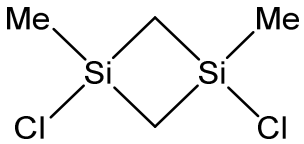
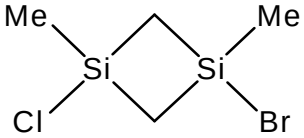
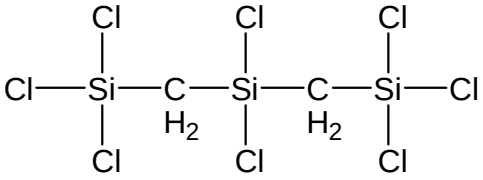
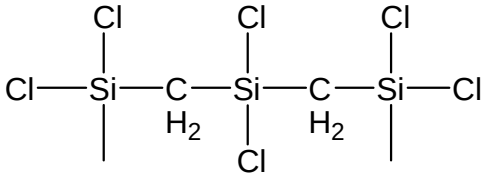
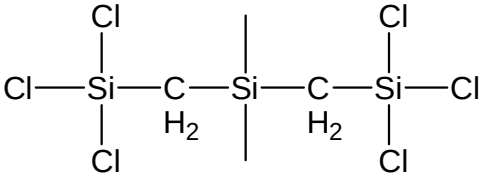
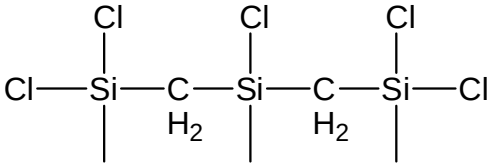
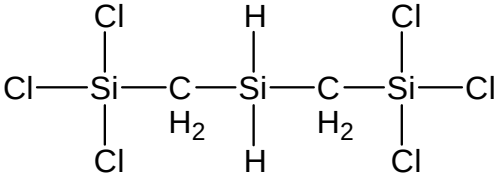
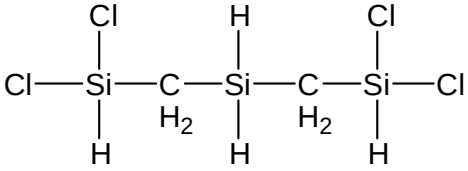
| | |
|---|---|
| <br>1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane | <br>1,3-bromo-1,3-dimethyl-1,3-disilacyclobutane |
| <br>1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane | <br>1,1,1,3,3,5,5,5-octachloro-1,5-dimethyl-1,3,5-trisilapentane |
| <br>1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane | <br>1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane |
| <br>1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane | <br>1,1,5,5-tetraachloro-1,3,5-trisilapentane |

and in at least one aspect of the invention, (b) at least one solvent. In certain embodiments of the composition described herein, exemplary solvents can include, without limitation, ether, tertiary amine, alkyl hydrocarbon, aromatic hydrocarbon, siloxanes, tertiary aminoether, and combinations thereof. In certain embodiments, the difference between the boiling point of the silicon compounds and the boiling point of the solvent is 40°C or less, less than about 30°C and in some cases less than about 20°C, preferably less than 10°C.

**[0020]** In another aspect, there is provided a method for depositing a film selected from a carbon-doped silicon oxide film and a carbon-doped silicon oxynitride film onto at least a surface of a substrate comprising:

placing the substrate into a reactor;

heating the reactor to one or more temperatures ranging from about 25°C to about 550°C;

introducing into the reactor a precursor comprising at least one compound selected from a silicon precursor listed in Table 1 and 2 and combinations thereof;

introducing into the reactor a nitrogen source to react with at least a portion of the precursor to form a carbon doped silicon nitride film; and

treating the carbon doped silicon nitride film with an oxygen source at one or more temperatures ranging from about 25°C to 1000°C or from about 100° to 400°C under conditions sufficient to convert the carbon doped silicon nitride film into the film. In certain embodiments, the carbon doped silicon oxide film or the carbon doped silicon oxynitride film has a carbon content of about 10 atomic weight percent (at. %) or greater as measured by XPS and an etch rate of at least 0.5 times less than thermal silicon oxide as measured in dilute hydrofluoric acid.

