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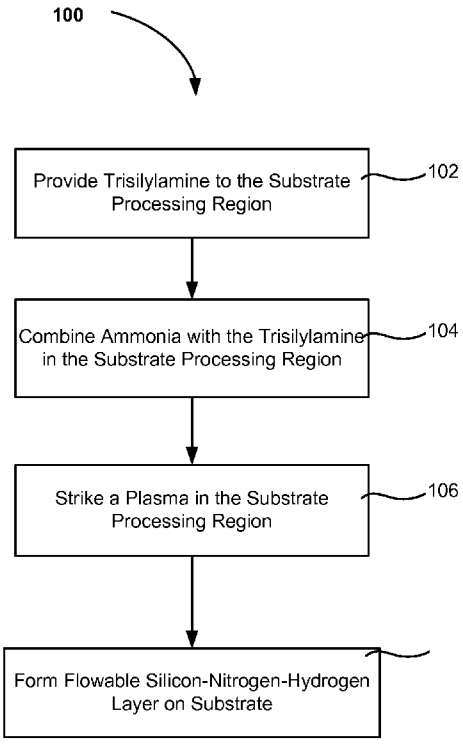

FIG. 1

(57) Abstract: A method of forming a dielectric layer is described. The method deposits a silicon- -containing film by chemical vapor deposition using a local plasma. The silicon-containing film is flowable during deposition at low substrate temperature. A silicon precursor (e.g. a silylamine, higher order silane or halogenated silane) is delivered to the substrate processing region and excited in a local plasma. A second plasma vapor or gas is combined with the silicon precursor in the substrate processing region and may include ammonia, nitrogen (N2), argon, hydrogen (H2) and/or oxygen (O2). The equipment configurations disclosed herein in combination with these vapor/gas combinations have been found to result in flowable deposition at substrate temperatures below or about 200C when a local plasma is excited using relatively low power.

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LOW COST FLOWABLE DIELECTRIC FILMS

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 61/699,495 by Chatterjee et al, filed September 11, 2012 and titled "LOW COST FLOWABLE DIELECTRIC FILMS" which is incorporated herein in its entirety for all purposes.

BACKGROUND OF THE INVENTION

[0002] Semiconductor device geometries have dramatically decreased in size since their introduction several decades ago. Modern semiconductor fabrication equipment routinely produce devices with 45 nm, 32 nm, and 28 nm feature sizes, and new equipment is being developed and implemented to make devices with even smaller geometries. The decreasing feature sizes result in structural features on the device having decreased spatial dimensions. The widths of gaps and trenches on the device have narrowed to a point where the aspect ratio of gap depth to its width becomes high enough to make it challenging to fill the gap with dielectric material. The depositing dielectric material is prone to clog at the top before the gap completely fills, producing a void or seam in the middle of the gap.

[0003] Over the years, many techniques have been developed to avoid having dielectric material clog the top of a gap, or to "heal" the void or seam that has been formed. One approach has been to start with highly flowable precursor materials that may be applied in a liquid phase to a spinning substrate surface (e.g., SOG deposition techniques). These flowable precursors can flow into and fill very small substrate gaps without forming voids or weak seams. However, once these highly flowable materials are deposited, they have to be hardened into a solid dielectric material.

[0004] In many instances, the hardening includes a heat treatment to remove carbon and hydroxyl groups from the deposited material to leave behind a solid dielectric such as silicon oxide. Unfortunately, the departing carbon and hydroxyl species often leave behind pores in the hardened dielectric that reduce the quality of the final material. In addition, the hardening dielectric also tends to shrink in volume, which can leave cracks and spaces at the interface of the dielectric and the surrounding substrate. In some instances, the volume of the hardened dielectric can decrease by 40% or more.

[0005] Spin-on dielectrics (SOD) have also been used to flow into features on a patterned substrate. The material is generally converted to silicon oxide from a silazane-type film which

contains silicon, nitrogen and hydrogen. Applying dielectric layers as a liquid results in very thick layers and makes it difficult to fill small gaps.

[0006] Thus, there is a need for new deposition processes and materials to form dielectric materials on structured substrates using vapor deposition techniques. This and other needs are addressed in the present application.

BRIEF SUMMARY OF THE INVENTION

[0007] A method of forming a dielectric layer is described. The method deposits a silicon- -containing film by chemical vapor deposition using a local plasma. The silicon-containing film is flowable during deposition at low substrate temperature. A silicon precursor (e.g. a silylamine, higher order silane or halogenated silane) is delivered to the substrate processing region and excited in a local plasma. A second plasma vapor or gas is combined with the silicon precursor in the substrate processing region and may include ammonia, nitrogen (N_2), argon, hydrogen (H_2) and/or oxygen (O_2). The equipment configurations disclosed herein in combination with these vapor/gas combinations have been found to result in flowable deposition at substrate temperatures below or about 200°C when a local plasma is excited using relatively low power. The process produces transient species which result in a flowable film during deposition before the film solidifies to fill gaps in a patterned substrate.

[0008] Embodiments of the invention include methods of forming a dielectric layer on a patterned substrate. The methods include flowing a silicon precursor into the substrate processing region. The methods further include flowing a plasma vapor/gas into a substrate processing region. The methods further include striking a plasma in the substrate processing region by applying a plasma power density less than or about 0.3 W/cm^2. The methods further include forming the dielectric layer on the patterned substrate. The dielectric layer includes silicon and one of carbon or nitrogen. The dielectric layer is flowable during deposition.

[0009] 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 invention. The features and advantages of the invention may be realized and attained by means of the instrumentalities, combinations, and methods described in the specification.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] A further understanding of the nature and advantages of the present invention may be realized by reference to the remaining portions of the specification and the drawings wherein like

reference numerals are used throughout the several drawings to refer to similar components. In some instances, a sublabel is associated with a reference numeral and follows a hyphen to denote one of multiple similar components. When reference is made to a reference numeral without specification to an existing sublabel, it is intended to refer to all such multiple similar components.

[0011] FIG. 1 is a flowchart illustrating selected steps for making a silicon oxide film according to embodiments of the invention.

