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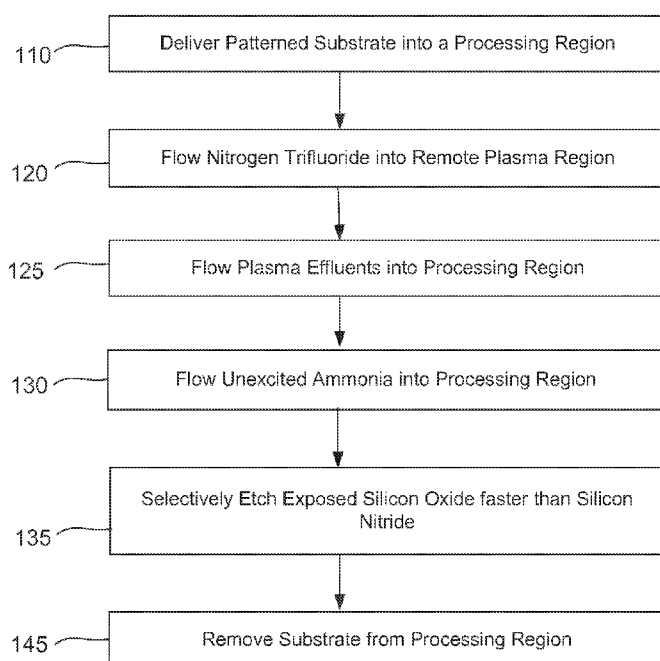


FIG. 1

(57) Abstract: A method of etching exposed silicon oxide on patterned heterogeneous structures is described and includes a remote plasma etch formed from a fluorine-containing precursor. Plasma effluents from the remote plasma are flowed into a substrate processing region where the plasma effluents combine with a nitrogen-and-hydrogen-containing precursor. Reactants thereby produced etch the patterned heterogeneous structures with high silicon oxide selectivity while the substrate is at high temperature compared to typical Siconi™ processes. The etch proceeds without producing residue on the substrate surface. The methods may be used to remove silicon oxide while removing little or no silicon, polysilicon, silicon nitride or titanium nitride.



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RADICAL-COMPONENT OXIDE ETCH

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Prov. Pat. App. No. 61/702,493 filed September 18, 2012, and titled "RADICAL-COMPONENT OXIDE ETCH," which is hereby
5 incorporated herein in its entirety by reference for all purposes.

BACKGROUND OF THE INVENTION

[0002] 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
10 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 which etches one material faster than another helping e.g. a pattern transfer process proceed. 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
15 selectivity towards a variety of materials.

[0003] 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 (plasmas within the substrate processing region) can penetrate more constrained trenches and exhibit less
20 deformation of delicate remaining structures. However, local plasmas can damage the substrate through the production of electric arcs as they discharge.

[0004] A SiconiTM etch is a remote plasma assisted dry etch process which involves the simultaneous exposure of a substrate to H₂, NF₃ and NH₃ plasma by-products. Remote plasma excitation of the hydrogen and fluorine species allows plasma-damage-free substrate processing.
25 The SiconiTM etch is largely conformal and selective towards silicon oxide layers but does not readily etch silicon regardless of whether the silicon is amorphous, crystalline or polycrystalline. Silicon nitride is typically etched at a rate between silicon and silicon oxide, but the selectivity of silicon oxide over silicon nitride is typically not as pronounced as the selectivity of silicon oxide over silicon. The selectivity provides advantages for applications such as shallow trench
30 isolation (STI) and inter-layer dielectric (ILD) recess formation. The SiconiTM process produces solid by-products which grow on the surface of the substrate as substrate material is removed.

The solid by-products are subsequently removed via sublimation when the temperature of the substrate is raised. As a consequence of the production of solid by-products, Siconi™ etch process can deform delicate remaining structures as well.

[0005] Methods are needed to selectively remove silicon oxide while not forming solid by-products on the surface since their formation may disturb delicate structures on a patterned substrate.

BRIEF SUMMARY OF THE INVENTION

[0006] A method of etching exposed silicon oxide on patterned heterogeneous structures is described and includes a remote plasma etch formed from a fluorine-containing precursor.

Plasma effluents from the remote plasma are flowed into a substrate processing region where the plasma effluents combine with a nitrogen-and-hydrogen-containing precursor. Reactants thereby produced etch the patterned heterogeneous structures with high silicon oxide selectivity while the substrate is at high temperature compared to typical Siconi™ processes. The etch proceeds without producing residue on the substrate surface. The methods may be used to remove silicon oxide while removing little or no silicon, polysilicon, silicon nitride or titanium nitride.

[0007] Embodiments of the invention include methods of etching patterned substrates in a substrate processing region of a substrate processing chamber. The patterned substrates have an exposed silicon oxide region. The methods include flowing a fluorine-containing precursor into a remote plasma region fluidly coupled to the substrate processing region while forming a remote plasma in the remote plasma region to produce plasma effluents. The methods further include flowing a nitrogen-and-hydrogen-containing precursor into the substrate processing region without first passing the nitrogen-and-hydrogen-containing precursor through the remote plasma region. The methods further include etching the exposed silicon oxide region with the combination of the plasma effluents and the nitrogen-and-hydrogen-containing precursor in the substrate processing region.

[0008] Additional embodiments and features are set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the specification or may be learned by the practice of the disclosed embodiments. The features and advantages of the disclosed embodiments may be realized and attained by means of the instrumentalities, combinations, and methods described in the specification.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] A further understanding of the nature and advantages of the disclosed embodiments may be realized by reference to the remaining portions of the specification and the drawings.

[0010] FIG. 1 is a flow chart of a silicon oxide selective etch process according to disclosed
5 embodiments.

[0011] FIG. 2A shows a substrate processing chamber according to embodiments of the invention.

[0012] FIG. 2B shows a showerhead of a substrate processing chamber according to embodiments of the invention.

10 [0013] FIG. 3 shows a substrate processing system according to embodiments of the invention.

[0014] In the appended figures, similar components and/or features may have the same reference label. Further, various components of the same type may be distinguished by following the reference label by a dash and a second label that distinguishes among the similar components. If only the first reference label is used in the specification, the description is
15 applicable to any one of the similar components having the same first reference label irrespective of the second reference label.

DETAILED DESCRIPTION OF THE INVENTION

[0015] A method of etching exposed silicon oxide on patterned heterogeneous structures is described and includes a remote plasma etch formed from a fluorine-containing precursor.

