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(54) **CROSSLINK CYCLO-SILOXANE
COMPOUND WITH LINEAR BRIDGING
GROUP TO FORM ULTRA LOW K
DIELECTRIC**

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(75) **Inventors: Lihua Li, San Jose, CA (US); Wen H. Zhu, Sunnyvale, CA (US); Tzu-Fang Huang, San Jose, CA (US); Li Qun Xia, Santa Clara, CA (US); Ellie Yieh, San Jose, CA (US)**

(57) **ABSTRACT**

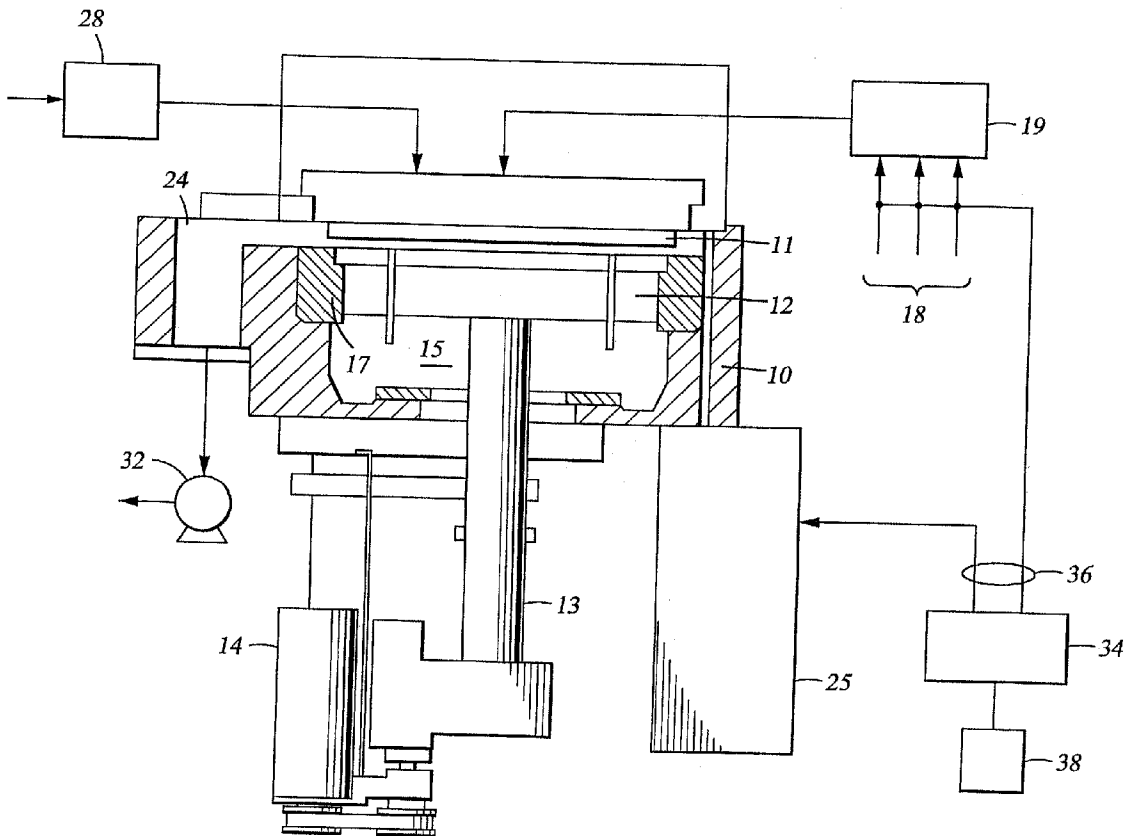
A method for depositing a low dielectric constant film having a dielectric constant of about 3.0 or less, preferably about 2.5 or less, is provided by using one or more cyclic organic precursors and one or more aliphatic precursors. In one aspect, a cyclic organosilicon compound, an aliphatic organosilicon, and an aliphatic hydrocarbon compound are reacted with an oxidizing gas at conditions sufficient to deposit a low dielectric constant film on the semiconductor substrate. The cyclic organosilicon compound includes at least one silicon-carbon bond. The aliphatic organosilicon compound includes a silicon-hydrogen bond or a silicon-oxygen bond.

Correspondence Address:
APPLIED MATERIALS, INC.
2881 SCOTT BLVD. M/S 2061
SANTA CLARA, CA 95050 (US)

(73) **Assignee: Applied Materials, Inc.**

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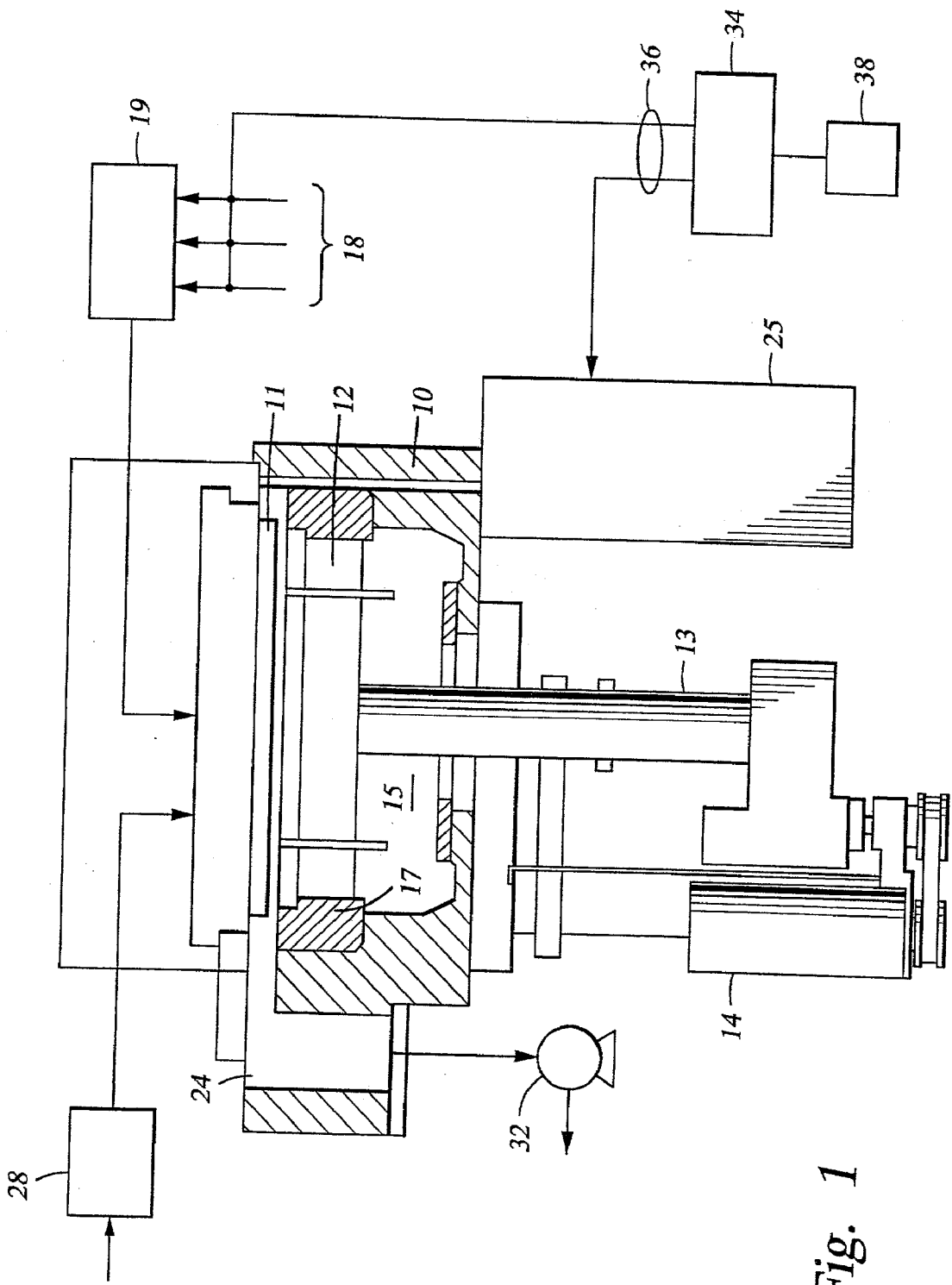