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

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

[0014] FIG. 3B shows a gas distribution showerhead according to embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0015] A method of forming a dielectric layer is described. The method deposits a silicon- -containing film by chemical vapor deposition using a local plasma. The silicon-containing film is flowable during deposition at low substrate temperature. A silicon precursor (e.g. a silylamine, higher order silane or halogenated silane) is delivered to the substrate processing region and excited in a local plasma. A second plasma vapor or gas is combined with the silicon precursor in the substrate processing region and may include ammonia, nitrogen (N_2), argon, hydrogen (H_2) and/or oxygen (O_2). The equipment configurations disclosed herein in combination with these vapor/gas combinations have been found to result in flowable deposition at substrate temperatures below or about 200°C when a local plasma is excited using relatively low power. The process produces transient species which result in a flowable film during deposition before the film solidifies to fill gaps in a patterned substrate.

[0016] Performing plasma chemical vapor deposition or plasma-enhanced chemical vapor deposition (PECVD) involves applying a "local" plasma within a substrate processing region to effect the deposition. Flowing a silicon precursor (e.g. a silylamine such as TSA) along with a plasma vapor/gas disclosed herein was found by the inventors to produce a dielectric layer including silicon, nitrogen, hydrogen. The film has been found to flow during deposition, which facilitates the filling of gaps common on patterned substrates used during semiconductor processing. Additional details about the methods and systems of forming the silicon oxide layer will now be described.

Exemplary Silicon Oxide Formation Process

[0017] FIG. 1 is a flowchart showing selected steps in a method 100 of making dielectric films according to embodiments of the invention. The exemplary method 100 includes providing trisilylamine to a substrate processing region 102. The method further includes flowing ammonia into the substrate processing region 104. The trisilylamine and the ammonia may be flowed concurrently into the substrate processing region and may not have been excited by a plasma prior to entry, in embodiments of the invention. Plasma excitation is provided by applying radio-frequency power to capacitive plates on either side of the substrate processing region 106. For example, the capacitive plates may be positioned above and below the substrate processing region. The plasma excitation of the combination of ammonia and the trisilylamine results in formation of a flowable dielectric layer (comprising silicon, nitrogen, hydrogen) on a patterned substrate surface.

[0018] Generally speaking, the trisilylamine may be referred to herein as a silicon precursor which contains a silylamine, but the silicon precursor may also contain carbon. The silicon precursor may contain one of trisilylamine, disilylamine or monosilylamine. The silicon precursor is delivered in the form in the gas phase in the form of a gas or vapor carried by a carrier gas. As will be discussed in detail shortly, an absence of carbon reduces the shrinkage of the deposited film. However, the silicon precursor and the dielectric film contain carbon in disclosed embodiments. Silicon carbide and silicon carbon nitride are desirable in some process flows and lie within the definition of flowable dielectric layers deposited using methods disclosed herein. That being said, the silicon precursor may be oxygen-free and carbon-free in disclosed embodiments. The lack of oxygen results in a lower or negligible concentration of silanol (Si-OH) groups in the flowable dielectric layer formed from the precursors. Excess silanol moieties in the deposited film can cause increased porosity and shrinkage during post deposition steps that remove the hydroxyl (-OH) moieties from the deposited layer.

[0019] Specific examples of silicon precursors may include silylamines such as $H_2N(SiH_3)$, $HN(SiH_3)_2$, and $N(SiH_3)_3$. The silicon precursor may also be a higher order silane, herein defined as Si_nH_{2n+2}, where n>=3. Silicon precursors may also be halogenated silanes and may be chlorinated silanes in embodiments of the invention. Halogenated silanes are defined herein as Si_nH_{2n+2}, where n>=1 or n>=2 in disclosed embodiments, where at least one of the hydrogen atomis is removed and replaced with a halogen. The silicon precursor is, for example, hexachlorodisilane Si_2Cl_6) in disclosed embodiments. The flow rates of a silicon precursor may be greater than or about 40 sccm, greater than or about 60 sccm or greater than or about 100 sccm

in different embodiments. All flow rates given herein refer to a dual chamber substrate processing system. Single wafer systems would require half these flow rates and other wafer sizes would require flow rates scaled by the processed area. The silicon precursor may be mixed with additional gases that may act as carrier gases, reactive gases, or both.

[0020] A plasma vapor/gas is combined with the silicon precursor and flowed into the substrate processing region or flowed separately into the substrate processing region where the combination of the silicon precursor and the plasma vapor/gas are excited in a plasma. Exemplary plasma vapor/gases include ammonia, H_2, N_2, O_2, H_2O, O_3, H_2O_2, N_2O, NO, He, and Ar, among other gases. The plasma vapor/gas may contain carbon in order to form silicon carbide and SiCN films, in which case the plasma vapor/gas may include methane, ethane, propane, butane, acetylene, or other hydrocarbon. The flow rate of the plasma vapor/gas may be greater than or about 25 sccm, greater than or about 40 sccm or greater than or about 50 sccm in disclosed embodiments. Sources of oxygen may not be included, in embodiments, to increase flowability.

[0021] As described in the example, the plasma may be ignited using a capacitively coupled plasma (CCP) configuration using radio frequencies near 13.56 MHz. However, other frequencies and excitation sources may be used such as higher and/or lower radio frequencies (e.g. 2.4 GHz in the microwave region or 350 kHz). An inductively coupled plasma (ICP) may be used in combination or in place of the CCP. The plasma power is relatively low to cause the formation of flow-inducing chemical transients in the forming film. For a 300 mm substrate, the power may be in the 10-350 W range. The power density may be less than or about 0.3 W per square centimeter, less than or about 0.25 W per square centimeter, less than or about 0.2 W per square centimeter or less than or about 0.15 W per square centimeter of patterned substrate area in embodiments of the invention. The power may be on continuously rather than pulsed in disclosed embodiments while during formation of the dielectric layer. In disclosed embodiments, striking the plasma means applying 0.025 W to 0.30 W (per square centimeter of patterned surface area) of plasma power to the substrate processing region. Patterned surface area is calculated as the area on a single plane passing through the patterned features (generally on the top surface of a substrate). The plasma excitation may also be effected by shining ultraviolet (UV) light into the substrate processing region.

