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(54) Title: PLASMA PROCESSING FOR POROUS SILICA THIN FILM

(57) Abstract: Low dielectric constant films with improved elastic modulus. The method of making such coatings involves providing a porous network coating produced from a resin containing at least 2 Si-H groups. The coating can be thermally cured and has a dielectric constant in the range of from about 1.1 to about 3.5. Plasma treatment of the thermally cured coating will convert the coating into porous silica. Plasma treatment of the thermally cured porous network coating yields a coating with improved modulus, but with a higher dielectric constant. The coating is plasma treated for between about 15 and about 120 seconds at a temperature less than about 350 °C. Porous network coatings can also be plasma cured without prior thermal curing. The coating can be plasma cured at a temperature between about 200 °C and about 250 °C for less than about 5 minutes. The thermally cured plasma treated coating or plasma cured coating can optionally be annealed. Annealing by rapid thermal processing (RTP) of the thermally cured plasma treated or plasma cured coating reduces the dielectric constant of the coating while maintaining an improved elastic modulus. The annealing temperature is preferably less than about 475 °C, and the annealing time is preferably no more than about 180 seconds. The annealed, thermally cured plasma treated or plasma cured coating has a dielectric constant in the range of from about 1.1 to about 3.5 and an improved elastic modulus.

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PLASMA PROCESSING FOR POROUS SILICA THIN FILM

This invention relates generally to coatings for use in electronic devices. More particularly, the invention relates to coatings having an improved elastic modulus and a low dielectric constant and to methods of making such coatings.

Thin film dielectric coatings on electric devices are known in the art. For instance, U.S. Patent Nos. 4,749,631 and 4,756,977, to Haluska et al., disclose silica based coatings produced by applying solutions of silicon alkoxides or hydrogen silsesquioxane, respectively, to substrates and then heating the coated substrates to a temperature between 200 and 1000°C. The dielectric constant of these coatings is often too high for certain electronic devices and circuits.

U.S. Patent Nos. 4,847,162 and 4,842,888, to Haluska et al., teach the formation of nitrided silica coatings by heating hydrogen silsesquioxane resin and silicate esters, respectively, to a temperature between 200 and 1000°C in the presence of ammonia. These references teach the use of anhydrous ammonia so that the resulting coating has about 1 to 2% by weight nitrogen incorporated therein.

Glasser et al., Journal of Non-Crystalline Solids, 64 (1984) pp. 209-221, teaches the formation of ceramic coatings by heating tetraethoxysilane in the presence of ammonia. This reference teaches the use of anhydrous ammonia and that the resulting silica coatings are nitrided.

U.S. Patent No. 4,636,440, to Jada, discloses a method of reducing the drying time for a sol-gel coated substrate comprising exposing the substrate to aqueous quaternary ammonium hydroxide and/or alkanol amine compounds. Jada requires that the coating be dried prior to heating. It is specifically limited to hydrolyzed or partially hydrolyzed silicon alkoxides and does not teach the utility of the process on coatings having Si-H bonds.

U.S. Patent Nos. 5,262,201, to Chandra, and 5,116,637, to Baney et al., teach the use of basic catalysts to lower the temperature necessary for the conversion of various preceramic materials, all involving hydrogen silsesquioxane, to ceramic coatings. These references teach the removal of solvent before the coating is exposed to the basic catalysts.

U.S. Patent No. 5,547,703, to Camilletti et al., teaches a method for forming low dielectric constant Si-O containing coatings on substrates comprising heating a hydrogen silsesquioxane resin successively under wet ammonia, dry ammonia, and oxygen. The

resultant coatings have dielectric constants as low as 2.42 at 1 MHz. This reference teaches the removal of solvent before converting the coating to a ceramic.

U.S. Patent No. 5,523,163, to Balance et al., teaches a method for forming Si-O containing coatings on substrates comprising heating a hydrogen silsesquioxane resin to convert it to a Si-O containing ceramic coating and then exposing the coating to an annealing atmosphere containing hydrogen gas. The resultant coatings have dielectric constants as low as 2.773. The reference teaches the removal of solvent before converting the coating to a ceramic.

U.S. Patent No. 5,618,878, to Syktich et al., discloses coating compositions containing hydrogen silsesquioxane resin dissolved in saturated alkyl hydrocarbons useful for forming thick ceramic coatings. The alkyl hydrocarbons disclosed are those up to dodecane. The reference does not teach exposure of the coated substrates to basic catalysts before solvent removal.

U.S. Serial No. 09/197,249, to Chung et al., entitled A METHOD OF FORMING COATINGS, filed November 20, 1998, discloses a method of making porous network coatings with low dielectric constants. The method comprises depositing a coating on a substrate with a solution comprising a resin containing at least 2 Si-H groups and a solvent in a manner in which at least 5 volume % of the solvent remains in the coating after deposition. The coating is then exposed to an environment comprising a basic catalyst and water. Finally, the solvent is evaporated from the coating to form a porous network. If desired, the coating can be cured by heating to form a ceramic. Films made by this process have dielectric constants in the range of 1.5 to 2.4 with an elastic modulus of about 2-3 GPa.

It has now been discovered that porous network coatings can be thermally cured and plasma treated, or plasma cured without prior thermal curing.

However, there remains a need for a method of making a porous network coating having an improved elastic modulus.

The present invention produces a coating with a low dielectric constant and an improved elastic modulus. The method of making the coating involves providing a porous network coating produced from a resin containing at least 2 Si-H groups.

The porous network coating can be thermally cured and plasma treated. In this case, the porous network coating is heated to a temperature in the range of from about 50°C to

about 1000°C for up to 6 hours. Typically, the porous network coating can be thermally cured by heating for about 1 hour at about 450°C.

The coating is then plasma treated to reduce the amount of Si-H bonds remaining in the coating. Plasma treatment of the thermally cured porous network coating yields a high elastic modulus of greater than about 4 GPa. The increase in the elastic modulus is typically at least about 50%, and more typically at least about 100% as compared to the thermally cured coating.

Alternatively, the porous network coating can be plasma cured by heating to a temperature in the range of about 200 to about 225°C for less than about 5 minutes. Typically, the porous network coating is plasma cured for about 2 minutes.

The thermally cured plasma treated coating or plasma cured coating can optionally be annealed. Thermal annealing of the thermally cured plasma treated coating or the plasma cured coating reduces the dielectric constant of the coating while maintaining the increase in the elastic modulus which was obtained when the coating was plasma treated or plasma cured. The annealing temperature is typically less than about 475°C, and the annealing time is typically no more than about 180 seconds.

The annealed, thermally cured plasma treated coatings and the annealed plasma cured coatings have a dielectric constant in the range of from about 1.1 to about 3.5 and an elastic modulus that is generally greater that about 4 GPa, and typically in the range of from about 4 GPa to about 10 GPa.

Accordingly, it is an object of the present invention to produce coatings having improved elastic modulus and low dielectric constant.

The manufacture of ultra low dielectric constant coatings having a dielectric constant of about 1.5 to about 2.4 is described in U.S. Patent Application Serial No. 09/197,249, which is incorporated herein by reference for its teaching on how to produce coatings having ultra low dielectric constants. This application describes a process in which pores are introduced into hydrogen silsesquioxane (HSQ) based films. HSQ based films produced according to the method taught in U.S. Serial No. 09/197,249, which have been cured under thermal conditions, contain about 20 to about 60% Si-H bonds density. When the dielectric constant of the coating is about 2.0, the coating has an elastic modulus of between about 2 and about 3 GPa. The present invention is based on the discovery that

plasma treating or plasma curing porous HSQ based films increases the elastic modulus of the film. Applying a plasma treatment to thermally cured HSQ based films, or plasma curing HSQ films which have not been thermally cured, reduces the amount of Si-H bonds remaining without losing the low density structure of the film.

The plasma treated films show improved elastic modulus as compared with the thermally cured coatings. However, the plasma treatment or the plasma cure can generate a notable amount of polar species in the film, resulting in an increase in the dielectric constant. This can be undesirable in some applications. The present invention is also based on the discovery that applying thermal annealing to thermally cured plasma treated or plasma cured coatings produces a low dielectric constant, improved modulus material.

