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THERMALLY STABLE DIELECTRIC COATINGS

This invention pertains to a method for producing thermally stable dielectric coatings comprising a first coating having a thickness of 1.25 to 2.25 μm produced from a hydrogen silsesquioxane resin (H-resin) and a second coating having a thickness of at least 100 nm comprised of silicon dioxide (SiO_2). It has been found that when a silicon dioxide coating having a thickness of at least 100 nm is applied over the H-resin coating that said coatings resist cracking in subsequent thermal processing. Thus, thermally stable dielectric coatings are conveniently produced.

A method for formation of multi-layer coatings of limited thicknesses for interlevel dielectrics and passivation on semiconductor devices is known in the art. Under the current method, as described in U.S. Patent 5,145,723, an H-resin is spun onto the semiconductor device and any solvent is removed to produce an H-resin film on said device. This film is then heated by placing the semiconductor device on hot plates (150°C. to 350°C.) to soften and flow the H-resin and finally a film is cured by heating in an oven at 400°C. to 450°C. for 1 hour. However, the method is effective for producing crack-free coatings only with thin layers (<1.2 μm) of H-resin ceramic. This thin layer does not adequately cover the metal layer and therefore it is required to apply a thick SiO_2 layer over said H-resin ceramic to produce a suitable interlevel dielectric.

Another method for producing multi-layer coatings on integrated circuits from H-resin is disclosed in U.S. Patent 4,756,977. According to '977 a first layer is produced by applying a solvent solution of H-resin to the device, the solvent is then removed and the coating is ceramified by heating to a temperature of between 150°C. and 1000°C. The H-resin based coatings produced by the method of '977 have a thickness of 3,000 to 5,000 angstroms (0.3 to 0.5 μm). A passivating coating is thereafter applied over the H-resin coating. The passivating coating may be a Si, SiN, SiC or SiCN.

It is desirable to have thicker coatings produced from H-resins to adequately cover the metallization. However, when thick coatings are produced using current processing methods, they contain undesirable cracks.

Other methods for curing H-resin are known in the art; however, these methods do not teach or suggest how to conveniently form thick coatings of 1.25 μm or greater. For example, U.S. Patents 5,380,567, 5,370,904 and 5,370,903 claim curing of H-resin in an inert atmosphere. U.S. Patent 5,380,567 reveals the cure of H-resin in an inert atmosphere at temperatures of 500°C. to 1000°C. (coating thickness 0.2 μm). U.S. Patent 5,370,904 provides a method for the formation of thick silicon oxide films wherein the method comprises forming an H-resin film on the surface and thereafter heating the film in an inert atmosphere at a temperature of from 250°C. to 500°C. until the SiH content in the silicon oxide product has reached ≤80% of the content

in the original H-resin (coating thicknesses 1.0 - 1.23 μm). U.S. Patent 5,370,903 is another method for the formation of thick silicon oxide films wherein the method comprises forming an H-resin film on the surface and thereafter heating said film in a mixed gas atmosphere (≤ 20% vol O_2) at a temperature of from 250°C. to 500°C. until the SiH content in the silicon oxide product has reached ≤80% of the SiH content in the starting H-resin (coating thicknesses 1.02 - 1.10 μm).

Additionally, U.S. Patent 5,059,448 incorporates the use of rapid thermal processing to produce coatings of 1 μm or less (0.13 to 0.945 μm). In '448 the H-resin film is exposed to a high intensity radiation to quickly heat the film at a temperature of 50°C to 1000°C.

Thicker coatings have also been produced by adding fillers to the H-resin. However, because of filler presence and the effect of the filler on the properties of the coating, these coatings are not necessarily suitable as interlevel dielectrics. For example, U.S. Patent 5,458,912 claims a method for forming tamper-proof coatings on electronic devices by applying to said device a coating comprising a silica precursor and a filler; and thereafter heating at a temperature sufficient to convert the silica precursor to a silica containing ceramic matrix. The coatings produced have thicknesses of 20 to 48 μm.