[0022] Flowing the silicon precursor comprises supplying a continuous flow of the silicon precursor to the substrate processing region throughout formation of the flowable dielectric layer. Similarly, striking the plasma comprises applying a plasma power continuously throughout formation of the flowable dielectric layer. It has been found that pulsing either (and, of course,

both) the silicon precursor flow or the plasma power results in a conformal film instead of the desirably flowable dielectric films described herein. The flow of plasma vapor/gas is also continuous throughout formation of the flowable dielectric layer, in embodiments of the invention.

[0023] In the substrate processing region, the silicon precursor and the plasma vapor/gas mix and react in the plasma to deposit the flowable dielectric film on the deposition substrate. The flowable dielectric film contains silicon, nitrogen, and hydrogen and may consist only of these elements in embodiments of the invention. The deposited dielectric film has flowable characteristics unlike conventional silicon nitride (Si_3N_4) film deposition techniques. The flowable nature during formation allows the film to flow into narrow features before solidifying. Nitrogen in the silicon-nitrogen-and-hydrogen-containing film may originate from both the plasma vapor/gas and the silicon precursor since both the silicon precursor and the nitrogen trifluoride can contain nitrogen.

[0024] The flowability of a silicon-containing film may be due to a variety of properties which result from mixing plasma vapor/gases with silicon precursor outlined herein in the presence of a low intensity local plasma as described above. These properties may include a presence of short chained polysilazane polymers which may have hydrogen and/or halogen termination. These short chains grow and network to form more dense dielectric material during and after the formation of the film. For example the deposited film may have a silazane-type, Si-NH-Si backbone (i.e., a carbon-free Si-N-H film).

[0025] In some embodiments, all precursors supplied to the plasma in the substrate processing region are carbon-free and therefore the deposited silicon-nitrogen-fluorine-and-hydrogen-containing film is also substantially carbon-free. Of course, "carbon-free" does not necessarily mean the film lacks even trace amounts of carbon. Carbon contaminants may be present in the precursor materials that find their way into the deposited silicon-and-nitrogen-containing precursor. The amount of these carbon impurities however are much less than would be found in a silicon precursor having a carbon moiety (e.g., TEOS, TMDSO, etc.).

[0026] The silicon precursor and plasma vapor/gas may also be selected to form silicon carbide or silicon carbon nitride (SiCN) rather than the aforementioned silicon nitride. In all cases, the silicon nitride, silicon carbide or SiCN may contain some hydrogen which may assist in the flowability of the film. The flowable dielectric film consists of silicon, carbon and hydrogen in disclosed embodiments. The flowable dielectric film may also consist of silicon and carbon. The flowable dielectric film consists of silicon, nitrogen and hydrogen in disclosed embodiments. The flowable dielectric film may also consist of silicon and nitrogen. The flowable dielectric film

consists of silicon, carbon, nitrogen and hydrogen in disclosed embodiments. The flowable dielectric film may also consist of silicon, carbon and nitrogen.

[0027] The temperature of the substrate during deposition of the flowable dielectric layer may be less than or about 200°C, less than or about 150°C, less than or about 125°C, less than or about 100°C, less than or about 75°C, less than or about 50°C, or less than or about 30°C in disclosed embodiments. For example, the substrate temperature may be less than 150°C while growing a silicon-nitrogen-hydride film from a silylamine and a plasma vapor/gas. For another example, the substrate temperature may be less than 80°C while growing a silicon-nitrogen-hydride film from a higher order silane and a plasma vapor/gas. Also in a disclosed embodiment, the substrate temperature may be less than 150°C while growing a silicon-nitrogen-hydride film from a halogenated silane of any order and a plasma vapor/gas.

[0028] The pressure in the substrate processing region during the deposition may be greater than or about 5 Torr, greater than or about 10 Torr, greater than or about 15 Torr or greater than or about 20 Torr in disclosed embodiments. The pressure in the substrate processing region during the deposition may be less than or about 50 Torr, less than or about 40 Torr or less than or about 30 Torr in disclosed embodiments. Upper limits may be combined with lower limits to arrive at additional pressure ranges according to embodiments of the invention. The deposition rate of the flowable dielectric film may be greater than or about 400Å/min, greater than or about 500Å/min, greater than or about 600Å/min or greater than or about 700Å/min in disclosed embodiments. The thickness of the deposited dielectric layer after solidification may be much less than is possible using bulk spin-on techniques (SOG, SOD). The thickness may be less than or about 25 nm, less than or about 20 nm, less than or about 15 nm or less than or about 10 nm in disclosed embodiments. These thicknesses are measured perpendicular to the major plane of the patterned substrate and after the flowable characteristics of the deposited film have abated.

[0029] Optional steps are now described and help to cure the film (to remove some components which made the nascent film flowable but are no longer needed). Following the deposition of the flowable dielectric film, the deposition substrate may treated at an elevated temperature to remove volatile species. The deposition substrate may remain in the substrate processing region for curing, or the substrate may be transferred to a different chamber where the heat treatment is performed. The curing temperature of the substrate may be less than or about 600°C, less than or about 400°C, less than or about 300°C, less than or about 250°C, less than or about 200°C or less than or about 150°C in disclosed embodiments. The temperature of the substrate may be greater than or about room temperature (25°C), greater than or about 50°C, greater than or about 100°C,

greater than or about 150°C or greater than or about 200°C in embodiments of the invention. Any of the upper bounds may be combined with any of the lower bounds to form additional ranges for the substrate temperature according to additional disclosed embodiments.