**[0021]** If desired, the invention further comprises treating the carbon doped silicon containing film with hydrogen or hydrogen/inert plasma at 25°C to 600°C.

**[0022]** One aspect of the invention relates to a composition comprising:

(a) at least one linear or cyclic silicon precursor compound having one Si-C-Si or two Si-C-Si linkages selected from the group consisting of 1,1,1,3,3,3-hexachloro-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-methyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2,2-dimethyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-ethyl-1,3-disilapropane, 1-chloro-1,3-disilacyclobutane, 1-bromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-disilacyclobutane, 1,3-dibromo-1,3-disilacyclobutane, 1,1,3-trichloro-1,3-disilacyclobutane, 1,1,3-tribromo-1,3-disilacyclobutane, 1,1,3,3-tetrachloro-1,3-disilacyclobutane, 1,1,3,3-tetrabromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, 1,3-bromo-1,3-dimethyl-1,3-disilacyclobutane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,5-dimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane, 1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane, 1,1,5,5-tetraachloro-1,3,5-trisilapentane; and;

(b) at least one solvent.

**[0023]** Another aspect of the invention relates to a method for forming a carbon doped silicon oxide film having carbon content ranging from 15 at % to 30 at.% via a thermal ALD process, the method comprising:

a) placing one or more substrates comprising a surface feature into a reactor;

b) heating to reactor to one or more temperatures ranging from ambient temperature to about 550°C and optionally maintaining the reactor at a pressure of 100 Torr or less;

c) introducing into the reactor at least one silicon precursor having two Si-C-Si linkages selected from the group consisting of 1-chloro-1,3-disilacyclobutane, 1-bromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-disilacyclobutane, 1,3-dibromo-1,3-disilacyclobutane, 1,1,3-trichloro-1,3-disilacyclobutane, 1,1,3-tribromo-1,3-disilacyclobutane, 1,1,3,3-tetrachloro-1,3-disilacyclobutane, 1,1,3,3-tetrabromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, 1,3-bromo-1,3-dimethyl-1,3-disilacyclobutane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,5-dimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane, 1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane, 1,1,5,5-tetraachloro-1,3,5-trisilapentane;

d) purge with an inert gas;

e) providing a nitrogen source into the reactor to react with the surface to form a carbon doped silicon nitride film;

f) purge with inert gas to remove reaction by-products

g) steps c to f are repeated to provide a desired thickness of carbon doped silicon nitride;

h) treating the resulting carbon doped silicon nitride film with an oxygen source at one or more temperatures ranging from about ambient temperature to 1000°C or from

disilacyclobutane, 1-bromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-disilacyclobutane, 1,3-dibromo-1,3-disilacyclobutane, 1,1,3-trichloro-1,3-disilacyclobutane, 1,1,3-tribromo-1,3-disilacyclobutane, 1,1,3,3-tetrachloro-1,3-disilacyclobutane, 1,1,3,3-tetrabromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, 1,3-bromo-1,3-dimethyl-1,3-disilacyclobutane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,5-dimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane, 1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane, 1,1,5,5-tetraachloro-1,3,5-trisilapentane; and; (b) at least one solvent. In certain embodiments of the composition described herein, exemplary solvents can include, without limitation, ether, tertiary amine, alkyl hydrocarbon, aromatic hydrocarbon, tertiary aminoether, siloxanes, and combinations thereof. In certain embodiments, the difference between the boiling point of the compound having one Si-C-Si or two Si-C-Si linkages and the boiling point of the solvent is 40°C or less. The wt % of silicon precursor compound in the solvent can vary from 1 to 99 wt %, or 10 to 90 wt%, or 20 to 80 wt %, or 30 to 70 wt %, or 40 to 60 wt %, to 50 to 50 wt %. In some embodiments, the composition can be delivered via direct liquid injection into a reactor chamber for silicon-containing film using conventional direct liquid injection equipment and methods.