20 Plasma effluents from the remote plasma are flowed into a substrate processing region where the plasma effluents combine with a nitrogen-and-hydrogen-containing precursor. Reactants thereby produced etch the patterned heterogeneous structures with high silicon oxide selectivity while the substrate is at high temperature compared to typical SiconiTM processes. The etch proceeds without producing residue on the substrate surface. The methods may be used to remove silicon
25 oxide while removing little or no silicon, polysilicon, silicon nitride or titanium nitride.

[0016] Selective remote gas phase etch processes have used a hydrogen source of ammonia (NH₃) and a fluorine source of nitrogen trifluoride (NF₃) which together flow through a remote plasma system (RPS) and into a reaction region. The flow rates of ammonia and nitrogen trifluoride are typically chosen such that the atomic flow rate of hydrogen is roughly twice that
30 of fluorine in order to efficiently utilize the constituents of the two process gases. The presence of hydrogen and fluorine allows the formation of solid byproducts of (NH₄)₂SiF₆ at relatively

low substrate temperatures. The solid byproducts are removed by raising the temperature of the substrate above the sublimation temperature. Remote gas phase etch processes remove oxide films much more rapidly than, e.g. silicon. However, the selectivity of traditional selective remote gas phase etch processes compared to silicon nitride may be poor. The inventors have discovered that the selectivity of silicon oxide over silicon nitride can be enhanced by exciting a fluorine-containing precursor in a remote plasma and combining the plasma effluents with ammonia which has not passed through a remote plasma system.

[0017] In order to better understand and appreciate the invention, reference is now made to FIG. 1 which is a flow chart of a silicon oxide selective etch process according to disclosed embodiments. Prior to the first operation, the substrate is patterned leaving exposed regions of silicon oxide and exposed regions of silicon nitride. The patterned substrate is then delivered into a substrate processing region (operation 110). A flow of nitrogen trifluoride is initiated into a plasma region separate from the processing region (operation 120). Other sources of fluorine may be used to augment or replace 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. 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 a compartment within the processing chamber. The plasma effluents formed in the remote plasma region are then flowed into the substrate processing region (operation 125). At this point, the gas phase etch would have little selectivity towards silicon oxide and would have limited utility. However, ammonia is simultaneously flowed into the substrate processing region (operation 130) to react with the plasma effluents. The ammonia is not passed through the remote plasma region and therefore is only excited by interaction with the plasma effluents.

[0018] The patterned substrate is selectively etched (operation 135) such that the silicon oxide is removed at a significantly higher rate than the silicon nitride. The reactive chemical species are removed from the substrate processing region and then the substrate is removed from the processing region (operation 145). Using the gas phase dry etch processes described herein, the inventors have established that etch selectivities of over 100:1 and up to 150:1 (SiO etch rate:SiN etch rate) are possible. Achievable selectivities using the methods described herein are at least four times greater than prior art methods. The silicon oxide etch rate exceeds the silicon nitride etch rate by a multiplicative factor of about 40 or more, about 50 or more, about 75 or more, or about 100 or more, in embodiments of the invention.

[0019] The gas phase dry etches described herein have also been discovered to increase etch selectivity of silicon oxide relative to silicon (including polysilicon). Using the gas phase dry etch processes described herein, the inventors have established that etch selectivities of over 100:1 and up to 500:1 (SiO etch rate:Si etch rate) are possible. Achievable selectivities using the methods described herein are at least five times greater than prior art methods. The silicon oxide etch rate exceeds the silicon etch rate by a multiplicative factor of about 100 or more, about 150 or more, about 200 or more, or about 300 or more, in embodiments of the invention.

[0020] Gas phase etches involving only fluorine (either remote or local) do not possess the selectivity needed to remove the silicon oxide while leaving other portions of the patterned substrate (e.g. made of silicon or silicon nitride) nearly undisturbed. The gas phase etches described herein have an added benefit, in that they do not produce solid residue. Elimination of solid residue avoids disturbing delicate features which may be supported by sacrificial silicon oxide. Elimination of solid residue also simplifies the process flows and decreases processing costs by removing the sublimation step. The fluorine-containing precursor is devoid of hydrogen in embodiments of the invention. The plasma effluents may also be devoid of hydrogen when no hydrogen precursors are included in the remote plasma region. This ensures minimal production of solid by-products on the patterned substrate.

[0021] Without wishing to bind the coverage of the claims to theoretical mechanisms which may or may not be entirely correct, some discussion of possible mechanisms may prove beneficial. Radical-fluorine precursors are produced by delivering a fluorine-containing precursor into the remote plasma region. Applicants suppose that a concentration of fluorine ions and atoms is produced and delivered into the substrate processing region. Ammonia (NH₃) may react with the fluorine to produce less reactive species such as HF₂⁻ which still readily remove silicon oxide but do not readily remove silicon and silicon nitride from the patterned substrate surface. The selectivity combined with the lack of solid byproducts, make these etch processes well suited for removing molds and other silicon oxide support structures from delicate non-silicon oxide materials while inducing little deformation in the remaining delicate structures.

[0022] Generally speaking, a nitrogen-and-hydrogen-containing precursor may be used in place of the ammonia. The nitrogen-and-hydrogen-containing precursor may consist only of nitrogen and hydrogen, e.g. ammonia (NH₃) used in the above example. The nitrogen-and-hydrogen-containing precursor may be hydrazine (N₂H₄) in disclosed embodiments.

[0023] The pressure in the substrate processing region may be above or about 0.1 Torr and less than or about 50 Torr, in disclosed embodiments, during the etching operation. The pressure

within the substrate processing region may also be below or about 40 Torr and above or about 5 Torr or 10 Torr in disclosed embodiments. Any of the upper limits can be combined with any of these lower limits to form additional embodiments of the invention. The temperature of the patterned substrate may be about 10°C or more and about 250°C or less, in disclosed
5 embodiments, during the etching operation. The temperature of the patterned substrate may be about 100°C or more and about 140°C or less during the etching operation in embodiments of the invention.

[0024] In addition to the fluorine-containing precursor, an oxygen-containing precursor may be delivered to the remote plasma region during the etching operation. The inventors have found
10 that adding the oxygen-containing precursor broadens the process window while maintaining the selectivity benefits outlined above. The pressure is the process parameter which can vary more widely through the addition of the oxygen-containing precursor. A broader pressure range is possible (while maintaining uniform selective etch process) when an oxygen-containing precursor is added to the remote plasma region during the etching operation. The oxygen-
15 containing precursor may be molecular oxygen (O₂), nitrous oxide (N₂O) or nitrogen dioxide (NO₂), for example, though other oxygen-containing precursors may be used.

