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(54) Title: LOW DIELECTRIC NANO–POROUS MATERIAL OBTAINABLE FROM POLYMER DECOMPOSITION

(57) Abstract

The present invention relates to novel low dielectric constant nanoporous dielectric films having improved mechanical strength, and to improved processes for producing the same on substrates suitable for use in the production of integrated circuits. The nanoporous dielectric films are prepared by a process of preparing a mixture of a spin–on–glass material with a suitable thermally degradable polymer in a compatible solvent or solvents. Applying the resulting mixture onto a substrate suitable for use in the production of an integrated circuit, to produce a coated substrate. The coated substrate is then heated for a time and at one or more temperatures effective to remove the thermally degradable polymer, so as to produce the desired low dielectric nanoporous dielectric film. Semiconductors, such as integrated circuits with films according to the invention, are also provided.

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LOW DIELECTRIC NANO–POROUS MATERIAL OBTAINABLE FROM POLYMER DECOMPOSITION

FIELD OF THE INVENTION

5 The present invention relates to novel low dielectric constant nanoporous films having improved mechanical strength, and to improved processes for producing the same on substrates suitable for use in the production of integrated circuits. The nanoporous films of the invention are prepared using silicon-based starting materials and thermally degradable polymers, copolymers and/or oligomers selected to be soluble in the employed 10 starting materials.

BACKGROUND OF THE INVENTION

As feature sizes in integrated circuits approach 0.25 µm and below, problems with interconnect RC delay, power consumption and signal cross-talk have become increasingly 15 difficult to resolve. It is believed that the integration of low dielectric constant materials for interlevel dielectric (ILD) and intermetal dielectric (IMD) applications will help to solve these problems. While there have been previous efforts to apply low dielectric constant materials to integrated circuits, there remains a longstanding need in the art for further improvements in processing methods and in the optimization of both the dielectric 20 and mechanical properties of such materials used in the manufacture of integrated circuits.

Nanoporous Films

One material with a low dielectric constant are nanoporous films prepared from silica, i.e., silicon-based materials. Air has a dielectric constant of 1, and when air is introduced into 25 a suitable silica material having a nanometer-scale pore structure, such films can be prepared with relatively low dielectric constants ("k"). Nanoporous silica materials are attractive because similar precursors, including organic-substituted silanes, e.g., tetraethoxysilane ("TEOS"), are used for the currently employed spin-on-glasses ("S.O.G.") and chemical vapor disposition ("CVD") of silica SiO_2. Nanoporous silica 30 materials are also attractive because it is possible to control the pore size, and hence the density, material strength and dielectric constant of the resulting film material. In addition to a low k, nanoporous films offer other advantages including: 1) thermal stability to 900°C, 2) substantially small pore size, i.e., at least an order of magnitude smaller in scale than the microelectronic features of the integrated circuit), 3) as noted above, preparation 35 from materials such as silica and TEOS that are widely used in semiconductors, 4) the

ability to "tune" the dielectric constant of nanoporous silica over a wide range, and 5) deposition of a nanoporous film can be achieved using tools similar to those employed for conventional S.O.G. processing.

5 Thus, high porosity in silica materials leads to a lower dielectric constant than would otherwise be available from the same materials in nonporous form. An additional advantage, is that additional compositions and processes may be employed to produce nanoporous films while varying the relative density of the material. Other materials requirements include the need to have all pores substantially smaller than circuit feature 10 sizes, the need to manage the strength decrease associated with porosity, and the role of surface chemistry on dielectric constant and environmental stability.

Density (or the inverse, porosity) is the key parameter of nanoporous films that controls the dielectric constant of the material, and this property is readily varied over a continuous 15 spectrum from the extremes of an air gap at a porosity of 100% to a dense silica with a porosity of 0%. As density increases, dielectric constant and mechanical strength increase but the degree of porosity decreases, and *vice versa*. This suggests that the density range of nanoporous films must be optimally balanced between for the desired range of low dielectric constant, and the mechanical properties acceptable for the desired application.

20

Nanoporous silica films have previously been fabricated by a number of methods. For example, nanoporous films have been prepared using a mixture of a solvent and a silica precursor, which is deposited on a substrate suitable for the purpose.

25 When forming such nanoporous films, e.g., by spin-coating, the film coating is typically catalyzed with an acid or base catalyst and additional water to cause polymerization/gelation ("aging") and to yield sufficient strength so that the film does not shrink significantly during drying.

30 Another previously proposed method for providing nanoporous silica films was based on the observation that film thickness and density/dielectric constant can be independently controlled by using a mixture of two solvents with dramatically different volatility. The more volatile solvent evaporates during and immediately after precursor deposition. The silica precursor, typically partially hydrolyzed and condensed oligomers of TEOS, is

applied to a suitable substrate and polymerized by chemical and/or thermal means until it forms a gel. The second solvent, called the Pore Control Solvent (PCS) is usually then removed by increasing the temperature until the film is dry. Assuming that no shrinkage occurs after gelation, the density/dielectric constant of the final film is fixed by the volume
5 ratio of low volatility solvent to silica, as described by EP patent application EP 0 775 669 A2. EP 0 775 669 A2 shows a method for producing a nanoporous silica film by solvent evaporation of one or more polyol solvents, e.g., glycerol, from a metal-based aerogel precursor, but nevertheless fails to provide a nanoporous silica film having sufficiently optimized mechanical and dielectric properties, together with a relatively even distribution
10 of material density throughout the thickness of the film.

Yet another method for producing nanoporous dielectrics is through the use of sol-gel techniques whereby a sol, which is a colloidal suspension of solid particles in a liquid, transforms into a gel due to growth and interconnection of the solid particles. One
15 theory that has been advanced is that through continued reactions within the sol, one or more molecules within the sol may eventually reach macroscopic dimensions so that they form a solid network which extends substantially throughout the sol. At this point, called the gel point, the substance is said to be a gel. By this definition, a gel is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. As the skeleton
20 is porous, the term "gel" as used herein means an open-pored solid structure enclosing a pore fluid. Removal of the pore fluid leaves behind empty pores.

Protecting the Surfaces of Nanometer Scale Pores

As the artisan will appreciate, a useful nanoporous film must meet a number of criteria,
25 including having a dielectric constant ("k") falling within the required value range, having a suitable thickness ("t") (e.g., measured in Ångstroms), having an ability to effectively fill gaps, such as, e.g., interconductor and/or intercomponent spaces, on patterned wafers, and having an effective degree of hydrophobicity. If the film is not strong enough, despite achieving the other requirements, the pore structure may collapse, resulting in high
30 material density and therefore an undesirably high dielectric constant. In addition, the surfaces of the resulting nanometer-scale pores carry silanol functional groups or moieties. Silanols, and the water that can be adsorbed onto the silanols from the environment, are highly polarizable and will raise the dielectric constant of the film. Thus,

the requirement for hydrophobicity arises from the requirement for a reduced range of dielectric constant relative to previously employed materials. For this reason, preparation of nanoporous dielectric films has previously required additional processing steps to silylate free silanols on surfaces, including pore surfaces, of the film, with a capping
5 reagent, e.g., trimethylsilyl [TMS, $(CH_3)_3SiO$-] or other suitable, art-known hydrophobic reagents.

Therefore, despite the availability of previous methods for preparing nanoporous silica films, the art recognizes a need for further, ongoing improvements in both nanoporous
10 silica films and methods for preparing the same. In particular, there remains a continuing need in the art for new processes which eliminate some or all of the aforementioned problems, such as providing methods for making silica nanoporous films of sufficient mechanical strength that are also optimized to have a desirably low and stable dielectric constant, without the need for further processing to make the film hydrophobic.
15

SUMMARY OF THE INVENTION

In order to solve the above mentioned problems and to provide other improvements, the invention provides novel nanoporous silica dielectric films with a low dielectric constant ("k"), e.g., typically ranging from about 1.5 to about 3.8, as well as novel new methods of producing
20 these dielectric films.

Broadly, the dielectric nanoporous films of the invention are prepared by mixing a non-volatile thermally degradable polymer with an organic and/or inorganic silicon-based material or mixture of such materials suitable for forming dielectric films. Such suitable
25 organic and/or inorganic silicon-based material or materials are referred to herein, for convenience and without limitation, as spin-on glass ("S.O.G.") material(s). The resulting mixture of the base material, i.e., one or more S.O.G. materials, and the thermally degradable component can optionally form a co-polymer, but, in any event, this mixture is applied by any art-known methods to a substrate suitable for use in preparing
30 an integrated circuit. The thermally degradable component is then is then subjected to a process of thermal treatments, leaving behind nanometer-scale voids in the solidified base material. The incorporated nanometer scale voids reduce the density of the base material to provide the desired low dielectric properties.

