excitation. Nitrogen trifluoride or another fluorine-containing precursor may be flowed into chamber plasma region 215 at rates between about 25 sccm and about 500 sccm, between about 50 sccm and about 150 sccm, or between about 75 sccm and about 125 sccm in different embodiments.

[0058] Combined flow rates of precursors into the chamber may account for 0.05% to about 20% by volume of the overall gas mixture; the remainder being carrier gases. The fluorine-containing precursor may be flowed into the remote plasma region, but the plasma effluents may have the same volumetric flow ratio in embodiments. In the case of the fluorine-containing precursor, a purge or carrier gas may be first initiated into the remote plasma region before the fluorine-containing gas to stabilize the pressure within the remote plasma region.

[0059] Substrate processing region 233 can be maintained at a variety of pressures during the flow of precursors, any carrier gases, and plasma effluents into substrate processing region 233. The pressure may be maintained between about 0.1 mTorr and about 100 Torr, between about 1 Torr and about 20 Torr or between about 1 Torr and about 5 Torr in different embodiments.

[0060] Embodiments of the deposition systems may be incorporated into larger fabrication systems for producing integrated circuit chips. **FIG. 3** shows one such system 300 of deposition, etching, baking, and curing chambers according to disclosed embodiments. In the figure, a pair of front opening unified pods (FOUPs) 302 supply substrates of a variety of sizes that are received by robotic arms 304 and placed into a low pressure holding area 306 before being placed into one of the substrate processing chambers 308a-f. A second robotic arm 310 may be used to transport the substrate wafers from the holding area 306 to the

substrate processing chambers 308a-f and back. Each substrate processing chamber 308a-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.

[0061] The substrate processing chambers 308a-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 chamber, e.g., 308c-d and 308e-f, may be used to deposit dielectric material on the substrate, and the third pair of processing chambers, e.g., 308a-b, may be used to etch the deposited dielectric. In another configuration, all three pairs of chambers, e.g., 308a-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.

[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 invention. 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.

[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 disclosed embodiments. Additionally, a number of well-known processes and elements have not been described in order to avoid unnecessarily obscuring the present invention. Accordingly, the above description should not be taken as limiting the scope of the invention.

[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. Each smaller range between any stated value or intervening value 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 invention, 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.

[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 "an aperture" includes a plurality of such apertures, and reference to "the plate" includes reference to one or more plates 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 intended to specify the presence of stated features, integers, components, or steps, but they do not preclude the presence or addition of one or more other features, integers, components, steps, acts, or groups.

WHAT IS CLAIMED IS:

1. A method of etching a patterned substrate in a substrate processing region of a substrate processing chamber, wherein the patterned substrate includes an exposed titanium nitride region and a region comprising an exposed second material, the method comprising:

flowing a fluorine-containing precursor into a remote plasma region fluidly coupled with the substrate processing region while forming a plasma in the remote plasma region to produce plasma effluents;

flowing at least one additional precursor into the substrate processing region; and

etching the exposed titanium nitride region with the precursor combination including the plasma effluents, wherein the titanium nitride is etched at a faster rate than the exposed second material.

2. The method of claim 1, wherein the at least one additional precursor is selected from the group consisting of helium, argon, and molecular hydrogen (H_2).

3. The method of claim 1, wherein the fluorine-containing precursor comprises a precursor selected from the group consisting of atomic fluorine, diatomic fluorine, nitrogen trifluoride, carbon tetrafluoride, hydrogen fluoride, and xenon difluoride.

4. The method of claim 1, wherein the plasma in the remote plasma region is a capacitively-coupled plasma.

5. The method of claim 1, wherein the substrate processing region is plasma-free during the etching process.

6. The method of claim 1, wherein the at least one additional precursor consists of either or both of helium and argon.

7. The method of claim 6, wherein the precursor combination including plasma effluents is substantially devoid of hydrogen.

8. The method of claim 6, wherein the exposed second material comprises silicon oxide and the selectivity of the etching operation (exposed titanium nitride region: exposed silicon oxide region) is greater than or about 5:1.

