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(54) Title: SILOXANE RESINS

(57) Abstract: This invention pertains to a siloxane resin composition comprising $R^1SiO_{3/2}$ siloxane units and $(R^2O)_bSiO_{(4-b)/2}$ siloxane units wherein R^1 is an alkyl group having 1 to 5 carbons; R^2 is a branched alkyl group having 3 to 30 carbons, b is from 1 to 3. The siloxane resin contains a molar ratio of $R^1SiO_{3/2}$ units to $(R^2O)_bSiO_{(4-b)/2}$ units of 1:99 to 99:1. The siloxane resin is useful to make insoluble porous resins and insoluble porous coatings. Heating a substrate coated with the siloxane resin at a sufficient temperature effects removal of the R^2O groups to form an an insoluble porous coating having a a dielectric constant in the range of 2.1 to 3, a porosity in the range of 2 to 40 volume percent and a modulus in the range of 1.9 to 20 GPa.

SILOXANE RESINS

FIELD OF THE INVENTION

[0001] This invention pertains to a siloxane resin composition comprising $R^1SiO_{3/2}$ siloxane units, and $(R^2O)_bSiO_{(4-b)/2}$ siloxane units wherein R^1 is independently selected from the group consisting of alkyl having 1 to 5 carbon atoms; R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and branched substituted alkyl groups having 3 to 30 carbon atoms, b is from 1 to 3. This invention further pertains to insoluble porous resins and insoluble porous coatings produced from the siloxane resin composition.

BACKGROUND OF THE INVENTION

[0002] Semiconductor devices often have one or more arrays of patterned interconnect levels that serve to electrically couple the individual circuit elements forming an integrated circuit (IC). The interconnect levels are typically separated by an insulating or dielectric coating. Previously, a silicon oxide coating formed using chemical vapor deposition (CVD) or plasma enhanced techniques (PECVD) was the most commonly used material for such dielectric coatings. However, as the size of circuit elements and the spaces between such elements decreases, the relatively high dielectric constant of such silicon oxide coatings (i.e. about 4) is inadequate to provide adequate electrical insulation.

[0003] In order to provide a lower dielectric constant than that of silicon oxide, dielectric coatings formed from siloxane-based resins have found use. An example of such coatings are those formed from hydrogen silsesquioxane resins as described for example in Collins et al., U.S. Patent No. 3,615,272 and Haluska et al. U.S. Patent No. 4,756,977. While such coatings provide lower dielectric constants than CVD or PECVD silicon oxide coatings and also provide other benefits namely enhanced gap filling and surface planarization, typically the dielectric constants of such coatings are limited to approximately 3 or greater.

[0004] It is well known that the dielectric constant of insulating coatings is an important factor where IC's with low power consumption, cross talk, and signal delay are required. As IC dimensions continue to shrink, this factor increases in importance. As a result, siloxane based resin materials and methods for making such materials that can provide electrically insulating coatings with dielectric constants below 3 are desirable. In addition it is desirable to have siloxane-based resins and methods for making such resins that provide coatings which have a high resistance to cracking. Also, it is desirable for such siloxane-based resins

to provide coatings by standard processing techniques namely spin coating. It is known that the dielectric constant of solid coatings decrease with a decrease in density of the coating material. A porous coating typically has a lower density than a corresponding solid coating.

[0005] Haluska, U.S. Patent No. 5,446,088 describes a method of co-hydrolyzing silanes of the formulas $HSi(OR)_3$ and $Si(OR)_4$ to form co-hydrolysates useful in the formation of coatings. The R group is an organic group containing 1-20 carbon atoms, which when bonded to silicon through the oxygen atom, forms a hydrolyzable substituent. Especially preferred hydrolyzable groups are methoxy and ethoxy. The hydrolysis with water is carried out in an acidified oxygen containing polar solvent. The co-hydrolyzates in a solvent are applied to a substrate, the solvent evaporated and the coating heated to 50 to 1000°C to convert the coating to silica. Haluska does not disclose silanes having branched alkoxy groups.

[0006] Chung et al., U.S. Patent No. 6,231,989 describe a method for forming a porous coating from hydrogen silsesquioxane resins. A porous network is formed by depositing a coating on a substrate with a solution comprising a hydrogen silsesquioxane resin 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; the solvent is evaporated from the coating to form a porous network with a dielectric constant in the range of about 1.5 to 2.4.

[0007] Smith et al., WO 98/49721, describe a process for forming a nanoporous dielectric coating on a substrate. The process comprises the steps of blending an alkoxysilane with a solvent composition and optional water; depositing the mixture onto a substrate while evaporating at least a portion of the solvent; placing the substrate in a sealed chamber and evacuating the chamber to a pressure below atmospheric pressure; exposing the substrate to water vapor at a pressure below atmospheric pressure and then exposing the substrate to base vapor.

[0008] Mikoshiba et al., U.S. Patent 6,022,814, describe a process for forming silicon oxide films on a substrate from hydrogen or methyl siloxane-based resins having organic substituents that are removed at a temperature ranging from 250°C to the glass transition point of the resin. Silicon oxide film properties reported include a density of 0.8 to 1.4 g/cm^3, an average pore diameter of 1 to 3 nm, a surface area of 600 to 1,500 m^2/g and a dielectric constant in the range of 2.0 to 3.0. The useful organic substituents that can be oxidized at a temperature of 250°C or higher that were disclosed include substituted and

unsubstituted alkyl or alkoxy groups exemplified by 3,3,3-triflouropropyl, ß-phenethyl group, t-butyl group, 2-cyanoethyl group, benzyl group, and vinyl group.

[0009] Mikoskiba et al., *J. Mat. Chem.*, 1999, 9, 591-598, report a method to fabricate angstrom size pores in methylsilsesquioxane coatings in order to decrease the density and the dielectric constant of the coatings. Copolymers bearing methyl (trisiloxysilyl) units and alkyl (trisiloxysilyl) units were spin-coated on to a substrate and heated at 250°C to provide rigid siloxane matrices. The coatings were then heated at 450°C to 500°C to remove thermally labile groups and holes were left corresponding to the size of the substituents, having a dielectric constant of about 2.3. Trifluoropropyl, cyanoethyl, phenylethyl, and propyl groups were investigated as the thermally labile substituents.

[0010] Ito et al., Japanese Laid-Open Patent (HEI) 5-333553, describe preparation of a siloxane resin containing alkoxy and silanol functionality by the hydrolysis of diacetoxydi(tertiarybutoxy)silane in the presence of a proton acceptor. The resin is radiation cured in the presence of a photo acid with subsequent thermal processing to form a SiO_2 like coating and can be used as a photo resist material for IC fabrication.

