FORMATION OF SILICON OXIDE USING NON-CARBON FLOWABLE CVD PROCESSES

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Pat. App. No. 12/840,768 filed July 21, 2010, and titled "FORMATION OF SILICON OXIDE USING NON-CARBON FLOWABLE CVD PROCESSES," and U.S. Prov. Pat. App. No. 61/231,729 filed August 6, 2009, and titled "FORMATION OF SILICON OXIDE USING NON-CARBON FLOWABLE CVD PROCESSES," which are incorporated herein by reference 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 produces 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 narrow 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 process 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 dielectic 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] Thus, there is a need for new deposition processes and materials to form dielectric materials on structured substrates without generating voids, seams, or both, in substrate gaps and trenches. There is also a need for materials and methods of hardening flowable dielectric materials with fewer pores and a lower decrease in volume. This and other needs are addressed in the present application.

BRIEF SUMMARY OF THE INVENTION

[0006] Methods, materials, and systems are described for forming silicon oxide layers from flowable materials with fewer pores and less shrinkage than produced by conventional SOG techniques. The methods may include the deposition of a silicon-and-nitrogen containing film (e.g., a silicon-nitrogen-hydrogen (Si-N-H) film) from a carbon-free silicon-and-nitrogen precursor and radical precursor. Because the silicon-and-nitrogen film is formed without carbon, the conversion of the film into hardened silicon oxide is done with less pore formation and less volume shrinkage.

[0007] The conversion of the silicon-and-nitrogen film to silicon oxide may be done by heating the silicon-and-nitrogen film in an oxygen-containing atmosphere. The oxygen-containing gases in this atmosphere may include radical atomic oxygen (O), molecular oxygen (O_2), ozone (O_3), and/or steam (H_2O), among other oxygen-containing gases. The heating temperatures, times, and pressures are sufficient to oxidize the silicon-and-nitrogen film into the silicon oxide film.

[0008] Embodiments of the invention include methods of forming a silicon oxide layer. The methods may include the steps of mixing a carbon-free silicon-and-nitrogen containing precursor with a radical precursor, and depositing a silicon-and-nitrogen containing layer on a substrate. The silicon-and-nitrogen containing layer is then converted to the silicon oxide layer through subsequent curing and/or annealing steps.

[0009] Embodiments of the invention may further include methods of forming a silicon oxide layer with reduced volume shrinkage. The methods may include providing a substrate containing a least one gap, and depositing a carbon-free silicon-and-nitrogen containing layer on the substrate. The substrate may be heated in an oxygen-containing atmosphere to convert the carbon-free silicon-and-nitrogen containing layer to the silicon oxide layer. The silicon oxide layer can retain a volume of about 85% or more of the carbon-free silicon-and-nitrogen containing layer deposited in the gap.

[0010] Embodiments of the invention still further include plasma chemical vapor deposition methods of forming a silicon oxide layer. The methods may include the steps of introducing a carbon-free silicon-and-nitrogen containing precursor, and a radical precursor to a reaction chamber containing a substrate. A plasma may be formed from a mixture comprising the carbon-free silicon-and-nitrogen containing precursor and the radical precursor. A silicon-and-nitrogen containing layer may be deposited on the substrate from the plasma, and the silicon-and-nitrogen containing layer may be converted into the silicon oxide layer.

[0011] 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

[0012] 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.

[0013] FIG. 1 is a flowchart illustrating selected steps for making a silicon oxide film according to embodiments of the invention.

[0014] FIG. 2 is another flowchart illustrating selected steps for forming a silicon oxide film in a substrate gap according to embodiments of the invention.

[0015] FIG. 3 is another flowchart illustrating selected steps in a plasma chemical vapor deposition method of making a silicon oxide film according to embodiments of the invention.

[0016] FIG. 4 shows a substrate processing system according to embodiments of the invention.

[0017] FIG. 5A shows a substrate processing chamber according to embodiments of the invention.