[0030] As already discussed, the curing operation may occur in the deposition chamber or the substrate may be transferred to an ex-situ curing chamber. In either case, the deposition operation and the curing operation may be repeated to form dep-cure-dep-cure process sequences. A plasma treatment may be present in the substrate processing region during the curing operation and the plasma may be an inductively coupled plasma (ICP) or a capacitively coupled plasma (CCP). The plasma may be a high-density plasma (HDP) in disclosed embodiments. The plasma treatment may be effected by applying power at a frequency in the radio-frequency (RF) range (e.g. 13.56 MHz) or in the microwave frequency range (e.g. 2.4 GHz). The plasma may be formed from various plasma input gases such as NH_3, Ar, N_2, Cl_2, or He in embodiments of the invention.

[0031] The patterned substrate may have a plurality of gaps for the spacing and structure of device components (e.g., transistors) formed on the substrate. The gaps may have a height and width that define an aspect ratio (AR) of the height to the width (i.e., H/W) that is significantly greater than 1:1 (e.g., 5:1 or more, 6:1 or more, 7:1 or more, 8:1 or more, 9:1 or more, 10:1 or more, 11:1 or more, 12:1 or more, etc.). In many instances the high AR is due to small gap widths of that range from about 90 nm to about 22 nm or less (e.g., less than 90 nm, 65 nm, 50 nm, 45 nm, 32 nm, 22 nm, 16 nm, etc.). The flowable dielectric layer is desirable since it can fill the exemplary narrow gaps more easily than non-flowable films or bulk flowable films using spin-on techniques, such as spin-on glass (SOG) and spin-on dielectric (SOD). Depositing thin layers of flowable material reduces the likelihood of prematurely clogging the top of a gap before it is completely filled to leave a void in the middle of the gap. The dielectric layer may be solidified after the flowable deposition. Additional parameters parameters may be introduced during the description of an exemplary silicon oxide deposition system.

Exemplary Silicon Oxide Deposition System

[0032] Deposition chambers that may implement embodiments of the present invention may include high-density plasma chemical vapor deposition (HDP-CVD) chambers, plasma enhanced chemical vapor deposition (PECVD) chambers, sub-atmospheric chemical vapor deposition (SACVD) chambers, and thermal chemical vapor deposition chambers, among other types of chambers. Specific examples of CVD systems that may implement embodiments of the invention include the CENTURA ULTIMA® HDP-CVD chambers/systems, and PRODUCER® PECVD chambers/systems, available from Applied Materials, Inc. of Santa Clara, Calif.

[0033] 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, 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.

[0034] Embodiments of the deposition systems may be incorporated into larger fabrication systems for producing integrated circuit chips. FIG. 2 shows one such system 1001 of deposition, baking and curing chambers according to disclosed embodiments. In the figure, a pair of FOUPs (front opening unified pods) 1002 supply substrate substrates (e.g., 300 mm diameter wafers) that are received by robotic arms 1004 and placed into a low pressure holding area 1006 before being placed into one of the wafer processing chambers 1008a-f. A second robotic arm 210 may be used to transport the substrate wafers from the holding area 1006 to the processing chambers 1008a-f and back.

[0035] The processing chambers 1008a-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., 1008c-d and 1008e-f) may be used to deposit the flowable dielectric material on the substrate, and the third pair of processing chambers (e.g., 1008a-b) may be used to anneal the deposited dielectric. In another configuration, the same two pairs of processing chambers (e.g., 1008c-d and 1008e-f) may be configured to both deposit and anneal a flowable dielectric film on the substrate, while the third pair of chambers (e.g., 1008a-b) may be used for UV or E-beam curing of the deposited film. In still another configuration, all three pairs of chambers (e.g., 1008a-f) may be configured to deposit and cure a flowable dielectric film on the substrate. In yet another configuration, two pairs of processing chambers (e.g., 1008c-d and 1008e-f) may be used for both deposition and UV or E-beam curing of the flowable dielectric, while a third pair of processing chambers (e.g. 1008a-b) may be used for annealing the dielectric film. Any one or more of the processes described may be carried out on chamber(s) separated from the fabrication system shown in different embodiments.

[0036] In addition, one or more of the process chambers 1008a-f may be configured as a wet treatment chamber. These process chambers include heating the flowable dielectric film in an atmosphere that includes moisture. Thus, embodiments of system 1001 may include wet treatment chambers 1008a-b and anneal processing chambers 1008c-d to perform both wet and dry anneals on the deposited dielectric film.

[0037] FIG. 3A is a substrate processing chamber 1101 according to disclosed embodiments. A remote plasma system (RPS) 1110 may process a gas which then travels through a gas inlet assembly 1111. Two distinct gas supply channels are visible within the gas inlet assembly 1111. A first channel 1112 carries a gas that passes through the remote plasma system (RPS) 1110, while a second channel 1113 bypasses the RPS 1110. The first channel 1112 may be used for the process gas and the second channel 1113 may be used for a treatment gas in disclosed embodiments. The lid (or conductive top portion) 1121 and a perforated partition (showerhead 1153) are shown with an insulating ring 1124 in between, which allows an AC potential to be applied to the lid 1121 relative to showerhead 1153. The process gas travels through first channel 1112 into chamber plasma region 1120 and may be excited by a plasma in chamber plasma region 1120 alone or in combination with RPS 1110. The combination of chamber plasma region 1120 and/or RPS 1110 may be referred to as a remote plasma system herein. The perforated partition (also referred to as a showerhead) 1153 separates chamber plasma region 1120 from a substrate processing region 1170 beneath showerhead 1153. Showerhead 1153 allows a plasma present in chamber plasma region 1120 to avoid directly exciting gases in substrate processing region 1170, while still allowing excited species to travel from chamber plasma region 1120 into substrate processing region 1170.

[0038] Showerhead 1153 is positioned between chamber plasma region 1120 and substrate processing region 1170 and allows plasma effluents (excited derivatives of precursors or other gases) created within chamber plasma region 1120 to pass through a plurality of through-holes 1156 that traverse the thickness of the plate. The showerhead 1153 also has one or more hollow volumes 1151 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 1155 into substrate processing region 1170 but not directly into chamber plasma region 1120. Showerhead 1153 is thicker than the length of the smallest diameter 1150 of the through-holes 1156 in this disclosed embodiment. In order to maintain a significant concentration of excited species penetrating from chamber plasma region 1120 to substrate processing region 1170, the length 1126 of the smallest diameter 1150 of the through-holes may be restricted by forming larger diameter portions of through-holes 1156 part way through the showerhead 1153. The length of the smallest diameter 1150 of the through-holes 1156 may be the same order of magnitude as the smallest diameter of the through-holes 1156 or less in disclosed embodiments.