Fig. 1

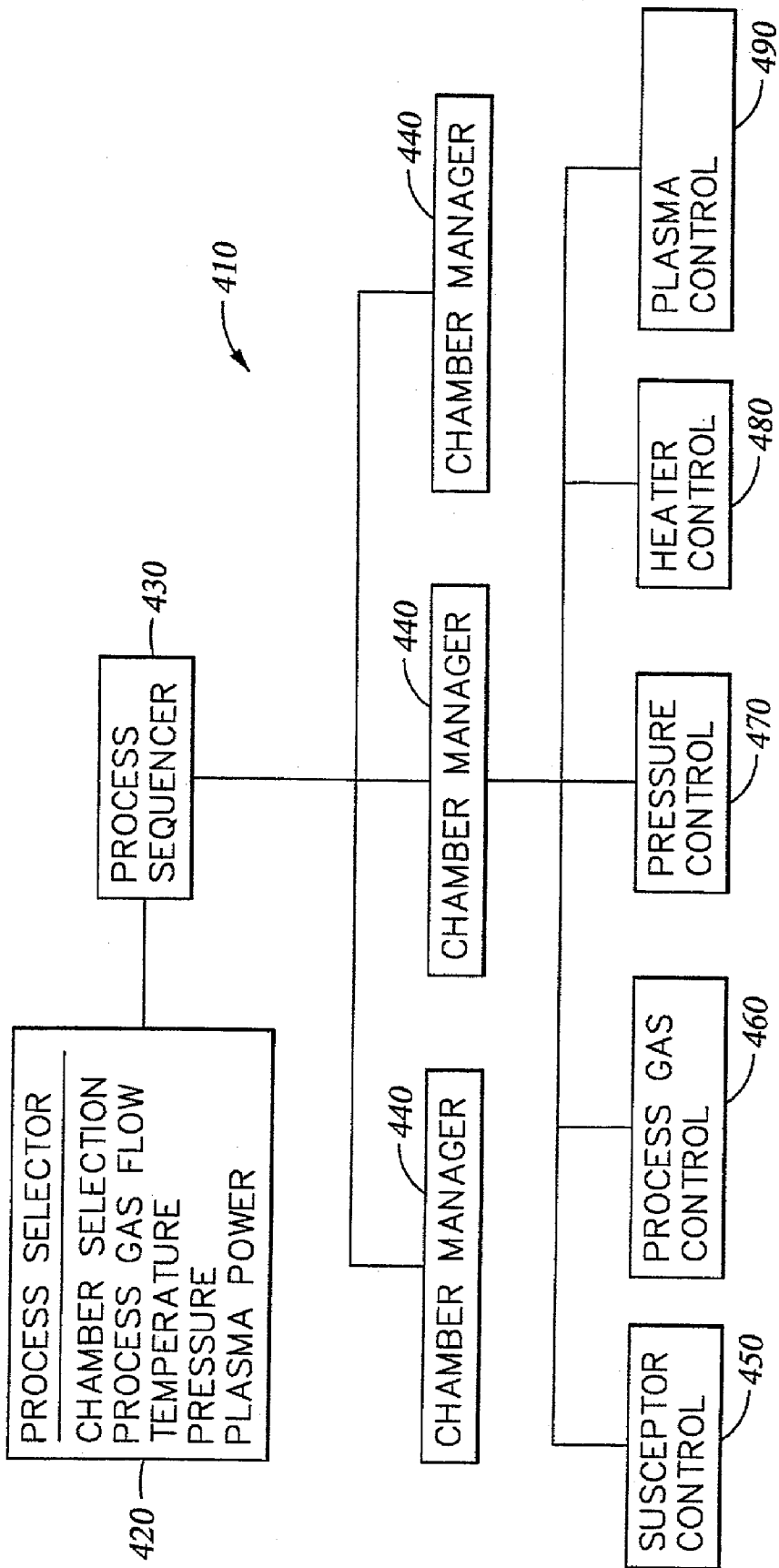
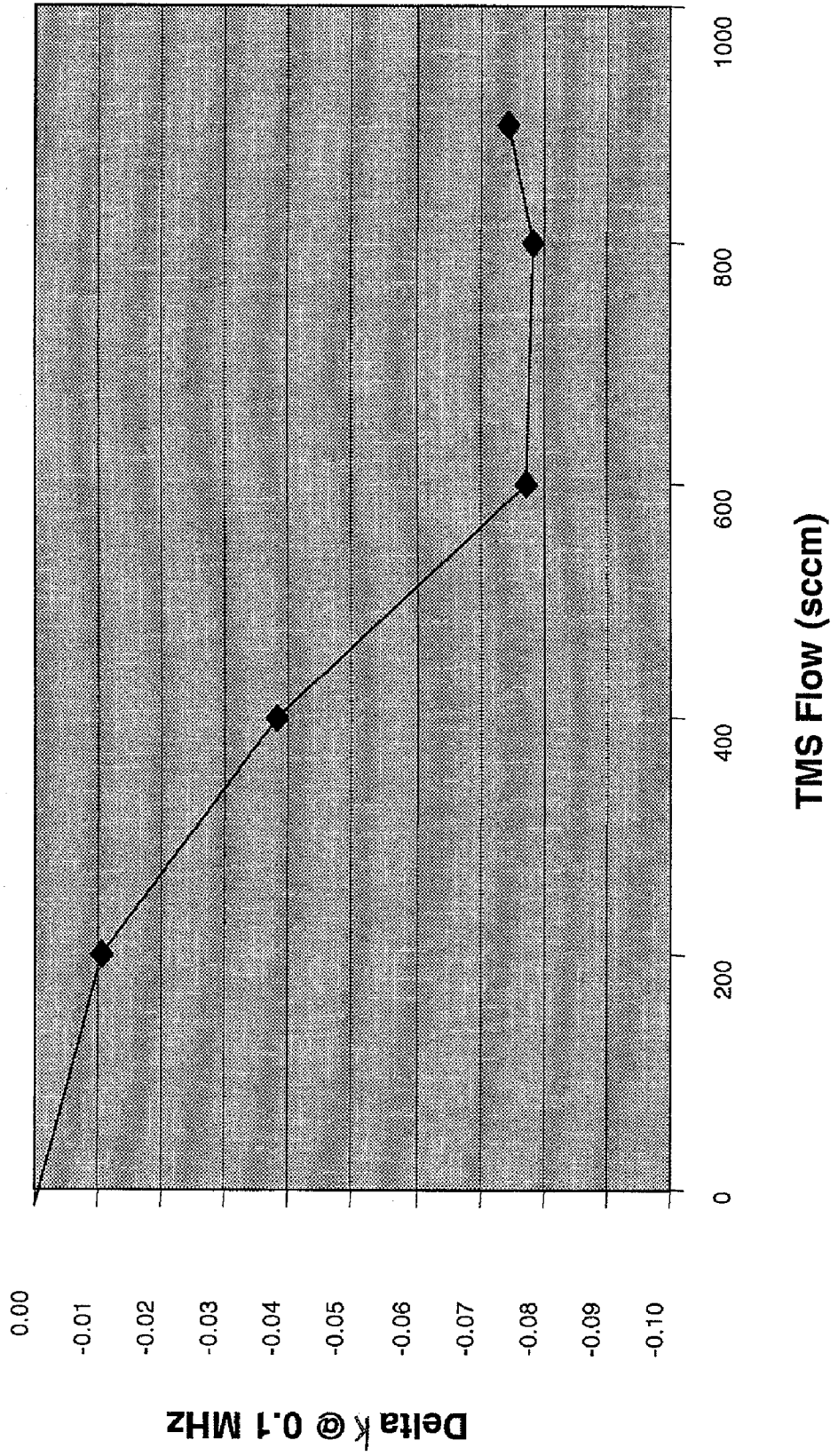