[0011] It has now been found that incorporation of branched alkoxy groups ($SiOR^2$), where R^2 is an alkyl group having 3 to 30 carbon atoms, into siloxane resins provides several advantages namely improved storage stability, increased modulus and increased porosity of the cured resins, while retaining a dielectric constant in the range of 2.1 to 3.0. It is therefore an object of this invention to show a siloxane resin composition having improved storage stability. It is also an object of this invention to show a method for making siloxane resins and a method for curing these resins to produce insoluble porous resins and insoluble porous coatings with a dielectric constant in the range of 2.1 to 3.0, porosity in the range of 2 to 40 volume percent and a modulus in the range of 1.9 to 20 GPa. These insoluble porous coatings have the advantage that they may be formed using conventional thin film processing.

SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a siloxane resin composition comprising $R^1SiO_{3/2}$ siloxane units, and $(R^2O)_bSiO_{(4-b)/2}$ siloxane units wherein R^1 is independently selected from the group consisting of alkyl having 1 to 5 carbon atoms; R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and branched substituted alkyl groups having 3 to 30 carbon atoms, b is from 1 to 3. The siloxane resin composition contains an average molar ratio of $R^1SiO_{3/2}$ units to $(R^2O)_bSiO_{(4-b)/2}$

units of 1:99 to 99:1. The sum of $R^1SiO_{3/2}$ units and $(R^2O)_bSiO_{(4-b)/2}$ units is at least 50 percent of the total siloxane units in the resin composition.

In a second aspect, the present invention provides

a method for preparing a siloxane resin comprising $R^1SiO_{3/2}$ siloxane units and $(R^2O)_bSiO_{(4-b)/2}$ siloxane units where b is from 1 to 3, which comprises:

combining

(a) a silane or a mixture of silanes of the formula R^1SiX_3, where each R^1 is independently selected from the group consisting of alkyl having 1 to 5 carbon atoms, where X is a independently a hydrolyzable group or a hydroxy group;

(b) a silane or a mixture of silanes of the formula $(R^2O)_cSiX_{(4-c)}$, where R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and branched substituted alkyl groups having 3 to 30 carbon atoms, c is from 1 to 3, X is a hydrolyzable group or a hydroxy group, silane (a) and silane (b) are present in a molar ration of silane (a) to silane (b) of 1:99 to 99:1; and

(c) water,

for a time and temperature sufficient to effect the formation of the siloxane resin.

In a third aspect, the present invention provides

a method of forming an insoluble porous resin, which comprises:

(A) heating the siloxane resin of the present invention for a time and temperature sufficient to effect curing of the siloxane resin,

(B) further heating the siloxane resin for a time and temperature sufficient to effect removal of the R^2O groups from the cured siloxane resin, thereby forming an insoluble porous resin.

In a fourth aspect, the present invention provides

a method of forming an insoluble porous coating on a substrate comprising the steps of

(A) coating the substrate with a coating composition comprising a siloxane resin composition comprising $R^1SiO_{3/2}$ siloxane units, and $(R^2O)_bSiO_{(4-b)/2}$ siloxane units wherein R^1 is independently selected from the group consisting of alkyl having 1 to 5 carbon atoms and R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and substituted branched alkyl groups having 3 to 30 carbon atoms, b is from 1 to 3, the siloxane resin composition contains a molar ratio of $HSiO_{3/2}$ units to $(R^2O)_bSiO_{(4-b)/2}$ units of 1:99 to 99:1 and the sum of $R^1SiO_{3/2}$ units and $(R^2O)_bSiO_{(4-b)/2}$ units is at least 50 percent of the total siloxane units in the resin composition;

(B) heating the coated substrate for a time and temperature sufficient to effect curing of the coating composition, and

(C) further heating the coated substrate for a time and temperature sufficient to effect removal of the R^2O groups from the cured coating composition, thereby forming an insoluble porous coating on the substrate.

In a fifth aspect, the present invention provides

an electronic substrate having an insoluble porous coating prepared by the method of the 4th aspect.

Disclosed herein, there is provided a method for making siloxane resins by reacting a silane or a mixture of silanes of the formula R^1SiX_3 where R^1 is independently selected from the group consisting of alkyl groups having 1 to 5 carbon atoms and a silane or a mixture of silanes of the formula $(R^2O)_cSiX_{(4-c)}$, where R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and substituted branched alkyl groups having 3 to 30 carbon atoms, c is from 1 to 3, and X is a hydrolyzable group or a hydroxy group.

Also disclosed herein, there is provided a method of forming an insoluble porous resin and to a method of forming an insoluble porous coating on a substrate. The dielectric constant of the insoluble porous coating is in the range of 2.1 to 3. The porosity of the insoluble porous resins and insoluble porous coatings ranges from 2 to 40 volume percent. The insoluble porous coatings have a modulus in the range of 1.9 to 20 GPa.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The siloxane resin composition comprises $R^1SiO_{3/2}$ siloxane units, and $(R^2O)_bSiO_{(4-b)/2}$ siloxane units wherein R^1 is selected from the group consisting of alkyl having 1 to 5 carbon atoms, R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and branched substituted alkyl groups having 3 to 30 carbon atoms, b is from 1 to 3. The siloxane resin contains a molar ratio of $R^1SiO_{3/2}$ units to $(R^2O)_bSiO_{(4-b)/2}$ units of 1:99 to 99:1. The sum of $R^1SiO_{3/2}$ units and $(R^2O)_bSiO_{(4-b)/2}$ units is at least 50 percent of the total siloxane units in the resin composition. It is preferred that the molar ratio of $R^1SiO_{3/2}$ units to $(R^2O)_bSiO_{(4-b)/2}$ units is 40:60 to 98:2 and more preferred is 50:50 to 85:15. It is preferred that the sum of $R^1SiO_{3/2}$ units and $(R^2O)_bSiO_{(4-b)/2}$ units is at least 70 percent of the total siloxane units in the siloxane resin composition..

[0016] The structure of the siloxane resin is not specifically limited. The siloxane resins may be essentially fully condensed or may be only partially reacted (i.e., containing less than 10 mole % Si-OR and/or less than 30 mole % Si-OH). The partially reacted siloxane resins ~~may be exemplified by, but not limited to, siloxane units such as $R^1Si(X)_dO_{(3-d/2)}$ and~~

$Si(X)_d(OR^2)_fO_{(4-d-f/2)}$; in which R1 and R2 are defined above; each X is independently a hydrolyzable group or a hydroxy group, and d and f are from 1 to 2. The hydrolyzable group is an organic group attached to a silicon atom through an oxygen atom (Si-OR) forming a silicon bonded alkoxy group or a silicon bonded acyloxy group. R is exemplified by, but not limited to, linear alkyl groups having 1 to 6 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl, or hexyl and acyl groups having 1 to 6 carbon atoms such as formyl, acetyl, propionyl, butyryl, valeryl or hexanoyl. The siloxane resin may also contain less than 10 mole % $SiO_{4/2}$ units.