Broadly, it has been found that a variety of solvent systems are readily employed in preparing films according to the invention. In one preferred embodiment of the invention, the thermally degradable component includes at least one polyalkylene oxide compound that is soluble in both the base material and that is soluble in a nonpolar solvent system, e.g., an organic-type solvent system. In another preferred embodiment, the low dielectric nanoporous film is produced by the process of preparing a mixture of at least one spin-on-glass material with a suitable thermally degradable polymer that is soluble in a polar solvent.

More preferably, in one aspect of the invention, the S.O.G. base material is a compound of Formula I:

$$[(SiO_2)_x - (R_1SiO_{1.5})_y - (R_2R_3SiO)_z]_n \qquad \text{Formula I}$$

wherein x, y, z and n are positive integers of independent values, R_1, R_2 and R_3 are independently H or organic, and at least one of R_1, R_2 and R_3 is H; and $1 \geq x \geq 0$; $1 \geq y \geq 0$; $1 \geq z \geq 0$, provided that x+y+z is 1.0.

When any of R_1, R_2 and R_3 are organic, the organic moiety is a C_1-C_6 alkyl. In addition, the value of n ranges from about 100 to about 800. Other suitable S.O.G. materials for preparing the dielectric films of the invention can include, simply by way of example, hydrogensiloxanes, hydroorganosiloxanes, alkylsiloxanes and polyhydridosilsesquioxanes, to name but a few.

Further, a thermally degradable polymer or mixture of polymers suitable for the compositions and processes of the invention range in molecular weight from about 200 to about 2,000,000 Daltons, but preferably from about 1,000 to about 30,000 Daltons. Within these general parameters, a suitable component for use in the compositions and methods of the invention includes one or more of the group consisting of a polyalkylene oxide, an aliphatic polyester, an acrylic polymer, an acetal polymer, and/or combinations thereof.

When the thermally degradable component is selected for solubility in a nonpolar solvent system, a suitable component includes one or more of the group consisting of a polyalkylene oxide, a poly(caprolatactone), a poly(valeractone), a poly(methyl methacrylate), a poly (vinylbutyral) and/or combinations thereof. Preferably, when the

component is a polyalkylene oxide, that compound includes a C_1 to about C_6 alkyl, e.g., polypropylene oxide.

When the thermally degradable component is selected for solubility in a polar solvent system,
5 the thermally degradable polymer is advantageously a polyalkylene oxide, e.g., a polymethylene oxide or polyethylene oxide.

As mentioned above, the low dielectric films of the invention are produced using a heating step to volatilize an oligomer and/or polymer component of the starting S.O.G. mixture.
10 Preferably, the heating step includes both a baking step and a curing step. In particular, the baking step includes a plurality of heating steps, ranging in temperature from about 60°C to about 300, or even 350°C, and each heating step is conducted for a time period ranging from about 0.5 to about 10 minutes or more particularly, from about 0.5 to about 4 minutes. For example, in one preferred aspect of the invention, the baking process
15 includes a first heating step of about 80°C, a second heating step of about 150°C, and a third heating step of about 200°C, each heating step being applied for a duration of about 1 minutes at each respective temperature.

When the processes of the invention include a curing step, curing is accomplished by
20 heating the baked film at a temperature of at least 400°C and for a time period ranging from about 10 to about 60 minutes.

The invention also provides for a substrate, e.g., an integrated circuit, that includes at least one low dielectric nanoporous film formed by the processes of the invention.
25 Further, the invention provides for methods for producing the above-described low dielectric nanoporous films on a substrate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Accordingly, nanoporous silica dielectric films having a dielectric constant, or k value,
30 ranging from about 1.5 to about 3.8, can be produced by the methods of the invention. The films produced by the processes of the invention have a number of advantages over those previously known to the art, including improved mechanical strength to withstand the further processing steps required to prepare integrated circuit on the treated substrate, and a low and stable dielectric constant. The property of a stable dielectric constant is

advantageously achieved without the need for further surface modification steps to render the film surface hydrophobic, thus confirming that the silica dielectric films as produced by the processes of the invention are sufficiently hydrophobic as initially formed.

5 As summarized in the "Description of the Prior Art" above, a number of methods for the preparation of nanoporous silica films on substrates are known to the art. In addition, a number of variations and improvement to these generally known methods for the preparation of nanoporous films are taught by co-owned U.S. Patent Application Ser. Nos., 09/046,475 and 09/046,473, both filed on March 25, 1998; U.S. Patent Application Ser. No. 09/054,262,
10 filed on April 3, 1998; and U.S. Patent Application Ser. Nos. 09/055,244 and 09/055,516, both filed on April 6, 1998, the disclosures of which are incorporated by reference herein in their entireties.

In order to better appreciate the scope of the invention, it should be understood that unless the
15 "SiO_2" functional group is specifically mentioned when the term "silica" is employed, the term "silica" as used herein, for example, with reference to nanoporous dielectric films, is intended to refer to dielectric films prepared by the inventive methods from an organic or inorganic glass base material, e.g., any suitable silicon-based material. It should also be understood that the use of singular terms herein is not intended to be so limited, but, where
20 appropriate, also encompasses the plural, e.g., exemplary processes of the invention may be described as applying to and producing a "film" but it is intended that multiple films can be produced by the described, exemplified and claimed processes, as desired.

Broadly, the processes of the invention are conducted by mixing a first component, formed of
25 a suitable base material, such as a silicon-based S.O.G. material or blend of materials, with a second component that is susceptible to thermal degradation after the film-forming mixture has been applied to a substrate and the resulting film is heated according to the processes described below. Further, the second component is formed of one or more relatively non-volatile, but thermally degradable, polymers, copolymers and/or oligomers, and is miscible
30 with the first component and any solvents, e.g., polar or nonpolar, that may be employed in that mixture. Further still, the thermally degradable component is preferably substantially nonvolatile at typical ambient environmental temperatures, e.g., from about 20 to about 200°C, so that no significant evaporation from the applied film will occur prior to heat induced volatilization and solidification of the surrounding film composition.

Thus, once the film-forming mixture is applied by art-standard methods to the substrate, the substrate and the resulting film is heated to a temperature and for a time period sufficient to thermally degrade and/or vaporize the second component so as to leave behind nanometer scale pore structures in the film. In one preferred embodiment the film is then cured. Optionally, the heating steps can be conducted in a plurality of stages, each stage utilizing similar or differing times and temperatures, or combined into a single process step. In a further option, the heating steps can also be conducted so as to combine the curing step and the vaporization of the thermally degradable second component.

The compositions and processes of the invention are described in further detail, as follows.

STARTING MATERIALS

Substrates

Broadly speaking, a "substrate" as described herein includes any suitable composition formed before a nanoporous silica film of the invention is applied to and/or formed on that composition. For example, a substrate is typically a silicon wafer suitable for producing an integrated circuit, and the base material from which the nanoporous silica film is formed is applied onto the substrate by conventional methods, e.g., including, but not limited to, the art-known methods of spin-coating, dip coating, brushing, rolling, and/or spraying. Prior to application of the base materials to form the nanoporous silica film, the substrate surface is optionally prepared for coating by standard, art-known cleaning methods.

Suitable substrates for the present invention non-exclusively include semiconductor materials such as gallium arsenide ("GaAs"), silicon and compositions containing silicon such as crystalline silicon, polysilicon, amorphous silicon, epitaxial silicon, and silicon dioxide ("SiO_2") and mixtures thereof. On the surface of the substrate is an optional pattern of raised lines, such as metal, oxide, nitride or oxynitride lines which are formed by well known lithographic techniques. Suitable materials for the lines include silica, silicon nitride, titanium nitride, tantalum nitride, aluminum, aluminum alloys, copper, copper alloys, tantalum, tungsten and silicon oxynitride. These lines form the conductors or insulators of an integrated circuit. Such are typically closely separated from one another at distances of about 20 micrometers or less, preferably 1 micrometer or less, and

more preferably from about 0.05 to about 1 micrometer. Other optional features of the surface of a suitable substrate include an oxide layer, such as an oxide layer formed by heating a silicon wafer in air, or more preferably, an SiO_2 oxide layer formed by chemical vapor deposition of such art-recognized materials as, e.g., plasma enhanced tetraethoxysilane ("PETEOS") silane oxide and combinations thereof, as well as one or more previously formed nanoporous silica dielectric films.