Fig. 2

Figure 3



CROSSLINK CYCLO-SILOXANE COMPOUND WITH LINEAR BRIDGING GROUP TO FORM ULTRA LOW K DIELECTRIC

BACKGROUND OF THE DISCLOSURE

[0001] 1. Field of the Invention

[0002] Embodiments of the present invention relate to the fabrication of integrated circuits. More particularly, embodiments of the present invention relate to a process for depositing dielectric layers on a substrate.

[0003] 2. Background of the Invention

[0004] Integrated circuit geometries have dramatically decreased in size since such devices were first introduced several decades ago. Since then, integrated circuits have generally followed the two year/half-size rule (often called Moore's Law), which means that the number of devices on a chip doubles every two years. Today's fabrication facilities are routinely producing devices having 0.13 μm and even 0.1 μm feature sizes, and tomorrow's facilities soon will be producing devices having even smaller feature sizes.

[0005] The continued reduction in device geometries has generated a demand for films having lower k values because the capacitive coupling between adjacent metal lines must be reduced to further reduce the size of devices on integrated circuits. In particular, insulators having low dielectric constants (k), less than about 4.0, are desirable. Examples of insulators having low dielectric constants include spin-on glass, such as un-doped silicon glass (USG) or fluorine-doped silicon glass (FSG), silicon dioxide, and polytetrafluoroethylene (PTFE), which are all commercially available.

[0006] More recently, organosilicon films having k values less than about 3.5 have been developed. In an attempt to further lower k values, Rose et al. (U.S. Pat. No. 6,068,884) disclosed a method for depositing an insulator by partially fragmenting a cyclic organosilicon compound to form both cyclic and linear structures in the deposited film. However, this method of partially fragmenting cyclic precursors is difficult to control and thus, product consistency is difficult to achieve.

[0007] There is a need, therefore, for a controllable process for making lower dielectric constant materials to improve the speed and efficiency of devices on integrated circuits.

SUMMARY OF THE INVENTION

[0008] Embodiments of the invention include a method for depositing a low dielectric constant film having a dielectric constant of about 3.0 or less, preferably about 2.5 or less, by blending one or more cyclic organosilicon precursors and one or more aliphatic precursors. In one aspect, a cyclic organosilicon compound, an aliphatic organosilicon, and an aliphatic hydrocarbon compound are reacted with an oxidizing gas at conditions sufficient to deposit a low dielectric constant film on the semiconductor substrate. The cyclic organosilicon compound includes at least one silicon-carbon bond. The aliphatic organosilicon compound includes a silicon-hydrogen bond or a silicon-oxygen bond. The aliphatic hydrocarbon includes at least one unsaturated carbon-carbon bond.

[0009] Embodiments of the invention also include reacting one or more meta-stable organic compounds with the blend of the one or more cyclic organosilicon precursors, and the one or more aliphatic precursors to form a low dielectric constant film having a dielectric constant of about 3.0 or less, preferably about 2.5 or less. In one aspect, a cyclic organosilicon compound, an aliphatic organosilicon, and a meta-stable organic compound are reacted with an oxidizing gas at conditions sufficient to deposit a low dielectric constant film on the semiconductor substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] So that the manner in which the above recited features of the present invention are attained and can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to the embodiments thereof which are illustrated in the appended drawings.

[0011] It is to be noted, however, that the description and appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0012] FIG. 1 is a cross-sectional diagram of an exemplary CVD reactor configured for use according to embodiments described herein.

[0013] FIG. 2 is a flow chart of a process control computer program product used in conjunction with the exemplary CVD reactor of FIG. 1.

[0014] FIG. 3 shows a relationship between dielectric constant and ratio of gases.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] Embodiments of the invention include a significant and unexpected reduction in dielectric constants for films containing silicon, oxygen, and carbon by blending one or more cyclic organosilicon compounds and one or more aliphatic compounds with an oxidizing gas at conditions sufficient to form an ultra low dielectric constant film (k less than 2.5). The films contain a network of —Si—O—Si— ring structures that are crosslinked with one or more linear organic compounds. Because of the crosslinkage, a reactively stable network is produced having a significant separation between ring structures and thus, the deposited films possess a significant degree of porosity.