**[0033]** In one embodiment of the method described herein, the carbon doped silicon oxide film having carbon content ranging from 5 at. % to 20 at. % is deposited using a thermal ALD process and a plasma comprising hydrogen to improve film properties. In this embodiment, the method comprises:

a. placing one or more substrates comprising a surface feature into a reactor;

b. heating to reactor to one or more temperatures ranging from ambient temperature to about 550°C and optionally maintaining the reactor at a pressure of 100 Torr or less;

c. introducing into the reactor at least one silicon precursor having one Si-C-Si linkage selected from the group consisting of 1,1,1,3,3,3-hexachloro-1,3-disilapropane,

b. heating to reactor to one or more temperatures ranging from ambient temperature to about 550°C and optionally maintaining the reactor at a pressure of 100 Torr or less;

c. introducing into the reactor at least one silicon precursor having two Si-C-Si linkages selected from the group consisting of 1-chloro-1,3-disilacyclobutane, 1-bromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-disilacyclobutane, 1,3-dibromo-1,3-disilacyclobutane, 1,1,3-trichloro-1,3-disilacyclobutane, 1,1,3-tribromo-1,3-disilacyclobutane, 1,1,3,3-tetrachloro-1,3-disilacyclobutane, 1,1,3,3-tetrabromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, 1,3-bromo-1,3-dimethyl-1,3-disilacyclobutane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,5-dimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane, 1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane, 1,1,5,5-tetraachloro-1,3,5-trisilapentane;

d. purge with an inert gas;

e. providing a nitrogen source into the reactor to react with the surface to form a carbon doped silicon nitride film;

f. purge with inert gas to remove reaction by-products;

g. steps c to f are repeated to provide a desired thickness of carbon doped silicon nitride;

h. providing post-deposition treating the carbon doped silicon nitride film with an oxygen source at one or more temperatures ranging from about ambient temperature to 1000°C or from about 100° to 400°C to convert the carbon doped silicon nitride film into a carbon doped silicon oxide film either in situ or in another chamber;

i. providing post-deposition exposing the carbon doped silicon oxide film to a plasma comprising hydrogen to improve at least one of the films' physical properties.

j. optionally post-deposition treating the carbon doped silicon oxide film with a thermal anneal at temperatures from 400° to 1000°C or a UV light source. In this or other

embodiments, the UV exposure step can be carried out either during film deposition, or once deposition has been completed.

**[0036]** In yet another further embodiment of the method described herein, the silicon containing film is deposited using a thermal ALD process with a catalyst comprising an ammonia or organic amine. In this embodiment, the method comprises:

a. placing one or more substrates comprising a surface feature into a reactor;

b. heating the reactor to one or more temperatures ranging from ambient temperature to about 150°C and optionally maintaining the reactor at a pressure of 100 Torr or less;

c. introducing into the reactor at least one silicon precursor having one or two Si-C-Si linkages selected from the group consisting of 1,1,1,3,3,3-hexachloro-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-methyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2,2-dimethyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-ethyl-1,3-disilapropane, 1-chloro-1,3-disilacyclobutane, 1-bromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-disilacyclobutane, 1,3-dibromo-1,3-disilacyclobutane, 1,1,3-trichloro-1,3-disilacyclobutane, 1,1,3-tribromo-1,3-disilacyclobutane, 1,1,3,3-tetrachloro-1,3-disilacyclobutane, 1,1,3,3-tetrabromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, 1,3-bromo-1,3-dimethyl-1,3-disilacyclobutane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,5-dimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane, 1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane, 1,1,5,5-tetraachloro-1,3,5-trisilapentane and a catalyst;

d. purge with an inert gas

e. providing vapors of water into the reactor to react with the precursor as well as a catalyst to form a carbon doped silicon oxide as-deposited film;

f. purge with inert gas to remove reaction by-products;

g. steps c to f are repeated to provide a desired thickness of carbon doped silicon oxide;

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $N_2$ dry + $H_2$ plasma | <0.02 | 1.58 | 36.39 | 35.43 | 25.68 | 0.54 | 1.9 |

**[00120]** The resulting film has film properties in Table 15. Film etch rates are very low, i.e. 0.12x thermal oxide, for as-deposited film with no anneal. The etch rates dropped to level below our detection limit after additional processing ($N_2$ dry or $N_2$ dry and plasma).

**[00121]** Film density for as-deposited film is 1.34 g/cc with slight densification with additional N2 dry or $N_2$ dry and $H_2$ plasma treatment. In all cases, the film has high carbon content 25-29% and low Cl content (< 2%).