[0025] Additional silicon oxide selective etch process parameters are disclosed in the course of describing an exemplary processing chamber and system.

Exemplary Processing System

[0026] Processing chambers that may implement embodiments of the present invention may be included within processing platforms such as the CENTURA® and PRODUCER® systems, available from Applied Materials, Inc. of Santa Clara, Calif. Examples of substrate processing chambers that can be used with exemplary methods of the invention may include those shown and described in co-assigned U.S. Provisional Patent App. No. 60/803,499 to Lubomirsky et al,
25 filed May 30, 2006, and titled "PROCESS CHAMBER FOR DIELECTRIC GAPFILL," the entire contents of which is herein incorporated by reference for all purposes. Additional exemplary systems may include those shown and described in U.S. Pat. Nos. 6,387,207 and 6,830,624, which are also incorporated herein by reference for all purposes.

[0027] FIG. 2A is a substrate processing chamber 1001 according to disclosed embodiments.
30 A remote plasma system (RPS 1010) may process the fluorine-containing precursor which then travels through a gas inlet assembly 1011. Two distinct gas supply channels are visible within the gas inlet assembly 1011. A first channel 1012 carries a gas that passes through the remote plasma system RPS 1010, while a second channel 1013 bypasses the RPS 1010. Either channel

may be used for the fluorine-containing precursor, in embodiments. On the other hand, the first channel 1002 may be used for the process gas and the second channel 1013 may be used for a treatment gas. The lid 1021 (e.g. a conducting top portion) and a perforated partition (showerhead 1053) are shown with an insulating ring 1024 in between, which allows an AC potential to be applied to the lid 1021 relative to showerhead 1053. The AC potential strikes a plasma in chamber plasma region 1020. The process gas may travel through first channel 1012 into chamber plasma region 1020 and may be excited by a plasma in chamber plasma region 1020 alone or in combination with RPS 1010. If the process gas (the fluorine-containing precursor) flows through second channel 1013, then only the chamber plasma region 1020 is used for excitation. The combination of chamber plasma region 1020 and/or RPS 1010 may be referred to as a remote plasma system herein. The perforated partition (also referred to as a showerhead) 1053 separates chamber plasma region 1020 from a substrate processing region 1070 beneath showerhead 1053. Showerhead 1053 allows a plasma present in chamber plasma region 1020 to avoid directly exciting gases in substrate processing region 1070, while still allowing excited species to travel from chamber plasma region 1020 into substrate processing region 1070.

[0028] Showerhead 1053 is positioned between chamber plasma region 1020 and substrate processing region 1070 and allows plasma effluents (excited derivatives of precursors or other gases) created within RPS 1010 and/or chamber plasma region 1020 to pass through a plurality of through-holes 1056 that traverse the thickness of the plate. The showerhead 1053 also has one or more hollow volumes 1051 which can be filled with a precursor in the form of a vapor or gas (such as a silicon-containing precursor) and pass through small holes 1055 into substrate processing region 1070 but not directly into chamber plasma region 1020. Showerhead 1053 is thicker than the length of the smallest diameter 1050 of the through-holes 1056 in this disclosed embodiment. In order to maintain a significant concentration of excited species penetrating from chamber plasma region 1020 to substrate processing region 1070, the length 1026 of the smallest diameter 1050 of the through-holes may be restricted by forming larger diameter portions of through-holes 1056 part way through the showerhead 1053. The length of the smallest diameter 1050 of the through-holes 1056 may be the same order of magnitude as the smallest diameter of the through-holes 1056 or less in disclosed embodiments.

[0029] In the embodiment shown, showerhead 1053 may distribute (via through-holes 1056) process gases which contain oxygen, hydrogen and/or nitrogen and/or plasma effluents of such process gases upon excitation by a plasma in chamber plasma region 1020. In embodiments, the process gas introduced into the RPS 1010 and/or chamber plasma region 1020 through first

channel 1012 may contain fluorine (e.g. CF₄, NF₃ or XeF₂). The process gas may also include a carrier gas such as helium, argon, nitrogen (N₂), 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.

5 **[0030]** In embodiments, the number of through-holes 1056 may be between about 60 and about 2000. Through-holes 1056 may have a variety of shapes but are most easily made round. The smallest diameter 1050 of through-holes 1056 may be between about 0.5 mm and about 20 mm or between about 1 mm and about 6 mm in disclosed embodiments. There is also latitude in choosing the cross-sectional shape of through-holes, which may be made conical, cylindrical
10 or a combination of the two shapes. The number of small holes 1055 used to introduce a gas into substrate processing region 1070 may be between about 100 and about 5000 or between about 500 and about 2000 in different embodiments. The diameter of the small holes 1055 may be between about 0.1 mm and about 2 mm.

[0031] FIG. 2B is a bottom view of a showerhead 1053 for use with a processing chamber
15 according to disclosed embodiments. Showerhead 1053 corresponds with the showerhead shown in FIG. 2A. Through-holes 1056 are depicted with a larger inner-diameter (ID) on the bottom of showerhead 1053 and a smaller ID at the top. Small holes 1055 are distributed substantially evenly over the surface of the showerhead, even amongst the through-holes 1056 which helps to provide more even mixing than other embodiments described herein.

20 **[0032]** An exemplary patterned substrate may be supported by a pedestal (not shown) within substrate processing region 1070 when fluorine-containing plasma effluents arriving through through-holes 1056 in showerhead 1053 combine with ammonia arriving through the small holes 1055 originating from hollow volumes 1051. Though substrate processing region 1070 may be equipped to support a plasma for other processes such as curing, no plasma is present during the
25 etching of patterned substrate, in embodiments of the invention.

[0033] A plasma may be ignited either in chamber plasma region 1020 above showerhead 1053 or substrate processing region 1070 below showerhead 1053. A plasma is present in chamber plasma region 1020 to produce the radical-fluorine precursors from an inflow of the fluorine-containing precursor. An AC voltage typically in the radio frequency (RF) range is
30 applied between the conductive top portion 1021 of the processing chamber and showerhead 1053 to ignite a plasma in chamber plasma region 1020 during deposition. An RF power supply generates a high RF frequency of 13.56 MHz but may also generate other frequencies alone or in combination with the 13.56 MHz frequency.