[0016] The cyclic organosilicon compounds include a ring structure having three or more silicon atoms and the ring structure may further comprise one or more oxygen atoms. Commercially available cyclic organosilicon compounds include rings having alternating silicon and oxygen atoms with one or two alkyl groups bonded to the silicon atoms. For example, the cyclic organosilicon compounds may include one or more of the following compounds:

[0017] 1,3,5-trisilano-2,4,6-trimethylene,
 $\text{—(—SiH}_2\text{CH}_2\text{—)}_3\text{—}$ (cyclic)

[0018] 1,3,5,7-tetramethylcyclotetrasiloxane
(TMCTS) $\text{—(—SiHCH}_3\text{—O—)}_4\text{—}$ (cyclic)

[0019] octamethylcyclotetrasiloxane (OMCTS),
 $\text{—(—Si(CH}_3)_2\text{—O—)}_4\text{—}$ (cyclic)

- [0020] 1,3,5,7,9-pentamethylcyclopentasiloxane,
—(—SiHCH₃—O—)₅— (cyclic)
- [0021] 1,3,5,7-tetrasilano-2,6-dioxy-4,8-dimethyl-
ene, —(—SiH₂—CH₂—SiH₂—O—)₂— (cyclic)
- [0022] hexamethylcyclotrisiloxane —(—Si(CH₃)₂—
O—)₃— (cyclic)

[0023] The aliphatic compounds include linear or branched (i.e. acyclic) organosilicon compounds having one or more silicon atoms and one or more carbon atoms and linear or branched hydrocarbon compounds having at least one unsaturated carbon bond. The structures may further comprise oxygen. Commercially available aliphatic organosilicon compounds include organosilanes that do not contain oxygen between silicon atoms and organosiloxanes that contain oxygen between two or more silicon atoms. For example, the aliphatic organosilicon compounds may include one or more of the following compounds:

- [0024] methylsilane, CH₃—SiH₃
- [0025] dimethylsilane, (CH₃)₂—SiH₂
- [0026] trimethylsilane, (CH₃)₃—SiH
- [0027] dimethyldimethoxysilane, (CH₃)₂—Si—
(OCH₃)₂
- [0028] ethylsilane, CH₃—CH₂—SiH₃
- [0029] disilanomethane, SiH₃—CH₂—SiH₃
- [0030] bis(methylsilano)methane, CH₃—SiH₂—
CH₂—SiH₂—CH₃
- [0031] 1,2-disilanoethane, SiH₃—CH₂—CH₂—SiH₃
- [0032] 1,2-bis(methylsilano)ethane, CH₃—SiH₂—
CH₂—CH₂—SiH₂—CH₃
- [0033] 2,2-disilanopropane, SiH₃—C(CH₃)₂—SiH₃
- [0034] 1,3-dimethyldisiloxane, CH₃—SiH₂—O—
SiH₂—CH₃
- [0035] 1,1,3,3-tetramethyldisiloxane (TMDSO),
(CH₃)₂—SiH—O—SiH—(CH₃)₂
- [0036] hexamethyldisiloxane (HMDS), (CH₃)₃—
Si—O—Si—(CH₃)₃
- [0037] 1,3-bis(silanomethylene)disiloxane, (SiH₃—
CH₂—SiH₂—)₂—O
- [0038] bis(1-methyldisiloxanyl)methane, (CH₃—
SiH₂—O—SiH₂—)₂—CH₂
- [0039] 2,2-bis(1-methyldisiloxanyl)propane, (CH₃—
SiH₂—O—SiH₂—)₂—C(CH₃)₂
- [0040] hexamethoxydisiloxane (HMDOS)
(CH₃O)₃—Si—O—Si—(OCH₃)₃
- [0041] diethylsilane ((C₂H₅)₂SiH₂),
- [0042] propylsilane (C₃H₇SiH₃),
- [0043] vinylmethylsilane (CH₂=CH)CH₃SiH₂),
- [0044] 1,1,2,2-tetramethyldisilane (HSi(CH₃)—
Si(CH₃)₂H),
- [0045] hexamethyldisilane ((CH₃)₃—Si(CH₃)₃),

- [0046] 1,1,2,2,3,3-hexamethyltrisilane
(H(CH₃)₂Si—Si(CH₃)₂—SiH(CH₃)₂),
- [0047] 1,1,2,3,3-pentamethyltrisilane (H(CH₃)₂Si—
SiH(CH₃)—SiH(CH₃)₂),
- [0048] dimethyldisilanoethane (CH₃—SiH₂—
(CH₂)₂—SiH₂—CH₃),
- [0049] dimethyldisilanopropane (CH₃—SiH—
(CH₂)₃—SiH—CH₃),
- [0050] tetramethyldisilanoethane ((CH₃)₂—SiH—
(CH₂)₂—SiH—(CH₃)₂),
- [0051] tetramethyldisilanopropane ((CH₃)₂—Si—
(CH₂)₃—Si—(CH₃)₂),

[0052] The aliphatic compounds also include aliphatic hydrocarbon compounds having between one and about 20 adjacent carbon atoms. The hydrocarbon compounds can include adjacent carbon atoms that are bonded by any combination of single, double, and triple bonds. For example, the organic compounds may include alkenes and alkynes having two to about 20 carbon atoms, such as ethylene, propylene, acetylene, and butadiene.

[0053] The one or more oxidizing gases may include oxygen (O₂), ozone (O₃), nitrous oxide (N₂O), carbon monoxide (CO), carbon dioxide (CO₂), water (H₂O), peroxide (H₂O₂) or combinations thereof. In one aspect, the oxidizing gas is oxygen gas. In another aspect, the oxidizing gas is ozone. When ozone is used as an oxidizing gas, an ozone generator converts from 6% to 20%, typically about 15%, by weight of the oxygen in a source gas to ozone, with the remainder typically being oxygen. Yet, the ozone concentration may be increased or decreased based upon the amount of ozone desired and the type of ozone generating equipment used. The one or more oxidizing gases are added to the reactive gas mixture to increase reactivity and achieve the desired carbon content in the deposited film.

[0054] The films contain a carbon content between about 5 and about 30 atomic percent (excluding hydrogen atoms), preferably between about 5 and about 20 atomic percent. The carbon content of the deposited films refers to atomic analysis of the film structure which typically does not contain significant amounts of non-bonded hydrocarbons. The carbon contents are represented by the percent of carbon atoms in the deposited film, excluding hydrogen atoms which are difficult to quantify. For example, a film having an average of one silicon atom, one oxygen atom, one carbon atom, and two hydrogen atoms has a carbon content of 20 atomic percent (one carbon atom per five total atoms), or a carbon content of 33 atomic percent excluding hydrogen atoms (one carbon atom per three total atoms).

[0055] One or more meta-stable compounds may be added to the mixture described above to further reduce the dielectric constant of the deposited film. The meta-stable compound first forms an unstable component within the film network and then is removed from the film network using an anneal treatment. The removal of the unstable component during the anneal treatment forms a void within the network leaving behind a film having a significantly lower dielectric constant. The meta-stable compound is also known as a “leaving group” because of the nature of the process whereby the meta-stable compound leaves the network to form one or more voids therein. Exemplary meta-stable

compounds may include t-butylethylene, 1,1,3,3-tetramethylbutylbenzene, t-butylether, methyl-methacrylate (MMA), and t-butylfurfurylether.

[0056] The anneal treatment removes the meta-stable component from the film network as well as reduces a moisture content of the film. Moisture content may arise due to exposure to ambient air or by-product formation, for example. Preferably, the film is subjected to a temperature between about 100° C. and about 400° C. for about 10 minutes to about 1 hour, preferably about 30 minutes. A non-reactive gas such as helium, hydrogen, nitrogen, or a mixture thereof is introduced at a rate of 100 to about 10,000 sccm. The chamber pressure is maintained between about 2 Torr and about 10 Torr. The RF power is about 200 W to about 1,000 W at a frequency of about 13.56 MHz, and the preferable substrate spacing is between about 300 mils and about 800 mils.