[0017] The siloxane resins have a weight average molecular weight in a range of 5,000 to 150,000 and preferably in a range of 10,000 to 50,000.

[0018] R^1 can be a linear alkyl group having 1 to 5 carbon atoms. The alkyl group is exemplified by, but not limited to, methyl, ethyl, propyl, butyl, and pentyl. It is preferred that R^1 is methyl.

[0019] R^2 is a substituted or unsubstituted branched alkyl group having 3 to 30 carbon atoms. The substituted branched alkyl group can be substituted with substituents in place of a carbon bonded hydrogen atom (C-H). Substituted R^2 groups are exemplified by, but not limited to, halogen such as chlorine and fluorine, alkoxycarbonyl such as described by formula $-(CH_2)_aC(O)O(CH_2)_bCH_3$, alkoxy substitution such as described by formula $-(CH_2)_aO(CH_2)_bCH_3$, and carbonyl substitution such as described by formula $-(CH_2)_aC(O)(CH_2)_bCH_3$, where $a \geq 0$ and $b \geq 0$. Unsubstituted R^2 groups are exemplified by, but not limited to, isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl, neopentyl, tert-pentyl, 2-methylbutyl, 2-methylpentyl, 2-methylhexyl, 2-ethylbutyl, 2-ethylpentyl, 2-ethylhexyl, etc. Preferably R^2 is a tertiary alkyl having 4 to 18 carbon atoms and more preferably R^2 is t-butyl.

[0020] The method for preparing the siloxane resin comprises:

combining

(a) a silane or a mixture of silanes of the formula R^1SiX_3, where each R^1 is independently selected from the group consisting of alkyl having 1 to 5 carbon atoms, where X is a independently a hydrolyzable group or a hydroxy group;

(b) a silane or a mixture of silanes of the formula $(R^2O)_cSiX_{(4-c)}$, where R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and branched substituted alkyl groups having 3 to 30 carbon atoms as described above, c is from 1 to 3, X is a hydrolyzable group or a hydroxy group; and

(c) water,

for a time and temperature sufficient to effect the formation of the siloxane resin.

[0021] Silane (a) is a silane or a mixture of silanes of the formula R^1SiX_3, where each R^1 is independently selected from the group consisting of alkyl having 1 to 5 carbon atoms. It is preferred that R^1 is methyl. X is a hydrolyzable group or a hydroxy group. By "hydrolyzable group" it is meant that greater than 80 mole percent of X reacts with water (hydrolyzes) under the conditions of the reaction to effect formation of the siloxane resin. The hydroxy group is a condensable group in which at least 70 mole percent reacts with another X group bonded to a different silicon atom to condense and form a siloxane bond (Si-O-Si). The hydrolyzable group is an amino group or an organic group attached to a silicon atom through an oxygen atom (Si-OR) forming a silicon bonded alkoxy group or a silicon bonded acyloxy group. When X is amino, it is typically used at less than 30 mole percent because the resulting siloxane resin may contain greater than 30 mole percent SiOH. R is exemplified by, but not limited to, linear alkyl groups having 1 to 6 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl, or hexyl and acyl groups having 1 to 6 carbon atoms such as formyl, acetyl, propionyl, butyryl, valeryl or hexanoyl. It is preferred that silane (a) be methyltrimethoxysilane or methyltriethoxysilane because of their easy availability.

[0022] Silane (b) is a silane or a mixture of silanes of the formula $(R^2O)_cSiX_{(4-c)}$, where R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and substituted branched alkyl groups having 3 to 30 carbon atoms as described above, c is from 1 to 3, and X is independently a hydrolyzable group or a hydroxy group as described above. It is preferred that silane (b) be di-t-butoxydihydroxysilane, di-t-butoxydimethoxysilane, di-t-butoxydiethoxysilane, di-t-butoxydiaminosilane and di-t-butoxydiacetoxysilane because of their easy availability. Silane (a) and silane (b) are present in a molar ratio of silane (a) to silane (b) of 1:99 to 99:1. It is preferred that silane (a) and silane (b) are present in a molar ratio of silane (a) to silane (b) of 40:60 to 98:2 and more preferred 50:50 to 85:15 on the same basis.

[0023] Water is present in an amount to effect hydrolysis of the hydrolyzable group, X. Typically water is present in an amount of 0.5 to 2.0 moles of water per mole of X in silanes (a) and (b) and more preferably is when the water is 0.8 to 1.2 moles, on the same basis.

[0024] The reaction to effect formation of the siloxane can be carried out in the liquid state with or without a solvent. If a solvent is used, it can include any suitable organic solvent that does not contain functional groups which may participate in the hydrolysis/condensation and is a solvent for silanes (a) and (b). The solvent is exemplified by, but not limited to, saturated aliphatics such as n-pentane, hexane, n-heptane, isooctane and dodecane; cycloaliphatics such as cyclopentane and cyclohexane; aromatics such as benzene, toluene, xylene and mesitylene; cyclic ethers such as tetrahydrofuran (THF) and dioxane; ketones such as methylisobutyl ketone (MIBK); halogen substituted alkanes such as trichloroethane; halogenated aromatics such as bromobenzene and chlorobenzene; and alcohols such as methanol, ethanol, propanol, butanol. Additionally, the above solvents may be used in combination as co solvents. Preferred solvents are aromatic compounds and cyclic ethers, with toluene, mesitylene and tetrahydrofuran being most preferred. When a solvent is used, it is generally used within a range of 40 to 95 weight percent based on the total weight of solvent and silanes (a) and (b). More preferred is 70 to 90 weight percent solvent on the above basis.

[0025] Combining components (a), (b), (c) and optionally a solvent (if it is present) may be done in any order as long as there is contact between any hydrolyzable groups (X) and water, so that the reaction may proceed to effect formation of the siloxane resin. Generally the silanes are dissolved in the solvent and then the water added to the solution. Some reaction usually occurs when the above components are combined. To increase the rate and extent of reaction, however, various facilitating measures such as temperature control and/or agitation are utilized.