The methods of the present invention are particularly applicable to the deposition of coatings on electronic devices or electronic circuits where they can serve as interlevel dielectric layers, doped dielectric layers to produce transistor like devices, pigment loaded binder systems containing silicon to produce capacitor and capacitor like devices, multilayer devices, 3-D devices, silicon on insulator devices, super lattice devices, and the like. However, the choice of substrates and devices to be coated by the instant invention is limited only by the need for thermal and chemical stability of the substrate at the temperature and pressure used in the present invention. As such, the coatings of the present invention can be used on substrates such as plastics including, for example, polyimides, epoxies, polytetrafluoroethylene and copolymers thereof, polycarbonates, acrylics and polyesters, ceramics, leather, textiles, metals, and the like.

As used in the present invention, the expression "ceramic" includes ceramics such as amorphous silica and ceramic-like materials such as amorphous silica-like materials that are not fully free of carbon and/or hydrogen but are otherwise ceramic in character. The expressions "electronic device" or "electronic circuit" include, but are not limited to, silica-based devices, gallium arsenide based devices, silicon carbide based devices, focal plane arrays, opto-electronic devices, photovoltaic cells and optical devices.

A porous network coating is needed as a starting material for the present invention. One method of making such a porous network coating is disclosed in U.S. Serial No. 09/197,249, which is described below.

The method of producing the porous network coating starts with depositing a coating on a substrate with a solution comprising a resin containing at least 2 Si-H groups and a solvent. The resins containing at least 2 Si-H groups are not particularly limited as long as the Si-H bonds can be hydrolyzed and at least partially condensed by the basic catalyst and water to form a crosslinked network that serves as the structure for the porous network. Generally, such materials have the formula:

$$\{R_3SiO_{1/2}\}_a\{R_2SiO_{2/2}\}_b\{RSiO_{3/2}\}_c\{SiO_{4/2}\}_d$$

wherein each R is independently selected from the group consisting of hydrogen, alkyl, alkenyl, or aryl groups, or alkyl, alkenyl, or aryl groups substituted with a hetero atom such as a halogen, nitrogen, sulfur, oxygen, or silicon, and a, b, c, and d are mole fractions of the particular unit and their total is 1, with the proviso that at least 2 R groups per molecule are hydrogen and the material is sufficiently resinous in structure to form the desired network. Examples of alkyl groups are methyl, ethyl, propyl, butyl, and the like, with alkyls of 1-6 carbons being typical. Examples of alkenyl groups include vinyl, allyl, and hexenyl. Examples of aryls include phenyl. Examples of substituted groups include $CF_3(CF_2)_nCH_2CH_2$, where n = 0-6.

Useful in the present invention are various hydridosiloxane resins, known as hydrogen silsesquioxane resins, comprising units of the formula $HSi(OH)_x(OR')_yO_{z/2}$. In this formula, each R' is independently selected from the group consisting of alkyl, alkenyl, or aryl groups, or alkyl, alkenyl, or aryl groups substituted with a hetero atom such as a halogen, nitrogen, sulfur, oxygen, or silicon. Examples of alkyl groups are methyl, ethyl, propyl, butyl, and the like, with alkyls of 1-6 carbons being typical. Examples of alkenyl groups include vinyl, allyl, and hexenyl. Examples of aryls include phenyl. Examples of substituted groups include $CF_3(CF_2)_nCH_2CH_2$, where n = 0-6. When these R' groups are bonded to silicon through the oxygen atom, they form a hydrolyzable substituent. In the above formula, x = 0 to 2, y = 0 to 2, z = 1 to 3, an x + y + z = 3. These resins may be essentially fully condensed $(HSiO_{3/2})_n$ where n is 8 or greater, or they may be only partially hydrolyzed (i.e., containing some Si-OR'), and/or partially condensed (i.e., containing some Si-OH).

The structure of the resin containing at least 2 Si-H groups is not limited. The structure may be what is generally known as ladder-type, cage-type, or mixtures thereof.

The HSQ resins may contain endgroups such as hydroxyl groups, triorganosiloxy groups, diorganohydrogensiloxy groups, trialkoxy groups, dialkoxy groups and others. The HSQ resin may also contain a small number (e.g., less than 10%) of the silicon atoms which have either 0 or 2 hydrogen atoms attached thereto and/or a small number of Si-C groups, such as $CH_3SiO_{3/2}$ or $HCH_3SiO_{2/2}$ groups.

The resins containing at least 2 Si-H groups and methods for their production are known in the art. For example, U.S. Patent No. 3,615,272, to Collins, teaches the production of an essentially fully condensed hydrogen silsesquioxane resin (which may contain up to 100-300 ppm silanol) by a process comprising hydrolyzing trichlorosilane in a benzenesulfonic acid hydrate hydrolysis medium, and then washing the resulting resin with water or aqueous sulfuric acid. Similarly, U.S. Patent No. 5,010,159 to Bank, teaches a method comprising hydrolyzing hydridosilanes in an arylsulfonic acid hydrate hydrolysis medium to form a resin which is then contacted with a neutralizing agent.

Other hydridosiloxane resins, such as those described in U.S. Patent No. 4,999,397, to Fry, and U.S. Patent No. 5,210,160, to Bergstrom, those produced by hydrolyzing an alkoxy or acyloxy silane in an acidic, alcoholic hydrolysis medium, those described in Japanese Kokai Patent Nos. 59-178749, 60-86017, and 63-107122, or any other equivalent hydridosiloxanes, will also function herein.

Specific molecular weight fractions of the Si-H containing resins may also be used. Such fractions and methods for their preparation are taught in U.S. Patent No. 5,063,267, to Hanneman, and U.S. Patent No. 5,416,190, to Mine. A typical fraction comprises material wherein at least 75% of the polymeric species have a number average molecular weight above about 1200, and a more typical fraction comprises material wherein at least 75% of the polymeric species have a number average molecular weight between about 1200 and about 100,000.

The Si-H containing resins may contain other components as long as these components do not interfere with the integrity of the coating. It should be noted, however, that certain materials may increase the dielectric constant of the coating. Known additives include catalysts such as platinum, rhodium, or copper catalyst which increase the rate and/or extent of cure of the resin, as described in U.S. Patent No. 4,822,697, to Haluska.

Ceramic oxide precursors may also be used in combination with the Si-H containing resins. The ceramic oxide precursors useful herein include compounds of various metals such as aluminum, titanium, zirconium, tantalum, niobium and/or vanadium, as well as various non-metallic compounds, such as those of boron or phosphorus, which may be dissolved in solution, hydrolyzed and subsequently pyrolyzed at relatively low temperature to form ceramic oxides. Ceramic oxide precursors useful herein are described in U.S. Patent Nos. 4,808,653, 5,008,320, and 5,290,394.

The Si-H containing resins are applied to the substrates as solvent dispersions to form a coating on the substrate ("SiH resin coating"). Solvents that may be used include any agent or mixture of agents that will dissolve or disperse the resin to form a homogeneous liquid mixture without affecting the resulting coating or the substrate. These solvents can include alcohols, such as ethyl alcohol or isopropyl alcohol; aromatic hydrocarbons, such as benzene or toluene; branched or linear alkanes, such as n-heptane, dodecane, or nonane; branched or linear alkenes, such as n-heptene, dodecene or tetradecene; ketones, such as methyl isobutyl ketone; esters; ethers, such as glycol ethers; or linear or cyclic siloxanes, such as hexamethyldisiloxane, octamethyldisiloxane, and mixtures thereof, or cyclic dimethylpolysiloxanes; or mixtures of any of the above solvents. The solvent is generally present in an amount sufficient to dissolve/disperse the resin to the concentration desired for application. Typically, the solvent is present in an amount of about 20 to about 99.9 wt%, and more typically from about 70 to about 95 wt% based on the weight of the resin and solvent.

If desired, other materials can be included in the resin dispersion. For instance, the dispersion can include fillers, colorants, adhesion promoters, and the like.

Specific methods for application of the resin dispersion to the substrate include, but are not limited to, spin coating, dip coating, spray coating, flow coating, screen printing, or others. A typical method is spin coating.

At least about 5 volume % of the solvent should remain in the coating until the resin is contacted with the basic catalyst and water. This solvent forms the pores of the porous network coating as the Si-H bonds are hydrolyzed and condensed. In some embodiments, it may be typical that at least about 10 volume % solvent remains, while in others, it may be

typical that at least about 15 volume % solvent remains, and in still others, it may be typical that at least about 25 volume % solvent remains.