[0057] Optionally, a second in-situ post treatment may be performed whereby the film is subjected to a temperature between about 100° C. and about 400° C. for about 2 seconds to about 10 minutes, preferably about 30 seconds. Helium, hydrogen, or a mixture thereof is flowed into the chamber at a rate of about 200 to about 10,000 sccm. The chamber pressure is maintained between about 2 Torr and about 10 Torr. The RF power is about 200 W to about 800 W at a frequency of about 13.56 MHz, and the preferable substrate spacing is between about 300 mils and about 800 mils. Preferably, the film is treated in one cycle using hydrogen gas.

[0058] The film may be deposited using any processing chamber capable of chemical vapor deposition (CVD). For example, FIG. 1 shows a vertical, cross-section view of a parallel plate CVD processing chamber 10. The chamber 10 includes a high vacuum region 15 and a gas distribution manifold 11 having perforated holes for dispersing process gases there-through to a substrate (not shown). The substrate rests on a substrate support plate or susceptor 12. The susceptor 12 is mounted on a support stem 13 that connects the susceptor 12 to a lift motor 14. The lift motor 14 raises and lowers the susceptor 12 between a processing position and a lower, substrate-loading position so that the susceptor 12 (and the substrate supported on the upper surface of susceptor 12) can be controllably moved between a lower loading/off-loading position and an upper processing position which is closely adjacent to the manifold 11. An insulator 17 surrounds the susceptor 12 and the substrate when in an upper processing position.

[0059] Gases introduced to the manifold 11 are uniformly distributed radially across the surface of the substrate. A vacuum pump 32 having a throttle valve controls the exhaust rate of gases from the chamber 10 through a manifold 24. Deposition and carrier gases, if needed, flow through gas lines 18 into a mixing system 19 and then to the manifold 11. Generally, each process gas supply line 18 includes (i) safety shut-off valves (not shown) that can be used to automatically or manually shut off the flow of process gas into the chamber, and (ii) mass flow controllers (also not shown) to measure the flow of gas through the gas supply lines 18. When toxic gases are used in the process, several safety shut-off valves are positioned on each gas supply line 18 in conventional configurations.

[0060] During deposition, a blend/mixture of one or more cyclic organosilicon compounds and one or more aliphatic

compounds are reacted with an oxidizing gas to form an ultra low k film on the substrate. Preferably, the cyclic organosilicon compounds are combined with at least one aliphatic organosilicon compound and at least one aliphatic hydrocarbon compound. For example, the mixture contains about 5 percent by volume to about 80 percent by volume of the one or more cyclic organosilicon compounds, about 5 percent by volume to about 15 percent by volume of the one or more aliphatic organosilicon compounds, and about 5 percent by volume to about 45 percent by volume of the one or more aliphatic hydrocarbon compounds. The mixture also contains about 5 percent by volume to about 20 percent by volume of the one or more oxidizing gases. More preferably, the mixture contains about 45 percent by volume to about 60 percent by volume of one or more cyclic organosilicon compounds, about 5 percent by volume to about 10 percent by volume of one or more aliphatic organosilicon compounds, and about 5 percent by volume to about 35 percent by volume of one or more aliphatic hydrocarbon compounds.

[0061] In one aspect, the one or more cyclic organosilicon compounds are introduced to the mixing system 19 at a flowrate of about 100 to about 10,000 sccm, preferably about 520 sccm. The one or more aliphatic organosilicon compounds are introduced to the mixing system 19 at a flowrate of about 100 to about 1,000 sccm, preferably about 600 sccm. The one or more aliphatic hydrocarbon compounds are introduced to the mixing system 19 at a flowrate of about 100 to about 10,000 sccm, preferably 2,000 sccm. The oxygen containing gas has a flowrate between about 100 and about 6,000 sccm, preferably 1,000 sccm. Preferably, the cyclic organosilicon compound is 2,4,6,8-tetramethylcyclotetrasiloxane, octamethylcyclotetrasiloxane, or a mixture thereof, and the aliphatic organosilicon compound is trimethylsilane, 1,1,3,3-tetramethyldisiloxane, or a mixture thereof. The aliphatic hydrocarbon compound is preferably ethylene.

[0062] In another aspect, the blend/mixture further includes one or more meta-stable precursors. The one or more meta-stable precursors are added in amounts of about 100 sccm to about 5,000 sccm. Preferably, the meta-stable organic precursor is t-butylether.

[0063] The deposition process can be either a thermal process or a plasma enhanced process. In a plasma enhanced process, a controlled plasma is typically formed adjacent the substrate by RF energy applied to the gas distribution manifold 11 using a RF power supply 25. Alternatively, RF power can be provided to the susceptor 12. The RF power to the deposition chamber may be cycled or pulsed to reduce heating of the substrate and promote greater porosity in the deposited film. The power density of the plasma for a 200 mm substrate is between about 0.03 W/cm² and about 3.2 W/cm², which corresponds to a RF power level of about 10 W to about 2,000 W. Preferably, the RF power level is between about 300 W and about 1,700 W.

[0064] The RF power supply 25 can supply a single frequency RF power between about 0.01 MHz and 300 MHz. Alternatively, the RF power may be delivered using mixed, simultaneous frequencies to enhance the decomposition of reactive species introduced into the high vacuum region 15. In one aspect, the mixed frequency is a lower frequency of about 12 kHz and a higher frequency of about

13.56 mHz. In another aspect, the lower frequency may range between about 300 Hz to about 1,000 kHz, and the higher frequency may range between about 5 mHz and about 50 mHz.

[0065] During deposition, the substrate is maintained at a temperature between about -20° C. and about 500° C., preferably between about 100° C. and about 450° C. The deposition pressure is typically between about 1 Torr and about 20 Torr, preferably between about 4 Torr and about 7 Torr. The deposition rate is typically between about 10,000 A/min and about 20,000 A/min.

[0066] When additional dissociation of the oxidizing gas is desired, an optional microwave chamber 28 can be used to input power from between about 50 Watts and about 6,000 Watts to the oxidizing gas prior to the gas entering the processing chamber 10. The additional microwave power can avoid excessive dissociation of the organosilicon compounds prior to reaction with the oxidizing gas. A gas distribution plate (not shown) having separate passages for the organosilicon compound and the oxidizing gas is preferred when microwave power is added to the oxidizing gas.

[0067] Typically, any or all of the chamber lining, distribution manifold 11, susceptor 12, and various other reactor hardware is made out of materials such as aluminum or anodized aluminum. An example of such a CVD reactor is described in U.S. Pat. No. 5,000,113, entitled "A Thermal CVD/PECVD Reactor and Use for Thermal Chemical Vapor Deposition of Silicon Dioxide and In-situ Multi-step Planarized Process," which is incorporated by reference herein.