[0026] The temperature at which the reaction is carried out is not critical as long as it does not cause significant gelation or cause curing of the siloxane resin product. Generally the temperature can be in a range of 20°C to 150°C, with a temperature of 20°C to 100°C being preferred. When X is an acyloxy group such as acetoxy, it is preferred to conduct the reaction at or below 85°C. The time to form the siloxane resin is dependent upon a number of factors such as, but not limited to, the specific silanes being used, the temperature and the mole ratio of R^1 and R^2O desired in the siloxane resin product of the reaction. Typically, the reaction time is from several minutes to several hours. To increase the molecular weight of the siloxane resin prepared and to improve the storage stability of the siloxane resin it is

preferred to carry out a bodying step subsequent to or as part of the above reaction. By "bodying" it is meant that the reaction is carried out over several hours with heating from 40°C up to the reflux temperature of the solvent to effect the increase in weight average molecular weight. It is preferred that the reaction mixture be heated such that the siloxane resin after heating has a weight average molecular weight in the range of 5,000 to 150,000.

[0027] When X is an acyloxy group such as acetoxy, the corresponding acid such as acetic acid is produced as a by-product of reaction. Since the presence of acetic acid may adversely affect the stability of the siloxane resin product, it is desirable that any acetic acid be neutralized. Neutralization of the by-product acetic acid may be effected by contacting the reaction mixture with a neutralizing agent or by removal via distillation. The distillation is generally accomplished by the addition of solvent such as toluene (if it is not already present) and removing the acetic acid under reduced pressure and heat (i.e. up to 50°C) as an azeotrope with the solvent. If a neutralizing agent is used, it must be sufficiently basic to neutralize any remaining acetic acid and yet insufficiently basic so that it does not catalyze rearrangement of the siloxane resin product. Examples of suitable bases include calcium carbonate, sodium carbonate, sodium bicarbonate, ammonium carbonate, ammonia, calcium oxide or calcium hydroxide. Neutralization may be accomplished by any suitable means such as stirring in a powdered neutralizing agent followed by filtration or by passing the reaction mixture and any additional solvent over or through a bed of particulate neutralizing agent of a size which does not impede flow.

[0028] The siloxane resin may be recovered in solid form by removing the solvent. The method of solvent removal is not critical and numerous approaches are well known in the art. For example, a process comprising removing the solvent by distillation under vacuum and heat (i.e. 50°C to 120°C) may be used. Alternatively, if it is desired to have the siloxane resin in a particular solvent, a solvent exchange may be done by adding a secondary solvent and distilling off the first solvent. The siloxane resins may also be stored in solid form.

[0029] An insoluble porous resin may be obtained by heating the siloxane resin for a time and temperature sufficient to effect curing of the siloxane resin and removal of the R^2O groups, thereby forming an insoluble porous resin. By "cured" it is meant that the resin is essentially insoluble in the solvent from which the siloxane resin was deposited onto the substrate or any solvent delineated above as being useful for the application of the siloxane resin. By "removal" it is meant that greater than 80 mole percent of the R^2O groups bonded to silicon atoms have been removed as volatile hydrocarbon and hydrocarbon fragments

which generate voids in the coating, resulting in the formation of an insoluble porous resin. The heating may be conducted in a single-step process or in a two-step process. In the two-step heating process the siloxane resin is first heated for a time and temperature sufficient to effect curing without significant removal of the R^2O groups. Generally this temperature can be in a range of from greater than 20°C to 350°C for several minutes to several hours. Then the cured siloxane resin is further heated for a time and temperature (for several minutes to several hours) within a range of greater than 350°C up to the lesser of the decomposition of the siloxane resin backbone or the R^1 groups bonded to silicon of the $R^1SiO_{3/2}$ siloxane units to effect removal of the R^2O groups from the silicon atoms. Typically, the removal step is conducted at a temperature in a range of greater than 350°C to 800°C. It is preferred that the removal step be conducted at a temperature in a range of greater than 350°C to 600°C, with 400°C to 550°C being more preferred. The porosity in the final insoluble porous resin can be controlled by the mole percent of OR^2 in the siloxane resin and how the siloxane resin is heated.

[0030] In the single-step process the curing of the siloxane resin and removal of the R^2O groups are effected simultaneously by heating for a time and temperature within a range of greater than 20°C up to the lesser of the decomposition of the siloxane resin backbone or the R^1 groups bonded to silicon atoms described herein above to effect removal of the R^2O groups from the cured siloxane resin. Generally, it is preferred that the curing/removal step be conducted at a temperature in a range of greater than 350°C to 600°C, with a temperature in a range of 400°C to 550°C being most preferred.

[0031] It is preferred that the heating takes place in an inert atmosphere, although other atmospheres may be used. Inert atmospheres useful herein include, but are not limited to, nitrogen, helium and argon with an oxygen level less than 50 parts per million and preferably less than 15 parts per million. Heating may also be conducted at any effective atmospheric pressure from vacuum to above atmospheric and under any effective oxidizing or non-oxidizing gaseous environment such as those comprising air, O_2, oxygen plasma, ozone, ammonia, amines, moisture, N_20, hydrogen, etc.

[0032] The insoluble porous resins may be useful as porous materials with controllable porosity and high temperature stability up to 550°C such as shape selective gas or liquid permeable membranes, catalyst supports, energy storage systems such as batteries and molecular separation and isolation. By the term "porous" it is meant an insoluble porous resin

having a porosity in a range of from 2 to 40 volume percent. The modulus of the insoluble porous resins ranges from 1.9 to 20 GPa.

[0033] The siloxane resins may be used to prepare an insoluble porous coating on a substrate by:

(A) coating the substrate with a coating composition comprising a siloxane resin composition comprising $R^1SiO_{3/2}$ siloxane units, and $(R^2O)_bSiO_{(4-b)/2}$ siloxane units wherein R^1 is independently selected from the group consisting of alkyl having 1 to 5 carbon atoms and R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and substituted branched alkyl groups having 3 to 30 carbon atoms, b is from 1 to 3. The siloxane resin contains an average molar ratio of $R^1SiO_{3/2}$ units to $(R^2O)_bSiO_{(4-b)/2}$ units of 1:99 to 99 to 1. The sum of $R^1SiO_{3/2}$ units and $(R^2O)_bSiO_{(4-b)/2}$ units is at least 50 percent of the total siloxane units in the resin composition;

(B) heating the coated substrate for a time and temperature sufficient to effect curing of the coating composition, and

(C) further heating the coated substrate for a time and temperature sufficient to effect removal of the R^2O groups from the cured coating composition, thereby forming an insoluble porous coating on the substrate.

