

STABILIZED ORGANOSILANE COMPOSITIONS AND METHODS OF USING
SAME TO FORM DENSE LOW-K FILMS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of US Provisional Application 63/519,635, filed 15 August 2023.

BACKGROUND

[0002] The present invention relates generally to stabilized organosilane compositions and the formation of dielectric films using stable compositions. More specifically, the invention relates to dielectric materials and films comprising same having a low dielectric constant and enhanced mechanical properties and methods for making same using stable compositions.

[0003] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0004] There is a continuing desire in the microelectronics industry to increase the circuit density in multilevel integrated circuit devices such as memory and logic chips to improve the operating speed and reduce power consumption. US Patent 10249489 B2 discloses low dielectric organosilicon films formed using, *inter alia*, alkoxyated disilyl-alkanes and -cycloalkanes. Such low dielectric materials are desirable for use, for example, as premetal dielectric layers or interlevel dielectric layers.

[0005] One class of organosilanes useful for low-k applications is alkoxyated disilacyclobutanes. However, some of such compounds have boiling points that require the film precursors to be heated to temperatures that are sufficiently high to promote polymerization, which limits the precursor's use as a stable and high-yield film forming compound.

[0006] US11393678 B Discloses methods for deposition of high-hardness low-k dielectric films. More particularly, a method of processing a substrate is provided. The method includes (1) flowing a precursor-containing gas mixture into a processing volume of a processing chamber having a substrate, wherein the precursors are silacyclobutane derivatives (2) maintaining the substrate at a pressure in a range of about 0.1 mtorr and about 20 torr and at a temperature in a range of about 200° to about 500°, and (3) generating a plasma at a substrate level to deposit a dielectric film on the substrate.

[0007] US5302734 A discloses synthesis of alkoxy-1,3-disilacyclobutane by pyrolysis.

[0008] US7381659 B discloses a method for reducing the tensile stress of a low-k dielectric. layer includes depositing an organosilicate layer on a substrate, the layer having an initial tensile stress value associated therewith. The layer is annealed in a reactive environment at a temperature and for a duration selected to result in the layer having a reduced tensile stress value with respect the initial tensile stress value following the completion of the annealing.

[0009] US10249489 B describes low dielectric materials and films comprising the same for improved performance when used as interlevel dielectric in integrated circuits as well as methods for making same. The formation of this organosilicate film involves the chemical vapor deposition of at least one organosilicon precursor.

[0010] Interrante, L. V., et al. (1998). "Linear and hyperbranched polycarbosilanes with Si-CH₂-Si bridging groups: a synthetic platform for the construction of novel functional polymeric materials." Appl. Organomet. Chem. **12**(10/11): 695-705. Describes synthetic routes to both linear and hyperbranched polycarbosilanes having a "[SiH₂CH₂]_n" compositional formula. The linear [SiH₂CH₂]_n polymer was prepared by ring-opening polymerization of a substituted disilacyclobutane.

[0011] There is a need to develop a composition comprising stabilized cyclodisilabutane for vapor deposition of silicon-containing low dielectric materials as the cyclodisilabutane disclosed in prior seems to potentially form polymeric species during its delivery.

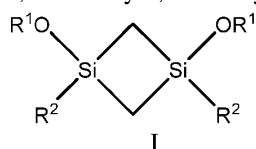
SUMMARY

[0012] The compositions or formulations described herein and methods using same overcome the problems of the prior art by depositing a silicon-containing film on at least a portion of the substrate surface that provides desirable film properties.

[0013] In one aspect, the present development provides stabilized organosilane compositions that are able to be used in the formation of dielectric films without being subject to polymerization to the extent that the precursors lose their utility. In another aspect, the invention relates to dielectric materials and films comprising the same having a low dielectric constant and enhanced mechanical properties, and methods for making the same using the stable organosilane compositions.

[0014] The above problems and others are overcome by a composition comprising:

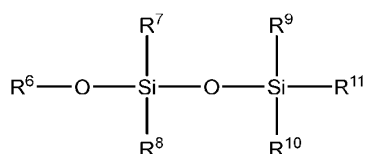
- (a) 1,3-dialkoxy-1,3-disilacyclobutane having the formula I below:



wherein each R^1 is independently a C_1 to C_{10} linear or branched alkyl, and each R^2 is independently hydrogen or a C_1 to C_{10} linear or branched alkyl; and

- (b) a polymerization inhibitor selected from the group consisting of

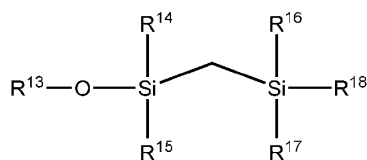
- (i) an antioxidant or free-radical scavenger;
- (ii) $\text{R}^3_n\text{R}^4_m\text{Si}(\text{OR}^5)_{4-n-m}$ wherein R^3 and R^4 are each independently selected from hydrogen and a C_1 to C_{10} linear or branched alkyl; and R^5 is selected from a C_1 to C_{10} linear or branched alkyl; n is 0, 1, 2, or 3; $m=0, 1, 2, 3$;
- (iii) an alkoxy-disiloxane having the formula below



wherein R^6 is selected from a linear or branched C_1 to C_6 alkyl, preferably methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, or tert-butyl, and a cyclic C_5 to C_6 alkyl; R^7 is selected from hydrogen, and a linear or branched C_1 to C_5 alkyl; R^{8-10} are each

selected independently from a linear or branched C₁ to C₅ alkyl, preferably methyl;
and R¹¹ is selected from hydrogen, a linear or branched C₁ to C₅ alkyl, or OR¹²
wherein R¹² is selected from a linear or branched C₁ to C₅ alkyl;

(iv) an alkoxy-carbosilane having the structure below



R¹³ is selected from a linear or branched C₁ to C₆ alkyl, preferably methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, or tert-butyl, and a cyclic C₅ to C₆ alkyl; R¹⁴ is selected from hydrogen, and a linear or branched C₁ to C₅ alkyl; R¹⁵⁻¹⁷ are selected independently from a linear or branched C₁ to C₅ alkyl, preferably methyl; and R¹⁸ is selected from hydrogen, a linear or branched C₁ to C₅ alkyl, or OR¹⁹ wherein R¹⁹ is selected from a linear or branched C₁ to C₅ alkyl; and

(v) an organoaminosilane R²⁰_nR²¹_mSi(NR²²R²³)_{4-n-m} wherein R²⁰ and R²¹ are each independently selected from hydrogen and a C₁ to C₁₀ linear or branched alkyl; and R²² and R²³ is selected from hydrogen, a C₁ to C₁₀ linear or branched alkyl; n is 0, 1, 2, or 3; m=0, 1, 2, 3.

[0015] In a preferred embodiment, the alkoxy groups in any of the polymerization inhibitor(s) (ii) to (v) are same as alkoxy group(s) in the 1,3-dialkoxy-1,3-disilacyclobutane to ensure that if alkoxy exchange reactions occur between the polymerization inhibitor(s) and the 1,3-dialkoxy-1,3-disilacyclobutane, the chemical structure of the 1,3-dialkoxy-1,3-disilacyclobutane does not change.