[0039] In the embodiment shown, showerhead 1153 may distribute (via through-holes 1156) process gases which contain a plasma vapor/gas such as ammonia and the silicon precursor. The precursors may not be excited in chamber plasma region 1120, in embodiments, since only a local

plasma is necessary. Note that any of the precursors may be supplied either via through-holes 1156 or via small holes 1155 into substrate processing region 1170 since this process involves excitation by a local plasma within substrate processing region 1170. The process gases enter substrate processing region 1170 where they are excited in a local plasma to form the flowable dielectric layer on the patterned substrate.

[0040] In embodiments, the number of through-holes 1156 may be between about 60 and about 2000. Through-holes 1156 may have a variety of shapes but are most easily made round. The smallest diameter 1150 of through-holes 1156 may be between about 0.5 mm and about 20 mm or between about 1 mm and about 6mm in disclosed embodiments. There is also latitude in choosing the cross-sectional shape of through-holes, which may be made conical, cylindrical or a combination of the two shapes. The number of small holes 1155 used to introduce a gas into substrate processing region 1170 may be between about 100 and about 5000 or between about 500 and about 2000 in different embodiments. The diameter of the small holes 1155 may be between about 0.1 mm and about 2 mm.

[0041] FIG. 3B is a bottom view of a showerhead 1153 for use with a processing chamber according to disclosed embodiments. Showerhead 1153 corresponds with the showerhead shown in FIG. 3A. Through-holes 1156 are depicted with a larger inner-diameter (ID) on the bottom of showerhead 1153 and a smaller ID at the top. Small holes 1155 are distributed substantially evenly over the surface of the showerhead, even amongst the through-holes 1156 which helps to provide more even mixing than other embodiments described herein.

[0042] An exemplary film is created on a substrate supported by a pedestal (not shown) within substrate processing region 1170 when plasma effluents arriving through through-holes 1156 in showerhead 1153 combine with a silicon-containing precursor arriving through the small holes 1155 originating from hollow volumes 1151. Though substrate processing region 1170 may be equipped to support a plasma for other processes such as curing, no plasma is present during the growth of the exemplary film.

[0043] A plasma may be ignited either in chamber plasma region 1120 above showerhead 1153 or substrate processing region 1170 below showerhead 1153. A plasma is present in chamber plasma region 1120 to produce the radical nitrogen precursor from an inflow of a nitrogen-and-hydrogen-containing gas. An AC voltage typically in the radio frequency (RF) range is applied between the conductive top portion (lid 1121) of the processing chamber and showerhead 1153 to ignite a plasma in chamber plasma region 1120 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.

[0044] The top plasma may be left at low or no power when the bottom plasma in the substrate processing region 1170 is turned on during the formation of the dielectric layer or while cleaning the interior surfaces bordering substrate processing region 1170. A plasma in substrate processing region 1170 is ignited by applying an AC voltage between showerhead 1153 and the pedestal or bottom of the chamber. A cleaning gas may be introduced into substrate processing region 1170 while the plasma is present.

[0045] 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.

[0046] 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.

[0047] The system controller controls all of the activities of the deposition system. 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.

[0048] A process for depositing a film stack on a substrate, converting a film to silicon oxide 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 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 computer system to load the code in memory. The CPU then reads and executes the code to perform the tasks identified in the program.

[0049] 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 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, may be used instead of or in addition to the touch-sensitive monitor to allow the user to communicate with the system controller.

[0050] As used herein "substrate" may be a support substrate with or without layers formed thereon. The support 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. A layer of "silicon oxide" may include minority concentrations of other elemental constituents such as nitrogen, hydrogen, carbon and the like. In some embodiments, silicon oxide consists 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. A gas in an "excited state" describes a gas wherein at least some of the gas molecules are in vibrationally-excited, dissociated and/or ionized states. A gas (or precursor) may be a combination of two or more gases (or precursors). 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-nitrogen precursor" is a radical precursor which contains nitrogen and a "radical-hydrogen precursor" is a radical precursor which contains hydrogen. 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.

[0051] The term "trench" is 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. The term "via" is used to refer to a low aspect ratio trench which may or may not be filled with metal to form a vertical electrical connection. As used herein, a conformal layer refers to a generally uniform layer of material on a surface in the same shape as the surface, i.e., the surface of the layer and the surface being covered are generally parallel. A person having ordinary skill in the art will recognize that the deposited material likely cannot be 100% conformal and thus the term "generally" allows for acceptable tolerances.

[0052] Having described 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 invention. 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.

[0053] 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.

[0054] 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 precursor" includes

reference to one or more precursor and equivalents thereof known to those skilled in the art, and so forth.

[0055] 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 forming a dielectric layer on a patterned substrate, the method comprising:

Transferring the patterned substrate into a substrate processing region;

flowing a silicon precursor into the substrate processing region;

flowing a plasma vapor/gas into the substrate processing region, wherein flowing the plasma vapor/gas and flowing the silicon precursor occur concurrently;

striking a plasma in the substrate processing region by applying a plasma power less than or about 0.3 W per square centimeter of patterned substrate area; and

forming the dielectric layer on the patterned substrate, wherein the dielectric layer comprises silicon and one of nitrogen or carbon and the dielectric layer is flowable during deposition,

wherein flowing the silicon precursor comprises supplying a continuous flow of the silicon precursor to the substrate processing region throughout formation of the flowable dielectric layer, and wherein striking a plasma comprises applying a plasma power continuously throughout formation of the flowable dielectric layer.

2. The method of claim 1 wherein a temperature of the patterned substrate is less than 200°C while forming the flowable dielectric layer.