[0034] The top plasma may be left at low or no power when the bottom plasma in the substrate processing region 1070 is turned on to either cure a film or clean the interior surfaces bordering substrate processing region 1070. A plasma in substrate processing region 1070 is ignited by applying an AC voltage between showerhead 1053 and the pedestal or bottom of the chamber. A cleaning gas may be introduced into substrate processing region 1070 while the plasma is present.

[0035] The pedestal may have a heat exchange channel through which a heat exchange fluid flows to control the temperature of the substrate. This configuration allows the substrate temperature to be cooled or heated to maintain relatively low temperatures (from room temperature through about 120°C). The heat exchange fluid may comprise ethylene glycol and water. The wafer support platter of the pedestal (preferably aluminum, ceramic, or a combination thereof) may also be resistively heated in order to achieve relatively high temperatures (from about 120°C through about 1100°C) using an embedded single-loop embedded heater element configured to make two full turns in the form of parallel concentric circles. 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 passes through the stem of the pedestal.

[0036] The substrate processing system is controlled by a system controller. In an exemplary embodiment, the system controller includes a hard disk drive, a floppy disk drive and a processor. The processor contains a single-board computer (SBC), analog and digital input/output boards, interface boards and stepper motor controller boards. Various parts of CVD system conform to the Versa Modular European (VME) standard which defines board, card cage, and connector dimensions and types. The VME standard also defines the bus structure as having a 16-bit data bus and a 24-bit address bus.

[0037] The system controller controls all of the activities of the etching chamber. The system controller executes system control software, which is a computer program stored in a computer-readable medium. Preferably, the medium is a hard disk drive, but the medium may also be other kinds of memory. The computer program includes sets of instructions that dictate the timing, mixture of gases, chamber pressure, chamber temperature, RF power levels, susceptor position, and other parameters of a particular process. Other computer programs stored on other memory devices including, for example, a floppy disk or other another appropriate drive, may also be used to instruct the system controller.

[0038] A process for depositing a film stack on a substrate or a process for cleaning a chamber can be implemented using a computer program product that is executed by the system controller. The computer program code can be written in any conventional computer readable programming language: for example, 68000 assembly language, C, C++, Pascal, Fortran or others. Suitable
5 program code is entered into a single file, or multiple files, using a conventional text editor, and stored or embodied in a computer usable medium, such as a memory system of the computer. If the entered code text is in a high level language, the code is compiled, and the resultant compiler code is then linked with an object code of precompiled Microsoft Windows® library routines. To execute the linked, compiled object code the system user invokes the object code, causing the
10 computer system to load the code in memory. The CPU then reads and executes the code to perform the tasks identified in the program.

[0039] The interface between a user and the controller is via a flat-panel touch-sensitive monitor. In the preferred embodiment two monitors are used, one mounted in the clean room wall for the operators and the other behind the wall for the service technicians. The two
15 monitors may simultaneously display the same information, in which case only one accepts input at a time. To select a particular screen or function, the operator touches a designated area of the touch-sensitive monitor. The touched area changes its highlighted color, or a new menu or screen is displayed, confirming communication between the operator and the touch-sensitive monitor. Other devices, such as a keyboard, mouse, or other pointing or communication device,
20 may be used instead of or in addition to the touch-sensitive monitor to allow the user to communicate with the system controller.

[0040] The chamber plasma region 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 to combine
25 with the ammonia. In embodiments, the ammonia is 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 to the ammonia.

[0041] In embodiments employing a chamber plasma region, the excited plasma effluents are
30 generated in a section of the substrate processing region partitioned from a deposition region. The deposition region, also known herein as the substrate processing region, is where the plasma effluents mix and react with the ammonia to etch the patterned substrate (e.g., a semiconductor wafer). The excited plasma effluents may also be accompanied by inert gases (in the exemplary

case, argon). The ammonia does not pass through a plasma before entering the substrate plasma region, in embodiments. The substrate processing region may be described herein as "plasma-free" during the etch of the patterned substrate. "Plasma-free" does not necessarily mean the region is devoid of plasma. Ionized species and free electrons created within the plasma region do travel through pores (apertures) in the partition (showerhead) but the ammonia is not substantially excited by the plasma power applied to the plasma region. The borders of the plasma in the chamber plasma region are hard to define and may encroach upon the substrate processing region through the apertures in the showerhead. In the case of an inductively-coupled plasma, a small amount of ionization may be effected within the substrate processing region directly. Furthermore, a low intensity plasma may be created in the substrate processing region without eliminating desirable features of the forming film. All causes for a plasma having much lower intensity ion density than the chamber plasma region (or a remote plasma region, for that matter) during the creation of the excited plasma effluents do not deviate from the scope of "plasma-free" as used herein.

[0042] Nitrogen trifluoride (or another fluorine-containing precursor) may be flowed into chamber plasma region 1020 at rates between about 25 sccm and about 200 sccm, between about 50 sccm and about 150 sccm or between about 75 sccm and about 125 sccm in disclosed embodiments. Ammonia may be flowed into substrate processing region 1070 at rates between about 25 sccm and about 200 sccm, between about 50 sccm and about 150 sccm or between about 75 sccm and about 125 sccm in disclosed embodiments. The optional oxygen-containing precursor may be flowed into chamber plasma region 1020 at rates between about 15 sccm and about 200 sccm, between about 25 sccm and about 150 sccm or between about 50 sccm and about 125 sccm in embodiments of the invention.

[0043] Combined flow rates of ammonia and fluorine-containing precursor 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 is flowed into the remote plasma region but the plasma effluents has 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 those of the fluorine-containing gas to stabilize the pressure within the remote plasma region.

[0044] Plasma power can be a variety of frequencies or a combination of multiple frequencies. In the exemplary processing system the plasma is provided by RF power delivered to lid 1021 relative to showerhead 1053. 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 500 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] Substrate processing region 1070 can be maintained at a variety of pressures during the flow of ammonia, any carrier gases and plasma effluents into substrate processing region 1070. The pressure may be maintained between about 500 mTorr and about 30 Torr, between about 1 Torr and about 20 Torr or between about 5 Torr and about 15 Torr in disclosed embodiments.

[0046] In one or more embodiments, the substrate processing chamber 1001 can be integrated into a variety of multi-processing platforms, including the ProducerTM GT, CenturaTM AP and EnduraTM platforms available from Applied Materials, Inc. located in Santa Clara, Calif. Such a processing platform is capable of performing several processing operations without breaking vacuum. Processing chambers that may implement embodiments of the present invention may include dielectric etch chambers or a variety of chemical vapor deposition chambers, among other types of chambers.