9. The method of claim 8, wherein the selectivity of the etching operation (exposed titanium nitride region: exposed silicon oxide region) is greater than or about 10:1.

10. The method of claim 6, wherein the substrate temperature is maintained at or below about 50°C during the etch process.

11. The method of claim 10, wherein the substrate temperature is maintained at or below about 10°C during the etch process.

12. The method of claim 1, wherein the at least one additional precursor comprises hydrogen.

13. The method of claim 12, wherein the exposed second material comprises tungsten and the selectivity of the etching operation (exposed titanium nitride region: exposed tungsten region) is greater than or about 50:1.

14. The method of claim 13, wherein the selectivity of the etching operation (exposed titanium nitride region: exposed tungsten region) is greater than or about 100:1.

15. The method of claim 13, wherein the patterned substrate further comprises an exposed silicon nitride region and the selectivity of the etching operation (exposed titanium nitride region: exposed silicon nitride region) is greater than or about 10:1.

16. The method of claim 13, wherein the patterned substrate further comprises an exposed silicon oxide region and the selectivity of the etching operation (exposed titanium nitride region: exposed silicon oxide region) is greater than or about 5:1.

17. The method of claim 13, wherein the patterned substrate further comprises an exposed tantalum nitride region and the selectivity of the etching operation (exposed titanium nitride region: exposed tantalum nitride region) is greater than or about 10:1.

18. The method of claim 12, wherein the substrate temperature is maintained at or above about 50°C during the etch process.

19. The method of claim 18, wherein the substrate temperature is maintained at or above about 200°C during the etch process.

20. The method of claim 12, wherein the hydrogen is flowed into the substrate processing region without being first excited in a remote plasma.

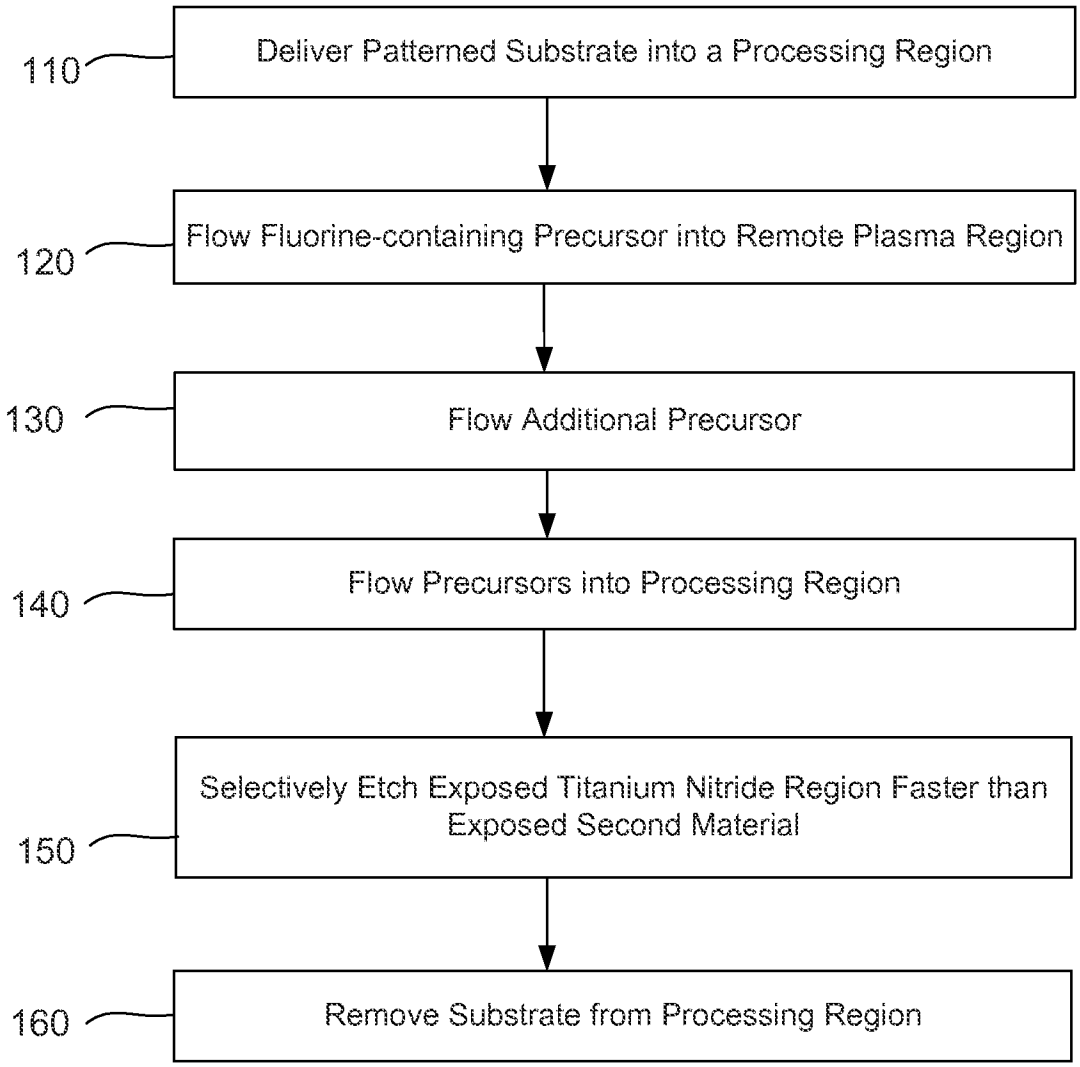
110
Deliver Patterned Substrate into a Processing Region
120
Flow Fluorine-containing Precursor into Remote Plasma Region
130
Flow Additional Precursor
140
Flow Precursors into Processing Region
150
Selectively Etch Exposed Titanium Nitride Region Faster than Exposed Second Material
160
Remove Substrate from Processing Region