[0016] The above problems and others are further solved by a chemical vapor deposition method for depositing an organosilicate film on at least a part of a substrate, the process comprising:

providing a substrate within a vacuum chamber;

introducing into the vacuum chamber the composition comprising (a) and (b)

as set forth above; and

applying energy to the gaseous structure forming composition in the vacuum chamber to induce reaction of at least the 1,3-dialkoxy-1,3-disilacyclobutane to deposit a film on at least a portion of the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1 is a graph that depicts precursor flow rate and corresponding piezoelectric control valve voltage associated with vaporizing both stabilized (Panels A and C) and un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane (Panels B and D) through a Horiba liquid source vaporization system.

[0018] FIG. 2 is a graph that depicts dielectric constants of films 1, 2, 3, and 4 deposited using stabilized (black hatched pattern) and un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane (solid black).

[0019] FIG. 3 is a graph that depicts hardness of films 1, 2, 3, and 4 deposited using stabilized (black hatched pattern) and un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane (solid black).

DETAILED DESCRIPTION

[0020] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (i.e., meaning "including, but not limited to,") unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (*e.g.*, "such as") provided herein, is intended merely to better illuminate the invention and does not

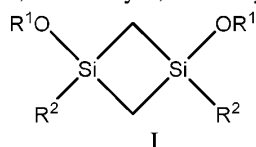
pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0021] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

[0022] In the claims, letters may be used to identify claimed method steps (e.g. a, b, and c). These letters are used to aid in referring to the method steps and are not intended to indicate the order in which claimed steps are performed, unless and only to the extent that such order is specifically recited in the claims.

[0023] In one aspect, the present development provides a composition comprising:

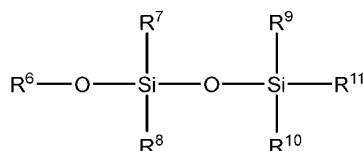
- (a) 1,3-dialkoxy-1,3-disilacyclobutane having the formula I below:



wherein each R^1 is independently a C_1 to C_{10} linear or branched alkyl, and each R^2 is independently hydrogen or a C_1 to C_{10} linear or branched alkyl; and

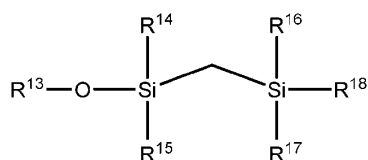
- (b) a polymerization inhibitor selected from the group consisting of
- (i) an antioxidant or free-radical scavenger;
 - (ii) $R^3_n R^4_m Si(OR^5)_{4-n-m}$ wherein R^3 and R^4 are each independently selected from hydrogen and a C_1 to C_{10} linear or branched alkyl; and R^5 is selected from a C_1 to C_{10} linear or branched alkyl; n is 0, 1, 2, or 3; $m=0, 1, 2, 3$;

(iii) an alkoxy-disiloxane having the formula below



wherein R^6 is selected from a linear or branched C_1 to C_6 alkyl, preferably methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, or tert-butyl, and a cyclic C_5 to C_6 alkyl; R^7 is selected from hydrogen, and a linear or branched C_1 to C_5 alkyl; R^{8-10} are each selected independently from a linear or branched C_1 to C_5 alkyl, preferably methyl; and R^{11} is selected from hydrogen, a linear or branched C_1 to C_5 alkyl, or OR^{12} wherein R^{12} is selected from a linear or branched C_1 to C_5 alkyl;

(iv) an alkoxy-carbosilane having the structure below



R^{13} is selected from a linear or branched C_1 to C_6 alkyl, preferably methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, or tert-butyl, and a cyclic C_5 to C_6 alkyl; R^{14} is selected from hydrogen, and a linear or branched C_1 to C_5 alkyl; R^{15-17} are selected independently from a linear or branched C_1 to C_5 alkyl, preferably methyl; and R^{18} is selected from hydrogen, a linear or branched C_1 to C_5 alkyl, or OR^{19} wherein R^{19} is selected from a linear or branched C_1 to C_5 alkyl; and

(v) an organoaminosilane $\text{R}^{20}_n\text{R}^{21}_m\text{Si}(\text{NR}^{22}\text{R}^{23})_{4-n-m}$ wherein R^{20} and R^{21} are each independently selected from hydrogen and a C_1 to C_{10} linear or branched alkyl; and R^{22} and R^{23} is selected from hydrogen, a C_1 to C_{10} linear or branched alkyl; n is 0, 1, 2, or 3; $m=0, 1, 2, 3$.

[0024] In a preferred embodiment, the alkoxy groups in any polymerization inhibitor(s) (ii) to (v) are the same as the alkoxy group(s) in the 1,3-dialkoxy-1,3-disilacyclobutane to ensure that if alkoxy exchange reactions occur between the

polymerization inhibitor(s) and the 1,3-dialkoxy-1,3-disilacyclobutane, the chemical structure of the 1,3-dialkoxy-1,3-disilacyclobutane does not change.

[0025] According to an exemplary embodiment, for the 1,3-dialkoxy-1,3-disilacyclobutane (a), R^1 and R^2 are each independently selected from the group consisting of hydrogen and C_1 to C_4 linear or branched alkyl. Examples include 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane, 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane, 1,3-di-n-propoxy-1,3-disilacyclobutane, 1,3-di-iso-propoxy-1,3-dimethyl-1,3-disilacyclobutane, 1,3-methoxy-1,3-diethyl-1,3-disilacyclobutane, 1,3-dipropoxy-1,3-disilacyclobutane, 1,3-diethoxy-1-methyl-1,3-disilacyclobutane, and 1,3-diethoxy-1-ethyl-1,3-disilacyclobutane, 1,3-diethoxy-1,3-disilacyclobutane, 1,3-dimethoxy-1,3-disilacyclobutane.

[0026] Polymerization inhibitor (b) is employed to stabilize the 1,3-dialkoxy-1,3-disilacyclobutane and can be selected from the group consisting of (i), (ii), (iii), (iv) and combinations thereof. The concentration of the polymerization inhibitor can range from about 1 ppm to about 50 wt%, or from about 1 ppm to about 40 wt%, or from about 1 ppm to about 30 wt%, or from about 1 ppm to about 20 wt%, or from about 1 ppm to about 10 wt%, or from about 1 ppm to about 5 wt%, or from about 1 ppm to about 2 wt%, or from about 1 ppm to about 1 wt%, or from about 1 ppm to about 0.5 wt%, or from about 1 ppm to about 0.1 wt%, or from 1 ppm to 100 ppm, or from 1 ppm to 50 ppm, or from 1 ppm to 10 ppm, depending on the polymerization inhibitor employed.

[0027] Examples of the antioxidant or free-radical scavenger (i) include, but are not limited to 2,6-di-tert-butyl-4-methyl phenol (or BHT for butylhydroxytoluene), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), 2-tert-butyl-4-hydroxyanisole, 3-tert-butyl-4-hydroxyanisole, propyl ester 3,4,5-trihydroxy-benzoic acid, 2-(1,1-dimethylethyl)-1,4-benzenediol, diphenylpicrylhydrazyl, 4-tert-butylcatechol, N-methylaniline, p-methoxydiphenylamine, diphenylamine, N,N'-diphenyl-p-phenylenediamine, p-hydroxydiphenylamine, phenol, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, tetrakis (methylene (3,5-di-tert-butyl)-4-hydroxy-hydrocinnamate) methane, phenothiazines, alkylamidonoisoureas, thiodiethylene bis (3,5-di-tert-butyl-4-hydroxy-hydrocinnamate, 1,2-bis (3,5-di-tert-butyl-4-

hydroxyhydrocinnamoyl) hydrazine, tris (2-methyl-4- hydroxy-5-tert-butylphenyl) butane, cyclic neopentanetetrayl bis (octadecyl phosphite), 4,4'-thiobis (6-tert-butyl-m-cresol), 2,2'- methylenebis (6-tert-butyl-p-cresol), oxalyl bis (benzylidenehydrazide) and naturally occurring antioxidants such as raw seed oils, wheat germ oil, tocopherols and combination thereof.