[0068] A system controller 34 controls the motor 14, the gas mixing system 19, and the RF power supply 25 which are connected therewith by control lines 36. The system controller 34 controls the activities of the CVD reactor and typically includes a hard disk drive, a floppy disk drive, and a card rack. The card rack contains a single board computer (SBC), analog and digital input/output boards, interface boards, and stepper motor controller boards. The system controller 34 conforms to the Versa Modular Europeans (VME) standard which defines board, card cage, and connector dimensions and types. The VME standard also defines the bus structure having a 16-bit data bus and 24-bit address bus.

[0069] FIG. 2 shows an illustrative block diagram of a hierarchical control structure of a computer program 410. The system controller 34 operates under the control of the computer program 410 stored on a hard disk drive 38. The computer program 410 dictates the timing, mixture of gases, RF power levels, susceptor position, and other parameters of a particular process. The computer program code can be written in any conventional computer readable programming language such as, for example, 68000 assembly language, C, C++, or Pascal. 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 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, from which the CPU reads and executes the code to perform the tasks identified in the program.

[0070] A user enters a process set number and process chamber number into a process selector subroutine 420 in response to menus or screens displayed on the CRT monitor by using the light pen interface. The process sets are predetermined sets of process parameters necessary to carry out specified processes, and are identified by predefined set numbers. The process selector subroutine 420 (i) selects a desired process chamber on the cluster tool, and (ii) selects a desired set of process parameters needed to operate the process chamber for performing the desired process. The process parameters for performing a specific process are provided to the user in the form of a recipe and relate to process conditions such as, for example, process gas composition, flow rates, temperature, pressure, plasma conditions such as RF bias power levels and magnetic field power levels, cooling gas pressure, and chamber wall temperature. The parameters specified by the recipe are entered utilizing the light pen/CRT monitor interface. The signals for monitoring the process are provided by the analog input and digital input boards of the system controller 34 and the signals for controlling the process are output to the analog output and digital output boards of the system controller 34.

[0071] A process sequencer subroutine 430 comprises program code for accepting the identified process chamber and set of process parameters from the process selector subroutine 420, and for controlling operation of the various process chambers. Multiple users can enter process set numbers and process chamber numbers, or a user can enter multiple process chamber numbers, so the sequencer subroutine 430 operates to schedule the selected processes in the desired sequence. Preferably the sequencer subroutine 430 includes computer readable program code to perform the steps of (i) monitoring the operation of the process chambers to determine if the chambers are being used, (ii) determining what processes are being carried out in the chambers being used, and (iii) executing the desired process based on availability of a process chamber and type of process to be carried out. Conventional methods of monitoring the process chambers can be used, such as polling. When scheduling a process execute, the sequencer subroutine 430 can be designed to take into consideration the present condition of the process chamber being used in comparison with the desired process conditions for a selected process, or the "age" of each particular user entered request, or any other relevant factor a system programmer desires to include for determining the scheduling priorities.

[0072] Once the sequencer subroutine 430 determines which process chamber and process set combination is going to be executed next, the sequencer subroutine 430 causes execution of the process set by passing the particular process set parameters to a chamber manager subroutine 440 which controls multiple processing tasks in a process chamber according to the process set determined by the sequencer subroutine 430. For example, the chamber manager subroutine 440 includes program code for controlling CVD process operations in the process chamber 10. The chamber manager subroutine 440 also controls execution of various chamber component subroutines that control operation of the chamber component necessary to carry out the selected process set. Examples of chamber component subroutines are susceptor control subroutine 450, process gas control subroutine 460, pressure control subroutine 470, heater control subroutine 480, and plasma control subroutine 490. Those having ordinary skill in the art would readily recognize that

other chamber control subroutines can be included depending on what processes are desired to be performed in a processing chamber.

[0073] In operation, the chamber manager subroutine **440** selectively schedules or calls the process component subroutines in accordance with the particular process set being executed. The chamber manager subroutine **440** schedules the process component subroutines similarly to how the sequencer subroutine **430** schedules which process chamber and process set is to be executed next. Typically, the chamber manager subroutine **440** includes steps of monitoring the various chamber components, determining which components needs to be operated based on the process parameters for the process set to be executed, and causing execution of a chamber component subroutine responsive to the monitoring and determining steps.

[0074] Operation of particular chamber component subroutines will now be described with reference to **FIG. 2**. The susceptor control positioning subroutine **450** comprises program code for controlling chamber components that are used to load the substrate onto the susceptor **12**, and optionally to lift the substrate to a desired height in the processing chamber **10** to control the spacing between the substrate and the gas distribution manifold **11**. When a substrate is loaded into the processing chamber **10**, the susceptor **12** is lowered to receive the substrate, and thereafter, the susceptor **12** is raised to the desired height in the chamber to maintain the substrate at a first distance or spacing from the gas distribution manifold **11** during the CVD process. In operation, the susceptor control subroutine **450** controls movement of the susceptor **12** in response to process set parameters that are transferred from the chamber manager subroutine **440**.

[0075] The process gas control subroutine **460** has program code for controlling process gas compositions and flow rates. The process gas control subroutine **460** controls the open/close position of the safety shut-off valves, and also ramps up/down the mass flow controllers to obtain the desired gas flow rate. The process gas control subroutine **460** is invoked by the chamber manager subroutine **440**, as are all chamber components subroutines, and receives from the chamber manager subroutine process parameters related to the desired gas flow rates. Typically, the process gas control subroutine **460** operates by opening the gas supply lines, and repeatedly (i) reading the necessary mass flow controllers, (ii) comparing the readings to the desired flow rates received from the chamber manager subroutine **440**, and (iii) adjusting the flow rates of the gas supply lines as necessary. Furthermore, the process gas control subroutine **460** includes steps for monitoring the gas flow rates for unsafe rates, and activating the safety shut-off valves when an unsafe condition is detected.

[0076] In some processes, an inert gas such as helium or argon is put into the processing chamber **10** to stabilize the pressure in the chamber before reactive process gases are introduced. For these processes, the process gas control subroutine **460** is programmed to include steps for flowing the inert gas into the chamber **10** for an amount of time necessary to stabilize the pressure in the chamber, and then the steps described above would be carried out.

[0077] Additionally, when a process gas is to be vaporized from a liquid precursor, such as OMCTS for example, the process gas control subroutine **460** would be written to

include steps for bubbling a carrier/delivery gas such as argon, helium, nitrogen, hydrogen, carbon dioxide, ethylene, or mixtures thereof, for example, through the liquid precursor in a bubbler assembly. The carrier gas typically has a flowrate between about 100 sccm to about 10,000 sccm, preferably 1,000 sccm.

[0078] For this type of process, the process gas control subroutine **460** regulates the flow of the delivery gas, the pressure in the bubbler, and the bubbler temperature in order to obtain the desired process gas flow rates. As discussed above, the desired process gas flow rates are transferred to the process gas control subroutine **460** as process parameters. Furthermore, the process gas control subroutine **460** includes steps for obtaining the necessary delivery gas flow rate, bubbler pressure, and bubbler temperature for the desired process gas flow rate by accessing a stored table containing the necessary values for a given process gas flow rate. Once the necessary values are obtained, the delivery gas flow rate, bubbler pressure and bubbler temperature are monitored, compared to the necessary values and adjusted accordingly.