It has now been unexpectedly found that when the cure conditions (time, temperature and environment) are controlled, a crack-free insoluble coating having a

thickness of greater than 1.25 μm is readily produced from H-resins. It has also been found that when a layer of silicon dioxide having a thickness of at least one nm is applied over the H-resin coating, the product coatings are surprisingly stable (remain crack-free) when exposed to subsequent thermal processing.

This invention pertains to a method for producing thermally stable multi-layer coatings and the coatings produced therefrom. The multi-layer coating is comprised of a first coating produced from H-resin having a thickness of 1.25 to 2.25 μm and a second coating comprising silicon dioxide (SiO_2) having a thickness of at least 100 nm.

The method for producing the first coating comprises applying a fillerless H-resin composition onto a substrate and thereafter heating said resin at a temperature of 150°C. to 500°C. for a sufficient period of time to produce a crack-free coating having a thickness of 1.25 μm to 2.25 μm. The second coating is produced by depositing, preferably by PECVD, silicon dioxide over the first coating at a thickness at least 100 nm. This multi-layer coating is surprisingly stable (remains crack-free) when exposed to subsequent thermal processing.

This invention pertains to a method for producing thermally stable multi-layer coatings and the coatings produced therefrom. The multi-layer coatings are useful on any substrate such as metals or ceramics but are particularly useful on electronic substrates. By "thermally stable", it is meant that the coatings do not develop cracks

when exposed to subsequent thermal processing (temperatures ≤ 450°C.), including cure processing (up to 4 cycles) and annealing (both O_2 and N_2). 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.

The multi-layer coatings produced herein may be applied to a wafer prior to the application of any metallization. They may also be applied over metallization as an interlevel dielectric or they may be applied as a top passivation coating to complete the formation of an integrated circuit.

Additionally, the electronic substrate can be bare (i.e. no passivation) or the substrate can have a primary passivation. Such primary passivation is typically ceramic coatings such as silica, silicon nitride, silicon carbide, silicon oxynitride, silicon oxycarbide, PSG, BPSG and others, deposited by CVD, PVD, PECVD or sol-gel approaches. Primary passivation and methods of their deposition are known in the art. Preferably, the electronic substrate has a primary passivation layer comprised of silica having a thickness of up to 300 nm, preferably 30 nm to 300 nm.

The first layer of our multi-layer coating of the instant invention is produced by applying a fillerless composition comprising H-resin onto a substrate. This resin

includes hydridosiloxane resins consisting of units of the formula $HSi(OH)_x(OR)_yO_{z/2}$, in which each R is independently an organic group or a substituted organic group which, when bonded to silicon through the oxygen atom, forms a hydrolyzable substituent, x = 0 to 2, y = 0 to 2, z = 1 to 3, x + y + z = 3. Examples of R include alkyls such as methyl, ethyl, propyl and butyl; aryls such as phenyl; and alkenyls such as allyl or vinyl. These resins may be essentially fully condensed, $(HSiO_{3/2})_n$ wherein n is 8 or greater or they may be only partially hydrolyzed (i.e., containing some Si-OR) and/or partially condensed (i.e., containing some Si-OH). Although not represented by this structure, these resins may also contain a small number (e.g., less than 10%) of silicon atoms which have either 0 or 2 hydrogen atoms attached thereto or a small number of SiC bonds due to various factors involved in their formation or handling.

The above H-resins and methods for their production are known in the art. For example, U.S. Patent 3,615,272 shows the production of a nearly fully condensed H-resin (which may contain up to 100-300 ppm silanol) by a process comprising hydrolyzing trichlorosilane in a benzenesulfonic acid hydrate hydrolysis medium and by then washing the resultant resin with water or aqueous sulfuric acid. Similarly, US Patent 5,010,159 provides an alternative method comprising hydrolyzing hydridosilanes in an arylsulfonic acid hydrate hydrolysis medium to form a resin which is then contacted with a neutralizing agent.