[0034] The siloxane resin is typically applied to a substrate as a solvent dispersion. Solvents which may be used include any agent or mixture of agents which will dissolve or disperse the siloxane resin to form a homogeneous liquid mixture without affecting the resulting coating or the substrate. The solvent can generally be any organic solvent that does not contain functional groups which may participate in a reaction with the siloxane resin, such as hydroxyl, exemplified by those discussed herein above for the reaction of the silane mixture with water.

[0035] The solvent is present in an amount sufficient to dissolve the siloxane resin to the concentration desired for a particular application. Typically the solvent is present in an amount of 40 to 95 weight percent, preferably from 70 to 90 weight percent based on the weight of the siloxane resin and solvent. If the siloxane resin has been retained in a solvent described herein above, the solvent may be used in coating the substrate, or if desired a simple solvent exchange may be performed by adding a secondary solvent and distilling off the first solvent.

[0036] Specific methods for application of the siloxane resin to a substrate include, but are not limited to spin coating, dip coating, spray coating, flow coating, screen printing or others. The preferred method for application is spin coating. When a solvent is used, the solvent is allowed to evaporate from the coated substrate resulting in the deposition of the siloxane resin coating on the substrate. Any suitable means for evaporation may be used such as simple air drying by exposure to an ambient environment, by the application of a vacuum, or heat (up to 50°C) or during the early stages of the curing process. When spin coating is used, the additional drying method is minimized since the spinning drives off the solvent.

[0037] Following application to the substrate, the siloxane resin coating is heated at a temperature sufficient to effect cure of the siloxane resin and removal of the R^2O groups bonded to silicon atoms, thereby forming a insoluble porous coating. By "cured coating" it is meant that the coating is essentially insoluble in the solvent from which the siloxane resin was deposited onto the substrate or any solvent delineated above as being useful for the application of the siloxane resin. By "removal" it is meant that greater than 80 mole percent of the R^2O groups bonded to silicon atoms have been removed as volatile hydrocarbon and hydrocarbon fragments which generate voids in the coating, resulting in the formation of a insoluble porous resin. The heating may be conducted in a single-step process or in a two-step process. In the two-step heating process the siloxane resin is first heated at a temperature sufficient to effect curing without significant removal of the R^2O groups. Generally this temperature can be in a range of from greater than 20°C to 350°C. Then the cured siloxane resin coating is further heated at a temperature within a range of greater than 350°C up to the lesser of the decomposition of the siloxane resin backbone or the R^1 groups bonded to silicon atoms described herein above to effect removal of the R^2O groups from the silicon atoms. Typically, the removal step is conducted at a temperature in the range of greater than 350°C to 800°C. It is preferred that the removal step be conducted at a temperature in a range of greater than 350°C to 600°C, with a temperature in a range of 400°C to 550°C being most preferred. During the curing and heating step greater than 90 mole percent of R^1 groups generally remain on the siloxane resin.

[0038] In the single-step process the curing of the siloxane resin and removal of the R^2O groups are effected simultaneously by heating at a temperature within a range of greater than 20°C up to the lesser of the decomposition of the siloxane resin backbone or the R^1 groups bonded to silicon atoms described herein above to effect removal of the R^2O groups from the

cured coating composition. Generally, it is preferred that the curing/removal step be conducted at a temperature in a range of greater than 350°C to 600°C, with a temperature in a range of 400°C to 550°C being most preferred.

[0039] It is preferred that the heating takes place in an inert atmosphere, although other atmospheres may be used. Inert atmospheres useful herein include, but are not limited to, nitrogen, helium and argon with an oxygen level less than 50 parts per million and preferably less than 15 parts per million. Heating may also be conducted at any effective atmospheric pressure from vacuum to above atmospheric and under any effective oxidizing or non-oxidizing gaseous environment such as those comprising air, O_2, oxygen plasma, ozone, ammonia, amines, moisture, N_20, hydrogen, etc.

[0040] Any method of heating such as the use of a quartz tube furnace, a convection oven, or radiant or microwave energy is generally functionally herein. Similarly, the rate of heating is generally not a critical factor, but it is most practical and preferred to heat the coated substrate as rapidly as possible.

[0041] The insoluble porous coatings produced herein may be produced on any substrate. However, the coatings are particularly useful on electronic substrates. By "electronic substrate" it is meant to include silicon based devices and gallium arsenide based devices intended for use in the manufacture of a semiconductor component including focal plane arrays, opto-electronic devices, photovoltaic cells, optical devices, transistor-like devices, 3-D devices, silicon-on-insulator devices, super lattice devices and the like.

[0042] By the above method a thin (less than 5 μm) insoluble porous coating is produced on the substrate. Preferably the coatings have a thickness of 0.3 to 2.5 μm and a thickness of 0.5 to 1.2 μm being more preferable. The coating smoothes the irregular surfaces of the various substrates and has excellent adhesion properties.

[0043] Additional coatings may be applied over the insoluble porous coating if desired. These can include, for example SiO_2 coatings, silicon containing coatings, silicon carbon containing coatings, silicon nitrogen containing coatings, silicon oxygen nitrogen containing coatings, silicon nitrogen carbon containing coatings and/or diamond like coatings produced from deposition (i.e. CVD, PECVD, etc.) of amorphous SiC:H, diamond, silicon nitride. Methods for the application of such coatings are known in the art. The method of applying an additional coating is not critical, and such coatings are typically applied by chemical vapor deposition techniques such as thermal chemical vapor deposition (TCVD), photochemical vapor deposition, plasma enhanced chemical vapor deposition (PECVD), electron cyclotron resonance

(ECR), and jet vapor deposition. The additional coatings can also be applied by physical vapor deposition techniques such as sputtering or electron beam evaporation. These processes involve either the addition of energy in the form of heat or plasma to a vaporized species to cause the desired reaction, or they focus energy on a solid sample of the material to cause its deposition.

[0044] The insoluble porous coatings formed by this method are particularly useful as coatings on electronic devices such is integrated circuits. The dielectric constant of the insoluble porous coatings ranges from 2.1 to 3.0, with 2.1 to 2.5 being more preferred for interlayer dielectric coatings. By the term "porous" it is meant an insoluble coating having a porosity of from 2 to 40 volume percent. The modulus of the insoluble porous coatings ranges from 1.9 to 20 GPa, with a preferred range from 4 to 13 GPa.