FIG. 1

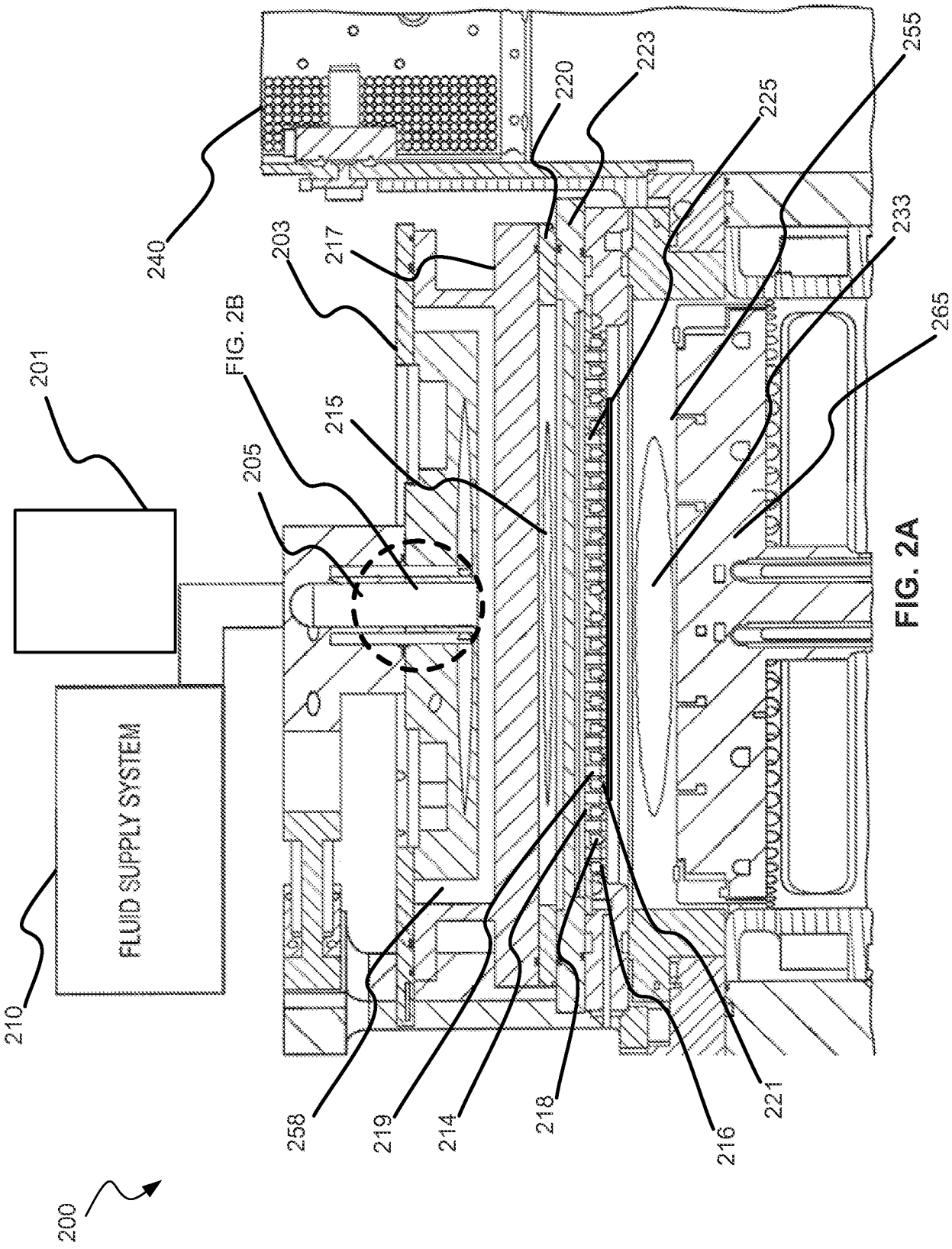
200
210
FLUID SUPPLY SYSTEM
201
205
FIG. 2B
215
203
217
240
220
223
225
255
233
265
258
219
214
218
216
221