The method of retaining the solvent is not particularly restricted. In a typical embodiment, a high boiling point solvent can be used alone or as a co-solvent with one of the solvents described above. In this manner, processing the resin dispersion as described above under normal conditions allows for at least about 5% residual solvent remaining. Typical high boiling solvents in this embodiment are those with boiling points above about 175°C including hydrocarbons, aromatic hydrocarbons, esters, ethers, and the like. Examples of specific solvents which can be used in this embodiment include saturated hydrocarbons, such as dodecane, tetradecane, hexadecane, etc., unsaturated hydrocarbons such as dodecene, tetradecene, etc., xylenes, mesitylene, 1-heptanol, dipentene, d-limonene, tetrahydrofurfuryl alcohol, mineral spirits, 2-octanol, stoddard solvent, Isopar H™, diethyl oxalate, diamyl ether, tetrahydropyran-2-methanol, lactic acid butyl ester, isooctyl alcohol, propylene glycol, dipropylene glycol monomethyl ether, diethylene glycol diethyl ether, dimethyl sulfoxide, 2,5-hexanedione, 2-butoxyethanol acetate, diethylene glycol monomethyl ether, 1-octanol, ethylene glycol, Isopar L™, dipropylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether, N-methylpyrrolidone, ethylene glycol dibutyl ether, gamma-butyrolactone, 1,3-butanediol, diethylene glycol monomethyl ether acetate, trimethylene glycol, triethylene glycol dimethyl ether, diethylene glycol monoethyl ether acetate, alpha-terpineol, n-hexyl ether, kerosene, 2-(2-n-butoxyethoxy)ethanol, dibutyl oxalate, propylene carbonate, propylene glycol monophenyl ether, diethylene glycol, catechol, diethylene glycol monobutyl ether acetate, ethylene glycol monophenyl ether, diethylene glycol dibutyl ether, diphenyl ether, ethylene glycol monobenzyl ether, hydroquinone, sulfolane, and triethylene glycol. Hydrocarbon solvents are particularly preferred.

The above processing (i.e., primarily deposition of the SiH resin coating solution) can be done in an environment that inhibits solvent evaporation prior to contact with the basic catalyst and water. For example, the spin coating can be performed in a closed environment such that the subsequent steps (i.e., contact with the basic catalyst and water) can occur before the solvent is completely evaporated.

The SiH resin coating containing at least about 5 volume % solvent is then contacted with a basic catalyst and water. Examples of basic catalysts include ammonia, ammonium hydroxide, as well as amines. The amines useful herein may include primary amines (RNH_2), secondary amines (R_2NH), and/or tertiary amines (R_3N) in which R is independently a saturated or unsaturated aliphatic, such as methyl, ethyl, propyl, vinyl, allyl, ethynyl, etc.; an alicyclic, such as cyclohexylmethyl; an aromatic, such as phenyl; a substituted hetero atom, such as oxygen, nitrogen, sulfur, etc.; or compounds in which the nitrogen atom is a member of a heterocyclic ring such as quinoline, pyrrolidine, or pyridine. In addition, any of the above amine compounds may be substituted with other hydrocarbon and/or hetero containing groups to form compounds such as diamines, amides, etc. Finally, it is also contemplated that compounds, which are converted to amines under the reactions conditions used, would function in an equivalent manner. For example, a compound such as an ammonium salt that yields an amine upon dissolution would provide the desired catalytic effect.

Examples of the amines that may used herein include methylamine, ethylamine, butylamine, allylamine, cyclohexylamine, aniline, dimethylamine, diethylamide, dioctylamine, dibutylamine, methylethylamine, saccharin, piperidine, trimethylamine, triethylamine, pyridine, diethyl toluidene ethylmethylpropylamine, imidazole, choline acetate, triphenyl phosphene analine, trimethylsilylimidazole, ethylenediamine, diethylhydroxylamine, triethylenediamine, n-methylpyrolidone, etc.

The basic catalyst can generally be used at any concentration sufficient to catalyze hydrolysis of the Si-H bonds. Generally, concentrations of the basic catalyst can be from about 1 ppm to about 100 wt% based on the weight of the resin, depending on the basic catalyst.

The water used can be that present in the ambient environment (e.g., > about 25% relative humidity), the ambient environment can be supplemented with additional water vapor (e.g., relative humidity up to about 100%), water can be used as a liquid, or a compound which generates water under the reaction conditions can be used.

Contact of the SiH resin coating with the basic catalyst and water can be accomplished by any means practical or desirable. For instance, the SiH resin coating can be contacted with vapors of the basic catalyst and water vapor. Alternatively, the SiH resin

coating can be contacted with the basic catalyst and water in the liquid state, such as by immersing the coating in an ammonium hydroxide solution.

The SiH resin coating is typically exposed to an environment comprising the basic catalyst and water in the vapor state, more typically ammonia and water vapor. For instance, the SiH resin coated substrate may be placed in a container and the appropriate environment introduced therein, or a stream of the basic catalyst and water may be directed at the SiH resin coating.

The method used to generate the basic catalyst and water environment is generally not significant in the present embodiment. Methods such as bubbling the basic catalyst (e.g., ammonia gas) through water or ammonium hydroxide solutions (to control the amount of water vapor present), heating a basic catalyst and water, or heating water and introducing the basic catalyst gas (e.g., ammonia gas) are all functional herein. It is also contemplated that methods, which generate basic catalyst vapors in situ, such as the addition of water to amine salts, or the addition of water to a silazane such as hexamethyldisilazane, will also be effective.

The basic catalyst used may be at any concentration desired. For example, the concentration may be from about 1 ppm up to a saturated atmosphere.

The exposure can be at any temperature desired from room temperature up to about 300°C. A temperature in the range of from about 20°C to about 200°C is typical, with a range of from about 20°C to about 100°C being more typical.

The SiH resin coating should be exposed to the basic catalyst and water environment for the time necessary to hydrolyze the Si-H groups to form silanols (Si-OH) and for the silanols to at least partially condense to form Si-O-Si bonds. Generally, exposures of up to about 20 minutes are typical, with exposures of at least about 1 second up to about 5 minutes being more typical. If the coatings are to be used as a dielectric layer, it is generally typical to have a shorter exposure, as longer exposures tend to increase the dielectric constant of the coating.

When the coating is exposed to the basic catalyst and water in the liquid state, the exposure is usually conducted by immersing the coated substrate in a solution. Other equivalent methods can be used, such as flushing the coating with a basic catalyst and water

solution. In addition, vacuum infiltration may also be used to increase penetration of the basic catalyst and water into the coating.

The basic catalyst solution used in this embodiment may be at any concentration desired. Generally when ammonium hydroxide is used, a concentrated aqueous solution of between about 28 and about 30% is typical since the duration of exposure is thereby shortened. When dilute solutions are used, the diluent is generally water.

Exposure to the basic catalyst and water solution in this embodiment may be conducted at any temperature and pressure desired. Temperatures from about room temperature (20-30°C) up to about the boiling point of the basic catalyst solution, and pressures from below to above atmospheric are all contemplated herein. From a practical standpoint, it is typical that the exposure occur at about room temperature and at about atmospheric pressure.

The resin coating is exposed to the basic catalyst solution in this embodiment for the time necessary to hydrolyze the Si-H groups to form silanols (Si-OH) and for the silanols to at least partially condense to form Si-O-Si bonds. Generally, exposures of up to about 2 hours are typical, with exposures of at least about 1 second up to about 15 minutes being more typical.

Alternatively, the coating may be exposed to both a liquid basic catalyst and water environment (e.g., ammonium hydroxide) and a gaseous basic catalyst and water vapor environment (ammonia gas and water vapor). The exposures may be either sequential or simultaneous, and are generally under the same conditions as those described above.

After the resin is exposed to one of the above environments, the solvent is then removed from the coating. This can be accomplished by any desired means, including but not limited to, heating the coating, and by vacuum. When the solvent is removed by heating the coating, condensation of the remaining silanols may be facilitated.

The coating produced by this process can be used as the starting material ("porous network coating") in the present invention. Porous network coatings which have not been thermally cured have the advantage of having a lower thermal budget, or thermal history, than cured films.

Alternatively, the porous network coating can be thermally cured if desired. If a cured coating is desired, the coating can be thermally cured by heating to a temperature

sufficient to convert the coating to a ceramic either before, during, or after solvent removal. Generally, the temperature is above room temperature, in the range of from about 50°C to about 1000°C. A typical temperature range is from about 50°C to about 500°C, with a range of about 200°C to about 500°C being more typical, and a range of about 350°C to about 450°C being more typical. Higher temperatures usually result in quicker and more complete conversion to a ceramic, but these temperatures can have detrimental effects on the various temperature sensitive substrates. The coatings are usually subjected to these temperatures for a time sufficient to ceramify the coating, generally up to about 6 hours, with a range of between about 5 minutes and about 6 hours being typical, and a range of between about 10 minutes and about 2 hours being more typical.