[0028] Examples of the polymerization inhibitor (ii) include, but are not limited to, tetramethoxysilane, trimethoxysilane, tetraethoxysilane, triethoxysilane, dimethoxymethylsilane, diethoxymethylsilane, methoxydimethylsilane, and ethoxydimethylsilane.

[0029] Examples of the polymerization inhibitor (iii) include, but are not limited to, 1,3-diethoxy-1,3-dimethyl-1,3-disiloxane, 1,3-diethoxy-tetramethyldisiloxane.

[0030] Examples of the polymerization inhibitor (iv) include, but are not limited to, 2,4,4-triethoxy-2,4-disilapentane, 2,4-diethoxy-4-methyl-2,4-disilapentane.

[0031] Examples of the polymerization inhibitor (v) include, but are not limited to, dimethylaminotrimethylsilane, diethylaminotrimethylsilane, bis(dimethylamino)dimethylsilane, tris(dimethylamino)methylsilane, dimethylaminodimethylsilane, and diethylaminodimethylsilane.

[0032] Throughout the invention, 1,3-dialkoxy-1,3-disilacyclobutane can be cis-cis, trans-trans, or cis-trans isomers, and mixture thereof. In this or other embodiments, the polymerization inhibitor has a boiling point (b.p.) similar to the b.p. of the 1,3-dialkoxy-1,3-disilacyclobutane or the difference between the b.p. of the polymerization inhibitor and the b.p. of the 1,3-dialkoxy-1,3-disilacyclobutane is 100 °C or less, 40 °C or less, 30 °C or less, or 20 °C or less, or 10 °C less, or 5 °C less. Alternatively, the difference between the boiling points ranges from any one or more of the following end-points: 0, 10, 20, 30, 40 °C, or 100 °C. Examples of suitable ranges of b.p. difference include without limitation, 0 to 100 °C, 0 to 40 °C, 1 to 10 °C, or 1 to 5 °C. Table 1 below lists some additional exemplary polymerization inhibitors (b) and their corresponding boiling points.

[0033] Table 1: Exemplary Polymerization Inhibitors

Chemical	B.P. (C)
1,3-diethoxy-1,3-dimethyl-1,3-disiloxane	185
2,4,4-triethoxy-2,4-disilapentane	240
1,3-diethoxy-tetramethyldisiloxane	183
2,4-diethoxy-4-methyl-2,4-disilapentane	178
Tetraethoxysilane	168
Sec-butoxy-pentamethyldisiloxane	161
Diethoxymethylsilane	98

[0034] An example of an organosilicate film deposited by the method of the present invention is a carbon-doped silicon oxide film. In the method of the present development, typically the first step is placing a substrate comprising at least one surface feature into a reactor which is at a temperature of from about 20 °C to about 600 °C, preferably 100 °C to about 550 °C, most preferably 100 °C to about 450 °C. Suitable substrates include, but are not limited to, semiconductor materials such as gallium arsenide (“GaAs”), boronitride (“BN”) silicon, and compositions containing silicon such as crystalline silicon, polysilicon, amorphous silicon, epitaxial silicon, silicon dioxide (“SiO₂”), silicon carbide (“SiC”), silicon oxycarbide (“SiOC”), silicon nitride (“SiN”), silicon carbonitride (“SiCN”), organosilicate glasses (“OSG”), organofluorosilicate glasses (“OFSG”), fluorosilicate glasses (“FSG”), and other appropriate substrates or mixtures thereof. Substrates may further comprise a variety of layers to which the film is applied thereto such as, for example, antireflective coatings, photoresists, organic polymers, porous organic and inorganic materials, metals such as copper, cobalt, ruthenium, tungsten, rhodium, and aluminum, or diffusion barrier layers, e.g., TiN, Ti, Ti(C)N, TaN, Ta(C)N, Ta, W, WN, TiSiN, TaSiN, SiCN, TiSiCN, TaSiCN, or W(C)N. The substrate may be a single crystal silicon wafer, a wafer of silicon carbide, a wafer of aluminum oxide (sapphire), a sheet of glass, a metallic foil, an organic polymer film or may be a polymeric, glass, silicon or metallic 3-dimensional article. The substrate may be coated with a variety of materials well known in the art including films of silicon oxide, silicon nitride, amorphous carbon, silicon oxycarbide, silicon oxynitride, silicon carbide, gallium arsenide, gallium nitride and the like. These coatings may completely coat the substrate, may be in multiple layers of various materials and may be partially etched

to expose underlying layers of material. The surface may also have on it a photoresist material that has been exposed with a pattern and developed to partially coat the substrate.

[0035] Examples of suitable deposition processes for the method disclosed herein include, but are not limited to, thermal chemical vapor deposition (CVD), plasma enhanced CVD (PECVD), atomic layer deposition (ALD), and plasma enhanced cyclic CVD (PECCVD) process. In one embodiment, the films are deposited using a plasma-based (e.g., remote generated or in situ) CVD process. The term “reactor” as used herein, includes without limitation, a reaction chamber or deposition chamber.

[0036] In certain embodiments, the substrate may be exposed to one or more pre-deposition treatments such as, but not limited to, a plasma treatment, thermal treatment, chemical treatment, ultraviolet light exposure, electron beam exposure, and combinations thereof to affect one or more properties of the films. These pre-deposition treatments may occur under an atmosphere selected from inert, oxidizing, and/or reducing.

[0037] Although the chemical reagents used herein may be sometimes described as “gaseous,” it is understood that the chemical reagents may be delivered directly as a gas to the reactor, delivered as vapors from vaporizing liquid or bubbling liquid using carrier gas such as nitrogen, helium or argon, vapors from subliming solid and/or transported by an inert carrier gas into the reactor.

[0038] In preferred embodiments, the organosilicate film deposited by the present method is a dense organosilicate glass (OSG) film which has a dielectric constant of from about 2.8 to about 3.1, which has a hardness of from about 3.2 to about 4.5 gigapascals (GPa) as measured using a MTS Nano Indenter. This is a significant decrease in dielectric constant over silicon dioxide films which typically have a dielectric constant of from about 3.8 to about 4.2 with a hardness of about 7 GPa.

[0039] The method of the present development includes the step of introducing into the vacuum chamber a composition as defined above, and applying energy to the gaseous structure forming composition in the vacuum chamber to induce reaction of the at least one organosilicon precursor to deposit a film on at least a portion of the substrate.

[0040] The composition described above and herein may be delivered to the reaction chamber such as a CVD or ALD reactor in a variety of ways. In one embodiment, a liquid delivery system may be utilized. In an alternative embodiment, a combined liquid delivery and flash vaporization process unit may be employed, such as, for example, the turbo vaporizer manufactured by MSP Corporation of Shoreview, MN, to enable low volatility materials to be volumetrically delivered, which leads to reproducible transport and deposition without thermal decomposition of the precursor. In liquid delivery formulations, the precursors described herein may be delivered in neat liquid form, or alternatively, may be employed in solvent formulations or compositions comprising same. Thus, in certain embodiments the precursor formulations may include solvent component(s) of suitable character as may be desirable and advantageous in a given end use application to form a film on a substrate.