FIG. 2A

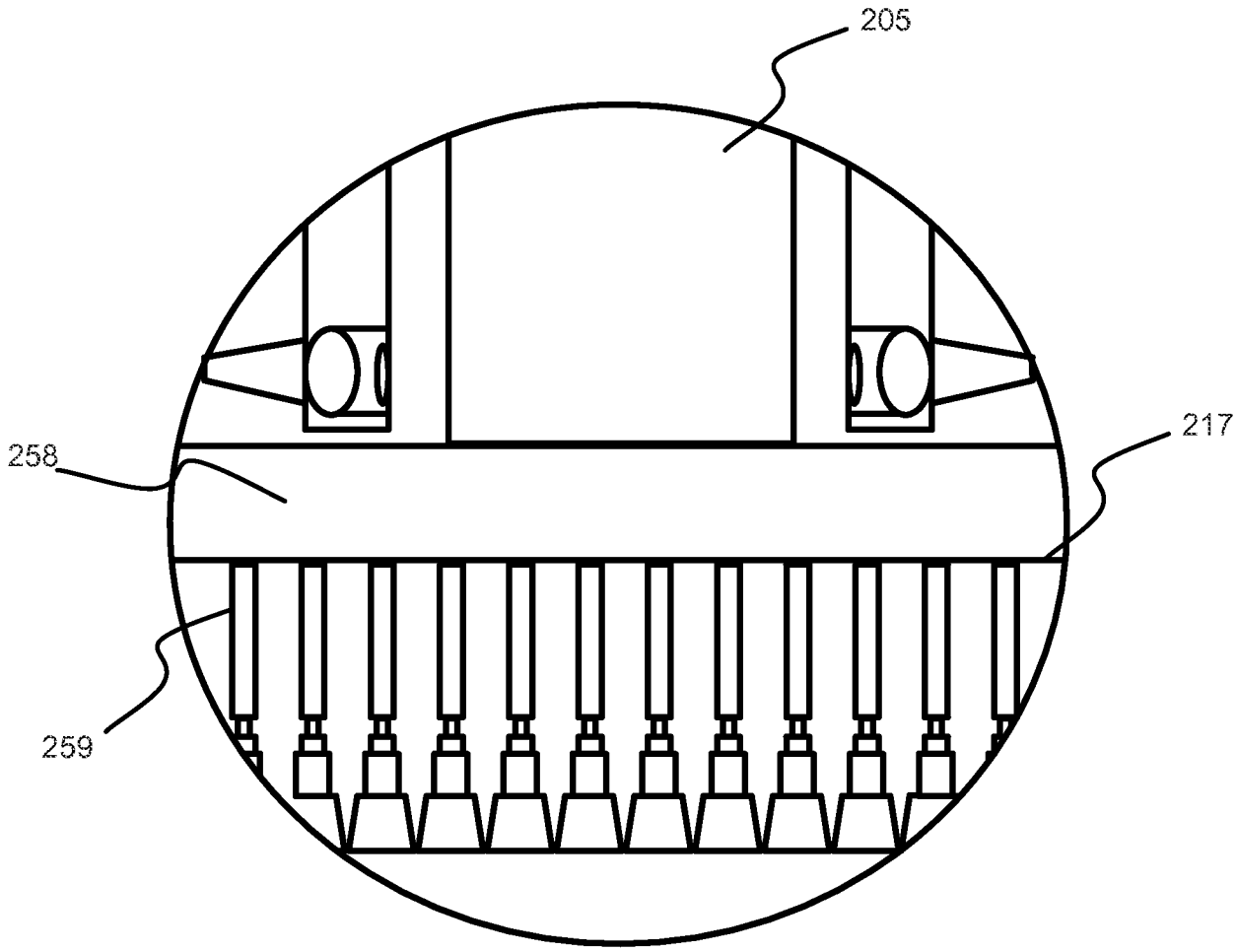

FIG. 2B