The heating may be conducted at any effective atmospheric pressure from vacuum to superatmospheric and under any effective gaseous environment, such as an inert gas (N_2, etc.). It is typical to heat under a nitrogen atmosphere.

Any method of heating, such as the use of a convection oven or radiant or microwave heat, is generally functional herein. The rate of heating is not critical, but it is most practical and typical to heat as rapidly as possible.

The resin coating may be simultaneously exposed to the basic catalyst and water environment (liquid or gaseous) and subjected to a temperature sufficient to convert it to a ceramic. The time and temperature for the exposure, as well as that necessary for the ceramification, are generally those described above.

In a typical procedure to produce a thermally cured porous network coating, a substrate is coated with the Si-H containing resin and solvent in a manner which ensures that at least about 5 volume % of the solvent remains in the coating. The coating is then exposed to the basic catalyst and water, and the solvent is evaporated. The coated substrate is placed in a convection oven, which is filled with an inert gas such as nitrogen. The temperature in the oven is then raised to the desired level (such as about 450°C) and maintained for the desired time under inert atmosphere (such as about 5 minutes to about 2 hours).

A thermally cured film formed as described above contains from about 20 to about 60% Si-H bond density remaining and has a dielectric constant of between about 1.1 and

about 3.5. It can have an elastic modulus of between about 2 and about 3 GPa when the dielectric constant is about 2.0.

Another method of making such a porous network coating is disclosed in U.S. Serial No. 09/458,739 to Zhong, entitled METHOD FOR MAKING NANOPOROUS SILICONE RESINS FROM ALKYLHYDRIDOSILOXANE RESINS, filed December 13, 1999. The method comprises contacting a hydridosilicon containing resin with a 1-alkene comprising about 8 to about 28 carbon atoms in the presence of a platinum group metal-containing hydrosilation catalyst, effecting formation of an alkylhydridosiloxane resin where at least about 5 percent of the silicon atoms are substituted with at least one hydrogen atom and heating the alkylhydridosiloxane prepared at a temperature sufficient to effect curing and thermolysis of alkyl groups from the silicon atoms, thereby forming a nanoporous silicone resin.

Although porous network coatings having low dielectric constants are desirable, it would be advantageous to have a coating with a higher elastic modulus.

In order to raise the elastic modulus of the thermally cured porous network coating, it is exposed to a plasma treatment. The plasma treatment can be done by radio frequency (RF), inductive coupled, RF capacitive coupled, helical resinator, microwave downstream, and microwave electron cyclotron resonance (ECR) plasma.

In a typical plasma process, the wafer is quickly heated in a rapid temperature ramp-up step to the desired temperature, and the wafer is plasma treated.

The exact conditions for the plasma treatment depend upon what type of plasma treatment is being used. Examples of typical microwave plasma treatment conditions for a 200mm wafer are shown below.

Microwave Plasma Power:	1000 W - 2000 W
Wafer Temperature:	80°C - 350°C
Process Pressure:	1.0 torr - 6.0 torr
Plasma Treatment Time:	>15 seconds
Plasma Gases:	$H_2/N_2/CF_4/O_2$
O_2 flow rate:	0-4000 sccm
CF_4 flow rate:	0-400 sccm
H_2/N_2 Gas Mixture flow rate:	>0-4000 sccm

The thermally cured plasma treated porous network coatings of the present invention have improved chemical stability and improved dimensional stability. By improved chemical stability, we mean that the coatings are more resistant to chemicals, such as cleaning solutions and chemical polishing solutions, and plasma damaging during photoresist ashing and dry etching processes.

Alternatively, porous network coatings which have not been thermally cured can be plasma cured by heating for less than about 5 minutes at a temperature that is between about 200 and about 225°C. Typically, the coating can be plasma cured by heating for about 2 minutes.

However, plasma treating or plasma curing can generate a notable amount of polar species in the film.

The thermally cured plasma treated or plasma cured coatings can be annealed using any type of thermal exposure to reduce the dielectric constant, if desired. For example, the thermally cured plasma treated or plasma cured coatings can be placed in a conventional oven until the polar species are removed, such as at 450°C for 30 minutes. Another process that can be used involves annealing the thermally cured plasma treated or plasma cured coatings in a Rapid Thermal Processing (RTP) chamber in order to reduce the dielectric constant. The plasma treated or plasma cured coating is annealed at a typical temperature for a sufficient time, and cooled to about 100°C.

Typical operating conditions for the RTP process are shown below.

Ramp rate:	150°C/sec
Wafer Temperature:	350 - 450°C
Annealing Time:	<180 seconds

The dielectric constant of the annealed, thermally cured plasma treated or plasma cured coatings is reduced as compared to the plasma treated or plasma cured porous network coatings. The dielectric constant of the annealed, thermally cured plasma treated or plasma cured coatings is typically in the range of from about 1.1 to about 3.5 and more typically in the range of from about 2 to about 2.5.

The elastic modulus of the annealed, thermally cured plasma treated coatings is increased as compared to thermally cured porous network coatings. This increase in elastic modulus is typically greater than about 50%, and more typically greater than about 100%.

The elastic modulus of the annealed, plasma cured coatings is comparable to the plasma cured coatings. Typically, the elastic modulus of the annealed, thermally cured plasma treated or plasma cured coating is greater than about 4 GPa and more typically between about 4 GPa and about 10 GPa.

The annealed, plasma treated coatings that were thermally cured by heating using RTP provides an advantage over those coatings that were thermally cured by other heating methods as the RTP thermal cure process lowers curing temperature and provides a much shorter curing time.

In order that the invention may be more readily understood, reference is made to the following examples, which are intended to illustrate the invention, but not limit the scope thereof.

Example 1

Two solutions of hydrogen silsesquioxane resin were prepared by the method of Collins et al., U.S. Patent No. 3,615,272. Solution 1 contained 12.7% resin by weight, 9.7% tetradecane ($C_{14}H_{30}$) by weight, and 77.6% methylpropyl ketone (MPK, $CH_3COC_3H_7$) by weight. Solution 2 contained 21.7% resin by weight, 16.6% tetradecane, and 61.7% methylisobutylketone (MIBK) by weight.

Solution 1 was spin coated on 8 inch single crystal Si wafers on a commercially available coater manufactured by Tokyo Electron Ltd. (TEL), Clean Track ACT™ 8 (ACT8) with optional Dielectric Aging Chamber (DAC).

After spinning the solution onto a wafer, the wafer was placed into the DAC where it was exposed to a moist ammonia atmosphere for 45 to 50 seconds at room temperature. After coating, the wafer was placed on a hotplate, which was preset to a temperature of 150°C, for one minute to remove the remaining solvent. The wafer was then removed from the coater and thermally treated by placing the wafer in a quartz tube furnace (QTF). The furnace was purged with inert atmosphere (N_2, with ultra-low O_2 content, <10 ppm) during cure. Cure temperature ranged from 400 to 450°C, and the time at temperature was 60 minutes. The thickness of the coating resulting from solution 1 averaged 5000 Å.

Solution 2 was spin coated on 8 inch single crystal Si wafers, on a commercially available DNS 80A spin coater. After spinning the solution onto a wafer, the wafer was

placed into a dielectric aging chamber (made in-house) where it was exposed to a moist ammonia atmosphere for 90 seconds at room temperature. After coating, the wafers were placed on a hotplate, which was preset to a temperature of 150°C, for one minute to remove the remaining solvent. The wafer was then removed from the coater and thermally treated by placing the wafer in a quartz tube furnace (QTF). The furnace was purged with inert atmosphere (N_2, with ultra-low O_2 content, <10 ppm) during cure. Cure temperature ranged from 400 to 450°C, and the time at temperature was 60 minutes. The thickness of the coating resulting from solution 2 averaged 10,000 Å.

The thermally cured coatings with 40-55% Si-H, a dielectric constant about 2.0 (5000 Å coating) and about 2.2 (10,000 Å coating) and an elastic modulus of about 3.0 GPa were treated with a microwave plasma under various conditions of time, temperature, microwave power, type of gas, and gas flow rate.