[0041] In one particular embodiment, a plasma enhanced chemical vapor deposition method for producing low k dielectric films, comprising: providing a substrate within a reaction chamber; introducing the reaction chamber gaseous composition comprising 1,3-dialkoxy-1,3-disilacyclobutane and at least one polymerization inhibitor with or without an oxidant; and applying energy to the gaseous composition in the reaction chamber to induce reaction of the gaseous composition to deposit a silicon-containing film on the substrate. The deposition process is typically conducted on a heated pedestal, at temperature(s) ranging from 100 °C to 600 °C, or from about 200 °C to 550 °C, or from about 250 °C to 450 °C, from about 200 °C to 400 °C.

[0042] An oxidant, such as oxygen (O₂), ozone (O₃), nitrous oxide (N₂O), nitric oxide (NO), nitrogen dioxide (NO₂), dinitrogen tetroxide (N₂O₄) and/or hydrogen peroxide (H₂O₂), can optionally be added.

[0043] One or more fluorine-providing gases may be used as an additive in the reaction or in a post-treatment. Examples of fluorine-providing gases are NF₃, F₂, CF₄, C₂F₆, C₄F₆, and C₆F₆.

[0044] In addition to the composition, and optionally the oxygen-providing gas and the fluorine-providing gas, additional materials can be charged into the vacuum chamber prior to, during and/or after the deposition reaction. Such materials include

reactive substances, such as gaseous or liquid organic substances, NH_3 , H_2 , CO_2 , CO , or fluorocarbons. Examples of organic substances are CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 , cyclopentane, cyclooctane, allene, propylene, alpha-terpinene, para-cymene, benzene, naphthalene, toluene and styrene.

[0045] The reagents (i.e., the composition, oxidant, etc.) can be carried into the reactor separately from distinct sources or as a mixture. The reagents can be delivered to the reactor system by any number of means, preferably using a pressurizable stainless steel vessel fitted with the proper valves and fittings to allow the delivery of liquid to the process reactor.

[0046] Energy is applied to the gaseous reagents to induce the gases to react and to form the film on at least a part of the substrate. Such energy can be provided by, e.g., thermal, plasma, pulsed plasma, helicon plasma, high density plasma, inductively coupled plasma, and remote plasma methods. A secondary rf frequency source can be used to modify the plasma characteristics at the substrate surface. Preferably, the film is formed by plasma enhanced chemical vapor deposition. It is particularly preferred to generate a capacitively coupled plasma at a frequency of 13.56 MHz. Plasma power is preferably from 0.02 to 7 watts/cm², more preferably 0.3 to 3 watts/cm², based upon a surface area of the substrate. It may be advantageous to employ a carrier gas which possesses a low ionization energy to lower the electron temperature in the plasma which in turn will cause less fragmentation in the OSG precursor and porogen. Examples of this type of low ionization gas include CO_2 , NH_3 , CO , CH_4 , Ar, Xe, and Kr.

[0047] In some embodiments where the energy is plasma energy, the plasma source is selected from but not limited to the group consisting of a carbon source plasma, including a hydrocarbon plasma, a plasma comprising hydrocarbon and helium, a plasma comprising hydrocarbon and argon, carbon dioxide plasma, carbon monoxide plasma, a plasma comprising hydrocarbon and hydrogen, a plasma comprising hydrocarbon and a nitrogen source, a plasma comprising hydrocarbon and an oxygen source, and mixture thereof.

[0048] The flow rate for each of the gaseous reagents preferably ranges from 10 to 5000 sccm, more preferably from 30 to 1000 sccm, per single 200 mm wafer. The

individual rates are selected so as to provide the desired amounts of structure-former and pore-former in the film. The actual flow rates needed may depend upon wafer size and chamber configuration, and are in no way limited to 200 mm wafers or single wafer chambers.

[0049] In some embodiments, the film is deposited at a rate of 50-250 nm/min.

[0050] The pressure in the vacuum chamber during deposition is preferably 0.01 to 600 torr, more preferably 1 to 15 torr.

[0051] The film is preferably deposited to a thickness of 0.002 to 10 microns, although the thickness can be varied as required. The blanket film deposited on a non-patterned surface has excellent uniformity, with a variation in thickness of less than 2% over 1 standard deviation across the substrate with a reasonable edge exclusion, wherein e.g. a 5mm outermost edge of the substrate is not included in the statistical calculation of uniformity.

[0052] In-situ or post-deposition treatments may be used to enhance materials properties like hardness, stability (to shrinkage, to air exposure, to etching, to wet etching, etc.), integrity, uniformity and adhesion. Such treatments can be applied to the film prior to, during and/or after porogen removal using the same or different means used for porogen removal. Thus, the term "post-treating" as used herein denotes treating the film with energy (e.g., thermal, plasma, photon, electron, microwave, etc.) or chemicals to remove porogens and, optionally, to enhance materials properties.

[0053] The conditions under which post-treating are conducted can vary greatly. For example, post-treating can be conducted under high pressure or under a vacuum ambient.

[0054] Thermal annealing is conducted under the following conditions. The environment can be inert (e.g., nitrogen, CO₂, noble gases (He, Ar, Ne, Kr, Xe), etc.), oxidizing (e.g., oxygen, air, dilute oxygen environments, enriched oxygen environments, ozone, nitrous oxide, etc.) or reducing (dilute or concentrated hydrogen, hydrocarbons (saturated, unsaturated, linear or branched, aromatics), etc.). The pressure is preferably about 1 Torr to about 1000 Torr, more preferably atmospheric pressure. However, a vacuum ambient is also possible for thermal

annealing as well as any other post-treating means. The temperature is preferably 200–500 °C, and the temperature ramp rate is from 0.1 to 100 °C/min. The total annealing time is preferably from 0.01 min to 12 hours.

[0055] Chemical treatment of the OSG film can also be conducted via use of fluorinating (HF, SiF₄, NF₃, F₂, COF₂, CO₂F₂, etc.), oxidizing (H₂O₂, O₃, etc.), chemical drying, methylating, or other chemical treatments that enhance the properties of the final material. Chemicals used in such treatments can be in solid, liquid, gaseous and/or supercritical fluid states.

[0056] In certain embodiments, the OSG film is subjected to annealing, preferably by heat, or radiation (i.e., photoannealing). In these embodiments, photoannealing is conducted under the following conditions. The environment can be inert (e.g., nitrogen, CO₂, noble gases (He, Ar, Ne, Kr, Xe), etc.), oxidizing (e.g., oxygen, air, dilute oxygen environments, enriched oxygen environments, ozone, nitrous oxide, etc.), or reducing (e.g., dilute or concentrated hydrocarbons, hydrogen, ammonia etc.). The power may range from 0 to 5000 W. The wavelength is preferably IR, visible, UV or deep UV (wavelength < 200nm). The temperature may range from ambient to 500°C. The pressure may range from 10 mtorr to atmospheric pressure. The total curing time may range from 0.01 min to 12 hours.

[0057] Plasma treating for chemical modification of the OSG film is conducted under the following conditions. The environment can be inert (nitrogen, CO₂, noble gases (He, Ar, Ne, Kr, Xe), etc.), oxidizing (e.g., oxygen, air, dilute oxygen environments, enriched oxygen environments, ozone, nitrous oxide, etc.), or reducing (e.g., dilute or concentrated hydrogen, hydrocarbons (saturated, unsaturated, linear or branched, aromatics), ammonia etc.). The plasma power is preferably 0–5000 W. The temperature is preferably ambient to 500°C. The pressure is preferably 10 mtorr to atmospheric pressure. The total curing time is preferably 0.01 min to 12 hours.