The nanoporous silica film of the invention can be applied so as to cover and/or lie between such optional electronic surface features, e.g., circuit elements and/or conduction pathways that may have been previously formed features of the substrate. Such optional substrate features can also be applied above the nanoporous silica film of the invention in at least one additional layer, so that the low dielectric film serves to insulate one or more, or a plurality of electrically and/or electronically functional layers of the resulting integrated circuit. Thus, a substrate according to the invention optionally includes a silicon material that is formed over or adjacent to a nanoporous silica film of the invention, during the manufacture of a multilayer and/or multicomponent integrated circuit.

In a further option, a substrate bearing a nanoporous silica film or films according to the invention can be further covered with any art known non-porous insulation layer, e.g., a glass cap layer.

First Component - Silicon-Based Polymers

In one embodiment, the starting materials, i.e., the first component, or silica starting material(s) for conducting the processes of the invention, includes organic and/or inorganic base materials suitable for use in coating a substrate. These are typically materials that are suitable for use as spin-on-glasses. Spin-on-glasses (S.O.G.) are silicon-based dielectric materials that are prepared in a solution form to be used for insulation, planarization and gap-filling in the fabrication of integrated circuits on a suitable substrate (e.g., wafer). S.O.G. solution materials can be applied onto a substrate by any art-known methods, including dipping, brushing, rolling, spraying, but are most typically applied by spin-coating.

Suitable S.O.G. materials for use in the methods of the invention are silicon-based materials that can be prepared from appropriate functional units, including, for example, at least one of the following.

SiO_2 (silica unit);
$Q_1SiO_{3/2}$ (silsesquioxane unit);
$Q_2Q_3SiO_2$ (siloxane unit); and
$Q_4Q_5Q_6SiO$ (end group)

5

wherein Q_1, Q_2, Q_3, Q_4, Q_5 and Q_6 are organic, and can be the same or different. The term "organic" encompasses any suitable organo-moiety, including alkyl, which can be straight, branched and/or cyclic alkyl, as well as arylalkyl, any of which can be substituted or unsubstituted, and combinations thereof. The "organic" term also encompasses aryl and
10 heteroaryl, substituted and unsubstituted organo-moieties.

Thus, in another embodiment of the invention, when any of Q_1, Q_2, Q_3, Q_4, Q_5 and Q_6 are organic, it is preferred that such moiety be an alkyl, preferably a C_{1-6} alkyl. In another embodiment, any of Q_1, Q_2, Q_3, Q_4, Q_5 and Q_6 can independently be an aryl moiety,
15 preferably a C_6-C_{12} aryl.

In yet a still further embodiment of the invention, the base material is a hydridosilsesquioxane or hydridosiloxane with the general structure of Formula I, as follows.

20

$$[(SiO_2)_x - (R_1SiO_{1.5})_y - (R_2R_3SiO)_z]_n \quad \text{Formula I}$$

wherein R_1, R_2 and R_3 are independently selected from H and/or an organic moiety, but at least one of R_1, R_2 and R_3 is H. Preferably, the organic moiety is an alkyl selected so that the base material is suitable for use as an S.O.G. material, as understood by the art. More preferably, the base material is a C_1-C_6 alkyl; and
25 x, y and z each independently range in value from 1 to zero, i.e.,

$1 \geq x \geq 0$; $1 \geq y \geq 0$; $1 \geq z \geq 0$

provided that x+y+z is 1.0.

In a preferred embodiment, n ranges from about 100 to about 800, yielding a molecular weight of from about 5,000 to about 45,000. More preferably, n ranges from about 250
30 to about 650 yielding a molecular weight of from about 14,000 to about 36,000.

Further, particular types of base materials each have a preferred range of values for the above described parameters of Formula I, as follows.

35 When the base material is a polyhydridosilsesquioxane ("PHSQ), y is 1 and R_1 is H.
When the base material is a silica, x is 1.
When the base material is a polymethylsilsesquioxane, y is 1 and R_1 is methyl.

When the base material is a polymethylhydridosilsesquioxane, y is 1 and R_1 is a mixture of H and methyl.

5 When the base material is a methylsiloxane such as, e.g., AMM512B, (Accuglass T-12B®), x, y and z > 0 and R_1, R_2 and R_3 are methyl.

When the base material is a methylsiloxane such as, e.g., AMM311, (Accuglass T-11®), x, y > 0 and z = 0 and R_1 is methyl.

10

In one particular embodiment of the invention, as exemplified herein, the S.O.G. materials include methylsiloxanes. Useful compositions that contain or include methylsiloxanes, and that are suitable for use as S.O.G. base materials, are readily available commercially, and include, for example, such products as AMM 311 (Accuglass T-11®); and 512B
15 (Accuglass T-12B®) S.O.G. materials. These are commercially available from Advanced Microelectronic Materials, a subsidiary of the Electronic Materials Division of Honeywell Corporation (Sunnyvale, California). The pertinent properties of AMM 311 and AMM 512B are set forth in Table 1, as follows.

Table 1
Properties of Commercially Available Methylsiloxanes

Material Properties	AMM 311	AMM 512B
Obtainable Film Thickness Range	2300-3500Å	4900 - 5200 Å
Metal Impurities	≤ 10 ppb	≤ 20 ppb
Shelf-Life	6 Months at 4□C	6 Months at 4□C
Filtration	0.1 μm	0.1 μm
% solid	10.5	14.7
Organic Content	10 wt%	14 wt%
Dielectric Constant	3.8	3.1
Refractive Index	1.39	1.38
Solvent System(wt%) -- ethanol, -- 2-propanol, -- acetone, -- water	 23 36 18 8	 32 30 14 10
Siloxanes: SiO_2 $CH_3SiO_{1.5}$ $(CH_3)_2SiO$	58.0 mole % 42.0 0	 46.3 mole % 46.7 7.0
Empirical composition after baking at 80, 150 and 250□C, in sequence.	$SiO_{1.78}(CH_3)_{0.42}$	$SiO_{1.7}(CH_3)_{0.6}$

In a further embodiment of the invention, base materials useful for the invention also include: hydrogensiloxanes polymers which have the structure of,

$$[(HSiO_{1.5})_{(a)}O_{(b)}]_n \quad \text{Formula II ;}$$

hydroorganosiloxanes which have one of the following formulae,

$$[(HSiO_{1.5})_{(a)}O_{(b)}(RSiO_{1.5})_{(c)}]_n \quad \text{Formula III}$$

In each of polymer formulae (II and III), (a) ranges from about 6 to about 20, (b) ranges from about 1 to about 3, (c) ranges from about 6 to about 20, n ranges from 1 to about 4,000, and each R (in Formula III, when n>1) is independently H, C_1-C_8 alkyl or C_6-C_{12} aryl. The weight average molecular weight may range from about 1,000 to about 220,000. In a preferred embodiment, for Formulas I, II and III, n ranges from about 100 to about 800, yielding a molecular weight of from about 5,000 to about 45,000. More preferably, n ranges from about 250 to about 650 yielding a molecular weight of from about 14,000 to about 36,000.

In a still further embodiment of the invention, the alkylsiloxanes can also include hydrogen alkylsiloxanes, such as, simply by way of example, hydrogenmethylsiloxane, hydrogenethylsiloxane, hydrogenpropylsiloxane, hydrogenbutylsiloxane, hydrogen*tert*-butylsiloxane, hydrogenphenylsiloxane and combinations thereof, to name but a few.

In yet a still further embodiment of the invention, the S.O.G. materials for conducting the processes of the invention include, for example hydrogensilsesquioxane, hydrogenmethylsilsesquioxane, hydrogenethylsilsesquioxane, hydrogenpropylsilsesquioxane, hydrogenbutylsilsesquioxane, hydrogen*tert*-butylsilsesquioxane and hydrogenphenylsilsesquioxane.

In a preferred embodiment of the invention, as exemplified below, the S.O.G. materials include polyhydridosilsesquioxane ("PHSQ") base materials. Porous polyhydridosilsequioxane (PHSQ) film is produced from the decomposition of the thermally degradable organic component in a polyhydridosilsequioxane/organic system. The polyhydridosilsequioxane is prepared from the hydrolysis of trialkoxysilane or trichlorosilane in a controlled reaction condition. The chemical composition of the polyhydridosilsesquioxane can be represented by the following formula:

$$(HSiO_{3/2})_n \qquad \text{Formula IV}$$

wherein n is an integer ranging from about 10 to about 4,000. In a preferred embodiment, n is an integer ranging from about 20 to about 1,000.