The testing was done in an Axcelis FusionGemini® ES microwave-downstream plasma asher. The system utilizes a 2.45 GHz source that efficiently couples microwave energy into the plasma, creating a high concentration of active radicals while minimizing energetic ions that might cause damage to the low dielectric constant materials. The system also employs fast ramping radiant heat heating to allow a wide range of process temperatures enabling multiple temperature process steps. This system is described in U.S. Patent No. 5,961,851.

The process conditions applied to the plasma treatment are shown below:

Microwave Plasma Power:	1500 W - 1800 W
Wafer Temperature:	80°C - 280°C
Process Pressure:	1.0 torr - 3.0 torr
Plasma Treatment Time:	15 seconds - 120 seconds
Plasma Gases:	$H_2/N_2/CF_4/O_2$
O_2 flow rate:	0-2510 sccm
CF_4 flow rate:	0-400 sccm
FG (5%H_2/95%N_2) flow rate:	0-3500 sccm

The results of this testing are shown in Tables 1-5.

Table 1. Thermally Cured Films with 40% Si-H and a thickness of 5000 Å at 450°C

	Plasma Treatment									
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	R.I @ 633nm	Si-H (%)	Modulus (GPa)
1	30	120	1800	0	15	1.2	3485	1.241	0	12.0
2	30	200	1800	0	15	1.2	3485	1.235	0	12.6
3	30	280	1800	0	15	1.2	3485	1.232	0	13.2
4	30	120	1800	0	150	1.2	3350	1.250	0	13.3
5	30	200	1800	0	150	1.2	3350	1.241	0	12.9
6	30	280	1800	0	150	1.2	3350	1.237	0	15.1
7	30	120	1800	200	150	1.2	3150	1.222	0	13.8
8	30	200	1800	200	150	1.2	3150	1.222	0	13.4
9	30	280	1800	200	150	1.2	3150	1.224	0	10.6
10	30	120	1800	200	15	1.2	3285	1.227	0	11.0
11	30	200	1800	200	15	1.2	3285	1.230	0	10.8
12	30	280	1800	200	15	1.2	3285	1.229	0	10.1

R.I. is refractive index.

Table 2. Thermally Cured Films with 55% Si-H and a thickness of 5000 Å at 450°C

	Plasma Treatment									
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	R.I @ 633nm	Si-H (%)	Modulus (GPa)
1	30	120	1800	0	150	1.2	3350	1.265	0	13.0
2	30	120	1800	0	150	1.2	3350	1.266	0	14.7
3	30	120	1800	0	150	1.2	3350	1.268	0	13.8
4	30	80	1800	0	150	1.2	3350	1.267	0	14.5
5	30	160	1800	0	150	1.2	3350	1.272	0	15.5
6	15	120	1800	0	150	1.2	3350	1.262	0	13.6
7	30	270	1800	0	150	1.2	3350	1.276	0	15.4

R.I. is refractive index.

Table 3. Thermally Cured Films with 55% Si-H and a thickness of 5000 Å at 450°C

	Plasma Treatment									
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	R.I @ 633nm	Si-H (%)	Modulus (GPa)
1	30	120	1500	0	150	2.1	3350	1.264	0	15.9
2	30	120	1500	0	150	2.1	3350	1.267	0	14.1

R.I. is refractive index.

Table 4. Thermally Cured Films with 40% Si-H and a thickness of 10,000 Å at 450°C

	Plasma Treatment									
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	R.I @ 633nm	Si-H (%)	Modulus (GPa)
1	60	270	1800	0	0	1.0	2000	1.264	12	6.3
5	20	200	1800	2510	5	1.5	240	1.267	0	6.6

R.I. is refractive index.

Table 5. Thermally Cured Films with 40% Si-H and a thickness of 10,000 Å at 400°C

	Plasma Treatment									
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	R.I @ 633nm	Si-H (%)	Modulus (GPa)
1	60	270	1800	0	0	1.0	2000	1.256	10	6.9
5	20	200	1800	2510	5	1.5	240	1.262	0	6.4

R.I. is refractive index.

The results of the testing shown in Tables 1-5 demonstrate that the coatings treated with the microwave plasma were either completely converted to porous silica or the amount of Si-H bonds was significantly reduced as compared to the initial level of Si-H bonds. The elastic modulus of the coatings were greatly improved (over 100%) under a wide variety of process conditions.

Example 2

Solution 1 (described in Example 1) was spin coated on 8 inch single crystal Si wafers on a commercially available coater manufactured by Tokyo Electron Ltd. (TEL), Clean Track ACT™ 8 (ACT8) with optional Dielectric Aging Chamber (DAC).

After spinning the solution onto a wafer, the wafer was placed into the DAC where it was exposed to a moist ammonia atmosphere for 45 to 50 seconds at room temperature. After coating, the wafer was then placed on a hotplate, which was preset to a temperature of 150°C, for one minute to remove the remaining solvent.

These film wafers, which were not thermally cured, were cured by a microwave plasma under various conditions of time, temperature, microwave power, type of gas, and gas flow rate. The Axcelis FusionGemini® ES microwave-downstream plasma asher described above was used to plasma cure the coatings which were not thermally cured. The

process conditions for the plasma cure were the same as those used for the thermally cured plasma treated coatings. The results of the testing are shown in Table 6.

Table 6. Films (No Thermal Cure) with 55% Si-H and a thickness of 5000 Å

	Plasma Cure									
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	Si-H (%)	R.I @ 633nm	Modulus (GPa)
17	30	120	1800	0	150	1.2	3350	0	1.288	14.7
19	30	170	1800	0	150	1.2	3350	0	1.289	16.1
23	30	270	1800	0	150	1.2	3350	0	1.286	16.3

R.I. is refractive index.

These coatings were completely converted to porous silica and the elastic modulus was significantly increased. They had a higher elastic modulus than the thermally cured coating after plasma curing. However, the thermal budget of plasma curing alone (without thermal curing) is much lower than that with thermal cure processing. Thus, plasma curing a coating without thermally curing it provides improved elastic modulus over thermally cured plasma treated coatings and a much lower thermal budget.

Example 3

Thermally cured coatings with 40-55% Si-H and a modulus of about 3.0 GPa from Example 1 and coatings which not been thermally cured from Example 2 were annealed by RTP after the microwave plasma treatment under various conditions shown below.

Pre-purge time:	>30 sec
Ramp rate:	150°C/sec
Wafer Temperature:	350 - 450 °C
Annealing Time:	<180 seconds

The results are shown in Tables 7-11.

Table 7. Thermally Cured Films with 40% Si-H and a thickness of 5000 Å at 450°C

	Plasma Treatment											RTP			
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	Si-H (%)	R.I @ 633nm	DK @ 1Mhz	Modulus (GPa)	Temp (C) /Time (min) /N2	R.I @ 633nm	DK @ 1MHz	Modulus (GPa)
1	30	200	1800	0	15	1.2	3485	0	1.235	3.79	12.6	450/ 2	1.211	3.38	ND
2	30	280	1800	0	15	1.2	3485	0	1.232	4.50	13.2	450/ 2	1.217	3.59	ND
3	30	120	1800	0	150	1.2	3350	0	1.250	3.10	13.3	450/ 2	1.194	2.09	ND
4	30	200	1800	0	150	1.2	3350	0	1.241	3.56	12.9	450/ 2	1.199	2.32	ND
5	30	280	1800	0	150	1.2	3350	0	1.237	4.04	15.1	450/ 2	1.208	2.61	ND
6	30	120	1800	200	150	1.2	3150	0	1.222	3.32	13.8	450/ 2	1.218	3.28	ND
7	30	200	1800	200	150	1.2	3150	0	1.222	6.17	13.4	450/ 2	1.222	3.64	ND
8	30	280	1800	200	150	1.2	3150	0	1.224	4.28	10.6	450/ 2	1.224	6.38	ND
9	30	200	1800	200	15	1.2	3285	0	1.230	5.43	10.8	450/ 2	1.229	4.91	ND

R.I. is refractive index.
DK is dielectric constant.
ND means not determined.

Table 8. Thermally Cured Films with 55% Si-H and a thickness of 5000 Å at 450°C.