3. The method of claim 1 wherein the plasma vapor/gas comprises one of ammonia, hydrogen (H_2), argon, nitrogen (N_2), a hydrocarbon or oxygen (O_2).

4. The method of claim 1 wherein the silicon precursor is one of trisilylamine, disilylamine or monosilylamine.

5. The method of claim 1 wherein the silicon precursor comprises a higher order silane containing three or more silicon atoms.

6. The method of claim 1 wherein the silicon precursor comprises a halogen-substituted silane.

7. The method of claim 6 wherein the halogen-substituted silane is hexachlorodisilane.

8. The method of claim 1 wherein the dielectric layer is one of silicon carbide, silicon nitride or SiCN.

9. The method of claim 1 wherein the dielectric layer consists of silicon, nitrogen, and hydrogen.

10. The method of claim 1 wherein the dielectric layer consists of silicon, carbon, nitrogen, and hydrogen.

11. The method of claim 1 wherein striking the plasma comprises applying radio frequencies (RF) to the substrate processing region by either capacitive or inductive means.

12. The method of claim 1 wherein striking the plasma comprises shining ultraviolet (UV) light into the substrate processing region.

13. The method of claim 1 wherein striking the plasma comprises applying 0.025 W to 0.30 W (per square centimeter of patterned surface area) of plasma power to the substrate processing region.

14. The method of claim 1 wherein striking the plasma comprises applying plasma power continuously throughout while forming the dielectric layer.

15. The method of claim 1 wherein the substrate is patterned and has a trench having a width of about 50 nm or less.

16. The method of claim 1 further comprising solidifying the dielectric layer after the operation of forming the dielectric layer.

17. The method of claim 16 wherein a thickness of the dielectric layer after solidification is about 25 nm or less perpendicular to the major plane of the patterned substrate.

18. The method of claim 1 wherein the silicon precursor, the plasma vapor/gas and the dielectric layer are each carbon-free.

19. The method of claim 1 wherein a temperature of the patterned substrate is less than 100°C while forming the flowable dielectric layer.

20. The method of claim 1 wherein a temperature of the patterned substrate is less than 30°C while forming the flowable dielectric layer.

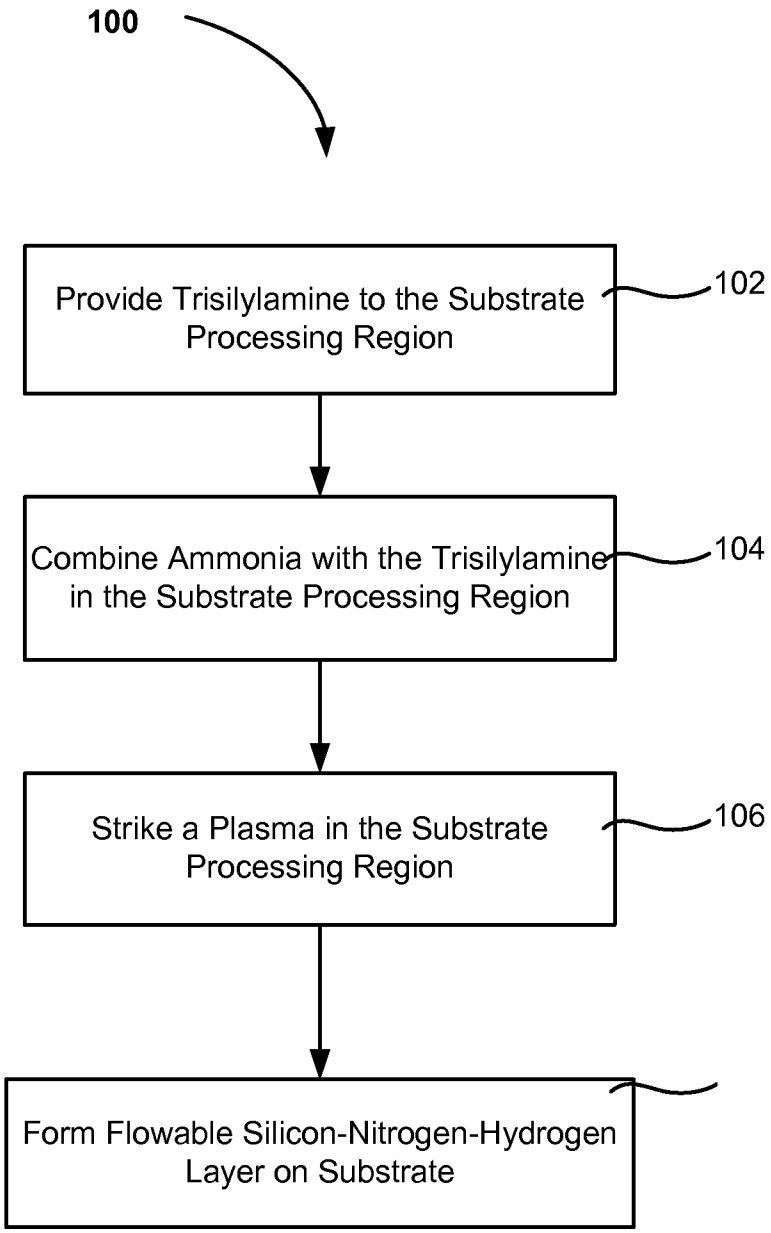
100
Provide Trisilylamine to the Substrate Processing Region
102
Combine Ammonia with the Trisilylamine in the Substrate Processing Region
104
Strike a Plasma in the Substrate Processing Region
106
Form Flowable Silicon-Nitrogen-Hydrogen Layer on Substrate