Second Component - Thermally Degradable Polymers

The second component is a thermally degradable component for use in the processes of the invention. The thermally degradable component is preferably miscible with the first component, and can optionally form a co-polymer therewith. The thermally degradable component is also sufficiently thermally degradable under the heating conditions employed according to the invention, for forming a useful nanoporous dielectric film on a substrate, so as to be useful for the manufacture of an integrated circuit. The thermally degradable component is also optionally selected to be soluble in either a polar or nonpolar solvent.

The terms, "degradable" or "thermally degradable" as employed herein, in reference to the component that is to be thermally degraded under the heating conditions of the inventive

process, includes both physical evaporation of a relatively volatile fraction of the thermally degradable component during the heating step(s) and/or degradation of the component(s) into more volatile molecular fragments. Without wishing to be bound by any theory or hypothesis, it is believed that the heating steps degrade the organic polymer component by either direct vaporization or chemical disruption of the polymer by the applied heat, or disruption of the polymer by any reactive species induced in the film structure by the applied heat. In any event, the thermal degradation of the organic polymer component forms nanometer-scale voids in the film structure.

It is also important that the thermally degradable component be substantially nonvolatile prior to the heating step, i.e., at room temperature. Thus, the thermally degradable component is not so volatile as to significantly evaporate prior to the time during the heating of the film when the silicon polymer(s) begins to achieve cross-linking. As confirmed by the Examples provided below, if significant evaporation does take place too early in the process, the resulting film density, and therefore the dielectric constant, will be higher than would otherwise be produced in that film. Thus, without meaning to be bound by any theory or hypothesis as to how the invention operates, it is believed that undesirable "significant" pre-heating evaporation is evaporation that takes place prior to the cross-linking of the S.O.G. material at such a rate and in such a proportion of the applied film, so as to result in the production of an undesirably dense dielectric film.

The term, "polymer" as employed herein also encompasses the terms oligomers and/or copolymers, unless expressly stated to the contrary.

Preferred thermally degradable polymers according to the invention will have molecular weights in a range that is effective to be thermally degraded in the temperature range of the heating steps, but the molecular weight should not be so low as to allow significant evaporation prior to the baking step(s), for the reasons discussed above. Preferably, thermally degradable polymer(s) employed according to the invention will have a molecular weight ranging from about 200 to about 2,000,000, or more, Daltons. More preferably, such a polymer will have a molecular weight ranging from about 1,000 to about 30,000 Daltons, or even from about 2,000 to about 10,000 Daltons.

Nonpolar Solvent Systems

Thermally Degradable Polymers

5 For processes employing a nonpolar solvent or solvent system, the thermally degradable polymer is soluble or miscible in the employed solvent and is, for example, a polyalkylene oxide. Preferably, the polyalkylene oxide includes an alkyl moiety, ranging, e.g., from C_1 to about C_6. More preferably, when the first component is a PHSQ, the degradable component is a polypropylene oxide ("PPO"). Other suitable thermally degradable polymers include,

10 without limitation, aliphatic polyesters, including, for example, poly(caprolactone) and poly(valeralactone); acrylic polymers, including, for example, poly(methyl methacrylate) and acetal polymers, including, for example, poly (vinylbutyral), to name but a few.

The thermally degradable polymers can also be chemically bonded to the silicon-based

15 polymers to form a copolymer, including, simply by way of example, PHSQ-polypropylene oxide copolymers, PHSQ-polycaprolactone copolymers and/or combinations thereof.

Nonpolar Solvents

In this embodiment of the invention, a suitable solvent or cosolvent optionally employed in the

20 film forming mixture that is applied to the substrate will, broadly, be a nonpolar solvent that has a boiling point of, e.g., 200°C or less, and preferably the boiling point will range from about 80 to about 160°C. Simply by way of example, and without limitation, nonpolar solvents useful according to the invention include acetates (ethyl acetate, isopropyl acetate, butyl acetate), ethers (dibutyl ether), and ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone).

25

In one particular embodiment the acetate solvent is an organic acetate or mixture of acetates. Preferably, the organic moiety of the organic acetate is a C_1 to C_6 alkyl, a C_5 to C_{12} aryl and or derivatives or combinations thereof. As shown in the examples below, the employed polypropylene oxide (PPO) is dissolved in ethyl acetate and/or a mixture of

30 ethyl and n-butyl acetate. The useful ratios of ethyl- to n-butyl acetate range generally from about 20:80 (wt/wt) to about 80:20 (wt/wt), and more preferably from about 50:50 to about 60:40. As exemplified below, a ratio of ethyl- to n-butyl acetate of about 70:30 (wt/wt) is readily employed.

The thermally degradable polymer is dissolved in the solvent in a percentage ranging, simply by way of example, from about 3 wt% to about 50 wt% or more particularly in a percentage ranging from about 5 wt% to about 30 wt%.

5 Polar Solvent Systems

Thermally Degradable Polymers

For processes employing a polar solvent or solvent system, the thermally degradable polymer is soluble or miscible in the employed solvent, and is e.g., a polyalkylene oxide. The

10 polyalkylene oxide includes an alkyl moiety, ranging, e.g., from C_2 to about C_6. Simply by way of example, in one embodiment, the thermally degradable component will include a polyethylene oxide and polypropylene oxide and copolymers thereof. Other thermally degradable polymers suitable for use in polar solvent systems include, without limitation, polyvinyl alcohol and water soluble polyethylene oxide/polypropylene oxide copolymers

15 and mixtures thereof.

Polar Solvents

In this embodiment, a suitable solvent or co-solvent optionally employed in the film forming mixture that is applied to the substrate will, broadly, be a polar solvent that has a

20 boiling point of 200°C or less, and preferably the boiling point will range from about 80°C to about 160°C. Simply by way of example, and without limitation, polar solvents useful according to the invention include water; alcohols, e.g., ethanol or isopropanol; ketones, e.g., acetone, and mixtures thereof.

25 Process Parameters

In the processes of the invention, a mixture of the S.O.G. i.e., silicone-based polymer(s), and thermally degradable polymer(s) and/or oligomers and optional solvent(s) is prepared in a suitable ratio. The prepared mixture of S.O.G. and degradable polymers and/or oligomers and optional solvent(s) is applied to a suitable substrate by an appropriate art-known means.

30

When the mixture is applied to the substrate by centrifugation, i.e., when it is spun-on, the conditions are those conventionally used for such application, e.g., the substrate is spun at about 2,000 to 4,000 rpms. The artisan will appreciate that specific conditions for application to a substrate will depend upon the selected materials, substrate and desired nanoscale pore

35 structure, as is readily determined by routine manipulation of these parameters.

The applied film broadly has a composition that includes a thermally degradable polymer component in a wt% ranging from about 10 wt% to about 80 wt%, more particularly from about 15 wt% to about 70 wt%, and even more particularly from about 30 wt% to about 5 70wt%.

The applied film is then baked and thereafter cured to form the nanoscale pore structures within the film, by thermally induced evaporation or decomposition of the thermally degradable polymer component. Baking/curing is done at a temperature and for a time period 10 effective to degrade and/or vaporize the degradable component, e.g., PPO, PEO, etc., and cause such nanometer scale pores to form. Preferably, the heating steps are conducted on a hot plate and/or in a oven, and optionally on a conveyer belt moving through a suitable hot zone. In a preferred embodiment, baking temperatures range from about 60°C to about 350°C, more preferably from about 70°C to about 300°C or from about 80°C to about 250°C.

15

Baking times will depend upon the materials selected and the desired results, but will generally range from about 30 seconds to about 10 minutes in the about 60°C to about 350°C temperature range; from about 0.5 to about 6 minutes in the about 70°C to about 300°C temperature range; and from about 0.5 to about 3 minutes in the about 80°C to about 250°C 20 temperature range.

The artisan will appreciate that specific temperature ranges and baking and/or curing conditions will depend upon the selected materials, substrate and desired nanoscale pore structure, as is readily determined by routine manipulation of these parameters. Generally, the curing step 25 comprises heating the baked film at a temperature of at least 400°C and for a time period ranging from about 10 to about 60 minutes.

Properties Of the Produced Nanoporous Silica Films

Nanoporous dielectric films formed on a substrate according to the invention are generally 30 formed with a pore size that ranges from about 1 nm to about 100 nm, more preferably from about 2 nm to about 30 nm, and most preferably from about 3 nm to about 20 nm. The density of the silicon-containing composition, including the pores, ranges from about 0.1 to about 1.9 g/cm^3, more preferably from about 0.25 to about 1.6 g/cm^3, and most preferably from about 0.4 to about 1.2 g/cm^3.