	Plasma Treatment											RTP			
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	Si-H (%)	R.I @ 633nm	DK @ 1Mhz	Modulus (GPa)	Temp (C) /Time (min) /N2	R.I @ 633nm	DK @ 1MHz	Modulus (GPa)
1	30	120	1500	0	150	2.1	3350	0	1.264	no	18.2	450/ 2	1.235	2.35	17.6
2	30	120	1500	0	150	2.1	3350	0	1.267	6.04	ND	450/ 2	1.233	2.22	12.6
3	40	120	1500	0	150	2.1	3350	0	1.271	5.78	ND	450/ 2	1.232	2.38	12.9
4	40	160	1200	0	200	1.2	3350	0	1.268	3.77	ND	450/ 2	1.205	2.39	12.7
5	30	120	1500	0	150	2.1	3350	0	1.267	4.28	13.2	450/ 2	1.238	2.35	13.6
6	20	80	1200	0	200	1.2	3350	0	1.259	2.98	ND	450/ 2	1.210	2.34	12.7
9	40	80	1200	0	100	1.2	3350	0	1.26	3.89	ND	450/ 2	1.202	2.35	13.8
10	30	160	1500	0	150	2.1	3350	0	1.263	4.17	ND	450/ 2	1.211	2.33	12.5
11	30	120	1500	0	150	2.1	3350	0	1.266	no	ND	450/ 2	1.247	2.39	13.6
16	20	80	1200	0	100	3	3350	0	1.272	no	ND	450/ 2	1.200	2.37	14.6
18	40	80	1200	0	200	3	3350	0	1.284	no	ND	450/ 2	1.233	2.42	15.5
19	30	80	1500	0	150	2.1	3350	0	1.285	no	ND	450/ 2	1.223	2.19	16.2
23	20	160	1800	0	200	1.2	3350	0	1.265	3.28	ND	450/ 2	1.227	2.37	13.4
24	30	120	1800	0	150	2.1	3350	0	1.241	3.23	ND	450/ 2	1.238	2.38	13.5
25	20	160	1800	0	100	3	3350	0	1.263	3.59	ND	450/ 2	1.256	2.34	13.2
27	30	120	1500	0	150	2.1	3350	0	1.264	no	ND	450/ 2	1.266	2.34	13.0
32	30	120	1500	0	150	2.1	3350	0	1.26	no	ND	450/ 2	1.271	2.34	13.5
1	30	120	1500	0	150	2.1	3350	0	1.264	no	18.2	350/ 2	1.235	2.35	11.0
5	30	120	1500	0	150	2.1	3350	0	1.267	4.28	13.2	350/ 2	1.238	2.35	11.1

R.I. is refractive index.
DK is dielectric constant.
ND means not determined.
No means not able to be determined.

Table 9. Thermally Cured Films with 40% Si-H and a thickness of 10,000 Å at 450°C.

	Plasma Treatment											RTP		
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	Si-H (%)	R.I @ 633nm	DK @ 1Mhz	Modulus (GPa)	Temp (C) /Time (min) /N2	DK @ 1MHz	Modulus (GPa)
1	60	270	1800	0	0	1.0	2000	0	1.264	4.28	6.5	450/ 2	2.75	ND
3	60	270	1800	0	100	1.0	2000	0	1.247	3.41	ND	450/ 2	2.30	6.8

R.I. is refractive index.
DK is dielectric constant.
ND means not determined.
No means not able to be determined.

Table 10. Thermally Cured Films with 40% Si-H and a thickness of 10,000 Å at 400°C.

	Plasma Treatment											RTP		
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	Si-H (%)	R.I @ 633nm	DK @ 1Mhz	Modulus (GPa)	Temp (C) /Time (min) /N2	DK @ 1MHz	Modulus (GPa)
1	60	270	1800	0	0	1.0	2000	10	1.256	5.27	6.9	450/ 2	3.92	ND
3	60	270	1800	0	100	1.0	2000	0	1.224	3.74	ND	450/ 2	2.27	5.8

R.I. is refractive index.
DK is dielectric constant.
ND means not determined.
No means not able to be determined.

Table 11. Films (No Thermal Cure) with 55% Si-H and a thickness of 5000 Å

Plasma Cure												RTP			
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	Si-H (%)	R.I @ 633nm	DK @ 1Mhz	Modulus (GPa)	Temp (C) /Time (min) /N2	R.I @ 633nm	DK @ 1MHz	Modulus (GPa)
17	30	120	1800	0	150	1.2	3350	0	1.288	4.65	14.7	450/ 2	1.213	2.68	ND
19	30	170	1800	0	150	1.2	3350	0	1.289	7.65	16.1	450/ 2	1.219	2.82	ND
23	30	270	1800	0	150	1.2	3350	0	1.286	3.48	16.3	450/ 2	1.237	2.88	ND

R.I. is refractive index.
DK is dielectric constant.
ND means not determined.
No means not able to be determined.

These results show that the plasma treated coatings were completely converted to porous silica or to a silica-like material. The elastic modulus was improved by the plasma treatment, but the dielectric constant was raised. The subsequent RTP annealing lowered the dielectric constant while maintaining a significantly improved elastic modulus as compared to the initial modulus of the original coating. Although the elastic modulus dropped somewhat from the elastic modulus of the plasma treated coatings in some cases, it remained significantly higher than the initial elastic modulus, still showing greater than 100% improvement.

Example 4

A thermally cured coating with 40-55% Si-H and a modulus of about 3.0 GPa was treated with plasma under the conditions listed below.

Plasma Power	400 watts
Wafer Temperature	Room Temperature
Process Pressure	1.2 torr
Plasma Treatment Time	120 seconds
Plasma Gases	Air

The testing was done in a an Branson/IPC plasma system (model IPC S4000 Series). The system utilizes a radio frequency (RF) source at 13.65 MHz which efficiently couples the RF energy into the plasma, creating a high concentration of active radicals.

The results of this testing are shown in Table 12.

Table 12. Thermally Cured Films with 55% Si-H and a thickness of 5000 Å at 450°C treated by radio frequency (RF) plasma with a BRANSON/IPC

	Plasma Treatment									
Run	Time (sec)	Temp (°C)	Power (watts)	Air (unit)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	Si-H (%)	R.I @ 633nm	Modulus (GPa)
1	120	room	400	50	0	1.2	0	0	1.236	7.4

R.I. is refractive index.

Example 5

A solution of alkylhydridosiloxane resin, prepared by the method of Zhong ,U.S. Serial No. 09/458739, with a resin composition of $\{HSiO_{3/2}\}_{33.5}\{RSiO_{3/2}\}_{21.5}\{SiO_{4/2}\}_{45}$ where R is equal to n-octadecyl, containing 16.3% resin by weight and 83.7% isobutyl isobutyrate by weight was continuously filtered through a 2.0 micrometer filter for 40 minutes prior to spin coating. Films were spun onto 8 inch single crystal Si wafers. Spin coating was performed on a Karl Suss RC8 spin coater. After spinning, the coated wafers were placed in a quartz tube furnace for thermal cure. The furnace was purged with nitrogen prior to ramping to achieve an oxygen content less than 10 ppm. The furnace was ramped to 450°C at 25°C/min with a 2 hour hold at 450°C. Samples were allowed to cool to below 100°C under flowing nitrogen before removal from the furnace. The coatings before plasma treatment had a dielectric constant of about 1.9 and an elastic modulus of about 1.8 GPa.

The plasma treatment was done in an Axcelis FusionGemini® ES microwave-downstream plasma asher described above. The process conditions applied to the plasma treatment are shown below:

Microwave Plasma Power:	1800 W
Wafer Temperature:	120°C - 280°C
Process Pressure:	2.1 torr
Plasma Treatment Time:	30 seconds
Plasma Gases:	$H_2/N_2/CF_4/O_2$
O_2 flow rate	0 sccm
CF_4 flow rate:	150 sccm
FG ($5\%H_2/95\%N_2$) flow rate:	3350 sccm

The results of this testing are shown in Table 13.

Table 13. Thermally Cured Films with a thickness of 7000 Å at 450°C

	Plasma Treatment									
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	R.I @ 633nm	Si-H (%)	Modulus (GPa)
1	30	120	1800	0	150	2.1	3350	1.339	0	3.6
2	30	200	1800	0	150	2.1	3350	1.159	0	3.1
3	30	280	1800	0	150	2.1	3350	1.187	0	5.4

R.I. is refractive index.

The results show that the coatings treated with the microwave plasma were completely converted to porous silica. The elastic modulus of the coating was significantly improved under a wide variety of process conditions.

Example 6

The thermally cured coatings obtained from Example 5 were annealed by RTP after the microwave plasma treatment under various conditions. The samples were nitrogen (ultra low O_2) purged for 30 seconds and ramped to the desired temperature.