[0058] Microwave post-treating is conducted under the following conditions. The environment can be inert (e.g., nitrogen, CO₂, noble gases (He, Ar, Ne, Kr, Xe), etc.), oxidizing (e.g., oxygen, air, dilute oxygen environments, enriched oxygen environments, ozone, nitrous oxide, etc.), or reducing (e.g., dilute or concentrated hydrocarbons, hydrogen, etc.). The temperature is preferably ambient to 500°C. The

power and wavelengths are varied and tunable to specific bonds. The total curing time is preferably from 0.01 min to 12 hours.

[0059] Electron beam post-treating is conducted under the following conditions. The environment can be vacuum, inert (e.g., nitrogen, CO₂, noble gases (He, Ar, Ne, Kr, Xe), etc.), oxidizing (e.g., oxygen, air, dilute oxygen environments, enriched oxygen environments, ozone, nitrous oxide, etc.), or reducing (e.g., dilute or concentrated hydrocarbons, hydrogen, etc.). The temperature is preferably ambient to 500°C. The electron density and energy can be varied and tunable to specific bonds. The total curing time is preferably from 0.001 min to 12 hours, and may be continuous or pulsed. Additional guidance regarding the general use of electron beams is available in publications such as: S. Chattopadhyay et al., *Journal of Materials Science*, 36 (2001) 4323-4330; G. Kloster et al., *Proceedings of IITC*, June 3-5, 2002, SF, CA; and U.S. Pat. Nos. 6,207,555 B1, 6,204,201 B1 and 6,132,814 A1. The use of electron beam treatment may provide for porogen removal and enhancement of film mechanical properties through bond-formation processes in matrix.

[0060] The invention will be illustrated in more detail with reference to the following Examples, but it should be understood that the present invention is not deemed to be limited thereto.

EXAMPLE 1 – Stabilization of 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane

[0061] 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane has a boiling point of 185 °C and must be heated to above 100 °C to have sufficient vapor pressure to enable practical vapor phase delivery. However, 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane has a tendency to polymerize when heated above 100 °C. More particularly, neat 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane will polymerize to form a gel if heated to 120 °C for several days. Thermogravimetric analysis (TGA) of 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane heated for 7 days reveals significant levels of non-volatile residue as compared to the pristine material which has non-detect levels of non-volatile residue. The polymeric thermal degradation product can also be measured by GPC (gel permeation chromatography). In contrast, 1,3-

diethoxy-1,3-dimethyl-1,3-disilacyclobutane spiked with butylated hydroxytoluene (BHT) or hydroquinone monomethylether (HQMMME) (aka 4-methoxy-phenol) exhibits substantially reduced or non-detect levels of non-volatile residue by TGA. 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane spiked with organosilanes such as DEMS or TEOS also exhibits substantially reduced or non-detect levels of non-volatile residue by TGA analysis. Doping 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane with antioxidant/free-radical scavengers or with organosilanes such as those described herein substantially increase the thermal stability of 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane, thus making it practical for use in low-k applications.

[0062] Table 2 below provides a listing of various compositions that include 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane (DEDMDSCB) and a polymerization inhibitor. The compositions were aged for 7 days at 120 °C or for up to 26 days at 110°C, inspected visually and analyzed by TGA for NVR (non-volatile content) after the thermal ageing.

[0063] Table 2

Sample description	Visual inspection after 1 day at 120°C	TGA NVR (%) after 1 day at 120°C	Visual inspection after 7 days at 120°C	TGA NVR (%) after 7 days at 120°C
99.8% DEDMDSCB	no gel	0.26	gel	~70
2 wt.% TEOS in AM-E DEDMDSCB	no gel	0.54	gel	--
10 wt.% TEOS in DEDMDSCB	no gel	0.30	no gel	0.75
0.1 wt.% DEMS in DEDMDSCB	no gel*	0.46*	no gel**	0.19**
0.5 wt.% DEMS in DEDMDSCB	no gel*	0.13*	no gel**	0.17**
2 wt.% DEMS in DEDMDSCB	no gel	0.06	no gel	0.09
10 wt.% DEMS in DEDMDSCB	no gel	0.06	no gel	0.29

1000 ppm BHT in DEDMDSCB	no gel	0.58	no gel	3.77
1000 ppm HQMME in DEDMDSCB	no gel	0.11	no gel	0.23
200 ppm HQMME in DEDMDSCB	no gel	0.14	gel	--

*1 day at 110°C

**26 days at 110°C

EXAMPLE 2

[0064] Additional tests were done to evaluate other potential stabilizers for DEDMDSCB, including BTBAS (bis(tert-butyl)aminosilane), 1-methoxy,1,1,3,3-tetramethyldisiloxane and 3,3,5,5-tetramethyl-2,6-dioxo-3,5-disilaheptane. DEDMDSCB was spiked with 0.5 wt.% BTBAS (bis(tert-butyl)aminosilane), 1-methoxy,1,1,3,3-tetramethyldisiloxane or 3,3,5,5-tetramethyl-2,6-dioxo-3,5-disilaheptane. The spiked samples were heated to 120°C for 24 hours, and then allowed to cool to room temperature to inspect for evidence of gel formation. If there was no indication of gel, the spiked DEDMDSCB was heated for an additional 6 days at 120°C. After a total of 7 days at 120°C the samples were evaluated by visual inspection, GC and TGA residue analysis for any indication of gel or formation of degradation products or non-volatile byproducts.

[0065] Table 3 below provides a listing of various compositions that include DEDMDSCB and the additives used as described above. The compositions were aged for 7 days at 120 °C. The ungeled compositions were inspected visually evaluated by TGA analysis after 1 day and 7 days at 120°C .

[0066] Table 3

Sample description	Visual inspection after 1 day at 120°C	TGA NVR (%) after 1d @ 120°C	Visual inspection after 7 day at 120°C	TGA NVR (%) after 7d @ 120°C
99.6% DEDMDSCB (1 of 2)	gel	Not analyzed	NA	NA
99.6% DEDMDSCB (2 of 2)	gel	Not analyzed	NA	NA

0.5 wt.% BTBAS in DEDMDSCB (1 of 2)	No gel	0.12 wt. %	No gel	0.17 wt. %
0.5 wt.% BTBAS in DEDMDSCB (2 of 2)	No gel	0.14 wt. %	No gel	0.12 wt. %
0.5 wt.% 1-methoxy,1,1,3,3-tetramethyldisiloxane in DEDMDSCB (1 of 2)	gel	Not analyzed	NA	NA
0.5 wt.% 1-methoxy,1,1,3,3-tetramethyldisiloxane in DEDMDSCB (2 of 2)	gel	Not analyzed	NA	NA
0.5 wt.% 3,3,5,5-tetramethyl-2,6-dioxa-3,5-disilaheptane in DEDMDSCB (1 of 2)	gel	Not analyzed	NA	NA
0.5 wt.% 3,3,5,5-tetramethyl-2,6-dioxa-3,5-disilaheptane in DEDMDSCB (2 of 2)	gel	Not analyzed	NA	NA

EXAMPLE 3

[0067] The liquid precursor, 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane, was vaporized using a Horiba liquid source vaporization system (LSVS). This system consists of two components: a liquid flow meter and a heated vaporizer (injector). Pressurized liquid is delivered to the liquid flow meter, the measured liquid flow is then delivered to the vaporizer, the gaseous output of the vaporizer is then delivered to a vacuum system. A piezoelectric control valve in the vaporizer (0 V = Fully Open, 120 V = Closed) opens or closes to adjust the liquid flow rate to its set point via a feedback loop. The temperature of the vaporizer is typically set to the lowest temperature that results in a stable vapor delivery flow rate. For 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane a vaporizer temperature of 110 °C was used.