Example 11. Low Dielectric Constant Carbon Doped Silicon Oxide Film Deposited from 1,1,3,3-Tetrachloro-1,3-Disilacyclobutane And Water/Pyridine

**[00122]** 1,1,3,3-tetrachloro-1,3-disilacyclobutane and $H_2O$ were used for film deposition. Pyridine was used as a reaction catalyst. The chemical (canister temp = 70$^o$C) was delivered with Ar sweeping through the precursor canister. Water temperature was 17 $^o$C (vapor pressure = 15 Torr) and water vapor was delivered with vapor draw, and pyridine temp was 25~35 $^o$C (vapor pressure= 15~25 Torr) and pyridine vapor was delivered with vapor draw. Main $N_2$ flow rate was 200 sccm, and Ar flow rate was 50 sccm.

**[00123]** The deposition process comprised of the steps described in Table 16.

Table 16. Deposition steps used in depositing Si-containing film from 1,1,3,3-tetrachloro-1,3-disilacyclobutane and water/pyridine.

| Steps | Descriptions | Time | Notes |
|---|---|---|---|
| 1 | Insert Si substrates into a reactor | | |
| 2 | Heat substrates to desired temperature | 5 minutes | T = 40 °C |

CLAIMS

1). A composition comprising:

(a) at least one silicon precursor compound having one Si-C-Si or two Si-C-Si linkages selected from the group consisting of 1,1,1,3,3,3-hexachloro-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-methyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2,2-dimethyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-ethyl-1,3-disilapropane, 1,1,3-trichloro-1,3-disilacyclobutane, 1,1,3-tribromo-1,3-disilacyclobutane, 1,3-bromo-1,3-dimethyl-1,3-disilacyclobutane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,5-dimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane, 1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane, 1,1,5,5-tetraachloro-1,3,5-trisilapentane; and;

(b) at least one solvent.

2). The composition of claim 1 where in the solvent comprises at least one member selected from the group consisting of ether, tertiary amine, siloxanes, alkyl hydrocarbon, aromatic hydrocarbon, and tertiary aminoether.

3). The composition of claim 1 wherein the difference between the boiling point of the silicon precursor and the boiling point of the solvent is 40°C or less.

4). The composition of claim 1 comprising less than 5ppm of at least one metal ions selected from the group consisting of $Al^{3+}$ ions, $Fe^{2+}$, $Fe^{3+}$, $Ni^{2+}$, and $Cr^{3+}$.

5). The composition of claim 1 where in the solvent comprises at least one member selected from the group consisting of heptane, octane, nonane, decane, dodecane, cyclooctane, cyclononane, cyclodecane, toluene, and mesitylene.

6). A method for forming a carbon doped silicon oxide film having carbon content ranging from 15 at. % to 30 at.% via a thermal ALD process, the method comprising:

a) placing one or more substrates comprising a surface feature into a reactor;

b) heating to reactor to one or more temperatures ranging from ambient temperature to 550°C and optionally maintaining the reactor at a pressure of 100 Torr or less;

c) introducing into the reactor at least one silicon precursor having two Si-C-Si linkages selected from the group consisting of 1-chloro-1,3-disilacyclobutane, 1-bromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-disilacyclobutane, 1,3-dibromo-1,3-disilacyclobutane, 1,1,3-trichloro-1,3-disilacyclobutane, 1,1,3-tribromo-1,3-disilacyclobutane, 1,1,3,3-tetrachloro-1,3-disilacyclobutane, 1,1,3,3-tetrabromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, 1,3-bromo-1,3-dimethyl-1,3-disilacyclobutane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,5-dimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane, 1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane, 1,1,5,5-tetraachloro-1,3,5-trisilapentane;

d) purge with an inert gas;

e) providing a nitrogen source into the reactor to react with the surface to form a carbon doped silicon nitride film;

f) purge with inert gas to remove reaction by-products;

g) steps c to f are repeated to provide a desired thickness of carbon doped silicon nitride;

h) treating the resulting carbon doped silicon nitride film with an oxygen source at one or more temperatures ranging from ambient temperature to 1000ºC or from 100ºC to 400ºC to convert the carbon doped silicon nitride film into a carbon doped silicon oxide film; and

i) providing post-deposition exposing the carbon doped silicon oxide film to a plasma comprising hydrogen.