Thus, the percentage of the nanoporous dielectric film produced by the methods of the invention that are represented by void space, i.e., nanometer scale pores, can range, e.g., from about 10 to about 70 percent, or greater, and preferably from about 20 to about 50 percent.

The refractive index is another indicator of the relative density of dielectric films produced from S.O.G. materials. The dielectric of the hydridosilsesquioxane or methyl silsesquioxane starting materials that are exemplified herein range from about 2.5 to about 3.3. The refractive index of dielectric films produced by the inventive methods range in value from about 1.15 to about 1.4, and more preferably from about 1.9 to about 1.31.

Given the low densities achieved by the methods and compositions of the invention, low dielectric constant or k values are attainable, ranging from about 1.5 to about 3.8, preferably from about 2.0 to about 2.8, and more preferably from about 1.8 to about 2.8.

EXAMPLES

Examples 1-6

For Examples 1-6, below, the exemplified S.O.G. base materials are the methylsiloxanes, AMM 512B and the AMM 311, discussed above. The exemplified organic component is polyethylene oxide ("PEO"). The artisan will appreciate that PEOs and/or a mixture of PEOs, are selected for use in the inventive processes to thermally degrade in a temperature range that is relatively low compared to the thermal tolerances of the employed substrate and S.O.G. materials, to be soluble in polar solvents that are compatible with the inventive processes, and to be miscible with the selected S.O.G. materials. Processing steps include dissolving the PEO in the S.O.G. in an appropriate amount, then casting the mixture onto the substrate by spinning, and then baking and optionally curing the spun film at a temperature range and for a time period or periods appropriate for the selected S.O.G. material.

The following non-limiting examples serve to illustrate the invention.

EXAMPLE 1

Films Formed by the Removal Of Polyethylene Oxide

Materials

A) Base Matrix Materials

5 Base matrix materials that form the backbone of the nanoporous foams were S.O.G. methylsiloxanes AMM 512B and 311. Table 2, below, lists the properties of the AMM methylsiloxanes.

Table 2
Properties of Methylsiloxanes

	AMM 311	AMM 512B
% solid	10.5	14.7
% water	8	10
Organic Content	10 wt%	14 wt%
Dielectric Constant	3.8	3.1
Refractive Index	1.39	1.38
Additional Solvents	Isopropyl alcohol, ethyl alcohol, acetone	isopropyl alcohol, ethyl alcohol, acetone

10 A) Thermally Degradable Components

Three polyethylene glycols with different molecular weights were used:

(i) MW= 200 (PEO-200) – liquid

(ii) MW=600 (PEO-600) – wax

(iii) MW=7500 (PEO-7500) – crystalline solid (mp=72°C)

15

A) Preparation of the Spin-On Solutions

Different amounts of PEO were employed, in amounts ranging from 1 to 22 percent by weight, relative to the methylsiloxane solutions. To dissolve PEO-7500, the solution was heated to above 60°C. For the other two PEOs, stirring at room

20 temperature was sufficient to complete dissolution. Symbol designated to describe the coating solutions is (base matrix)-(MW of PEO)-(wt. % of PEO) in as-spun form. For example, 512B-7500-26 represents a composition of 26 wt% of PEO-7500 and 74 wt% of 512B in the as-spun form (sample "I" in Table 3, below). For convenience in description, each combination is also given an alphabetic designation. The

25 following samples were prepared, as listed in Table 3, below.

Table 3
Coating Mixtures

Sample No.	Base Matrix Solution	Wt Base Solution (grams)	MW PEO	Wt of PEO (grams)	(Summary)
A	311	10.10	200	0.55	311-200-34
B	311	10.21	200	1.18	311-200-51
C	311	30.00	600	1.71	311-600-35
D	311	30.67	600	3.15	311-600-49
E	311	30.05	7500	0.34	311-7500-10
F	311	21.78	7500	2.31	311-7500-49
G	311	16.99	7500	2.61	311-7500-57
H	311	19.50	7500	4.43	311-7500-65
I	512B	30.00	7500	1.55	512B-7500-26
J	512B	21.68	7500	2.17	512B-7500-39
K	512B	28.97	7500	4.35	512B-7500-48
L	512B	29.10	7500	6.40	512B-7500-56

The prepared samples, as described by Table 3, above, were then spun onto suitable test substrates, which were flat wafers of about 4 or 6 inch oxide-coated silicon wafers.

5

Bake/Cure Cycles

Hot plate bake temperatures were 80, 150, and 250°C for 2 minutes at each temperature. The as-spun films were hazy, but the films became clear after the 250°C bake. However, there was smoking during the 150 and 250°C bake steps, resulting
10 from the volatilization and removal of the PEG. The baked films were then cured at 400°C for 30 minutes in flowing nitrogen.

EXAMPLE 2
Analysis of Films by Fourier
15 Transformed Infrared ("FTIR") Spectroscopy

The film samples were prepared as described above in Example 1 using the F and J starting materials. The spun-on films were then treated with 80, 150 and 250°C, as

baking steps and were subjected to FTIR analysis [spectra not shown] after each baking step. A broad absorption peak was obtained between 2800 cm^{-1} to 3000 cm^{-1} that confirmed the presence of the organic PEO in the film. The peak intensity, i.e., amplitude of the PEO signal, remained essentially constant until the 250°C baking
5 step, as is recorded in Table 4, below.

Table 4
FTIR Analysis
Peak High Ratio Between Peaks at 2830 cm^{-1} to 1050 cm^{-1}

Baking Step	Sample F (311-7500-49) Peak Height Amplitude*	Sample J (512B-7500-39) Peak Amplitude*
80 Deg. C	0.322	0.243
150 Deg. C	0.332	0.257
250 Deg. C	0**	0**
	*Absolute value above baseline ** Minor bump in nearly level curve at approximately 2970 cm^{-1} - this is indicative of the organic moiety from the 311 or 512B	

As shown in Table 4, above, peak measurements confirmed that PEO was still present in the film in substantial amounts after the bake at 150°C, but was almost completely
10 removed after the last bake at 250°C. Therefore, it is believed that the porous structure took shape during the third bake step.

Additional FTIR of the films produced from F and J, after they were cured at 400°C, showed virtually no trace of the PEO component in the 2800 cm^{-1} to 3000 cm^{-1} band
15 (except for a miniscule blip at approximately 2970 cm^{-1}). Thus, the 400°C cured films yielded FTIR spectra for both the 311 and the 512B derived films which are essentially the same as those of pure AMM311 and AMM512B.

EXAMPLE 3

20 Measurements Of Thickness Of Produced Films

Film thickness was measured using Nanospec, Tencor, and Gaertner instruments. Data from Nanospec and Tencor appeared to give inconsistent results. A more reliable film thickness can be obtained from the Gaertner machine in double-angle mode. Thickness of one selected film was measured in SEM. The SEM thickness was in line with the result

obtained from the Gaertner elipsometer. The major shrinkage occurred in the 250°C bake step. The thickness of the nanoporous film that resulted after each processing step using mixtures F and J, respectively, are listed in Table 5, as follows.

Table 5
Bake/Cure Film - Thickness in Ångstroms

Sample No.	Total solid in Solution (%)	Spin Speed (rpm)	Thickness after 80°C	Thickness after 150°C	Thickness after 250°C	Thickness after 400°C
F	19.1	3000	12860 Å	12350 Å	7770 Å	7156 Å
J	22.5	5000	12550 Å	12100 Å	8400 Å	7880 Å

5

EXAMPLE 4
Measurements Of Refractive Index

10 Refractive indexes ("R.I.") were measured using a Gaertner elipsometer and are tabulated in Table 6, below. The refractive indexes of the cured base materials AMM311 and AMM512B were determined by this method to be 1.39 and 1.38, respectively.

EXAMPLE 5
15 Measurements Of Dielectric Constant

The dielectric constant (k) of the cured films was calculated from the capacitance of each film with thickness (t) under aluminum dot, using a Hewlett-Packard LCR meter model HP4275A. The dielectric constant (k) was calculated according to the
20 following equation:

$$k = C\,t/(E_o\,A),$$

where A is the area of the Al dot (cm^2), C is the capacitance (Farad), t is the film thickness (cm) and E_o is the permittivity of free space (8.85419×10^{-14} F/cm). Dielectric constants with an error bar of about ±0.1 are listed in the last column of
25 Table 6, as follows.