[0018] FIG. 5B shows a showerhead of a substrate processing chamber according to embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0019] The formation of a silicon oxide layer with reduced porosity and shrinkage from a flowable silicon-and-nitrogen containing layer is described. The flowable silicon-and-nitrogen containing layer may be formed substantially free of carbon from precursors that lack carbon-containing moieties. When the substantially carbon free silicon-and-nitrogen containing layer is converted to a silicon oxide layer, the absence of carbon in the layer results is less pore formation and shrinkage of the oxide layer compared to the starting silicon-and-nitrogen containing layer. Additional details about the methods and systems of forming the silicon oxide layer will now be described.

Exemplary Silicon Oxide Formation Process

[0020] FIG. 1 is a flowchart showing selected steps in methods 100 of making silicon oxide films according to embodiments of the invention. The method 100 includes providing a carbon-free silicon precursor to a reaction chamber 102. The carbon-free silicon precursor may be, for example, a silicon-and-nitrogen precursor, a silicon-and-hydrogen precursor, or a silicon-nitrogen-and-hydrogen containing precursor, among other classes of silicon precursors. Specific examples of these precursors may include silyl-amines such as $H_2N(SiH_3)$, $HN(SiH_3)_2$, and $N(SiH_3)_3$, among other silyl-amines. These silyl-amines may be mixed with additional gases that may act as carrier gases, reactive gases, or both. Examples of additional gases may include H_2, N_2, NH_3, He, and Ar, among other gases. Examples of carbon-free silicon precursors may also include silane (SiH_4) either alone or mixed with other silicon-containing gases (e.g., $N(SiH_3)_3$),

hydrogen-containing gases (e.g., H_2), and/or nitrogen-containing gases (e.g., N_2, NH_3). Carbon-free silicon precursors may also include disilane, trisilane, higher-order silanes, and chlorinated silanes, alone or in combination with one another or the previously mentioned carbon-free silicon precursors.

[0021] The silicon-precursor may be oxygen-free in addition to carbon-free. The lack of oxygen results in a lower concentration of silanol (Si-OH) groups in the silicon-and-nitrogen 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.

[0022] A radical-nitrogen precursor is also provided to the reaction chamber 104. The radical-nitrogen precursor is a nitrogen-radical containing species that was generated outside the reaction chamber from a more stable nitrogen precursor. For example, a relatively stable nitrogen precursor such a NH_3 and/or hydrazine (N_2H_4) may be activated in a plasma unit outside the reaction chamber to form the radical-nitrogen precursor, which is then transported into the reaction chamber. The stable nitrogen precursor may also be a mixture comprising NH_3 & N_2, NH_3 & H_2, NH_3 & N_2 & H_2 and N_2 & H_2, in different embodiments. Hydrazine may also be used in place of or in combination with NH_3 in the mixtures with N_2 and H_2. The radical-nitrogen precursor produced may be one or more of $\cdot N$, $\cdot NH$, $\cdot NH_2$, etc., and may also be accompanied by ionized species formed in the plasma.

[0023] Generally speaking, a radical precursor which does not include nitrogen will also allow a silicon-and-nitrogen-containing layer to be formed. A radical precursor may be a radical-nitrogen precursor if it includes nitrogen supplied with the aforementioned precursors to the remote plasma region. The radical precursor is generated in a section of the reaction chamber partitioned from a deposition region where the precursors mix and react to deposit the silicon-and-nitrogen layer on a deposition substrate (e.g., a semiconductor wafer). In an embodiment where the radical precursor is a radical-nitrogen precursor, a stable nitrogen precursor is flowed into the remote plasma region and excited by a plasma. The stable nitrogen precursor (and the radical-nitrogen precursor) may also be accompanied by a carrier gas such as hydrogen (H_2), nitrogen (N_2), argon, helium, etc. A radical-nitrogen precursor formed from an input gas consisting essentially of nitrogen (N_2) (with or without additional inert carrier gases) has also been found to produce beneficial films in disclosed embodiments. The radical-nitrogen

precursor may also be replaced by a radical precursor formed from an input gas consisting essentially of hydrogen (H_2) (and optionally inert carrier gases) in embodiments where the silicon-containing precursor comprises nitrogen.