[0047] Embodiments of the deposition systems may be incorporated into larger fabrication systems for producing integrated circuit chips. FIG. 3 shows one such system 1101 of deposition, baking and curing chambers according to disclosed embodiments. In the figure, a pair of FOUPs (front opening unified pods) 1102 supply substrate substrates (e.g., 300 mm diameter wafers) that are received by robotic arms 1104 and placed into a low pressure holding area 1106 before being placed into one of the substrate processing chambers 1108a-f. A second robotic arm 1110 may be used to transport the substrate wafers from the holding area 1106 to the substrate processing chambers 1108a-f and back. Each substrate processing chamber 1108a-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.

[0048] The substrate processing chambers 1108a-f may include one or more system components for depositing, annealing, curing and/or etching a flowable dielectric film on the substrate wafer. In one configuration, two pairs of the processing chamber (e.g., 1108c-d and 1108e-f) may be used to deposit dielectric material on the substrate, and the third pair of

processing chambers (e.g., 1108a-b) may be used to etch the deposited dielectric. In another configuration, all three pairs of chambers (e.g., 1108a-f) may be configured to etch a dielectric film on the substrate. Any one or more of the processes described may be carried out on chamber(s) separated from the fabrication system shown in different embodiments.

- 5 **[0049]** System controller 1157 is used to control motors, valves, flow controllers, power supplies and other functions required to carry out process recipes described herein. A gas handling system 1155 may also be controlled by system controller 1157 to introduce gases to one or all of the substrate processing chambers 1108a-f. System controller 1157 may rely on feedback from optical sensors to determine and adjust the position of movable mechanical
- 10 assemblies in gas handling system 1155 and/or in substrate processing chambers 1108a-f. Mechanical assemblies may include the robot, throttle valves and susceptors which are moved by motors under the control of system controller 1157.

- [0050]** In an exemplary embodiment, system controller 1157 includes a hard disk drive (memory), USB ports, a floppy disk drive and a processor. System controller 1157 includes
- 15 analog and digital input/output boards, interface boards and stepper motor controller boards. Various parts of multi-chamber processing system 1101 which contains processing chamber 1001 are controlled by system controller 1157. The system controller executes system control software in the form of a computer program stored on computer-readable medium such as a hard disk, a floppy disk or a flash memory thumb drive. Other types of memory can also be used.
- 20 The computer program includes sets of instructions that dictate the timing, mixture of gases, chamber pressure, chamber temperature, RF power levels, susceptor position, and other parameters of a particular process.

- [0051]** A process for etching, depositing or otherwise processing a film on a substrate or a process for cleaning chamber can be implemented using a computer program product that is
- 25 executed by the controller. The computer program code can be written in any conventional computer readable programming language: for example, 68000 assembly language, C, C++, Pascal, Fortran or others. Suitable program code is entered into a single file, or multiple files, using a conventional text editor, and stored or embodied in a computer usable medium, such as a memory system of the computer. If the entered code text is in a high level language, the code is
- 30 compiled, and the resultant compiler code is then linked with an object code of precompiled Microsoft Windows® library routines. To execute the linked, compiled object code the system user invokes the object code, causing the computer system to load the code in memory. The CPU then reads and executes the code to perform the tasks identified in the program.

[0052] The interface between a user and the controller may be via a touch-sensitive monitor and may also include a mouse and keyboard. In one embodiment two monitors are used, one mounted in the clean room wall for the operators and the other behind the wall for the service technicians. The two monitors may simultaneously display the same information, in which case only one is configured to accept input at a time. To select a particular screen or function, the operator touches a designated area on the display screen with a finger or the mouse. The touched area changes its highlighted color, or a new menu or screen is displayed, confirming the operator's selection.

[0053] As used herein "substrate" may be a support substrate with or without layers formed thereon. The patterned substrate may be an insulator or a semiconductor of a variety of doping concentrations and profiles and may, for example, be a semiconductor substrate of the type used in the manufacture of integrated circuits. Exposed "silicon oxide" of the patterned substrate is predominantly SiO₂ but may include concentrations of other elemental constituents such as nitrogen, hydrogen, carbon and the like. In some embodiments, silicon oxide films etched using the methods disclosed herein consist essentially of silicon and oxygen. The term "precursor" is used to refer to any process gas which takes part in a reaction to either remove material from or deposit material onto a surface. "Plasma effluents" describe gas exiting from the chamber plasma region and entering the substrate processing region. Plasma effluents are in an "excited state" wherein at least some of the gas molecules are in vibrationally-excited, dissociated and/or ionized states. A "radical precursor" is used to describe plasma effluents (a gas in an excited state which is exiting a plasma) which participate in a reaction to either remove material from or deposit material on a surface. A "radical-fluorine precursor" is a radical precursor which contains fluorine but may contain other elemental constituents. A "radical-oxygen precursor" is a radical precursor which contains oxygen but may contain other elemental constituents. The phrase "inert gas" refers to any gas which does not form chemical bonds when etching or being incorporated into a film. Exemplary inert gases include noble gases but may include other gases so long as no chemical bonds are formed when (typically) trace amounts are trapped in a film.

[0054] The terms "gap" and "trench" are used throughout with no implication that the etched geometry has a large horizontal aspect ratio. Viewed from above the surface, trenches may appear circular, oval, polygonal, rectangular, or a variety of other shapes. A trench may be in the shape of a moat around an island of material (e.g. a substantially cylindrical TiN pillar). The term "via" is used to refer to a low aspect ratio trench (as viewed from above) which may or may not be filled with metal to form a vertical electrical connection. As used herein, a conformal etch process refers to a generally uniform removal of material on a surface in the same shape as the

surface, i.e., the surface of the etched layer and the pre-etch surface are generally parallel. A person having ordinary skill in the art will recognize that the etched interface likely cannot be 100% conformal and thus the term "generally" allows for acceptable tolerances.

[0055] 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.

[0056] Where a range of values is provided, it is understood that each intervening value, to the tenth 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 these 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.

[0057] As used herein and in the appended claims, the singular forms "a", "an", and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a process" includes a plurality of such processes and reference to "the dielectric material" includes reference to one or more dielectric materials and equivalents thereof known to those skilled in the art, and so forth.

[0058] Also, the words "comprise," "comprising," "include," "including," and "includes" 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 has an exposed silicon oxide region, the method comprising:

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

flowing a nitrogen-and-hydrogen-containing precursor into the substrate processing region without first passing the nitrogen-and-hydrogen-containing precursor through the remote plasma region; and

etching the exposed silicon oxide region with the combination of the plasma effluents and the nitrogen-and-hydrogen-containing precursor in the substrate processing region.