Table 6
Refractive Index and Dielectric Constant

Sample No.	Wt %PEO in S.O.G.	Wt% PEO In as-spun film	Refractive Index				Dielectric constant
			512-7500	311-200	311-600	311-7500	
A	5.1	34		1.372			--*
B	10.4	51		1.314			--
C	5.4	35			1.268		--
D	9.5	49			1.224		--
D	9.5	49			1.219		2.63
E	1.1	10				1.326	--
F-1	9.5	49				1.186	2.32
F-2	9.5	49				1.202	2.43
G	13.5	57				1.19	2.19
H	18.5	65				1.173	2.11
I	4.9	26	1.309				2.73
J	9.1	39	1.235				2.36
K-1	13	48	1.228				2.18
K-2	13	48	1.214				2
L	18	56	1.197				2.02

* "--" no data

Analysis

As can be seen in Table 6, above, the resulting films have dielectric constants ranging from 2 to 2.73. The degree of porosity of each film can be estimated from the weight
5 percent of the thermally degradable component (PEO), in the as-spun film by assuming that the densities of the base material and the thermally degradable component are the same and that no loss of the evaporative component either through evaporation or degradation mechanism occurs before the crosslinking of the base material. The weight percent of the PEO in various films is listed in the third column of Table 6 and can be
10 used as an indicator of the degree of porosity of the film, with the exception of the PEO 200 samples, where there was evidence, as discussed below, that the more volatile PEO 200 evaporated prior to the 200°C heating step. Thus, Samples I, J, K-1, K-2 and L, prepared using AMM 512B, and which had PEO (7500) weight percentages in the as-spun films of 26, 39, 48 and 56, respectively, were determined to have dielectric constant
15 values of 2.73, 2.36, 2.18, 2 and 2.02, respectively (two different films were produced and measured using Sample K). Within this series, it can be appreciated that as the PEO

weight percentages in the as-spun films increases, the measured dielectric constant decreases. Analogous results were seen with samples F-1, F-2, G, and H, prepared using AMM 311, and which had PEO (7500) weight percentages of 49, 57 and 65, with measured dielectric constants declining from 2.43 to 2.11 as the weight percentages of PEO in the as-spun film rose to 65, thus confirming the effectiveness of the instant methods. In contrast, it should be noted that the dielectric constants of the base materials 400°C cured 311 and 512B are 3.8 and 3.1, respectively.

The dielectric constants for the films produced using the 311 series and the 512B series, as shown in Table 6, were plotted against the weight percent of the PEO to produce [plotted figures not shown]. The resulting plots of the Table 6 data confirm that dielectric films produced using both the AMM 311 and 512B methylsiloxane S.O.G. materials exhibit reduced dielectric constant properties in roughly linear proportion to the weight percentage of the thermally degradable component of the as-spun film. The plotted data also confirms that the nanoporous films produced using AMM 512B base material exhibited k values that were lower, by about 0.3, than the k values of the nanoporous films produced using the AMM base material 311. This lower range of k values seems to be consistent with the lower dielectric constant of the unmodified 512B base material. Since the exact degree of porosity is not determined, quantitative analysis of the relationship between dielectric constant and porosity for these systems cannot be established. However, as confirmed by the tabulated data, the dependence of k on the percentage of PEO in the as-spun film is understood and controllable.

The refractive index vs. the weight percent of PEO, as shown in Table 6, was plotted [figure not shown] for the films produced using both the AMM 311 and AMM 512B series of base materials. The plotted data confirms that the refractive index for both film series falls into the same line. However, when the refractive index data for the film produced using the PEO 200 starting mixture is compared to the linear plots of the other data, the PEO 200 refractive index falls substantially outside of (and above) the values predicted by the linear relationship between the refractive index and PEO weight % of the other films. Without meaning to be bound by any theory or hypothesis, it is believed that this non-linear elevation in refractive index confirms that the film formed using PEO 200

is simply denser than would otherwise be expected, because less PEO 200 remained in the film prior to formation of the pore structures.

Conclusions

5 (1) For the series of films produced using starting mixtures incorporating PEO compounds having molecular weights of 600 and 7500, and the AMM311 and AMM512B base materials, respectively, the refractive indexes of the films are similar, at the same respective PEO weight fraction. While not wishing to be bound by any theory or hypothesis, it is believed that this may indicate a similar degree of porosity in the 10 respective films, since the refractive indexes of the two base materials are also very close (1.38 vs. 1.39).

(2) The dielectric constant of the series of films produced using the AMM512B base material is lower than that of the 311 series when the respective films are compared at the same PEO loading. Judging from results from the k and R.I. data, it can be inferred that 15 at the same loading of PEO 600 and 7500, a similar level of porosity is obtainable from either 311 and 512B, but that the porous film of similar porosity exhibits different k value due to the differences in base material.

(3) PEO 200 is a viscous liquid with appreciable vapor pressure at 200°C. The refractive indexes of the two films prepared from the PEO 200 were higher than the 20 predicted value based on the no-loss assumption. Although the dielectric constant of these films was not measured it is reasonable to conclude that if a substantial amount of the PEO 200 evaporated during the baking step due to its volatility, then the final porosity will be much less than the value calculated from the proportion of PEO 200 present in the as-spun film composition.

25 The absolute volume fraction in the porous film is not known, but the weight fraction of PEO is believed to be proportional to the volume fraction, or the degree of porosity, although the exact value of the porosity has not determined to date.

EXAMPLE 6
Scanning Electron Microscopic
(SEM) Examination of Film Surface

5 A nanoporous film was prepared using sample K (512B-7500-13). A sufficient quantity of sample K was spin-coated onto a substrate, which was a flat silicon wafer with a thickness of 9580Å, and the film was finished as described above for Example 1.

The surface of the film was then prepared for SEM by standard, art-known methods The film surface was examined using a Joel JSM-6300 F scanning electron microscope
10 ("SEM") at 2.5 kilovolts, with a magnification of 50,000, and a field width of 10 nm. Under these conditions, the surface of the dielectric film exhibited a uniform texture, with no cracking and no large pores [image not shown].

EXAMPLE 7
Stud Pull Test

15 Methods

The stud pull test was conducted by the following method.

A film to be tested is placed on substrate wafer, and an epoxy test stud was epoxied to the top of the film. Once the epoxy has cured, the stud was pulled away from the film, with a measured force, until some component broke. The measured pull force at the moment
20 just prior to breakage was the stud pull strength.

Tests

The stud pull test was performed on 7500-8000Å films spun from the PEO 7500-containing formulation. A 6" silicon wafer with a 500Å thermal oxide layer was used. In
25 addition, a 1 □m layer of aluminum was deposited on top of the film prior to attaching the stud to the wafer. Stud pull results are shown in Table 7, below.

Table 7
Stud Pull Results

AMM/PEG Mixture	Stud Pull Strength, Kpsi*	Standard Deviation
F	1.5	1.0
G	1.1	0.5
H	1.6	1.1
J	2.4	1.1
K	1.5	1.2
	*kilopounds/inch^2	

Analysis of Stud Pull Results

The tested films all failed at the interface between the thermal oxide and the film, not in the film itself. However, it should be appreciated that the stud pull tests obtained even under the interphase failure conditions are still significantly higher than respective porous
5 nanosilica films at the same k value. For example, the stud pull test result for sample H having a k of 2.11 was 1.6 Ksi, which would be much higher than the projected stud pull of less than 0.5 Ksi for the corresponding nanosilica dielectric film having a k of 2.1.

Furthermore, for experimental convenience, in the test samples as prepared above, the
10 dielectric films were deposited on the substrate over a thermal oxide layer, formed by simply heating the silicon wafer in air. For actual production of integrated circuits, art-known chemical vapor deposition ("CVD") materials are preferably employed, such as, e.g., plasma enhanced CVD tetraethoxysilane oxide ("PETEOS") or silane oxide and combinations thereof, to form the layer between the wafer and the applied nanoporous
15 dielectric film. With these alternative materials, the adhesion between the oxide layer of the wafer and the nanoporous film is significantly enhanced.

Conclusion

Porous methylsiloxane films were produced by heating a thermally degradable component of a methylsiloxane precursor/polyethylene oxide blend, leaving behind a foam structure
20 with the methylsiloxane as the skeleton. A conventional, art known coater and furnace were used for the processing. In this example, dielectric constants ranging from 2.8 to 2.0 were achieved by adjusting the amount of thermally degradable component in the polymer blend. When methylsiloxane 512B was employed, the as-spun film, containing 50 wt% polyethylene oxide, produced a k value of about 2.1. Films with a k lower than
25 2.1 can be prepared by increasing the amount of polyethylene oxide at expense of further decreasing the mechanical strength of the film. Of course, the above-described stud pull test confirms that the nanoporous films produced by the process is internally cohesive, at least in the tested ranges of PEO weight percentages. In conclusion, the foregoing examples demonstrate that polyethylene oxide is an excellent thermally labile, thermally
30 degradable component for making low-k methylsiloxane spin-on dielectrics.