[0068] The degree of residue buildup or clogging in a vaporizer for a given precursor can be monitored by tracking the voltage of the piezoelectric control valve for a fixed liquid flow rate as function of time (that is, as a function of the mass of the precursor vaporized). As residue builds up in the piezoelectric valve, the valve must open further to maintain the same liquid flow rate. Thus, if the voltage of the piezoelectric valve begins to rapidly decrease (0 V = Fully Open) for a fixed liquid flow rate the vaporizer is clogging.

[0069] To test the stability of 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane in the Horiba LSVS over time, a fixed liquid flow condition (1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane = 600 mg/min; He = 700 sccm) was run at the beginning of the workday. During this daily standard the liquid flow rate and piezoelectric voltage were recorded. After the daily standard was completed, various flow rates of 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane (500 – 1100 mg/min) were vaporized through the Horiba LSVS; vaporization times ranges from 72 to 380 sec. After a vaporization run was completed, the vaporizer was purged with N₂ prior to the next run. Changes in the piezoelectric voltage of the daily standard over time were used to gauge the degree of residue buildup (i.e., clogging) in the vaporizer.

[0070] The stability of vaporizing 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane in a Horiba LSVS was monitored for both un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane and stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane. Stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane refers to a mixture of 99.5 w % 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane and 0.5 w % of a polymerization inhibitor (DEMS®). The results are presented in FIG. 1, which shows the precursor flow rate and the voltage of the piezoelectric valve from the daily standard as a function of the day (0 to 60) during the evaluation period. There are four panels in FIG. 1. The top two panels (Panels A and B) show the trends in the precursor flow rate and the bottom two panels (Panels C and D) show the trends in the voltage of the piezoelectric valve. The two panels on the right side of FIG. 1 (Panels B and D) show trends for un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane with the original vaporizer. The two panels on the left side of FIG. 1 (Panels A and C) show the trends for the stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane with a new vaporizer. A new vaporizer was needed to test stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane because the original vaporizer clogged after vaporizing ~ 140 g of un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane.

[0071] Consider the data for un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane collected with the original injector (Panels B and D). While the precursor flow of the daily standard for days 1 – 23 is stable within expected experimental error (Panel B), the decrease in the voltage of the piezoelectric valve

(Panel D) required to maintain stable flow indicates that residue was building up in the piezoelectric valve as the un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane vaporized. This is clearly illustrated by considering the rapid decrease in piezoelectric valve voltage on a weekly basis (W1, W2, and W3). Data from the first week of testing (W1) shows a rapid linear decrease in the piezoelectric valve voltage. Prior to running un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane through the vaporizer in the second week of testing (W2), N₂ was cycled through the vaporizer hundreds of times and the vaporizer allowed to sit idle at temperature for four days. Apparently, this allowed the vaporizer to recover somewhat, as the initial valve voltage at the start of W2 (day 9) was greater than the valve voltage at the end of W1 (day 4). However, the initial valve voltage at the start of W2 is still much lower than the initial valve voltage at the start of W1, indicative of residue buildup remaining in the piezoelectric control valve. Data from the second week of testing (W2) again shows a rapid linear decrease in the piezoelectric valve voltage. Limited data was collected during the third week of testing (W3), as the injector clogged after two additional days of testing. Approximately 140 g of un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane was vaporized before the vaporizer clogged. These data clearly indicate that vaporizing un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane readily leads to residue buildup and clogging of the piezoelectric control valve in a Horiba LSVS.

[0072] Contrast this to the behavior of stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane shown in Panels A and C of FIG. 1. While the precursor flow of the daily standard for days 39 – 58 is stable within expected experimental error (Panel A), only a small gradual decrease in the voltage of the piezoelectric valve (Panel C) is observed. Further, the data in Panels A and C corresponds to vaporizing over 200 g of stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane. These data clearly indicate that stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane results in a significantly smaller rate of residue building up in the piezoelectric control valve relative to un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane.

[0073] All vaporization and deposition experiments were performed on a 300 mm AMAT Producer[®] SE, which deposits films on two wafers at the same time. Thus, the precursor and gas flow rates correspond to the flow rates required to deposit films

on two wafers at the same time. The stated RF power per wafer is correct, as each wafer processing station has its own independent RF power supply. The stated deposition pressure is correct, as both wafer processing stations are maintained at the same pressure.

[0074] Thickness was measured on a Woollam model M2000 Spectroscopic Ellipsometer. Dielectric constant was determined using a Hg probe on mid-resistivity p-type wafers (range 8-12 ohm-cm). Mechanical properties were determined using a KLA iNano Nano Indenter.

[0075] In the examples listed below the same deposition conditions were used to deposit films with un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane and stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane.

EXAMPLE 4: Deposition of a Dense OSG, Film 1, from un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane and stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane.

[0076] A dense film was deposited using un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane using the following process conditions for 300 mm processing. The un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane precursor was delivered to the reaction chamber via direct liquid injection (DLI) at a flow rate of 1100 mg/min using 1500 standard cubic centimeters per minute (sccm) He carrier gas flow, 10 sccm O₂, 400 milli-inch showerhead/heated pedestal spacing, 400 °C pedestal temperature, 4.5 Torr chamber pressure to which a 300 Watt 13.56 MHz plasma was applied. The same deposition conditions were used to deposit a dense film using stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane in place of un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane. Various attributes of the two films (e.g., dielectric constant (k) and hardness) were obtained as described above and are shown graphically in FIG. 2 and FIG. 3.

EXAMPLE 5: Deposition of a Dense OSG, Film 2, from un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane and stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane

[0077] A dense film was deposited using un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane using the following process conditions for 300 mm processing.

The un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane precursor was delivered to the reaction chamber via direct liquid injection (DLI) at a flow rate of 1100 mg/min using 1000 standard cubic centimeters per minute (sccm) He carrier gas flow, 100 sccm O₂, 300 milli-inch showerhead/heated pedestal spacing, 400 °C pedestal temperature, 8.5 Torr chamber pressure to which a 300 Watt 13.56 MHz plasma was applied. The same deposition conditions were used to deposit a dense film using stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane in place of un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane. Various attributes of the two films (e.g., dielectric constant (k) and hardness) were obtained as described above and are shown graphically in FIG. 2 and FIG. 3.

[0078] EXAMPLE 6: Deposition of a Dense OSG, Film 3, from un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane and stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane.

[0079] A dense film was deposited using un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane using the following process conditions for 300 mm processing. The un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane precursor was delivered to the reaction chamber via direct liquid injection (DLI) at a flow rate of 1100 mg/min using 1500 standard cubic centimeters per minute (sccm) He carrier gas flow, 20 sccm O₂, 330 milli-inch showerhead/heated pedestal spacing, 400 °C pedestal temperature, 7.3 Torr chamber pressure to which a 400 Watt 13.56 MHz plasma was applied. The same deposition conditions were used to deposit a dense film using stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane in place of un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane. Various attributes of the two films (e.g., dielectric constant (k) and hardness) were obtained as described above and are shown graphically in FIG. 2 and FIG. 3.