[0024] In the reaction chamber, the carbon-free silicon precursor and the radical-nitrogen precursor mix and react to deposit a silicon-and-nitrogen containing film on the deposition substrate 106. The deposited silicon-and-nitrogen-containing film may deposit conformally with some recipe combinations in embodiments. In other embodiments, the deposited silicon-and-nitrogen containing film has flowable characteristics unlike conventional silicon nitride (Si_3N_4) film deposition techniques. The flowable nature of the formation allows the film to flow into narrow gaps trenches and other structures on the deposition surface of the substrate.

[0025] The flowability may be due to a variety of properties which result from mixing a radical-nitrogen precursors with carbon-free silicon precursor. These properties may include a significant hydrogen component in the deposited film and/or the presence of short chained polysilazane polymers. 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 Si-N-H film). When both the silicon precursor and the radical-nitrogen precursor are carbon-free, the deposited silicon-and-nitrogen 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 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] Following the deposition of the silicon-and-nitrogen containing layer, the deposition substrate may be introduced to a oxygen-containing atmosphere 108. The deposition substrate may remain in the reaction chamber when the oxygen-containing atmosphere is introduced, or the substrate may be transferred to a different chamber where the oxygen-containing atmosphere is introduced. The oxygen-containing atmosphere may include one or more oxygen containing gases such as molecular oxygen (O_2), ozone (O_3), water vapor (H_2O), and nitrogen-oxides (NO, NO_2, etc.), among other oxygen-containing gases. The oxygen-containing atmosphere may also include radical oxygen and hydroxyl species such as atomic oxygen (O), hydroxides (OH), etc.,

that may be generated remotely and transported into the substrate chamber. Ions of oxygen-containing species may also be present.

[0027] The oxygen-containing atmosphere provides oxygen to convert the silicon-and-nitrogen containing film into the silicon oxide (SiO_2) film 110. As noted previously, the lack of carbon in the silicon-and-nitrogen containing film results in significantly fewer pores formed in the final silicon oxide film. It also results in less volume reduction (i.e., shrinkage) of the film during the conversion to the silicon oxide. For example, where a silicon-nitrogen-carbon layer formed from carbon containing silicon precursors may shrink by 40 vol.% or more when converted to silicon oxide, the substantially carbon-free silicon-and-nitrogen films may shrink by about 15 vol.% or less.

[0028] Referring now to FIG. 2, another flowchart is shown illustrating selected steps in methods 200 for forming a silicon oxide film in a substrate gap according to embodiments of the invention. The method 200 may include providing a substrate comprising a gap 202. The 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., about 90 nm, 65 nm, 45 nm, 32 nm, 22 nm, 16 nm, etc.).

[0029] A flowable silicon-and-nitrogen containing layer may be deposited on the substrate 204. Because the layer is flowable, it can fill gaps with high aspect ratios without creating voids or weak seams around the center of the filling material. For example, a depositing flowable material is less likely to prematurely clog the top of a gap before it is completely filled to leave a void in the middle of the gap.

[0030] The deposited silicon-and-nitrogen containing layer may then be heated in an oxygen-containing atmosphere. The heating temperature may range from room temperature to about 1100°C (e.g., above one of 200°C, 300°C, 400°C, 500°C, 600°C, 700°C, 800°C, 900°C or 1000°C, in different embodiments) The oxygen-containing atmosphere may include substantially pure oxygen in the form of atomic oxygen (O), molecular oxygen (O_2), ozone (O_3) and mixtures thereof. The atmosphere may also contain a mixture of oxygen and steam (H_2O).

For example, the deposited silicon-and-nitrogen layer may be heated in an atmosphere containing ozone (O_3) and steam (H_2O).

[0031] Embodiments may include multiple heating stages with different temperatures and atmospheres. For example, a first heating stage may be performed at a lower first temperature in an atmosphere that includes steam (H_2O), while a second heating stage may be performed at a higher second temperature in a dry oxygen-containing atmosphere which substantially lacks water vapor. A third heating stage may also be conducted in a non-oxygen containing atmosphere (e.g., dry N_2, He, Ar, etc.).

[0032] Heating the deposited silicon-and-nitrogen containing layer in an oxygen-containing atmosphere forms a silicon oxide layer on the substrate, including the substrate gap 208. As noted above, the silicon oxide layer has fewer pores and less volume reduction than similar layers formed with carbon-containing precursors that have significant quantities of carbon present in the layer before the heat treatment step. In many cases, the volume reduction is slight enough (e.g., about 15 vol.% or less) to avoid post heat treatment steps to fill, heal, or otherwise eliminate spaces that form in the gap as a result of the shrinking silicon oxide.