Examples 8-9

For examples 8 and 9, porous methylsiloxane coatings are produced from the removal of a thermally degradable, organic component from a film prepared from a mixture of an S.O.G. and a thermally degradable organic polymer in a nonpolar solvent. The exemplified S.O.G. base materials for the following examples are polyhydridosilsesquioxanes ("PHSQs") and the exemplified thermally degradable polymer is polypropylene oxide ("PPO"). The artisan will appreciate that PPOs and/or a mixture of PPO and polyethylene oxide ("PEO") copolymers useful for the inventive processes, are selected to thermally degrade in a temperature range that is relatively low compared to the thermal tolerances of the employed substrate and S.O.G. materials. The PPO and/or a mixture of PPO/PEOs are also selected to be soluble in nonpolar solvents that are compatible with the inventive processes, and to be miscible with the selected S.O.G. materials.

Processing steps include dissolving appropriate quantities of, e.g., a PPO into, e.g., a PHSQ solution, then casting the mixture onto a substrate by a suitable method, such as spinning, and then baking and optionally curing the spun film at a temperature range and for a time period or periods appropriate for the selected PHSQ material.

EXAMPLE 8
Preparation of Polyhydridosilsesquioxane

160 gm of triethoxysilane was mixed with 800 gm acetone. 11.7 gm of water and 14.6 gm of 0.02N nitric acid were added to the triethoxysilane/water solution. The final solution was stored at 22°C for 10 days.

After a 10-day reaction at 22°C, the by-product ethanol was vacuum distilled off at temperature between 22 and 25°C while ethyl acetate was continuously adding to the solution to replace the leaving ethanol. After distillation, n-butyl acetate was added to adjust the final composition to be 10 wt% PHSQ resin, 63 wt% ethyl acetate, and 27 wt% n-butyl acetate. This is the PHSQ solution. These proportions are equivalent to 70 wt% ethyl acetate and 30 wt% n-butyl acetate, if the 10% PHSQ resin is omitted.

EXAMPLE 9

Preparation and Composition of the Spinning Solutions

1. Base Matrix Materials

Polyhydridosilsesquioxane resin as prepared in Example 8 was dissolved in mixture of
5 ethyl acetate and butyl acetate in a ratio of 70:30, by weight was used.

2. Decomposable Components

Polypropylene oxide was dissolved in ethyl acetate at four different percents: 5, 10, 15, and 20% (wt/wt). The PPO solutions were then mixed with the PHSQ solution as
10 prepared in Example 8, in a 50:50 (wt/wt) ratio.

Three polypropylene oxide polymers with molecular weights of 425, 1000 and 4000, respectively, were used. The polypropylene oxide was dissolved in ethyl acetate.

15 3. Composition of the as-spun film

Symbols designated to describe the coating solutions are (base matrix)-(MW of the PPO)-(wt. % of PPO). For example, PHSQ-1000-33.3 represents 33.3 wt. % of polypropylene oxide of molecular weight 1000 and 66.7% PHSQ in the as-spun film. The following six samples were prepared:

20 PHSQ (control)

PHSQ - 425-50%
PHSQ - 425-66.6%
PHSQ - 1000-33.3%
PHSQ - 1000-50%
25 PHSQ - 1000-60%
PHSQ - 4000- 50%
PHSQ - 1000-66.60%

4. Spin and Bake/Cure Cycles

30 Samples were spun at 3000 rpm for 20 seconds, baked at 80°C/150°C/200°C for 60 seconds and cured at 400°C for 30 minutes in flowing nitrogen.

5. Refractive Index and Dielectric Constant

Refractive index and film thickness was measured by a Woolam elipsometer and dielectric
35 constant was calculated from the capacitance using a Hewlett-Packard LCR meter (Model HP4275A). The PPO%, and the measured thickness, refractive index and dielectric constants of the cured films are listed in the following table.

Table 7

	Wt.% of PPO in SOG	Wt% of PPO in as-spun film	Cured Film Thickness, Å	R.I.*	k **
PHSQ	0	0	3280	1.383	3.1
PHSQ-425-50%	5	50	3980	1.341	--
PHSQ-425-66.6%	10	66.6	5070	1.286	--
PHSQ-1000-33.3%	2.5	33.3	2200	1.291	2.8
PHSQ-1000-50%	5	50	3200	1.237	2.5
PHSQ-1000-60%	7.5	60	3300	1.226	2.3
PHSQ-4000-50%	5	50	3200	1.227	2.4
PHSQ-4000-66.6%	10	66.6	5200	1.175	2.0

*Refractive Index; **Dielectric Constant

6. Discussion & Conclusion

It can be appreciated from the data presented by Table 2, above, that when the PPO molecular weights are 1000 and 4000, the refractive index ("R.I.") and dielectric constant
5 ("k") of the produced PHSQ films decrease proportionately as the amount of the PPO in the initial composition is increased. Thus, a porous film with dielectric constant around 2.0 can be obtained at 66 weight percent of PPO in the solid of the as-spun film.

It should also be noted that the refractive index measurements for the PPO 425 series are
10 about 0.1 higher than the measurements obtained from similar loading with higher molecular weight PPO. This increase corresponds to an increase of 0.5 in the measured higher dielectric constant. This can be attributed to the partial physical evaporation of volatile species in the low molecular weight PPO during baking steps, resulting in actually less degradable component in the post-bake films.

15

Based on the same principle, it will be appreciated that films with a dielectric constant of less than 2.0 can readily be obtained by incorporating a higher loading of the decomposable polymer. This approach can also be applied to other low k silsesquioxane films with a general structure of R $SiO_{3/2}$ where R can be chosen independently from
20 hydrogen or alkyl or mixture of both.

WHAT IS CLAIMED IS:

1. A low dielectric nanoporous film comprising a spin-on-glass material, said film having been produced by a process comprising the steps of

(a) preparing a mixture of at least one spin-on-glass material with a thermally degradable polymer in a compatible solvent,

(b) applying the mixture of step (a) onto a substrate to produce a coated substrate,

(c) heating the coated substrate of step (b) for a time and at one or more temperatures effective produce the desired low dielectric nanoporous film.

2. The low dielectric nanoporous film of claim 1 having a dielectric constant ranging from about 1.5 to about 3.8.

3. The low dielectric nanoporous film of claim 1 having a refractive index ranging from about 1.15 to about 1.40.

4. The low dielectric nanoporous film of claim 1 produced from a spin-on glass base material of Formula I:

$$[(SiO_2)_x - (R_1SiO_{1.5})_y - (R_2R_3SiO)_z]_n \qquad \text{Formula I}$$

wherein x, y, z and n are positive integers of independent values, R_1, R_2 and R_3 are independently H or organic, and at least one of R_1, R_2 and R_3 is H; and $1 \geq x \geq 0$; $1 \geq y \geq 0$; $1 \geq z \geq 0$, provided that x+y+z is 1.0.

5. The low dielectric nanoporous film of claim 4 wherein the organic moiety is a $C_1.C_6$ alkyl, and n ranges from about 100 to about 800.

6. The low dielectric nanoporous film of claim 1 produced from a hydrogensiloxane spin-on glass base material of Formula II

$$[(HSiO_{1.5})_{(a)}O_{(b)}]_n \qquad \text{Formula II ;}$$

wherein (a) ranges from about 6 to about 20, (b) ranges from about 1 to about 3, (c) ranges from about 6 to about 20, and n ranges from 1 to about 4,000.

7. The low dielectric nanoporous film of claim 1 produced from a hydroorganosiloxane spin-on glass base material of Formula III

$$[(HSiO_{1.5})_{(a)}O_{(b)}(RSiO_{1.5})_{(c)}]_n \qquad \text{Formula III}$$

wherein (a) ranges from about 6 to about 20, (b) ranges from about 1 to about 3, (c) ranges from about 6 to about 20, and n ranges from 1 to about 4,000, and when n>1, each R is independently H, C_1-C_8 alkyl or C_6-C_{12} aryl.

8. The low dielectric nanoporous film of claim 1 produced from an alkylsiloxane spin-on
5 glass base material selected from the group consisting of hydrogenmethylsiloxane, hydrogenethylsiloxane, hydrogenpropylsiloxane, hydrogenbutylsiloxane, hydrogen*tert*-butylsiloxane, hydrogenphenylsiloxane and combinations thereof.