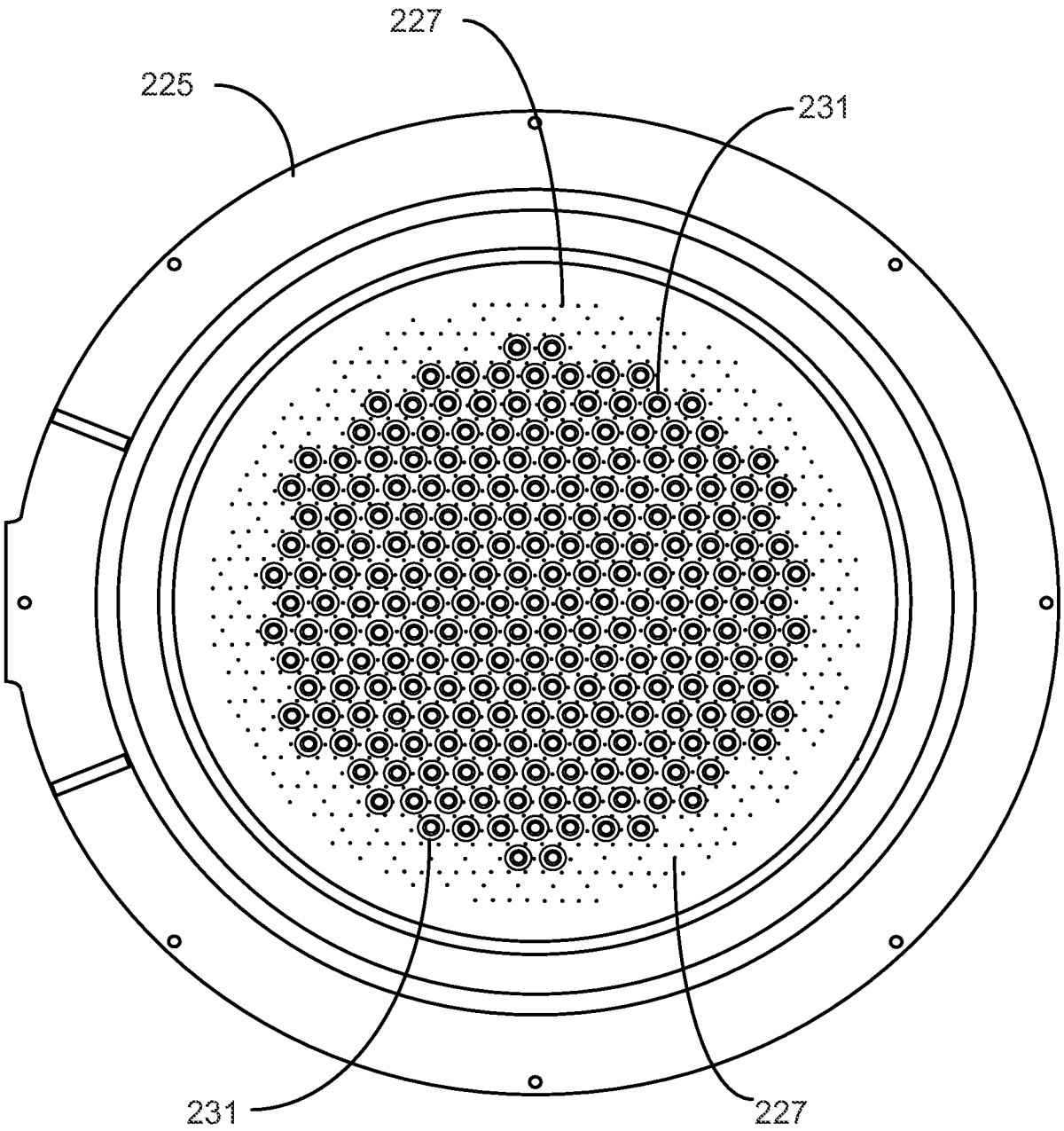

FIG. 2C

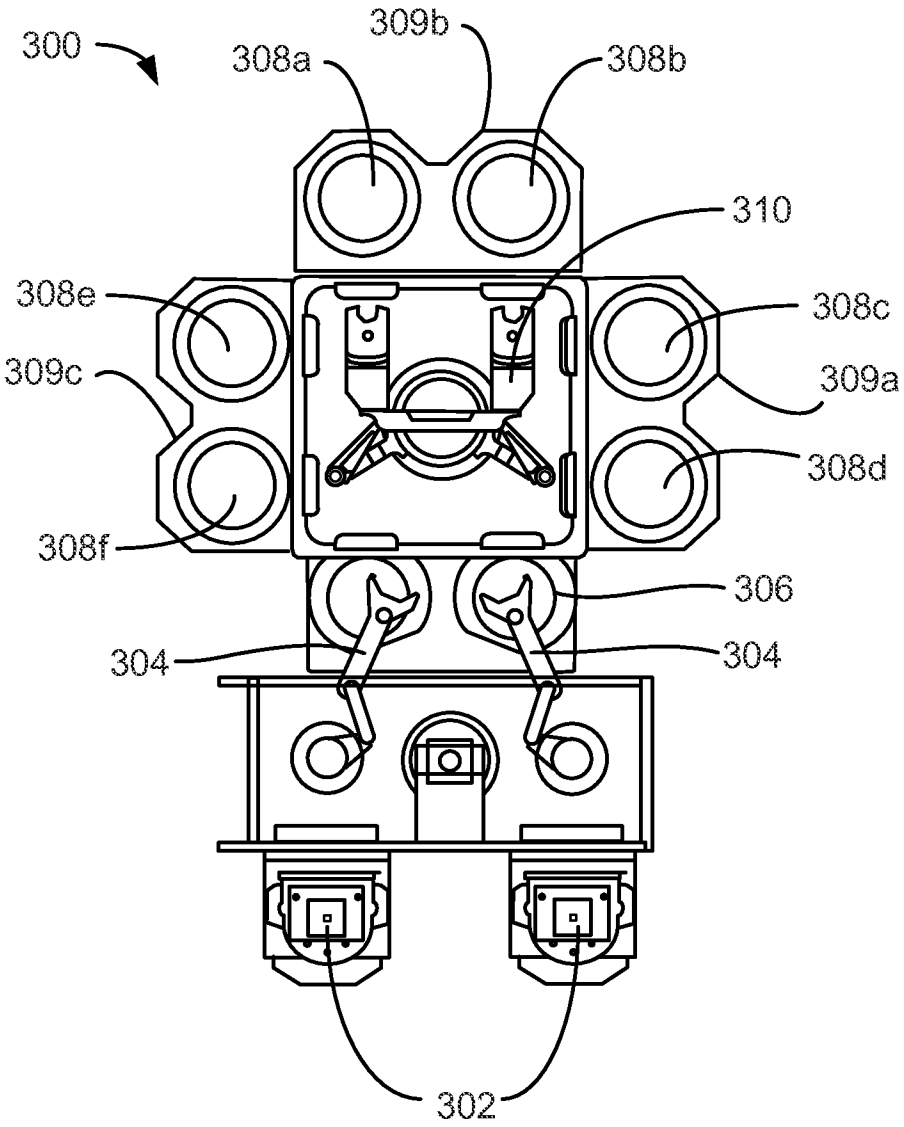
300
309b
308a
308b
310
308e
308c
309c
309a
308d
308f
306
304
304
302