EXAMPLES

[0045] The following non-limiting examples are provided so that one skilled in the art may more readily understand the invention. In the Examples weights are expressed as grams (g). Molecular weight is reported as weight average molecular weight (Mw) and number average molecular weight (Mn) determined by Gel Permeation Chromatography. Analysis of the siloxane resin composition was done using ^{29}Si nuclear magnetic resonance (NMR). Nitrogen sorption porosimetry measurements were performed using a QuantaChrome Autosorb 1 MP system. The cured siloxane resins were ground into fine powders before being placed into the sample cell, degassed for several hours, and loaded into the analysis station. The surface area was determined by the Brunauer-Emmett-Teller method. The total pore volume was determined from the amount of vapor adsorbed into the pores at a relative pressure close to unity (P/Po = 0.995) with the assumption that the pores filled with adsorbate. Skeletal density was measured using a helium gas pycnometer. Skeletal density represents the true density of the siloxane resin solid structure excluding any interior voids, cracks or pores in the measurement. The percent porosity was calculated from the skeletal density and the total pore volume. Refractive Index (RI) and coating thickness were measured using a Woollam M-88 Spectroscopic Ellipsometer.

[0046] In the following examples Me stands for methyl and tBu stands for tertiarybutyl, Ac stands for acetoxy, and Et stands for ethyl. In the following tables, n.m. indicates the specified property was not measured.

Example 1.

[0047] This example illustrates the formation of a siloxane resin composition where R^1 is Me and R^2 is t-butyl. 10.00 g of $(HO)_2Si(OtBu)_2$ and 6.44 g of $MeSi(OMe)_3$ were added to

22.20 g of THF in a flask under an argon atmosphere. 1.75 g of deionized water was then added slowly to the reaction mixture at room temperature. After stirring at room temperature for 1 hour, the reaction mixture was heated to reflux for 6 hours. The solvent was removed using a rotary evaporator to yield a siloxane resin as a viscous oil. The oil was heated at 150°C under vacuum for 12 hours; the temperature was raised to 200°C and maintained under vacuum for an additional 5 hours. A 9.37 g yield of solid resin was obtained, having a Mw of 13,100, a Mn of 4,900. Composition as determined by ^{29}Si NMR was $(MeSiO_{3/2})_{0.36}((ZO)SiO_{3/2})_{0.14}((tBuO)_bSiO_{4-b/2})_{0.5}$ where ZO = OH or OMe.

Example 2

[0048] This example illustrates the formation of an insoluble porous resin. A sample (1.9744 g) of the siloxane resin prepared in Example 1 was weighed into an alumina crucible and transferred into a quartz tube furnace. The furnace was evacuated to <20 mmHg (<2666 Pa) and backfilled with argon. The sample was heated to 450°C at a rate of 10°C/minute and held at 450°C for 1 hour before cooling to room temperature while under an argon purge. The cured material obtained in 47.2 weight percent yield (9319 g). Composition as determined ^{29}Si NMR was $(MeSiO_{3/2})_{0.47}(SiO_{4/2})_{0.53}$. BET surface area was 584 m^2/g and pore volume was 0.40 cc/g.

Example 3

[0049] This example illustrates the formation of a siloxane resin composition where R^1 is Me and R^2 is t-butyl. $MeSi(OMe)_3$ (A), $(H_2N)_2Si(OtBu)_2$ (B) and THF were added to a flask under an argon atmosphere in the amounts described in Table 1. Deionized water was then slowly added to the flask and the mixture stirred for one hour at room temperature, the mixture was heated to 65°C. Temperature was maintained at 65°C for two hours, and then cooled to room temperature. Volatile components were removed using a rotary evaporator at room temperature under vacuum (1 mm Hg). The product was dissolved in toluene and azeotroped dried and the solution held at reflux for 30 minutes, cooled and filtered through a 0.45 micrometer syringe filter. The solvent was vacuum (1 mm Hg) evaporated at 25°C to yield the siloxane resin. Analysis of the siloxane resin structure and molecular weight is shown in Table 2.

Table 1. Summary of Resin Synthesis

Example No.	(A) (g)	(B) (g)	THF (g)	H_2O (g)	Toluene in reflux step (g)	Yield (g)	Appearance
3-1	20.0	1.5	30.3	11.1	50	11.8	Wax
3-2	20.1	3.0	30.2	11.6	50	12.8	Oil
3-3	20.0	7.6	29.9	13.2	50	16.8	Oil
3-4	20.0	12.0	30.0	14.8	50	21.7	Oil

Table 2.

Analysis of $(MeSiO_{3/2})_f((tBuO)_b\ SiO_{4-b/2})_g$ Resins

Example	Molar ratio of f/g Based on reactant	Molar ratio of f/g (^{29}Si NMR)	Mw	Mn	Tg (°C)
3-1	95.3/4.7	96.0/4.0	109,700	2,460	-43.9
3-2	91.0/9.0	n.m.	>100,000*	n.m.	-13.4
3-3	80.0/20.0	80.0/20.0	17,600	1,480	-28.9
3-4	71.8/28.2	75.0/25.0	7,310	1,090	-39.4

* The molecular weight data was inconclusive because the material was gel-like, however it could still be re-dissolved in solvent.

Example 4

[0050] This example illustrates the formation of an insoluble porous resin. Resins prepared in Example 3 (2 to 3 g) were weighed into an alumina crucible and transferred into a quartz tube furnace. The furnace was evacuated to <20 mmHg (<2666 Pa) and backfilled with argon. The samples were was heated to the temperatures shown in Table 3 at a rate of 10°C/minute and held at temperature for 1 hour before cooling to room temperature while under an argon purge. The pyrolysis temperature, Char Yield and porosity data are shown in Table 3. Char Yield is expressed as weight percent retained after analysis at the specified temperature and is a measure of the shrinkage of the bulk siloxane resin upon heating.

Table 3. Porosity and char yields of cured resins.

Example No.	Resin Sample No.	Temp. (°C)	Char Yield (Wt %)	Pore Volume (cm^3/g)	Surface Area, BET, (m^2/g)
4-1	3-1	400	80.2	0.157	142
4-2	3-1	450	79.7	0.161	160
4-3	3-2	400	79.3	n.m.	n.m.
4-4	3-2	450	76.8	0.265	413
4-5	3-3	380	71.4	0.214	272
4-6	3-3	400	66.3	n.m.	n.m.
4-7	3-3	450	62.6	0.295	486
4-8	3-4	380	69.4	0.056	35
4-9	3-4	400	60.9	0.227	277
4-10	3-4	450	49.5	0.213	348

Example 5

[0051] This example illustrates the formation of a siloxane resin composition where R^1 is Me and R^2 is t-butyl.$MeSi(OMe)_3$ (A), $(AcO)_2Si(OtBu)_2$ (B) and THF were added to a flask under an argon atmosphere in the amounts described in Table 4. Deionized water was then added to the flask and the mixture was stirred at room temperature for 1 hour. 75 g of toluene was added to the reaction mixture. The solvent was removed using a rotary evaporator to yield the product as viscous oil, which was immediately dissolved into 150 g of toluene. Residual acetic acid was removed as an azeotrope with toluene under reduced pressure (azeotrope boiling point at 38°C). The resin was again dissolved into 110 g of toluene and azeotropically dried and refluxed for 1h. The solution was filtered and the solvent removed by evaporation to yield the final resin product. A summary of the resin synthesis is shown in Table 4. The molecular weight information for the resins is shown in Table 5.