7) The method of Claim 6 wherein the silicon precursor comprises a composition comprising,

(a) at least one silicon precursor compound having one Si-C-Si or two Si-C-Si linkages selected from the group consisting of 1,1,1,3,3,3-hexachloro-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-methyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2,2-dimethyl-1,3-disilapropane, 1,1,1,3,3,3-hexachloro-2-ethyl-1,3-disilapropane, 1-chloro-1,3-disilacyclobutane, 1-bromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-1,3-disilacyclobutane, 1,3-dibromo-1,3-disilacyclobutane, 1,1,3-trichloro-1,3-disilacyclobutane, 1,1,3-tribromo-1,3-disilacyclobutane, , 1,1,3,3-tetrabromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, 1,3-bromo-1,3-dimethyl-1,3-disilacyclobutane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,5-dimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane, 1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane, 1,1,5,5-tetraachloro-1,3,5-trisilapentane; and;

(b) at least one solvent.

8) A film formed according to the method of claim 6 having 50 Å or less damage layer when exposed to oxygen ashing process.

9) A film formed according to the method of claim 6 having 20 Å or less damage layer when exposed to oxygen ashing process.

10) A film formed according to the method of claim 6 having 10 Å or less damage layer when exposed to oxygen ashing process.

11) A film formed according to the method of claim 6 having 5 Å or less damage layer when exposed to oxygen ashing process.

12. The film of any one of claims 8 to 11 having a k of less than 4.

13. The film of any one of claims 8 to 12 having an etch rate of at least 0.5 times less than thermal silicon oxide.

14. The film of any one of claims 8 to 12 having an etch rate of at least 0.1 times less than thermal silicon oxide.

15. The film of any one of claims 8 to 12 having an etch rate of at least 0.05 times less than thermal silicon oxide.

16. The film of any one of claims 8 to 12 having an etch rate of at least 0.01 times less than thermal silicon oxide.

17) A stainless steel container housing the composition of claim 1.

18) A method for forming a carbon doped silicon oxide film having carbon content ranging from 15 at % to 30 at.% via a thermal ALD process, the method comprising:

a. placing one or more substrates comprising a surface feature into a reactor;

b. heating the reactor to one or more temperatures ranging from ambient temperature to 150°C and optionally maintaining the reactor at a pressure of 100 Torr or less;

c. introducing into the reactor at least precursor having two Si-C-Si linkages selected from the group consisting of 1-chloro-1,3-disilacyclobutane, 1-bromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-disilacyclobutane, 1,3-dibromo-1,3-disilacyclobutane, 1,1,3-trichloro-1,3-disilacyclobutane, 1,1,3-tribromo-1,3-disilacyclobutane, 1,1,3,3-tetrachloro-1,3-disilacyclobutane, 1,1,3,3-tetrabromo-1,3-disilacyclobutane, 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, 1,3-bromo-1,3-dimethyl-1,3-disilacyclobutane, 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane, 1,1,1,3,3,5,5,5-octachloro-1,5-dimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-3,3-dimethyl-1,3,5-trisilapentane, 1,1,3,5,5-pentachloro-1,3,5-trimethyl-1,3,5-trisilapentane, 1,1,1,5,5,5-hexachloro-1,3,5-trisilapentane, 1,1,5,5-tetraachloro-1,3,5-trisilapentane and a catalyst;

d. purge with an inert gas

e. providing vapors of water into the reactor to react with the precursor as well as a catalyst to form a carbon doped silicon oxide as-deposited film;

f. purge with inert gas to remove reaction by-products;

g. steps c to f are repeated to provide a desired thickness of carbon doped silicon oxide.

19. The method of Claim 18 further comprising post-deposition treatment of the carbon doped silicon oxide film with a thermal anneal at temperatures from 300 to 700$^{o}$C.

20. The method of Claim 18 further comprising hydrogen plasma treatment of the carbon doped silicon oxide film with a plasma comprising hydrogen.