[0079] The pressure control subroutine **470** comprises program code for controlling the pressure in the processing chamber **10** by regulating the size of the opening of the throttle valve in the exhaust pump **32**. The size of the opening of the throttle valve is set to control the chamber pressure to the desired level in relation to the total process gas flow, size of the process chamber, and pumping set point pressure for the exhaust pump **32**. When the pressure control subroutine **470** is invoked, the desired, or target pressure level is received as a parameter from the chamber manager subroutine **440**. The pressure control subroutine **470** operates to measure the pressure in the processing chamber **10** by reading one or more conventional pressure manometers connected to the chamber, compare the measure value(s) to the target pressure, obtain PID (proportional, integral, and differential) values from a stored pressure table corresponding to the target pressure, and adjust the throttle valve according to the PID values obtained from the pressure table. Alternatively, the pressure control subroutine **470** can be written to open or close the throttle valve to a particular opening size to regulate the processing chamber **10** to the desired pressure.

[0080] The heater control subroutine **480** comprises program code for controlling the temperature of the heat modules or radiated heat that is used to heat the susceptor **12**. The heater control subroutine **480** is also invoked by the chamber manager subroutine **440** and receives a target, or set point, temperature parameter. The heater control subroutine **480** measures the temperature by measuring voltage output of a thermocouple located in a susceptor **12**, compares the measured temperature to the set point temperature, and increases or decreases current applied to the heat module to obtain the set point temperature. The temperature is obtained from the measured voltage by looking up the corresponding temperature in a stored conversion table, or by calculating the temperature using a fourth order polynomial. The heater control subroutine **480** gradually controls a ramp up/down of current applied to the heat module. The gradual ramp up/down increases the life and reliability of the heat module. Additionally, a built-in-fail-safe mode can be

included to detect process safety compliance, and can shut down operation of the heat module if the processing chamber 10 is not properly set up.

[0081] The plasma control subroutine 490 comprises program code for setting the RF bias voltage power level applied to the process electrodes in the processing chamber 10, and optionally, to set the level of the magnetic field generated in the reactor. Similar to the previously described chamber component subroutines, the plasma control subroutine 490 is invoked by the chamber manager subroutine 440.

[0082] The pretreatment and method for forming a pretreated layer of the present invention is not limited to any specific apparatus or to any specific plasma excitation method. The above CVD system description is mainly for illustrative purposes, and other CVD equipment such as electrode cyclotron resonance (ECR) plasma CVD devices, induction-coupled RF high density plasma CVD devices, or the like may be employed. Additionally, variations of the above described system such as variations in susceptor design, heater design, location of RF power connections and others are possible. For example, the substrate could be supported and heated by a resistively heated susceptor.

EXAMPLES

[0083] The following examples illustrate the low dielectric films of the present invention. The films were deposited using a chemical vapor deposition chamber that is part of an integrated processing platform. In particular, the films were deposited using a "Producer" system, available from Applied Materials, Inc. of Santa Clara, Calif.

Example 1

[0084] A low dielectric constant film was deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of about 400° C.

[0085] Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;

[0086] Trimethylsilane (TMS), at about 200 sccm;

[0087] Ethylene, at about 2,000 sccm;

[0088] Oxygen, at about 1,000 sccm; and

[0089] Helium, at about 1,000 sccm

[0090] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The film was deposited at a rate of about 12,000 A/min, and had a dielectric constant (k) of about 2.54 measured at 0.1 MHz.

Example 2

[0091] A low dielectric constant film was deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of about 400° C.

[0092] Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;

[0093] Trimethylsilane (TMS), at about 400 sccm;

[0094] Ethylene, at about 2,000 sccm;

[0095] Oxygen, at about 1,000 sccm; and

[0096] Helium, at about 1,000 sccm;

[0097] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The film was deposited at a rate of about 12,000 A/min, and had a dielectric constant (k) of about 2.51 measured at 0.1 MHz.

Example 3

[0098] A low dielectric constant film was deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of about 400° C.

[0099] Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;

[0100] Trimethylsilane (TMS), at about 600 sccm;

[0101] Ethylene, at about 2,000 sccm;

[0102] Oxygen, at about 1,000 sccm; and

[0103] Helium, at about 1,000 sccm

[0104] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The film was deposited at a rate of about 12,000 A/min, and had a dielectric constant (k) of about 2.47 measured at 0.1 MHz.

Example 4

[0105] A low dielectric constant film was deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of about 400° C.

[0106] Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;

[0107] Trimethylsilane (TMS), at about 800 sccm;

[0108] Ethylene, at about 2,000 sccm;

[0109] Oxygen, at about 1,000 sccm; and

[0110] Helium, at about 1,000 sccm

[0111] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The film was deposited at a rate of about 12,000 A/min, and had a dielectric constant (k) of about 2.47 measured at 0.1 MHz.

Example 5

[0112] A low dielectric constant film was deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of about 400° C.

[0113] Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;

[0114] Trimethylsilane (TMS), at about 900 sccm;

- [0115] Ethylene, at about 2,000 sccm;
 [0116] Oxygen, at about 1,000 sccm; and
 [0117] Helium, at about 1,000 sccm

[0118] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The film was deposited at a rate of about 12,000 Å/min, and had a dielectric constant (k) of about 2.48 measured at 0.1 MHz.

Example 6

[0119] A low dielectric constant film was deposited on a substrate from the following reactive gases at a chamber pressure of about 14 Torr and substrate temperature of 350° C.

- [0120] Octamethylcyclotetrasiloxane (OMCTS), at about 210 sccm;
 [0121] Trimethylsilane (TMS), at about 400 sccm;
 [0122] Oxygen, at about 600 sccm; and
 [0123] Helium, at about 800 sccm

[0124] The substrate was positioned 450 mils from the gas distribution showerhead. A power level of 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The deposited film had a dielectric constant (k) of about 2.67 measured at 0.1 MHz.

Example 7

[0125] A low dielectric constant film was deposited on a substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of 400° C.

- [0126] Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;
 [0127] Ethylene, at about 2,000 sccm;
 [0128] Oxygen, at about 1,000 sccm; and
 [0129] Helium, at about 1,000 sccm

[0130] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The deposited film had a dielectric constant (k) of about 2.55 measured at 0.1 MHz.

[0131] FIG. 3 illustrates the effect of varying the flow rate of TMS in Examples 1-5 described above. It was surprisingly found that the dielectric constant significantly decreased as the flow rate of TMS increased between about 200 sccm to about 600 sccm. The low dielectric constants were achieved with a ratio of aliphatic hydrocarbon compound to aliphatic organosilicon compound of about 15:1 to about 1:1. As illustrated with Example 6 and shown in FIG. 3, the addition of a sufficient amount of the aliphatic hydrocarbon compound to the cyclic organosilicon and aliphatic organosilicon compounds provided a dielectric constant at least 7% lower than a dielectric constant obtained by omitting the aliphatic hydrocarbon compound. Further,

the addition of a sufficient amount of the aliphatic organosilicon compound to the cyclic organosilicon and aliphatic hydrocarbon compounds provided a dielectric constant about 3% lower than a dielectric constant obtained by omitting the aliphatic organosilicon compound as shown in Example 7.