2. The method of claim 1 further comprising flowing an oxygen-containing precursor into the remote plasma region during the formation of the remote plasma.

3. The method of claim 1 further comprising flowing one of molecular oxygen, nitrogen dioxide or nitrous oxide into the remote plasma region during the formation of the remote plasma.

4. The method of claim 1 wherein the nitrogen-and-hydrogen-containing precursor consists of nitrogen and hydrogen.

5. The method of claim 1 wherein the nitrogen-and-hydrogen-containing precursor comprises ammonia.

6. The method of claim 1 wherein the patterned substrate further comprises an exposed polysilicon region and the selectivity of the etching operation (exposed silicon oxide region: exposed polysilicon region) is greater than or about 50:1.

7. The method of claim 1 wherein the patterned substrate further comprises an exposed polysilicon region and the selectivity of the etching operation (exposed silicon oxide region: exposed polysilicon region) is greater than or about 100:1.

8. The method of claim 1 wherein the patterned substrate further comprises an
5 exposed silicon nitride region and the selectivity of the etching operation (exposed silicon oxide region: exposed silicon nitride region) is greater than or about 30:1.

9. The method of claim 1 wherein the patterned substrate further comprises an exposed silicon nitride region and the selectivity of the etching operation (exposed silicon oxide region: exposed silicon nitride region) is greater than or about 70:1.

10. The method of claim 1 wherein the substrate processing region is plasma-free.

11. The method of claim 1 wherein the nitrogen-and-hydrogen-containing precursor is not excited by any remote plasma formed outside the substrate processing region.

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

13. The method of claim 1 wherein the fluorine-containing precursor and the plasma effluents are essentially devoid of hydrogen.

14. The method of claim 1 wherein the fluorine-containing precursor flowed through through-holes in a dual-zone showerhead and the ammonia passes through separate zones in the
20 dual-zone showerhead, wherein the separate zones open into the substrate processing region but not into the remote plasma region.

15. The method of claim 1 wherein a temperature of the patterned substrate is greater than or about 10°C and less than or about 250°C during the etching operation.

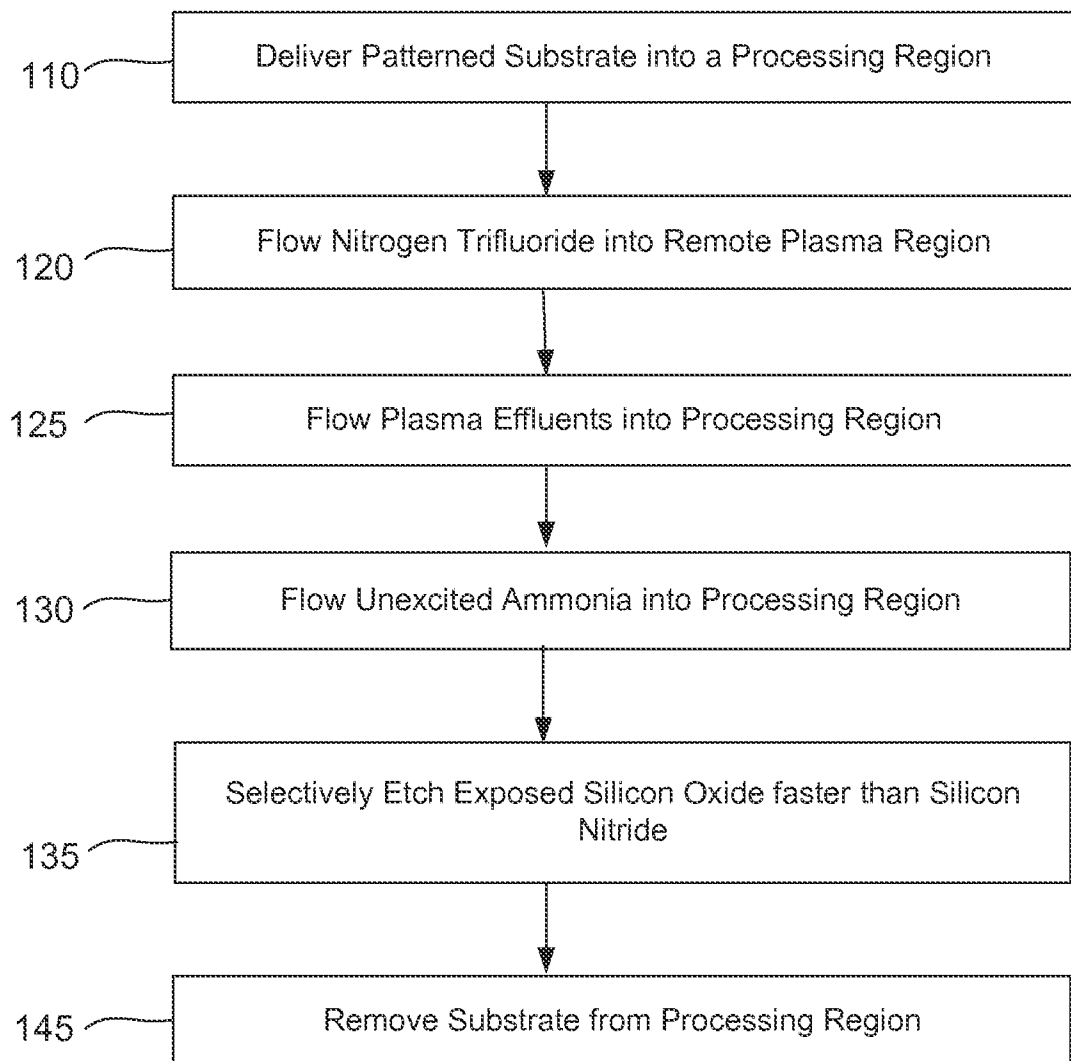
16. The method of claim 1 wherein a temperature of the patterned substrate is greater than or about 100°C and less than or about 140°C during the etching operation.

17. The method of claim 1 wherein a pressure within the substrate processing region is below or about 50 Torr and above or about 0.1 Torr during the etching operation.

5 18. The method of claim 1 wherein forming a plasma in the remote plasma region to produce plasma effluents comprises applying RF power between about 10 Watts and about 2000 Watts to the plasma region.