9. The low dielectric nanoporous film of claim 1 produced from an alkylsiloxane spin-on glass base material selected from the group consisting of hydrogensilsesquioxane,
10 hydrogenmethylsilsesquioxane, hydrogenethylsilsesquioxane, hydrogenpropylsilsesquioxane, hydrogenbutylsilsesquioxane, hydrogen*tert*-butylsilsesquioxane, hydrogenphenylsilsesquioxane, and combinations thereof.

10. The low dielectric nanoporous film of claim 1 produced from a polyhydridosilsesquioxane spin-on glass base material of Formula IV

15 $$(HSiO_{3/2})_n \qquad \text{Formula IV}$$

wherein n is an integer ranging from about 10 to about 4,000.

11. The low dielectric nanoporous film of claim 1 wherein the thermally degradable polymer ranges in molecular weight from about 200 to about 2,000,000 Daltons.

12. The low dielectric nanoporous film of claim 11 wherein the thermally degradable
20 polymer ranges in molecular weight from about 1,000 to about 30,000 Daltons.

13. The low dielectric nanoporous film of claim 1 wherein the compatible solvent is a nonpolar solvent, and the thermally degradable polymer is soluble in the nonpolar solvent and miscible with the spin-on-glass material.

14. The low dielectric nanoporous film of claim 13 wherein the thermally degradable
25 polymer is selected from the group consisting of polyalkylene oxide, aliphatic polyester, acrylic polymer, acetal polymer, and combinations thereof.

15. The low dielectric nanoporous film of claim 13 wherein the thermally degradable polymer is selected from the group consisting of poly(caprolatactone), poly(valeractone), poly(methyl methacrylate), poly (vinylbutyral).

16. The low dielectric nanoporous film of claim 14 wherein the polyalkylene oxide
5 comprises a C_1 to about C_6 alkyl.

17. The low dielectric nanoporous film of claim 16 wherein the thermally degradable polymer is a polypropylene oxide.

18. The low dielectric nanoporous film of claim 13 wherein the nonpolar solvent is an organic acetate comprising a C_1 to C_6 alkyl, a C_5 to C_{12} aryl and combinations and
10 derivatives thereof.

19. The low dielectric nanoporous film of claim 13 wherein the nonpolar solvent is selected from the group consisting of ethyl acetate, isopropyl acetate, butyl acetate, dibutyl ether, acetone, methyl ethyl ketone, methyl isobutyl ketone and combinations thereof.

15 20. The low dielectric nanoporous film of claim 1 wherein the compatible solvent is a polar solvent, and the thermally degradable polymer is soluble in the polar solvent and miscible with the spin-on-glass material.

21. The low dielectric nanoporous film of claim 1 wherein the spin-on glass comprises a silicon-based polymer comprising a subunit selected from the group consisting of, SiO_2;
20 Q_1SiO_3 ; $Q_2Q_3SiO_2$; and $Q_4Q_5Q_6SiO$ and combinations thereof, wherein Q_1, Q_2, Q_3, Q_4, Q_5 and Q_6 are independently organic.

22. The low dielectric nanoporous film of claim 19 wherein when any of Q1, Q2, Q3, Q4, Q5 and Q6 is organic, the organic moiety is a C1-6 alkyl.

23. The low dielectric nanoporous film of claim 4 wherein the spin-on-glass base material
25 comprises an SiO2 moiety, and x is 1.

24. The low dielectric nanoporous film of claim 4 wherein the spin-on-glass base material comprises a polymethylsilsesquioxane, and y is 1 and R_1 is methyl.

25. The low dielectric film coating of claim 4 wherein the spin-on-glass base material comprises at least one alkylsiloxane.

26. The low dielectric nanoporous film of claim 25 wherein the alkylsiloxane is a methylsiloxane.

5 27. The low dielectric nanoporous film of claim 26 wherein the methylsiloxane has a formula according to Formula I, wherein x, y and z are all greater than zero, and R_1, R_2 and R_3 are methyl.

28. The low dielectric nanoporous film of claim 20 wherein the thermally degradable polymer is a polyalkylene oxide.

10 29. The low dielectric nanoporous film of claim 28 wherein the polyalkylene oxide is selected from the group consisting of polyethylene oxide and polyethylene oxide/propylene oxide copolymers.

30. The low dielectric nanoporous film of claim 20 wherein the polar solvent is selected from the group consisting of water, alcohol, ketones and mixtures thereof.

15 31. The low dielectric nanoporous film of claim 1 wherein the heating of step (c) comprises a baking step and a curing step.

32. The low dielectric nanoporous film of claim 30 wherein the baking step comprises a plurality of heating steps, ranging in temperature from about 60°C to about 350°C, and each heating step is for a time period ranging from about 0.5 to about 10 minutes.

20 33. The low dielectric nanoporous film of claim 30 wherein the baking comprises a first heating step of about 80oC, a second heating step of about 150oC, and a third heating step of about 200oC, each heating step being applied for a duration of about 1 minutes at each respective temperature.

34. The low dielectric nanoporous film of claim 1 wherein the substrate comprises a
25 semiconductor material selected from the group consisting of gallium arsenide, silicon, and mixtures thereof.

35. The low dielectric nanoporous film of claim 34 wherein the silicon material is selected from the group consisting of crystalline silicon, polysilicon, amorphous silicon, epitaxial silicon, and silicon dioxide.

36. The low dielectric nanoporous film of claim 34 wherein the substrate comprises a
5 surface layer applied by chemical vapor deposition selected from the group consisting of plasma enhanced tetraethoxysilane, silane oxide and combinations thereof.

37. An integrated circuit comprising at least one low dielectric nanoporous film of claim 1.

38. A method of producing a low dielectric nanoporous film on a substrate comprising
10 the steps of

(a) preparing a mixture of at least one spin-on-glass material with a suitable thermally degradable polymer soluble in a compatible solvent,

(b) applying the mixture of step (a) onto a substrate to produce a coated substrate,

(c) heating the coated substrate of step (b) for a time and at one or more temperatures
15 effective produce the desired low dielectric nanoporous film.

PATENT COOPERATION TREATY

PCT

REC'D 18 AUG 2000
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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below	
30-4538		
International application No.	International filing date (day/month/year)	(Earliest) Priority Date (day/month/year)
PCT/US 00/10214	14/04/2000	14/04/1999
Applicant		
ALLIEDSIGNAL INC.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

      [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

      [ ] contained in the international application in written form

      [ ] filed together with the international application in computer readable form.

      [ ] furnished subsequently to this Authority in written form

      [ ] furnished subsequently to this Authority in computer readble form.

      [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

      [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [X] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

   [ ] the text is approved as submitted by the applicant.

   [X] the text has been established by this Authority to read as follows:

   LOW DIELECTRIC NANO-POROUS MATERIAL OBTAINABLE FROM POLYMER DECOMPOSITION

5. With regard to the **abstract**,

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ______

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/10214

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C18/12 H01L21/316 C08L83/04 C09D183/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C C08L C09D H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 470 801 A (KAPOOR ASHOK K ET AL) 28 November 1995 (1995-11-28) column 8, line 5 - line 30	33-36
A	EP 0 775 669 A (TEXAS INSTRUMENTS INC) 28 May 1997 (1997-05-28) page 2, line 3 - line 10 page 6, line 48 - line 52 page 10; table 1 page 11; table 2	33-36

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 August 2000	10/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hoepfner, W

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/10214

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claims Nos.: 1-32, 37, 38
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-32, 37, 38

Present claims 1-3, 37 relate to a product and/or compound and/or method defined by reference to a desirable characteristic or property, namely nanoporous, dielectric constant, thermally degradable polymer, compatible solvent, effective time and temperature and refractive index. The claims cover all products and/or compounds and/or methods having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such products and/or compounds and/or methods. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the product and/or compound and/ormethod by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed (see the following parapraph).

Present claims 1-32, 37, 38 relate to an extremely large number of possible compounds and/or products and/or methods. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds and/or products and/or methods claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds and/or products and/or methods described in the description and in the worked Examples on pages 8-30 and being claimed in claims 33-36, i.e. nanoporous silica films and methods for their preparation.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No
PCT/US 00/10214

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5470801	A	28-11-1995	US	5598026 A	28-01-1997
			US	5864172 A	26-01-1999
EP 0775669	A	28-05-1997	US	5736425 A	07-04-1998
			JP	10070121 A	10-03-1998
			US	5955140 A	21-09-1999
			JP	10087316 A	07-04-1998