The process conditions applied to the RTP were in the following ranges:

Pre-purge time:	>30 sec
Ramp rate:	150°C/sec
Wafer Temperature:	350 - 450 °C
Annealing Time:	<180 seconds

The results are shown in Table 14.

Table 14. Thermally Cured Films with 40% Si-H and a thickness of 5000 Å at 450°C

	Plasma Treatment									RTP		
Run	Time (sec)	Temp (°C)	Power (watts)	O_2 (sccm)	CF_4 (sccm)	Pressure (torr)	FG (sccm)	Si-H (%)	R.I @ 633nm	DK @ 1Mhz	Modulus (GPa)	Temp (C) /Time (min) /N2	DK @ 1MHz	Modulus (GPa)
1	30	120	1800	0	150	2.1	3350	0	1.339	2.87	3.6	450/ 2	2.04	ND
2	30	200	1800	0	150	2.1	3350	0	1.159	6.25	3.1	450/ 2	2.07	ND
3	30	280	1800	0	150	2.1	3350	0	1.187	no	5.4	450/ 2	2.34	ND

R.I. is refractive index.
DK is dielectric constant.
ND means not determined.
No means not able to be determined.

Example 7

Porous network coatings were produced from hydrogen silsesquioxane resin by spinning onto silicon wafers and treating with NH_3 followed by 1 minute 150°C hotplate thermal treatments. The plasma conversion was done in an Axcelis FusionGemini® ES plasma asher. After the plasma conversion, porous silica films with low dielectric constant and high modulus have been obtained. The results are shown in Table 15.

The plasma conditions are 2-4 torr in pressure. The temperatures are controlled between 195-230°C. The forming gas is $N_2/H_2/CF_4$. The plasma power and gas flow data are listed in Table 15.

The results indicate that, after plasma curing, the dielectric constants are in a range of 2.0 to 2.8. The plasma conditions at 210°C always yield the films of lower dielectric constants, lower than 2.4. The films processed at 195, 225, and 230°C showed dielectric constants higher than 2.4. The modulus of the plasma cured films are from 6 to 9 GPa. The plasma curing process took off approximately 10% of the film thickness. However, the uniformity of the plasma cured film is typically within 2%. The FTIR spectra suggest that Si-H bonds were completely removed from the films during the plasma curing at the pressures 2-3 torr, implying that porous silica films were made from the plasma curing process. Typically, the films with the dielectric constants of 2.0-2.3 include less than 1% SiOH.

Table 15. Plasma Cure of Films (Example 7)

	Pre-Plasma Heating			Plasma Cure Conditions									
Wafer	Time (sec)	Pressure (torr)	Temperature (°C)	Time (sec)	Pressure (torr)	Temperature (°C)	Power (W)	H_2N_2 (sccm)	CF_4 (sccm)	DK	Modulus (GPa)	Refractive Index	Thickness (Å)
1	120	2.0	210	90	2.0	210	1800	2000	100	2.30	7.3	1.202	4302
2	120	3.0	210	90	3.0	210	1800	2000	100	2.13	7.0	1.196	4265
3	120	3.0	210	90	3.0	210	1800	2000	100	2.27	8.2	1.258	3628
4	120	2.5	210	90	2.5	210	1800	2000	100	2.29	7.9	1.247	3671
5	120	4.0	210	90	4.0	210	1800	2000	100	2.16	6.7	1.205	3676
6	120	4.0	210	90	4.0	210	1800	2000	100	2.24	6.5	1.182	4403
7	120	2.5	230	90	2.5	230	1800	2000	100	2.80	8.8	1.244	3652
8	120	2.0	225	90	2.0	225	1800	2000	100	2.88	7.6	1.203	4442
9	120	2.5	225	90	2.5	225	1800	2000	100	2.57	7.2	1.212	4315
10	120	3.0	225	90	3.0	225	1800	2000	100	2.43	7.2	1.197	4400
11	120	2.0	195	90	2.0	195	1800	2000	100	2.59	6.8	1.215	4351
12	120	2.5	195	90	2.5	195	1800	2000	100	2.74	7.3	1.216	4315
13	120	3.0	195	90	3.0	195	1800	2000	100	2.73	7	1.203	4296
14	0	2.5	210	90	2.5	210	1800	2000	100	2.10	6.9	1.216	3733
15	0	3.0	210	90	3.0	210	1800	2000	100	2.02	6.6	1.212	3766

Example 8

Porous network coatings were produced from hydrogen silsesquioxane by spinning onto silicon wafers and treating with NH_3 followed by 1 minute 150°C hotplate thermal treatments. The NH_3 aging time was 1/2 to 2/3 of standard recipes specified in both the TEL spin tool and the DNS spin tool. The plasma conversion was done in an Axcelis FusionGemini® ES plasma asher. After the plasma conversion, porous silica films with low dielectric constant and high modules have been obtained. The results are shown in Table 16.

The plasma conditions are 2-4 torr in pressure. The temperatures are controlled at 210°C. The forming gas is $N_2/H_2/CF_4$. The plasma power and gas flow data are listed in Table 16.

The plasma curing can also convert the initial films into porous silica films even if the initial films were aged for a short time under moist NH_3. The plasma cured films with less than standard aging time show dielectric constants under 2.3. The modulus values are from 5.7 to 9 GPa. Again, from FTIR spectra, Si-H bonds were removed during the plasma curing so that porous silica films were obtained. The SiOH level in these films are typically smaller than 1%.

Table 16. Plasma Cure of Films (Example 8)

	Pre-Plasma Heating			Plasma Cure Conditions									
Wafer	Time (sec)	Pressure (torr)	Temperature (°C)	Time (sec)	Pressure (torr)	Temperature (°C)	Power (W)	H_2N_2 (sccm)	CF_4 (sccm)	DK	Modulus (GPa)	Refractive Index	Thickness (Å)
2/3 NH_3 Treatment in TEL													
1	120	3.0	210	90	3.0	210	1800	2000	100	2.6	8.8	1.258	3521
2	120	2.5	210	90	2.5	210	1800	2000	100	2.32	9.0	1.261	3577
3	120	2.5	210	90	2.5	210	1800	2000	100	2.27	8.2	1.258	3628
4	120	4.0	210	90	4.0	210	1800	2000	100	2.23	5.7	1.214	3570
5	120	2.5	230	90	2.5	230	1800	2000	100	2.24	8.5	1.257	3654
6	60	2.5	210	90	2.5	210	1800	2000	100	2.21	9.1	1.254	3599
7	0	2.5	210	90	2.5	210	1800	2000	100	2.24	9.0	1.270	3550
1/2 NH_3 Treatment in DNS													
8	120	2.5	210	90	2.5	210	1800	2000	100	2.27	8.4	1.219	4269
9	120	3.0	210	90	3.0	210	1800	2000	100	2.39	8.0	1.218	4186

Example 9

Porous network coatings were produced from hydrogen silsesquioxane by spinning onto silicon wafers and treating with excessive NH_3 followed by 1 minute 150°C hotplate thermal treatments. The NH_3 aging time was twice as long as that specified in the standard recipes for both the TEL spin tool and the DNS spin tool. The plasma conversion was done in an Axcelis FusionGemini® ES plasma asher. The results are shown in Tables 17A and 17B.

The plasma conditions are 2.5-3 torr in pressure. The temperatures are controlled at 210° C. The forming gas is $N_2/H_2/CF_4$. The plasma power and gas flow data are listed in Tables 17A and 17B.

After longer NH_3 aging, the dielectric constants of the plasma cured porous films are 2.5 or higher, and the moduli are approximately 7-8 GPa. The SiOH content is typically around 1.5-2.5%, as calculated from FTIR spectra. The Si-H bonds were completed removed.

In Examples 7-9, the infrared spectra of the annealed, plasma cured coatings that were thermally annealed by heating using RTP are virtually identical to those coatings that were thermally annealed by other heating methods. The features in the spectra indicate that this plasma cured film is silica in nature. The SiOH content is smaller than 1 weight percent as calculated from the infrared spectra. The refractive index (RI) of the RTP annealed coatings (1.20 to 1.22) is consistent with the RI value of coatings that were thermally annealed by other heating methods. The elastic modulus of the plasma cured coatings that were thermally annealed by RTP can be two or three times higher (as high as 7-8 GPa) than the initial elastic modulus. The dielectric constants of these coatings range from 2.1 to 2.3.