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/071417

A. CLASSIFICATION OF SUBJECT MATTER

H01L 21/3065(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 21/3065; H01L 21/308; H01L 21/306; C23F 1/02; H01L 27/108; C03C 15/00; H01L 27/04; B44C 1/22; H01L 21/00

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: remote plasma, titanium nitride, selectively etch, rate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-2008-0013174 A (HYNIX SEMICONDUCTOR INC.) 13 February 2008 See abstract; paragraphs [0033]-[0056]; claims 1-12 and figures 3a-3e.	1-20
Y	US 2012-0211462 A1 (JINGCHUN ZHANG et al.) 23 August 2012 See abstract; paragraphs [0020]-[0047]; claims 1-14 and figures 4A-4B.	1-20
Y	JP 2009-044129 A (TOKYO OHKA KOGYO CO., LTD.) 26 February 2009 See abstract; paragraphs [0039], [0048]-[0049]; table 1 and claims 1, 11.	12-20
A	US 5948702 A (ANTONIO L. P. ROTONDARO) 07 September 1999 See abstract; column 2, line 50 - column 4, line 38; claims 1, 3, 6 and figures 1-2E.	1-20
A	US 4877482 A (JAMES H. KNAPP et al.) 31 October 1989 See abstract; column 2, line 8 - column 3, line 8 and claims 1-6.	1-20

☐ 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
"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	Date of mailing of the international search report
08 April 2014 (08.04.2014)	**08 April 2014 (08.04.2014)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
CHOI, Sang Won
Telephone No. +82-42-481-8291

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/071417

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 10-2008-0013174 A	13/02/2008	None	
US 2012-0211462 A1	23/08/2012	CN 103380485 A	30/10/2013
		TW 201248720 A	01/12/2012
		WO 2012-115750 A2	30/08/2012
		WO 2012-115750 A3	15/11/2012
JP 2009-044129 A	26/02/2009	JP 2009-019255 A	29/01/2009
		JP 5047881 B2	10/10/2012
		JP 5364250 B2	11/12/2013
		US 2009-0017636 A1	15/01/2009
		US 8623236 B2	07/01/2014
US 5948702 A	07/09/1999	None	
US 4877482 A	31/10/1989	EP 0388749 A1	26/09/1990
		EP 0388749 B1	21/06/1995
		JP 02-305977 A	19/12/1990
		JP 2903607 B2	07/06/1999
		KR 10-0204199 B1	15/06/1999