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

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**FIG. 1**

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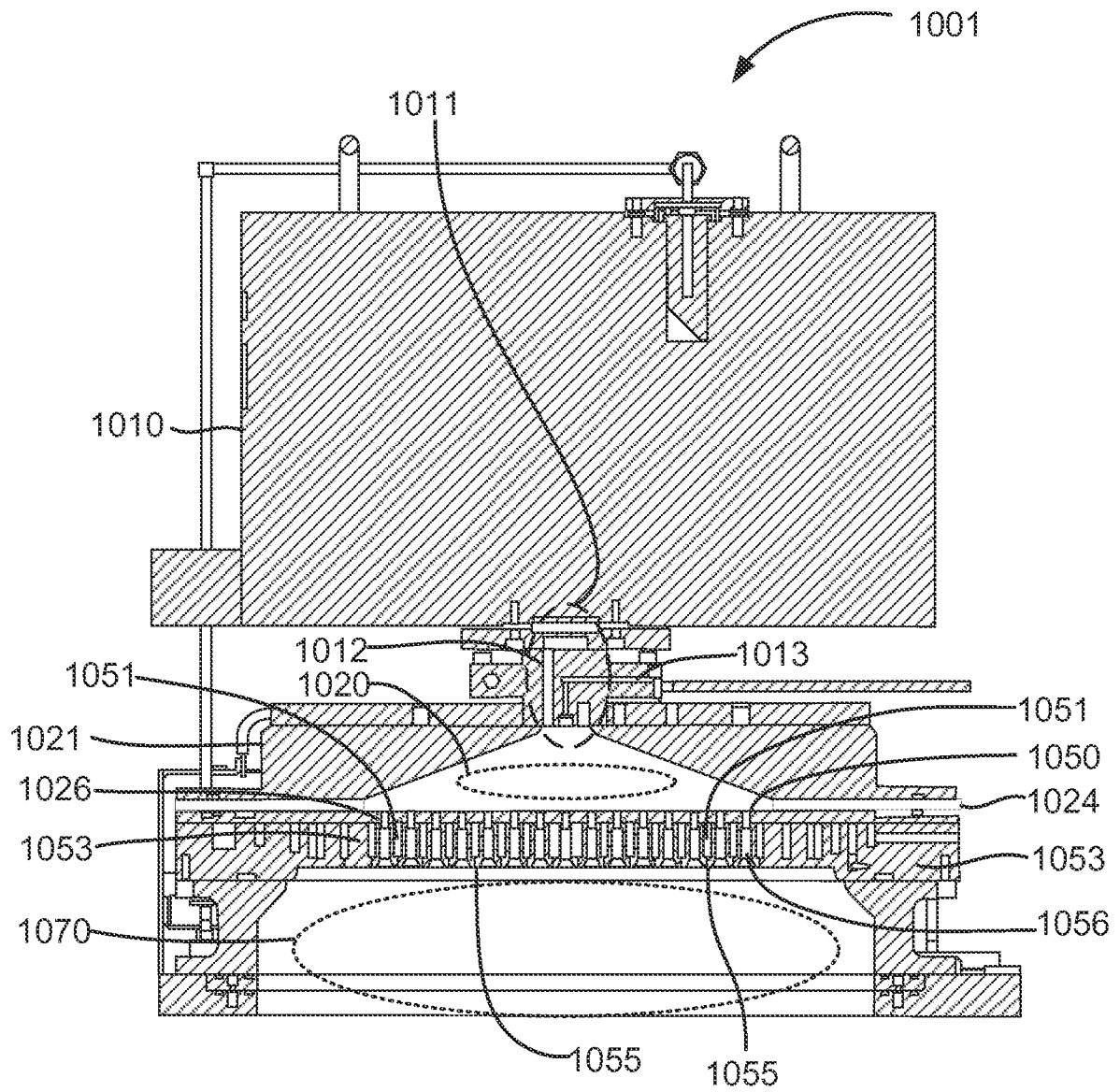