[0080] EXAMPLE 7: Deposition of a Dense OSG, Film 4, from un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane and stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane.

[0081] A dense film was deposited using un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane using the following process conditions for 300 mm processing. The un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane precursor was

delivered to the reaction chamber via direct liquid injection (DLI) at a flow rate of 1100 mg/min using 1500 standard cubic centimeters per minute (sccm) He carrier gas flow, 13 sccm O₂, 330 milli-inch showerhead/heated pedestal spacing, 375 °C pedestal temperature, 7.3 Torr chamber pressure to which a 400 Watt 13.56 MHz plasma was applied. The same deposition conditions were used to deposit a dense film using stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane in place of un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane. Various attributes of the two films (e.g., dielectric constant (k) and hardness) were obtained as described above and are shown graphically in FIG. 2 and FIG. 3.

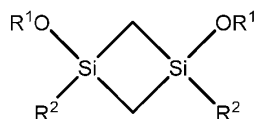
[0082] As shown in FIG. 2 and FIG. 3, comparing the k and hardness of Films 1, 2, 3, and 4 deposited using un-stabilized and stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane indicates that stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane does not increase the k or decrease the mechanical properties of as deposited films relative to the same films deposited using un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane. Indeed, the data in FIG. 2 and FIG. 3 indicates that films deposited using the stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane have a slightly lower k and a slightly higher hardness relative to films deposited using the un-stabilized 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane.

[0083] Although the principles of the invention have been described above in connection with preferred embodiments, it is to be clearly understood that this description is made only by way of example and not as a limitation of the scope of the invention.

CLAIMS

1. A composition comprising:

(a) 1,3-dialkoxy-1,3-disilacyclobutane according to Formula I:

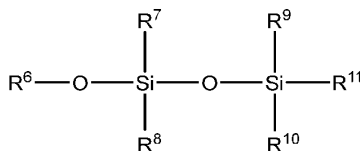


Formula I

wherein each R^1 is independently a C_1 to C_{10} linear or branched alkyl, and each R^2 is independently hydrogen or a C_1 to C_{10} linear or branched alkyl; and

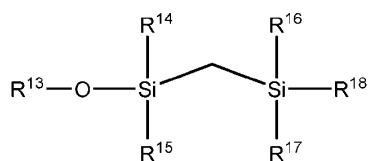
(b) a polymerization inhibitor selected from the group consisting of

- (i) an antioxidant or free-radical scavenger;
- (ii) $R^3_n R^4_m Si(OR^5)_{4-n-m}$ wherein R^3 and R^4 are each independently selected from hydrogen and a C_1 to C_{10} linear or branched alkyl; and R^5 is selected from a C_1 to C_{10} linear or branched alkyl; n is 0, 1, 2, or 3; $m=0, 1, 2, 3$;
- (iii) an alkoxy-disiloxane having the formula below



wherein R^6 is selected from a linear or branched C_1 to C_6 alkyl, preferably methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, or tert-butyl, and a cyclic C_5 to C_6 alkyl; R^7 is selected from hydrogen, and a linear or branched C_1 to C_5 alkyl; R^{8-10} are each selected independently from a linear or branched C_1 to C_5 alkyl, preferably methyl; and R^{11} is selected from hydrogen, a linear or branched C_1 to C_5 alkyl, or OR^{12} wherein R^{12} is selected from a linear or branched C_1 to C_5 alkyl;

- (iv) an alkoxy-carbosilane having the structure below



R^{13} is selected from a linear or branched C_1 to C_6 alkyl, preferably methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, or tert-butyl, and a cyclic C_5 to C_6 alkyl; R^{14} is selected from hydrogen, and a linear or branched C_1 to C_5 alkyl; R^{15-17} are selected independently from a linear or branched C_1 to C_5 alkyl, preferably methyl; and R^{18} is selected from hydrogen, a linear or branched C_1 to C_5 alkyl, or OR^{19} wherein R^{19} is selected from a linear or branched C_1 to C_5 alkyl; and

(v) an organoaminosilane $R_n^{20}R_m^{21}Si(NR^{22}R^{23})_{4-n-m}$ wherein R^{20} and R^{21} are each independently selected from hydrogen and a C_1 to C_{10} linear or branched alkyl; and R^{22} and R^{23} is selected from hydrogen, a C_1 to C_{10} linear or branched alkyl; n is 0, 1, 2, or 3; $m=0, 1, 2, 3$.

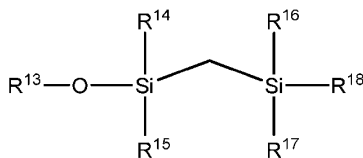
2. The composition of claim 1 wherein for the (a) 1,3-dialkoxy-1,3-disilacyclobutane according to Formula I, each R^1 is selected from methyl and ethyl, and R^2 is methyl.

3. The composition of claim 1 wherein for the (a) 1,3-dialkoxy-1,3-disilacyclobutane according to Formula I, each R^1 is ethyl.

4. The composition of claim 1 wherein the (b) polymerization inhibitor is selected from

(ii) $R_n^3R_m^4Si(OR^5)_{4-n-m}$ with the R^3 , R^4 , and R^5 substituents as defined; and

(iv) the alkoxy-carbosilane having the structure below



with the R^{13} , R^{14} , R^{15} , R^{16} , R^{17} and R^{18} substituents as defined.

5. The composition of claim 1 wherein the (b) polymerization inhibitor is (i) and is selected from the group consisting of 2,6-di-tert-butyl-4-methyl phenol, butylhydroxytoluene, 2,2,6,6-tetramethyl-1-piperidinyloxy, 2-tert-butyl-4-hydroxyanisole, 3-tert-butyl-4-hydroxyanisole, propyl ester 3,4,5-trihydroxy-benzoic acid, 2-(1,1-dimethylethyl)-1,4-benzenediol, diphenylpicrylhydrazyl, 4-tert-butylcatechol, N-methylaniline, p-methoxydiphenylamine, diphenylamine, N,N'-diphenyl-p-phenylenediamine, p-hydroxydiphenylamine, phenol, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, tetrakis (methylene (3,5-di-tert-butyl)-4-hydroxy-hydrocinnamate) methane, phenothiazines, alkylamidonoisoureas, thiodiethylene bis (3,5-di-tert-butyl-4-hydroxy-hydrocinnamate, 1,2-bis (3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl) hydrazine, tris (2-methyl-4-hydroxy-5-tert-butylphenyl) butane, cyclic neopentetetrayl bis (octadecyl phosphite), 4,4'-thiobis (6-tert-butyl-m-cresol), 2,2'-methylenebis (6-tert-butyl-p-cresol), oxalyl bis (benzylidenehydrazide) and naturally occurring antioxidants such as raw seed oils, wheat germ oil, tocopherols and combination thereof.

6. The composition of claim 1 wherein the (b) polymerization inhibitor is (ii) and is selected from the group consisting of tetramethoxysilane, trimethoxysilane, tetraethoxysilane, triethoxysilane, dimethoxymethylsilane, diethoxymethylsilane, methoxydimethylsilane, and ethoxydimethylsilane.

7. The composition of claim 1 wherein the (b) polymerization inhibitor is (iii) and is selected from the group consisting of 1,3-diethoxy-1,3-dimethyl-1,3-disiloxane, and 1,3-diethoxy-tetramethyldisiloxane.