Table 4. Summary of Resin Synthesis

Example No.	(A) (g)	(B) (g)	THF (g)	H_2O (g)	Yield (g)	Appearance
5-1	18.6	40.0	72.0	11.1	23.6	Solid
5-2	27.9	40.0	80.0	14.5	26.0	Solid
5-3	43.5	40.3	90.0	20.0	40.0	Solid
5-4	92.9	39.9	120.3	28.3	67.3	Wax

Table 5.

Analysis of $(MeSiO_{3/2})_f((tBuO)_bSiO_{4-b/2})_g$ Resins.

Example	Molar ratio of f/g Based on reactants	Molar ratio of f/g Based on ^{29}Si NMR	Mn	Mw
5-1	0.50/0.50	0.44/0.56	2,990	17,700
5-2	0.60/0.40	0.55/0.44	2,010	46,000
5-3	0.70/0.30	0.69.0.31	n.m.	>100,000*
5-4	0.85/0.15	0.83/0.17	3,400	32,100

* The molecular weight data was inconclusive because the material was gel-like, however it could still be re-dissolved in solvent.

Example 6

[0052] This example illustrates the formation of an insoluble porous resin. Resins prepared in Example 5 (2 to 3 g) were weighed into an alumina crucible and transferred into a quartz tube furnace. The furnace was evacuated to <20 mmHg (<2666 Pa) and backfilled with argon. The samples were was heated to 450°C at a rate of 10°C/minute and held at 450°C for 1 hour before cooling to room temperature while under an argon purge. The cured siloxane resins were obtained as transparent or slightly opaque thick films. The pyrolysis temperature, char yield and porosity data are shown in Table 6. Char Yield is expressed as weight percent retained after analysis at the specified temperature.

Table 6. Porosity and char yields of cured resins.

Example No.	Resin Sample No.	Skeletal Density (g/cm^3)	Char Yield (Wt %)	Pore Volume (cm^3/g)	Porosity (%)	Surface Area, BET, (m^2/g)
6-1	5-1	1.693	60.5	0.271	31.4	461
6-2	5-2	1.624	72.5	0.280	31.3	481
6-3	5-3	1.505	78.0	0.249	27.2	425
6-4	5-4	1.398	76.5	0.125	14.9	168

Example 7

[0053] This example illustrates the formation of an insoluble porous coating. Resins prepared in Example 5 (2 to 3g) were dissolved in MIBK to form a clear solution containing 25 weight % as resin. The solution was filtered through a 1.0 μm syringe membrane filter followed by a 0.2 μm syringe membrane filter to remove any large particles. The solution was applied to a silicon wafer by spin coating at 2000 rpm for 20 seconds. The coated silicon wafers were put into a quartz tube furnace and the furnace was purged with nitrogen. The furnace was heated to 400°C, 425°C or 450°C (50 to 60°C/minute) and held at temperature for 2 hours, then cooled to room temperature while maintaining the nitrogen purge. The coated wafers were stored under a nitrogen atmosphere before the property measurements. Modulus and dielectric constants (Dk) of the thin films are shown in Table 7.

Table 7. Thin film Properties of resins on silicon wafers

Example No.	Resin Sample No.	Temperature °C	Dk	Modulus, Gpa	Hardness, Gpa	Thickness, Å	RI
7-1	5-1	450	2.32	7.9	0.91	6,300	1.273
7-2	5-1	425	2.36	9.0	1.11	6,728	1.276
7-3	5-1	400	2.48	8.7	0.95	6,826	1.271
7-4	5-2	450	2.16	3.5	0.51	6,199	1.252
7-5	5-2	425	2.48	5.5	0.65	6,374	1.307
7-6	5-2	400	2.55	4.8	0.53	6,333	1.338
7-7	5-3	450	2.61	7.4	1.11	8,551	1.347
7-8	5-3	425	2.52	6.9	1.08	9,025	1.350
7-9	5-3	400	2.38	7.4	1.19	9,413	1.336
7-10	5-4	450	2.88	7.8	1.4	10,500	1.368
7-11	5-4	425	2.71	6.0	1.19	10,525	1.383
7-12	5-4	400	2.63	7.1	1.25	10,892	1.375

Comparative Example 1

[0054] This examples illustrates the preparation of a $(MeSiO_{3/2})_h(CF_3CH_2CH_2)SiO_{3/2})_i$ resin prepared according to U.S. Patent No. 6,022,814 and formation of thin films from the resin. 0.5 g of trifluoropropyltrimethoxy silane, 9.5 g of methyltrethoxy silane, 10 g of isopropyl alcohol, 3.4 g of butanol and 0.10 g oxalic acid dihidrate were mixed in a flask. 3.4 g of water was then added into the reaction flask via a syringe. A slight increase in temperature from 24 to 30°C was observed. The reaction mixture was heated to 70°C and maintained at 70°C for 2 hrs, followed by cooling to room temperature. The solvent was then removed under vacuum at 35°C, yielding a 4.98 g of product.

[0055] The product obtained was dissolved into 10 g butanol and 2.56 g isopropanol to form a solution. The solution was applied to single crystal silicon wafers by spin coating at 1500, 2000, and 3000 rpm, resulting in silicon wafers having poor quality films for which no characterization data could be generated. The films contained numerous circular defects of different sizes dispersed over the entire surface of the wafer. Using optical microscopy these defects also appeared to be present below the surface of the film.

[0056] Another sample of the recovered product prepared was dissolved into MIBK to form a 25 wt.% solution. The solution was filtered through a 1.0 μm syringe membrane filter followed by a 0.2 μm syringe membrane filter to remove any large particles. The solution was applied to a silicon wafer by spin coating at 2000 rpm for 20 seconds. The coated silicon wafers were put into a quartz tube furnace and the furnace was purged with nitrogen. The furnace was heated to 450°C (at 25°C/minute) and held at temperature for 2 hours, then cooled to room temperature while maintaining the nitrogen purge. The coated wafers were stored under a nitrogen atmosphere before the property measurements. The modulus and dielectric constant of the thin films are shown in Table 8.