[0132] While the foregoing is directed to preferred embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims which follow.

What is claimed is:

1. A method for depositing a low dielectric constant film having a dielectric constant of about 3.0 or less, comprising:

reacting a gas mixture comprising:

- one or more cyclic organosilicon compounds;
- one or more aliphatic compounds; and
- one or more oxidizing gases; and

delivering the gas mixture to a substrate surface at conditions sufficient to deposit the low dielectric constant film on the substrate surface.

2. The method of claim 1, wherein the one or more cyclic organosilicon compounds comprise at least one silicon-carbon bond.

3. The method of claim 1, wherein the one or more aliphatic compounds comprise a silicon-hydrogen bond or an unsaturated carbon-carbon bond.

4. The method of claim 1, wherein the one or more aliphatic compounds comprise organosilicon compounds, hydrocarbon compounds, or a mixture thereof.

5. The method of claim 1, wherein the one or more cyclic organosilicon compounds is selected from the group consisting of 3,5-trisilano-2,4,6-trimethylene, 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), 1,3,5,7,9-pentamethylcyclopentasiloxane, 1,3,5,7-tetrasilano-2,6-dioxy-4,8-dimethylene, and hexamethylcyclotrisiloxane.

6. The method of claim 4, wherein the organosilicon compounds are selected from the group consisting of methylsilane, dimethylsilane, trimethylsilane, dimethyldimethoxysilane, ethylsilane, disilanoethane, bis(methylsilano)methane, 1,2-disilanoethane, 1,2-bis(methylsilano)ethane, 2,2-disilanoethane, 1,3-dimethylidisiloxane, 1,1,3,3-tetramethyldisiloxane (TMDSO), hexamethyldisiloxane (HMDS), 1,3-bis(silano)methylene)disiloxane, bis(1-methyldisiloxanyl)methane, 2,2-bis(1-methyldisiloxanyl)propane, diethylsilane, propylsilane, vinylmethylsilane, 1,1,2,2-tetramethyldisilane, hexamethyldisilane, 1,1,2,2,3,3-hexamethyltrisilane, 1,1,2,3,3-pentamethyltrisilane, dimethyldisilanoethane, dimethyldisilanoethane, tetramethyldisilanoethane, and tetramethyldisilanoethane.

7. The method of claim 4, wherein the hydrocarbon compounds are selected from the group consisting of ethylene, propylene, acetylene, ethylene, propylene, acetylene, butadiene, t-butylethylene, 1,1,3,3-tetramethylbutylbenzene, t-butylether, methyl-methacrylate (MMA), and t-butyl-furfuryl ether.

8. The method of claim 1, wherein the one or more cyclic organosilicon compounds is 3,5-trisilano-2,4,6-trimethyl-

ene, 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), or a mixture thereof.

9. The method of claim 1, wherein the one or more aliphatic compounds comprises ethylene, methylsilane, dimethylsilane, trimethylsilane, or a mixture thereof.

10. The method of claim 1, wherein the one or more aliphatic compounds comprises ethylene and trimethylsilane.

11. The method of claim 1, wherein the conditions comprise a power density ranging from about 0.03 W/cm² to about 3.2 W/cm².

12. The method of claim 1, wherein the conditions comprise a substrate temperature of about 100° C. to about 400° C.

13. The method of claim 1, wherein the conditions comprise a pressure of about 4 Torr to about 6 Torr.

14. The method of claim 1, wherein the gas mixture comprises:

about 5 percent by volume to about 80 percent by volume of the one or more cyclic organosilicon compounds;

about 5 percent by volume to about 15 percent by volume of one or more aliphatic organosilicon compounds;

about 5 percent by volume to about 45 percent by volume of one or more aliphatic hydrocarbon compounds; and

about 5 percent by volume to about 20 percent by volume of the one or more oxidizing gases.

15. The method of claim 1, wherein the gas mixture comprises:

about 5 percent by volume to about 80 percent by volume of the one or more cyclic organosilicon compounds;

about 5 percent by volume to about 15 percent by volume of one or more aliphatic organosilicon compounds;

about 5 percent by volume to about 45 percent by volume of ethylene; and

about 5 percent by volume to about 20 percent by volume of the one or more oxidizing gases.

16. The method of claim 1, wherein the gas mixture comprises:

about 5 percent by volume to about 80 percent by volume of the one or more cyclic organosilicon compounds;

about 5 percent by volume to about 15 percent by volume of trimethylsilane;

about 5 percent by volume to about 45 percent by volume of ethylene; and

about 5 percent by volume to about 20 percent by volume of the one or more oxidizing gases.

17. The method of claim 1, wherein the gas mixture comprises:

about 5 percent by volume to about 80 percent by volume of octamethylcyclotetrasiloxane;

about 5 percent by volume to about 15 percent by volume of trimethylsilane;

about 5 percent by volume to about 45 percent by volume of ethylene; and

about 5 percent by volume to about 20 percent by volume of the one or more oxidizing gases.

18. The method of claim 1, wherein the gas mixture comprises:

about 15 percent by volume to about 60 percent by volume of the one or more cyclic organosilicon compounds;

about 5 percent by volume to about 10 percent by volume of the one or more aliphatic organosilicon compounds;

about 5 percent by volume to about 35 percent by volume of the one or more aliphatic hydrocarbon compounds; and

about 5 percent by volume to about 20 percent by volume of the one or more oxidizing gases.

19. The method of claim 1, wherein the gas mixture comprises:

about 15 percent by volume to about 60 percent by volume of octamethylcyclotetrasiloxane;

about 5 percent by volume to about 10 percent by volume of trimethylsilane;

about 5 percent by volume to about 35 percent by volume of ethylene; and

about 5 percent by volume to about 20 percent by volume of the one or more oxidizing gases.

20. A method for depositing a low dielectric constant film having a dielectric constant of about 3.0 or less, comprising:

reacting a gas mixture comprising:

one or more cyclic organosilicon compounds;

one or more aliphatic compounds;

one or more meta-stable organic compounds; and

one or more oxidizing gases;

delivering the gas mixture to a substrate surface at conditions sufficient to transform the meta-stable organic compound to an unstable component within a network of the film; and

annealing the film to remove the unstable component from the film.

21. The method of claim 20, wherein annealing the film occurs at a temp. between about 100° C. to about 400° C. for about 2 seconds to about 10 minutes.

22. The method of claim 20, wherein the meta-stable compound is one of more compounds selected from the group consisting of t-butylethylene, 1,1,3,3-tetramethylbutylbenzene, t-butylether, methyl-methacrylate (MMA), and t-butylfurfurylether.

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