8. The composition of claim 1 wherein the (b) polymerization inhibitor is (iv) and is selected from the group consisting of 2,4,4-triethoxy-2,4-disilapentane and 2,4-diethoxy-4-methyl-2,4-disilapentane.

9. The composition of claim 1 wherein the (b) polymerization inhibitor is (v) and is selected from the group consisting of dimethylaminotrimethylsilane, diethylaminotrimethylsilane, bis(dimethylamino)dimethylsilane, and tris(dimethylamino)methylsilane.

10. The composition of claim 1 wherein the (a) 1,3-dialkoxy-1,3-disilacyclobutane and the (b) polymerization inhibitor have respective boiling points that differ by 100 °C or less.

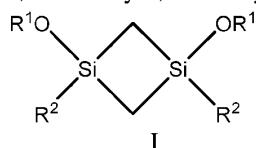
11. The composition of claim 1 wherein any alkoxy groups in any polymerization inhibitor(s) (ii) to (v) are the same as any alkoxy group(s) in the 1,3-dialkoxy-1,3-disilacyclobutane according to Formula I.

12. A chemical vapor deposition method for depositing an organosilicate film on at least a part of a substrate, the process comprising:

providing a substrate within a vacuum chamber;

introducing into the vacuum chamber a composition comprising:

(a) 1,3-dialkoxy-1,3-disilacyclobutane having the formula I below:



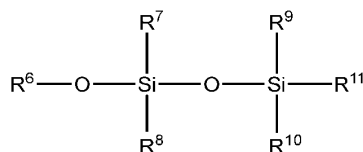
wherein each R¹ is independently a C₁ to C₁₀ linear or branched alkyl, and each R² is independently hydrogen or a C₁ to C₁₀ linear or branched alkyl; and

(b) a polymerization inhibitor selected from the group consisting of

- (i) an antioxidant or free-radical scavenger;
- (ii) R³_nR⁴_mSi(OR⁵)_{4-n-m} wherein R³ and R⁴ are each independently selected from hydrogen and a C₁ to C₁₀ linear or branched

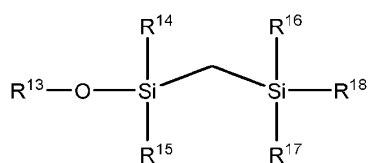
alkyl; and R^5 is selected from a C_1 to C_{10} linear or branched alkyl; n is 0, 1, 2, or 3; $m=0, 1, 2, 3$;

(iii) an alkoxy-disiloxane having the formula below



wherein R^6 is selected from a linear or branched C_1 to C_6 alkyl, preferably methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, or tert-butyl, and a cyclic C_5 to C_6 alkyl; R^7 is selected from hydrogen, and a linear or branched C_1 to C_5 alkyl; R^{8-10} are each selected independently from a linear or branched C_1 to C_5 alkyl, preferably methyl; and R^{11} is selected from hydrogen, a linear or branched C_1 to C_5 alkyl, or OR^{12} wherein R^{12} is selected from a linear or branched C_1 to C_5 alkyl;

(iv) an alkoxy-carbosilane having the structure below



R^{13} is selected from a linear or branched C_1 to C_6 alkyl, preferably methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, or tert-butyl, and a cyclic C_5 to C_6 alkyl; R^{14} is selected from hydrogen, and a linear or branched C_1 to C_5 alkyl; R^{15-17} are selected independently from a linear or branched C_1 to C_5 alkyl, preferably methyl; and R^{18} is selected from hydrogen, a linear or branched C_1 to C_5 alkyl, or OR^{19} wherein R^{19} is selected from a linear or branched C_1 to C_5 alkyl; and

(v) an organoaminosilane $R_n^{20}R_m^{21}Si(NR^{22}R^{23})_{4-n-m}$ wherein R^{20} and R^{21} are each independently selected from hydrogen and a C_1 to C_{10} linear or branched alkyl; and R^{22} and R^{23} is selected from hydrogen, a C_1 to C_{10} linear or branched alkyl; n is 0, 1, 2, or 3; $m=0, 1, 2, 3$; and

applying energy to the gaseous structure forming composition in the vacuum chamber to induce reaction of at least the 1,3-dialkoxy-1,3-disilacyclobutane to deposit a film on at least a portion of the substrate.

13. The method of claim 12 wherein for the (a) 1,3-dialkoxy-1,3-disilacyclobutane according to Formula I, each R1 is selected from methyl and ethyl, and R2 is methyl.

14. The method of claim 12 wherein the (b) polymerization inhibitor is (i) and is selected from the group consisting of 2,6-di-tert-butyl-4-methyl phenol, butylhydroxytoluene, 2,2,6,6-tetramethyl-1-piperidinyloxy, 2-tert-butyl-4-hydroxyanisole, 3-tert-butyl-4-hydroxyanisole, propyl ester 3,4,5-trihydroxy-benzoic acid, 2-(1,1-dimethylethyl)-1,4-benzenediol, diphenylpicrylhydrazyl, 4-tert-butylcatechol, N-methylaniline, p-methoxydiphenylamine, diphenylamine, N,N'-diphenyl-p-phenylenediamine, p-hydroxydiphenylamine, phenol, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, tetrakis (methylene (3,5-di-tert-butyl)-4-hydroxy-hydrocinnamate) methane, phenothiazines, alkylamidonoisoureas, thiodiethylene bis (3,5-di-tert-butyl-4-hydroxy-hydrocinnamate, 1,2-bis (3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl) hydrazine, tris (2-methyl-4-hydroxy-5-tert-butylphenyl) butane, cyclic neopentetetrayl bis (octadecyl phosphite), 4,4'-thiobis (6-tert-butyl-m-cresol), 2,2'-methylenebis (6-tert-butyl-p-cresol), oxalyl bis (benzylidenehydrazide) and naturally occurring antioxidants such as raw seed oils, wheat germ oil, tocopherols and combination thereof.

15. The method of claim 12 wherein the (b) polymerization inhibitor is (ii) and is selected from the group consisting of tetramethoxysilane, trimethoxysilane, tetraethoxysilane, triethoxysilane, dimethoxymethylsilane, and diethoxymethylsilane.

16. The method of claim 12 wherein the (b) polymerization inhibitor is (iii) and is selected from the group consisting of 1,3-diethoxy-1,3-dimethyl-1,3-disiloxane, and 1,3-diethoxy-tetramethyldisiloxane.

17. The method of claim 12 wherein the (b) polymerization inhibitor is (iv) and is selected from the group consisting of 2,4,4-triethoxy-2,4-disilapentane and 2,4-diethoxy-4-methyl-2,4-disilapentane.

18. The method of claim 12 wherein the (b) polymerization inhibitor is (v) and is selected from the group consisting of dimethylaminotrimethylsilane, diethylaminotrimethylsilane, bis(dimethylamino)dimethylsilane, tris(dimethylamino)methylsilane, dimethylaminodimethylsilane, and diethylaminodimethylsilane.

19. The method of claim 12 wherein the (a) 1,3-dialkoxy-1,3-disilacyclobutane and the (b) polymerization inhibitor have respective boiling points that differ by 100 °C or less.

20. The method of claim 12 wherein any alkoxy groups in any polymerization inhibitor(s) (ii) to (v) are the same as any alkoxy group(s) in the 1,3-dialkoxy-1,3-disilacyclobutane according to Formula I.