Table 17A. Long Aging Time 2x Standard Time on the DNS Tool (Example 9)

Pre-Plasma Heating				Plasma Cure Conditions									
Wafer	Time (sec)	Pressure (torr)	Temperature (°C)	Time (sec)	Pressure (torr)	Temperature (°C)	Power (W)	H_2N_2 (sccm)	CF_4 (sccm)	DK	Modulus (GPa)	Refractive Index	Thickness (Å)
1	120	3.0	210	90	3.0	210	1800	2000	100	2.63	8.0	1.197	4369
2	120	2.5	210	90	2.5	210	1800	2000	100	2.53	8.2	1.197	4685

Table 17B. Long Aging Time 1.5x Standard Time on the DNS Tool (Example 9)

Pre-Plasma Heating				Plasma Cure Conditions									
Wafer	Time (sec)	Pressure (torr)	Temperature (°C)	Time (sec)	Pressure (torr)	Temperature (°C)	Power (W)	H_2N_2 (sccm)	CF_4 (sccm)	DK	Modulus (GPa)	Refractive Index	Thickness (Å)
3	120	3.0	210	90	3.0	210	1800	2000	100	2.54	8.4	1.200	4429
4	120	2.5	210	90	2.5	210	1800	2000	100	2.53	8.7	1.199	4454

By the above methods, a thin (less than 5 microns) SiO_2 containing coating is produced on the substrate. The coating has an improved elastic modulus. Furthermore, with the annealing step, the coating can have an improved elastic modulus and a low dielectric constant.

The coating smooths the irregular surfaces of various substrates and has excellent adhesion. In addition, the coating may be covered by other coatings, such as further SiO_2 coatings, SiO_2/modifying ceramic oxide layers, silicon containing coatings, carbon containing coatings, and/or diamond like coatings.

These coatings posses low defect density and are useful on electronic devices as dielectric layers in, for example, multilayer devices.

While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the compositions and methods disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims.

CLAIMS

1. A method of making a plasma treated coating having improved properties comprising:

providing a thermally cured porous network coating produced from a resin containing at least 2 Si-H groups, wherein the porous network coating has an initial dielectric constant and an initial elastic modulus; and

plasma treating the porous network coating to reduce the amount of Si-H bonds and to provide a plasma treated coating having a second dielectric constant which is greater than the initial dielectric constant, and a second elastic modulus which is greater than the initial elastic modulus.

2. The method of claim 1 further comprising annealing the plasma treated coating to provide an annealed, plasma treated coating having a third dielectric constant which is less than the second dielectric constant and a third elastic modulus which is greater than the initial elastic modulus.

3. The method of claim 2 wherein the plasma treated coating is annealed at a temperature less than about 475°C.

4. The method of claim 2 wherein the plasma treated coating is annealed at a temperature in the range of about 350°C to about 450°C.

5. The method of claim 2 wherein the plasma treated coating is annealed for no more than about 180 seconds.

6. The method of claim 1 wherein the second elastic modulus of the plasma treated coating is at least about 50% greater than the initial elastic modulus.

7. The method of claim 1 wherein the second elastic modulus of the plasma treated coating is at least about 100% greater than the initial elastic modulus.

8. The method of claim 2 wherein the third elastic modulus of the annealed, plasma treated coating is at least about 50% greater that the initial elastic modulus.

9. The method of claim 2 wherein the third elastic modulus of the annealed, plasma treated coating is at least about 100% greater than the initial elastic modulus

10. The method of claim 1 wherein the thermally cured porous network coating is cured by heating to a temperature sufficient to convert the porous network coating into a ceramic.

11. The method of claim 10 wherein the thermally cured porous network coating is cured by heating to a temperature of about 50°C to about 1000°C for up to about 6 hours.

12. The method of claim 11 wherein the thermally cured porous network coating is cured by heating to a temperature in the range of about 50°C to about 500°C for between 10 minutes and about 2 hours.

13. The method of claim 11 wherein the thermally cured porous network coating is cured by heating to a temperature in the range of about 350°C to about 450°C for between 10 minutes and about 1 hour.

14. The method of claim 1 wherein the thermally cured porous network coating is plasma treated for a time in the range of about 15 to about 120 seconds.

15. The method of claim 1 wherein the thermally cured porous network coating is plasma treated at a temperature less than about 350°C.

16. The method of claim 1 wherein the thermally cured porous network coating is plasma treated at a temperature in the range of about 80°C to about 280°C.

17. The method of claim 2 wherein the third dielectric constant of the annealed, plasma treated coating is in the range of from about 1.1 to about 3.5.

18. The method of claim 2 wherein the third dielectric constant of the annealed, plasma treated coating is in the range of from about 2.0 to about 2.5.

19. The method of claim 2 wherein the third elastic modulus of the annealed, plasma treated coating is greater than about 4 GPa.

20. The method of claim 2 wherein the third elastic modulus of the annealed, plasma treated coating is greater than about 10 GPa.

21. The method of claim 2 wherein the third elastic modulus of the annealed, plasma treated coating is between about 4 GPa and about 10 Gpa.

22. A method of making a plasma cured coating having improved properties comprising: providing a porous network coating produced from a resin containing at least 2 Si-H groups; and

plasma curing the porous network coating to reduce the amount of Si-H bonds and to produce an SiO_2-containing plasma cured coating having a first dielectric constant and having a first elastic modulus.

23. The method of claim 22 further comprising annealing the plasma cured coating to provide an annealed, plasma cured coating having a second dielectric constant which is less than the first dielectric constant and having a second elastic modulus which is comparable to the first elastic modulus.

24. The method of claim 23 wherein the plasma cured coating is annealed at a temperature less than about 475°C.

25. The method of claim 23 wherein the plasma cured coating is annealed at a temperature in the range of about 350°C to about 450°C.

26. The method of claim 23 wherein the plasma cured coating is annealed for no more than about180 seconds.

27. The method of claim 22 wherein the porous network coating is plasma cured for a time in the range of about 15 to about 120 seconds.

28. The method of claim 22 wherein the porous network coating is plasma cured at a temperature less than about 350°C.

29. The method of claim 22 wherein the porous network coating is plasma cured at a temperature in the range of about 80°C to about 280°C.

30. The method of claim 22 wherein the porous network coating is plasma cured at a temperature in the range of about 195°C to about 230°C.

31. The method of claim 23 wherein the second dielectric constant of the annealed, plasma cured coating is in the range of from about 1.1 to about 3.5.

32. The method of claim 23 wherein the second dielectric constant of the annealed, plasma cured coating is in the range of from about 2 to about 2.5.

33. The method of claim 23 wherein the second elastic modulus of the annealed, plasma cured coating is greater than about 4 Gpa.

34. The method of claim 23 wherein the second elastic modulus of the annealed, plasma cured coating is greater than about 10 GPa.

35. The method of claim 23 wherein the second elastic modulus of the annealed, plasma cured coating is between about 4 GPa and about 10 GPa.

36. A porous coating having a dielectric constant of from about 2.0 to about 3.5 and an elastic modulus of greater than about 4 GPa.

37. The porous coating of claim 36 wherein the elastic modulus is greater than about 10 Gpa.

38. A plasma treated coating prepared by the method of claim 1.

39. An annealed, plasma treated coating prepared by the method of claim 2.

40. A plasma cured coating prepared by the method of claim 22.

41. An annealed, plasma cured coating prepared by the method of claim 23.

42. An electronic device containing a plasma treated coating prepared by the method of claim 1.

43. An electronic device containing a plasma cured coating prepared by the method of claim 22.

44. A substrate having a plasma treated coating prepared by the method of claim 1.

45. A substrate having a plasma cured coating prepared by the method of claim 22.

46. A porous SiO_2-containing plasma treated coating having a dielectric constant of about 1.1 to about 3.5 and an elastic modulus of about 4 GPa to about 10 GPa.

47. A porous SiO_2-containing plasma treated coating having a dielectric constant of about 2.0 to about 2.9 and an elastic modulus of about 5.7 GPa to about 9.1 GPa.

48. A porous SiO_2-containing plasma cured coating having a dielectric constant of about 1.1 to about 3.5 and an elastic modulus of about 4 GPa to about 10 GPa.

49. A porous SiO_2-containing plasma cured coating having a dielectric constant of about 2.0 to about 2.9 and an elastic modulus of about 5.7 GPa to about 9.1 Gpa.