Table 8. Thin film Properties of resins on silicon wafers

Example No.	Dk	Modulus, Gpa	Thickness, Å	RI
C1-1	n.m.	n.m.	5632	1.3738
C1-2	2.58	1.50	5149	1.3878
C1-3	2.63	1.60	5202	1.3736

[0057] The thin films prepared from the $(MeSiO_{3/2})_h(CF_3CH_2CH_2)SiO_{3/2})_i$ resin had higher Dk than that reported in Patent No. 6,022,814. Modulus was much lower than the modulus of the insoluble porous coating of the present invention.

Comparative Example 2

[0058] This example illustrates the formation of a $(MeSiO_{3/2})$ resin and formation of thin films made from the resin. 2560 g (140 mol) of deionized water and 1536 g (15.4 mol) of (MIBK) were added to a flask. The mixture was cooled to –4 °C while stirring. 512 g (5.12 mol) of MIBK and 817 g of methyltrichlorsilane (5.46 mol) were added to the flask at a rate of (5.5 g/min) over 4 h while stirring. During the addition, the temperature increased to about 8 °C. After the addition was finished, the temperature was raised to 56 °C, during a 2 hr period and maintained at 56 °C for an additional 2 hrs. The reaction solution was clear at 56 °C. The reaction solution was cooled to below 30 °C, at which time a phase separation was observed. The water layer containing HCl was drained off through a bottom valve in the flask. The solvent layer containing the siloxane resin product was washed with 1L deionized water while stirring, followed by removal of the water. This washing step was repeated 4

times until the PH value of washed water was about 4. The MIBK solvent, water, and any residual HCl was removed using a rotary evaporator at 40 °C leaving the methyl silsesquioxane resin product, which was then dissolved in toluene. The toluene was removed using a rotary evaporator. The siloxane resin product was further dried under vacuum at room temperature overnight. The resin was kept in a refrigerator for further characterization and thin film evaluation. GPC analysis of the resulting resin showed Mw of 13,500 and Mn of 3,500.

[0059] 2 to 3g of the methyl silsesquioxane resin product was dissolved in MIBK to form a clear solution containing 25 weight % as resin. The solution was filtered through a 1.0 μm syringe membrane filter followed by a 0.2 μm syringe membrane filter to remove any large particles. The solution was applied to silicon wafers by spin coating at 2000 rpm for 20 seconds. The coated silicon wafers were put into a quartz tube furnace and the furnace was purged with nitrogen. The furnace was heated to 450°C (25°C/minute) and held at temperature for 2 hours, then cooled to room temperature while maintaining the nitrogen purge. The coated wafers were stored under a nitrogen atmosphere before the property measurements. The modulus and dielectric constant of the thin films are shown in Table 9.

Table 9. Thin film Properties of resins on silicon wafers

Example No.	Dk	Modulus, Gpa	Hardness, Gpa	Thickness, Å	RI
C2-1	2.50	1.50	0.26	9402	1.3652
C2-2	2.51	1.50	0.30	9286	1.3787
C2-3	n.m.	n.m.	n.m.	9707	1.3842

This comparative Example illustrates that nonporous thin films made from a ($MeSiO_{3/2}$) resin resulted in similar dielectric constant as thin films of the present invention, however, much lower modulus (<2 GPa).

CLAIMS:

1. A siloxane resin composition comprising $R^1SiO_{3/2}$ siloxane units and $(R^2O)_bSiO_{(4-b)/2}$ siloxane units wherein R^1 is independently selected from the group consisting of alkyl having 1 to 5 carbon atoms, R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and branched substituted alkyl groups having 3 to 30 carbon atoms, b is from 1 to 3, the siloxane resin contains a molar ratio of $R^1SiO_{3/2}$ units to $(R^2O)_bSiO_{(4-b)/2}$ units of 1:99 to 99:1 and the sum of $R^1SiO_{3/2}$ units and $(R^2O)_bSiO_{(4-b)/2}$ units is at least 50 percent of the total siloxane units in the resin composition.

2. The siloxane resin composition as claimed in claim 1, wherein R^2 is t-butyl.

3. A method for preparing a siloxane resin comprising $R^1SiO_{3/2}$ siloxane units and $(R^2O)_bSiO_{(4-b)/2}$ siloxane units where b is from 1 to 3, which comprises:

combining

(a) a silane or a mixture of silanes of the formula R^1SiX_3, where each R^1 is independently selected from the group consisting of alkyl having 1 to 5 carbon atoms, where X is a independently a hydrolyzable group or a hydroxy group;

(b) a silane or a mixture of silanes of the formula $(R^2O)_cSiX_{(4-c)}$, where R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and branched substituted alkyl groups having 3 to 30 carbon atoms, c is from 1 to 3, X is a hydrolyzable group or a hydroxy group, silane (a) and silane (b) are present in a molar ration of silane (a) to silane (b) of 1:99 to 99:1; and

(c) water,

for a time and temperature sufficient to effect the formation of the siloxane resin.

4. The method as claimed in claim 3, wherein R^1 is methyl and R^2 is t-butyl.

5. A method of forming an insoluble porous resin, which comprises:

(A) heating the siloxane resin of claims 1 or 2 for a time and temperature sufficient to effect curing of the siloxane resin,

(B) further heating the siloxane resin for a time and temperature sufficient to effect removal of the R^2O groups from the cured siloxane resin, thereby forming an insoluble porous resin.

6. A method of forming an insoluble porous coating on a substrate comprising the steps of

(A) coating the substrate with a coating composition comprising a siloxane resin composition comprising $R^1SiO_{3/2}$ siloxane units, and $(R^2O)_bSiO_{(4-b)/2}$ siloxane units wherein R^1 is independently selected from the group consisting of alkyl having 1 to 5 carbon atoms and R^2 is independently selected from the group consisting of branched alkyl groups having 3 to 30 carbon atoms and substituted branched alkyl groups having 3 to 30 carbon atoms, b is from 1 to 3, the siloxane resin composition contains a molar ratio of $HSiO_{3/2}$ units to $(R^2O)_bSiO_{(4-b)/2}$ units of 1:99 to 99:1 and the sum of $R^1SiO_{3/2}$ units and $(R^2O)_bSiO_{(4-b)/2}$ units is at least 50 percent of the total siloxane units in the resin composition;

(B) heating the coated substrate for a time and temperature sufficient to effect curing of the coating composition, and

(C) further heating the coated substrate for a time and temperature sufficient to effect removal of the R^2O groups from the cured coating composition, thereby forming an insoluble porous coating on the substrate.

7. The method according to claims 5 or 6, where the curing of the siloxane resin and removal of the R^2O groups from the cured siloxane resin is done in a single step.

8. An electronic substrate having an insoluble porous coating prepared by the method of claim 6.