[0033] FIG. 3 is another flowchart illustrating selected steps in a plasma chemical vapor deposition methods 300 of making a silicon oxide film according to embodiments of the invention. The methods 300 may include introducing a carbon-free silicon precursor and a radical-nitrogen precursor into a plasma chemical vapor deposition chamber 302. The radical-nitrogen precursor may be generated outside the plasma CVD deposition chamber, for example, from a stable nitrogen-containing gas (e.g., ammonia, molecular nitrogen (N_2), a mixture of N_2 and H_2, etc.) passing through a remote plasma system externally coupled to the CVD deposition chamber.

[0034] A plasma may be formed from the silicon precursor and the radical-nitrogen precursor in the plasma CVD chamber 304. A substrate also positioned in the chamber may be exposed to the plasma, which deposits a silicon-and-nitrogen containing layer on the substrate 306. The deposited layer may include a flowable silazane type material with a Si-NH-Si backbone that permits the layer to fill gaps and other structured elements of the substrate with fewer voids and weak seams than a conventional PECVD deposition of a silicon oxide film.

[0035] Following the deposition of the silicon-and-nitrogen containing film, oxygen-containing gases may be introduced into the plasma CVD chamber to convert the deposited silicon-and-nitrogen layer into a silicon oxide layer. The oxygen-containing gases may include molecular oxygen, ozone and water vapor, among other gases. In some instances, a plasma may be struck from a mixture that includes the oxygen-containing gases, while in other instances no plasma is formed from the gases.

[0036] The oxygen-containing gas entering the CVD chamber may include one or more compounds that have been activated (e.g., radicalized, ionized, etc.) before entering the chamber. For example, the oxygen-containing gas may include radical oxygen species, radical hydroxyl species, etc., activated by exposing more stable precursor compounds through a remote plasma source. The more stable precursors may include water vapor and hydrogen peroxide (H_2O_2) that produce hydroxyl (OH) radicals and ions, and molecular oxygen and/or ozone that produce atomic oxygen (O) radicals and ions.

Exemplary Silicon Oxide Deposition System

[0037] 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.

[0038] 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.

[0039] Embodiments of the deposition systems may be incorporated into larger fabrication systems for producing integrated circuit chips. FIG. 4 shows one such system 400 of deposition,

baking and curing chambers according to disclosed embodiments. In the figure, a pair of FOUPs (front opening unified pods) 402 supply substrate substrates (e.g., 300 mm diameter wafers) that are received by robotic arms 404 and placed into a low pressure holding area 406 before being placed into one of the wafer processing chambers 408a-f. A second robotic arm 410 may be used to transport the substrate wafers from the holding area 406 to the processing chambers 408a-f and back.

[0040] The processing chambers 408a-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., 408c-d and 408e-f) may be used to deposit the flowable dielectric material on the substrate, and the third pair of processing chambers (e.g., 408a-b) may be used to anneal the deposited dielectic. In another configuration, the same two pairs of processing chambers (e.g., 408c-d and 408e-f) may be configured to both deposit and anneal a flowable dielectric film on the substrate, while the third pair of chambers (e.g., 408a-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., 408a-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., 408c-d and 408e-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. 408a-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.

[0041] In addition, one or more of the process chambers 408a-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 400 may include wet treatment chambers 408a-b and anneal processing chambers 408c-d to perform both wet and dry anneals on the deposited dielectric film.