FIG. 2A

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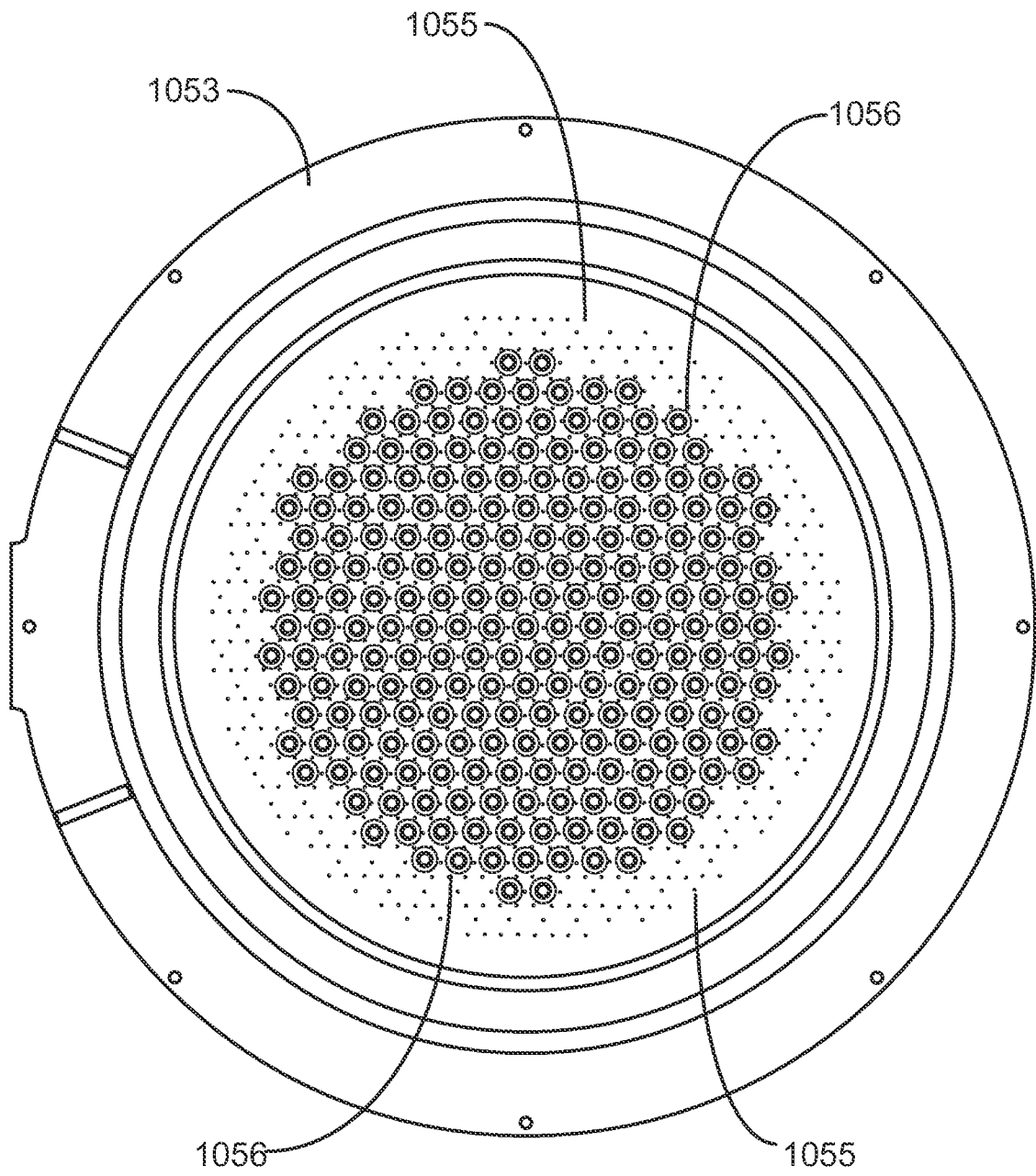
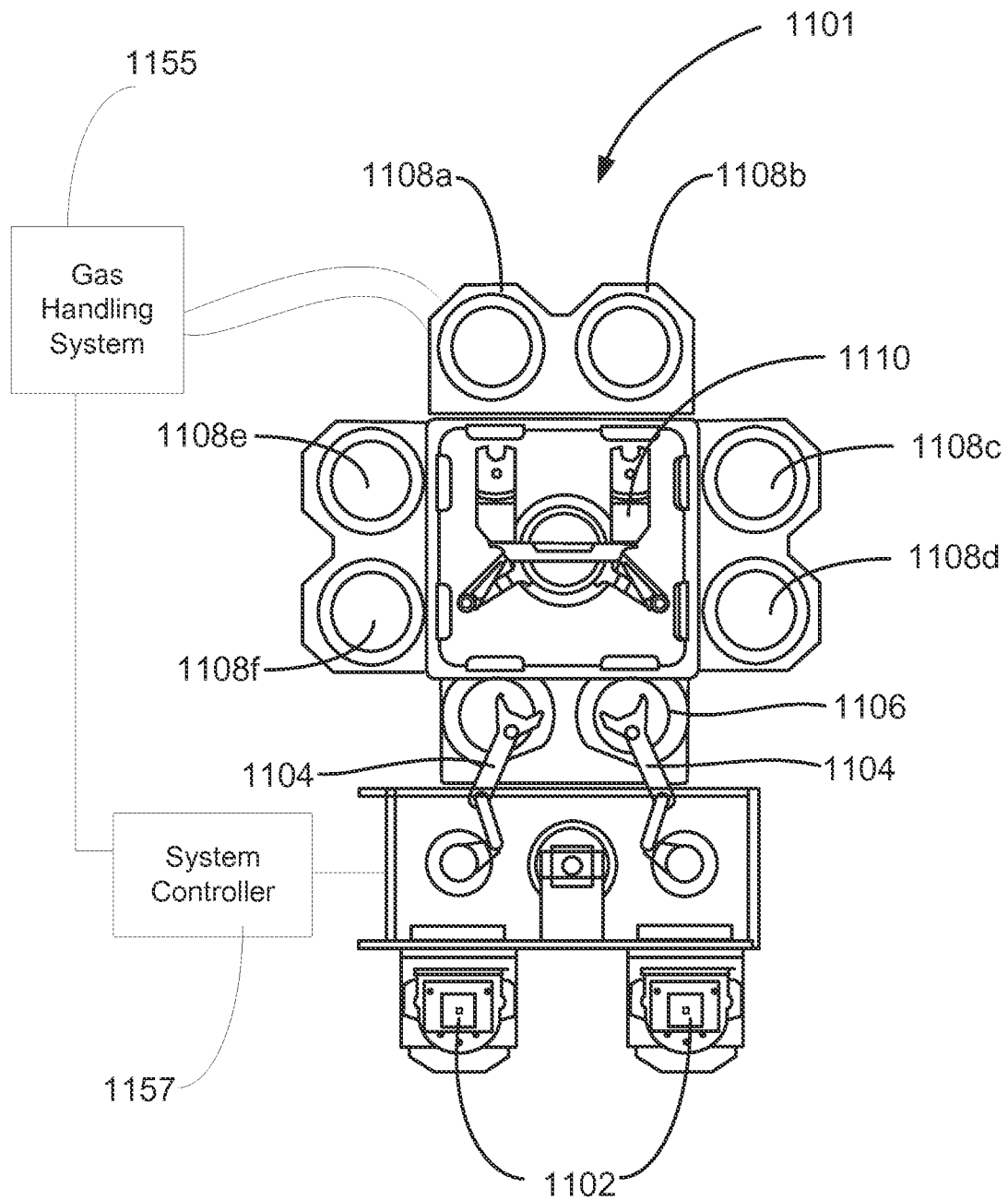


FIG. 2B

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**FIG. 3**

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 21/302; C23F 1/02

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: etch, remote plasma, silicon oxide, nitrogen-and-hydrogen-containing precursor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-2003-0054726 A (JUSUNG ENGINEERING CO., LTD.) 02 July 2003 See abstract; pages 2-3 and figure 2.	1-19
Y	US 2012-0211462 A1 (JINGCHUN ZHANG et al.) 23 August 2012 See abstract; paragraphs [0020]-[0047], claims 1-14 and figures 4A-4B.	1-19
A	KR 10-2011-0086540 A (IN SUK CHO) 28 July 2011 See abstract; paragraphs [0001], [0007]-[0014] and figure 1.	1-19
A	US 2001-0008803 A1 (TOSHI TAKAMATSU et al.) 19 July 2001 See abstract; paragraphs [0019]-[0059], [0078], [0081]-[0085] and figures 1-2.	1-19
A	US 2011-0294300 A1 (JINGCHUN ZHANG et al.) 01 December 2011 See abstract; paragraphs [0018]-[0025], [0030]-[0051] and figures 1-2B, 4, 7.	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

24 December 2013 (24.12.2013)

Date of mailing of the international search report

27 December 2013 (27.12.2013)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/056636

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US 2001-0008803 A1	19/07/2001	US 6551939 B2	22/04/2003
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