FIG. 1

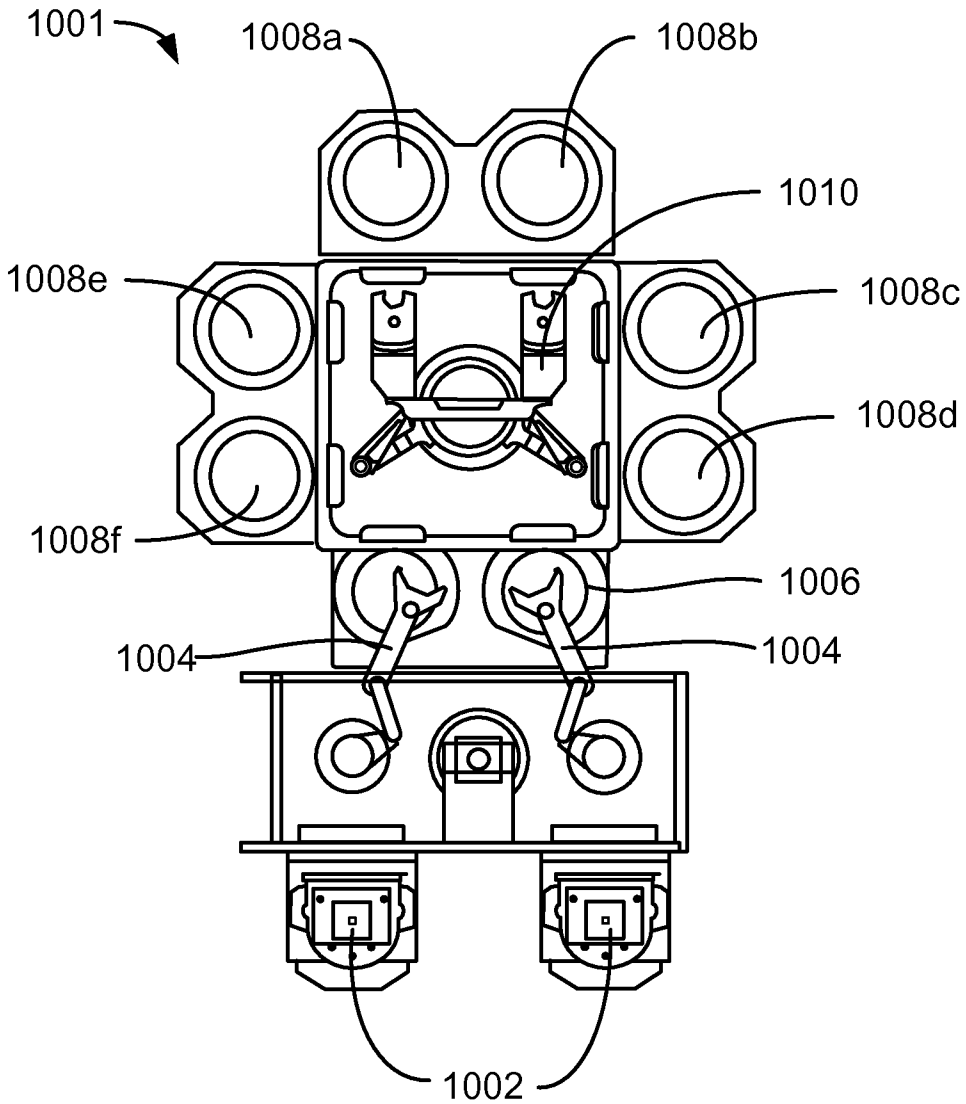
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FIG. 2

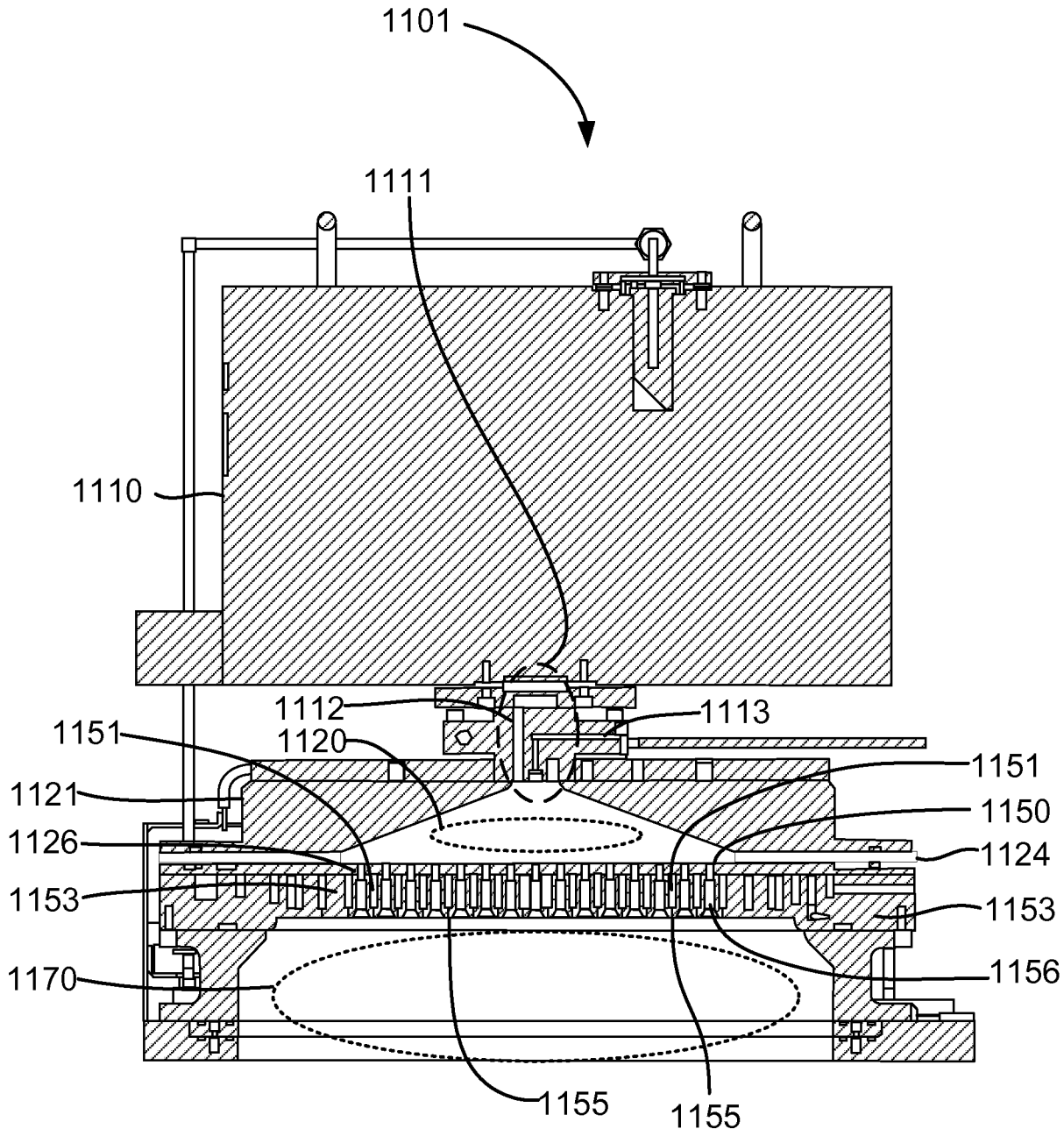
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FIG. 3A