[0042] FIG. 5A is a substrate processing chamber 500 according to disclosed embodiments. A remote plasma system (RPS) 510 may process a gas which then travels through a gas inlet assembly 511. Two distinct gas supply channels are visible within the gas inlet assembly 511. A first channel 512 carries a gas that passes through the remote plasma system RPS 510, while a second channel 513 bypasses the RPS 500. First channel 512 may be used for the process gas and second channel 513 may be used for a treatment gas in disclosed embodiments. The lid (or

conductive top portion) 521 and a perforated partition 553 are shown with an insulating ring 524 in between, which allows an AC potential to be applied to the lid 521 relative to perforated partition 553. The process gas travels through first channel 512 into chamber plasma region 520 and may be excited by a plasma in chamber plasma region 520 alone or in combination with RPS 510. The combination of chamber plasma region 520 and/or RPS 510 may be referred to as a remote plasma system herein. The perforated partition (also referred to as a showerhead) 553 separates chamber plasma region 520 from a substrate processing region 570 beneath showerhead 553. Showerhead 553 allows a plasma present in chamber plasma region 520 to avoid directly exciting gases in substrate processing region 570, while still allowing excited species to travel from chamber plasma region 520 into substrate processing region 570.

[0043] Showerhead 553 is positioned between chamber plasma region 520 and substrate processing region 570 and allows plasma effluents (excited derivatives of precursors or other gases) created within chamber plasma region 520 to pass through a plurality of through holes 556 that traverse the thickness of the plate. The showerhead 553 also has one or more hollow volumes 551 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 555 into substrate processing region 570 but not directly into chamber plasma region 520. Showerhead 553 is thicker than the length of the smallest diameter 550 of the through-holes 556 in this disclosed embodiment. In order to maintain a significant concentration of excited species penetrating from chamber plasma region 520 to substrate processing region 570, the length 526 of the smallest diameter 550 of the through-holes may be restricted by forming larger diameter portions of through-holes 556 part way through the showerhead 553. The length of the smallest diameter 550 of the through-holes 556 may be the same order of magnitude as the smallest diameter of the through-holes 556 or less in disclosed embodiments.

[0044] In the embodiment shown, showerhead 553 may distribute (via through holes 556) 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 520. In embodiments, the process gas introduced into the RPS 510 and/or chamber plasma region 520 through first channel 512 may contain one or more of oxygen (O_2), ozone (O_3), N_2O, NO, NO_2, NH_3, N_xH_y including N_2H_4, silane, disilane, TSA and DSA. The process gas may also include a carrier gas such as helium, argon, nitrogen (N_2), etc. The second channel 513 may also deliver a process gas and/or a carrier gas, and/or a film-curing gas used to remove an unwanted component from the growing

or as-deposited film. Plasma effluents may include ionized or neutral derivatives of the process gas and may also be referred to herein as a radical-oxygen precursor and/or a radical-nitrogen precursor referring to the atomic constituents of the process gas introduced.

[0045] In embodiments, the number of through-holes 556 may be between about 60 and about 2000. Through-holes 556 may have a variety of shapes but are most easily made round. The smallest diameter 550 of through holes 556 may be between about 0.5mm and about 20mm or between about 1mm 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 555 used to introduce a gas into substrate processing region 570 may be between about 100 and about 5000 or between about 500 and about 2000 in different embodiments. The diameter of the small holes 555 may be between about 0.1 mm and about 2 mm.

[0046] FIG. 5B is a bottom view of a showerhead 553 for use with a processing chamber according to disclosed embodiments. Showerhead 553 corresponds with the showerhead shown in FIG. 5A. Through-holes 556 are depicted with a larger inner-diameter (ID) on the bottom of showerhead 553 and a smaller ID at the top. Small holes 555 are distributed substantially evenly over the surface of the showerhead, even amongst the through-holes 556 which helps to provide more even mixing than other embodiments described herein.

[0047] An exemplary film is created on a substrate supported by a pedestal (not shown) within substrate processing region 570 when plasma effluents arriving through through-holes 556 in showerhead 553 combine with a silicon-containing precursor arriving through the small holes 555 originating from hollow volumes 551. Though substrate processing region 570 may be equipped to support a plasma for other processes such as curing, no plasma is present during the growth of the exemplary film.

[0048] A plasma may be ignited either in chamber plasma region 520 above showerhead 553 or substrate processing region 570 below showerhead 553. A plasma is present in chamber plasma region 520 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 521 of the processing chamber and showerhead 553 to ignite a plasma in chamber plasma region 520 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.

[0049] The top plasma may be left at low or no power when the bottom plasma in the substrate processing region 570 is turned on to either cure a film or clean the interior surfaces bordering substrate processing region 570. A plasma in substrate processing region 570 is ignited by applying an AC voltage between showerhead 553 and the pedestal or bottom of the chamber. A cleaning gas may be introduced into substrate processing region 570 while the plasma is present.

[0050] 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 0°C 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.

[0051] 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.

[0052] The system controller controls all of the activities of the CVD machine. 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.

[0053] 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 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.

[0054] 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.

[0055] The chamber plasma region or a region in an RPS may be referred to as a remote plasma region. In embodiments, the radical-nitrogen precursor is created in the remote plasma region and travels into the substrate processing region where the carbon-free silicon-containing precursor is excited by the radical-nitrogen precursor. In embodiments, the carbon-free silicon-containing precursor is excited only by the radical-nitrogen precursor. Plasma power may essentially be applied only to the remote plasma region, in embodiments, to ensure that the radical-nitrogen precursor provides the dominant excitation to the carbon-free silicon-containing precursor.

[0056] In embodiments employing a chamber plasma region, the excited plasma effluents are 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 carbon-free silicon-containing precursor to deposit the silicon-and-nitrogen layer on a deposition substrate (e.g., a semiconductor wafer). The excited plasma effluents are also accompanied by an inert gases (in the exemplary case, argon). The carbon-free silicon-containing precursor 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 growth of the silicon-and-nitrogen-containing layer. "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 carbon-free silicon-containing precursor 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.

[0057] 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" is used as a shorthand for and interchangeably with a silicon-and-oxygen-containing material. As such, silicon oxide may include 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 may be a combination of two or more gases. 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. The phrase "inert gas" refers to any gas which does not form chemical bonds when 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.

[0058] 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.

[0059] 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.

[0060] 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.

[0061] 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.

[0062] 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 silicon oxide layer, the method comprising:
mixing a carbon-free silicon-and-nitrogen containing precursor with a radical precursor;
depositing a silicon-and-nitrogen containing layer on a substrate; and
converting the silicon-and-nitrogen containing layer to the silicon oxide layer.

2. The method of claim 1 wherein the radical precursor is a radical-nitrogen precursor.

3. The method of claim 1 wherein the radical precursor comprises hydrogen but essentially no nitrogen.

4. The method of claim 1 wherein the carbon-free silicon-and-nitrogen containing precursor comprises a silyl-amine.

5. The method of claim 4 wherein the silyl-amine comprises $N(SiH_3)_3$.

6. The method of claim 1 wherein the radical precursor is generated from a nitrogen-and-hydrogen containing gas using a plasma before being mixed with the carbon-free silicon-and-nitrogen containing precursor.

7. The method of claim 6 wherein the nitrogen-and-hydrogen containing gas comprises a gas selected from the group consisting of hydrazine, ammonia, N_2 and H_2.

8. The method of claim 1 wherein the silicon-and-nitrogen containing layer is converted to the silicon oxide layer by exposing the silicon-and-nitrogen containing layer to an oxygen-containing atmosphere.

9. The method of claim 8 wherein the oxygen-containing atmosphere comprises one or more gases selected from the group consisting of oxygen (O_2), ozone (O_3), and steam (H_2O).

10. A method of forming a silicon oxide layer with reduced volume shrinkage, the method comprising:
providing a substrate containing a least one gap;

depositing a carbon-free silicon-and-nitrogen containing layer on the substrate; and

heating the substrate in an oxygen-containing atmosphere to convert the carbon-free silicon-and-nitrogen containing layer to the silicon oxide layer, wherein the silicon oxide layer retains a volume of about 85% or more of the carbon-free silicon-and-nitrogen containing layer deposited in the gap.

11. The method of claim 10 wherein the carbon-free silicon-and-nitrogen containing layer is deposited on the substrate by the reaction of a silicon-and-nitrogen precursor with a radical precursor.

12. The method of claim 11 wherein the silicon-and-nitrogen precursor comprises $N(SiH_3)_3$ and the radical precursor is formed from plasma-activated NH_3.

13. The method of claim 10 wherein the carbon-free silicon-and-nitrogen containing layer comprises a Si-N-H layer.

14. The method of claim 10 wherein the substrate gap has a width of about 50 nm or less.

15. The method of claim 10 wherein the silicon oxide layer in the gap is substantially void-free.