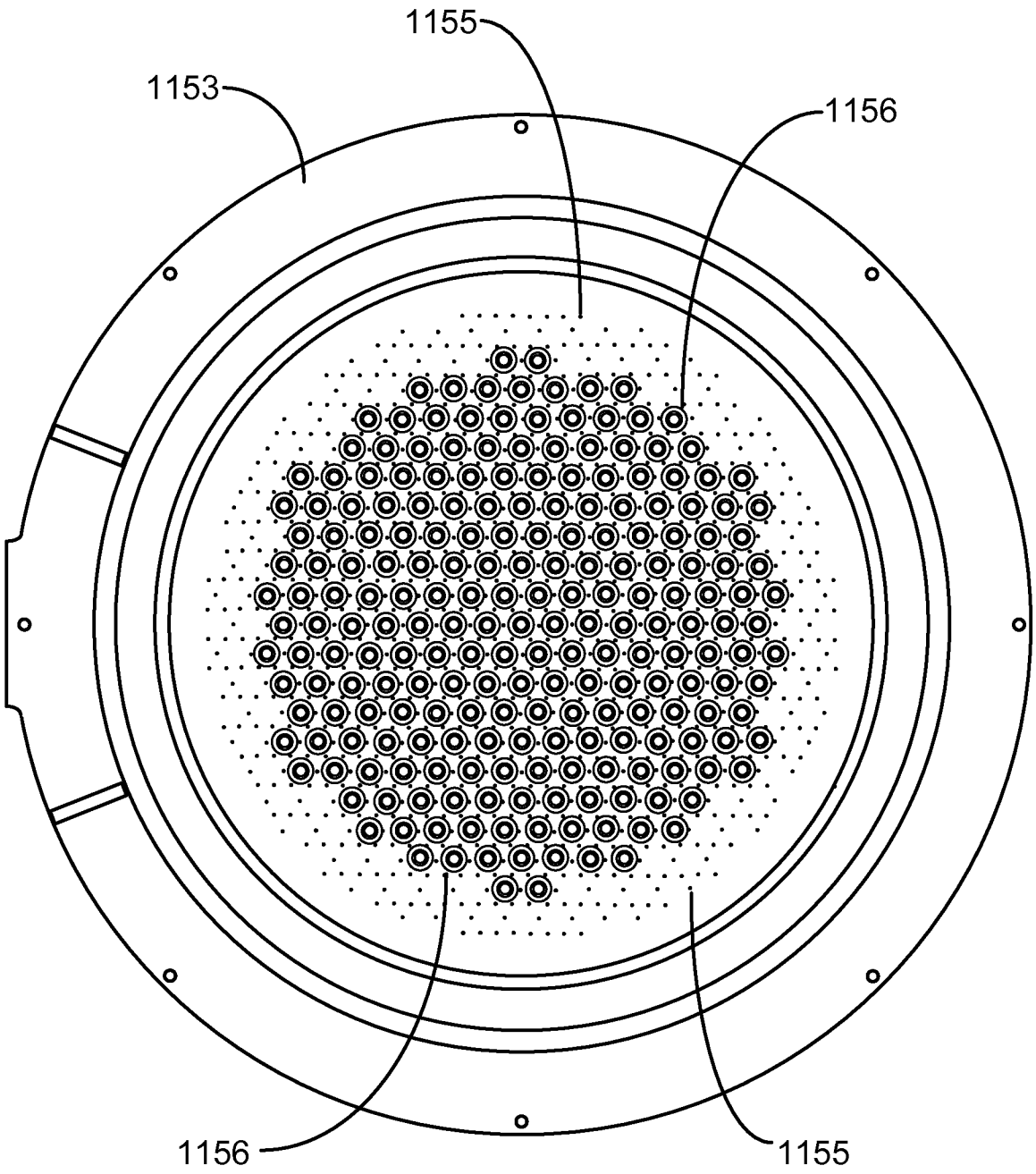

FIG. 3B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/055802

A. CLASSIFICATION OF SUBJECT MATTER

H01L 21/205(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 21/205; H01L 21/4757; B05C 11/00; H01L 21/762; H01L 21/316; H01L 21/31; H01L 21/76

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: silicon, precursor, plasma, vapor, dielectric, gap, fill and flowable

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2012-0142192 A1 (DONGQING LI et al.) 07 June 2012 See abstract, paragraphs [0017]-[0033], claims 1-15 and figures 1-3B.	1-20
A	US 7888233 B1 (VISHAL GAURI et al.) 15 February 2011 See abstract, column 4, line 15 - column 12, line 35, claims 1-20 and figures 2-6.	1-20
A	US 2012-0009802 A1 (ADRIEN LAVOIE et al.) 12 January 2012 See abstract, paragraphs [0094]-[0114], [0158]-[0164] and figures 1-4, 10-13.	1-20
A	US 2007-0111470 A1 (JOHN A. SMYTHE III et al.) 17 May 2007 See abstract, paragraphs [0028]-[0064] and figures 1-8.	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 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
27 November 2013 (27.11.2013)	**28 November 2013 (28.11.2013)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/055802

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PCT/US2013/055802

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