Other hydridosiloxane resins, such as those described by US Patents 4,999,397 and 5.210,160; those produced by hydrolyzing an alkoxy or acyloxy silane in an acidic, alcoholic hydrolysis medium; those described in JP-As 59-178749, 60-86017 and 63-107122; or any other equivalent hydridosiloxane, will also suitably function herein.

Specific molecular weight fractions of the above H-resins may also be used in this invention. Such fractions and methods for their preparation are taught in U.S. Patents 5,063,267 and 5,416,190. A preferred fraction comprises material wherein at least 75% of the polymeric species have a number average molecular weight of at least 1200 and a more preferred fraction comprises material wherein at least 75% of the polymeric species have a number average molecular weight between 1200 and 100,000.

The H-resin may further contain a platinum, rhodium or copper catalyst to increase the rate and extent of cure of said resin. Generally, any platinum, rhodium or copper compound or complex which can be solubilized is useful herein. For instance, platinum acetylacetonate, rhodium catalyst $RhCl_3[S(CH_2CH_2CH_2CH_3)_2]_3$, obtained from Dow Corning Corporation, Midland, Mich. or cupric naphthenate are suitable. These catalysts are generally added in an amount of between 5 to 1000 ppm platinum, rhodium or copper, based on the weight of the H-resin. Platinum and rhodium catalysts useful herein are further described in U.S. Patent 4,822,697.

Ceramic oxide precursors may also be used in combination with the H-resin herein. The ceramic oxide precursors contemplated include compounds of various metals, such as aluminum, titanium, zirconium, tantalum, niobium and/or vanadium, as well as various non-metallic compounds such as those of boron or phosphorous, which may be dissolved in solution, hydrolyzed and subsequently pyrolyzed at relatively low temperatures to form ceramic oxides.

The above ceramic oxide precursors generally have one or more hydrolyzable groups bonded to the above metal or non-metal, depending on the valence of the metal. The number of hydrolyzable groups included in these compounds is not critical as long as the compound is soluble or dispersable in the solvent. Likewise, selection of the exact hydrolyzable substituent is not critical since the substituents are either hydrolyzed or pyrolyzed out of the system. Typical hydrolyzable groups are alkoxy, such as methoxy, propoxy, butoxy and hexoxy; acyloxy such as acetoxy; other organic groups bonded to said metal or non-metal through an oxygen, such as acetylacetonate or amino groups. Specific compounds, therefore, include zirconium tetracetylacetonate, titanium dibutoxy diacetylacetonate, aluminum triacetylacetonate, tetraisobutoxy titanium and $Ti(N(CH_3)_2)_4$. The ceramic oxide precursors useful herein are further described and manufactured by the teachings in U.S. Patents 4,808,653, 5,008,320 and 5,290,354.

When ceramic oxide precursors are combined with H-resin, it is generally used in an amount such that the final coating contains 0.1 to 30 percent by weight of ceramic oxide precursor.

The H-resin is normally applied to the substrate as a solvent dispersion. Solvents include any agent or mixture of agents which will dissolve said resin to form a homogeneous liquid mixture without affecting the resulting coating. These solvents include alcohols such as ethyl alcohol or isopropyl alcohol; aromatic hydrocarbons such as benzene or toluene; alkanes such as n-heptane, dodecane or nonane; ketones such as methyl iso-butyl ketone; esters; glycol ethers and siloxanes such as cyclic dimethylpolysiloxanes and linear dimethylpolysiloxanes (e.g. hexamethyldisiloxane, octamethyltrisiloxane and mixtures thereof). The solvent is present in an amount sufficient to dissolve the H-resin to the concentration desired for application. Typically, the solvent is present in an amount of 20 to 99 wt%, preferably from 50 to 80 wt%, and most preferably at 55 to 75 wt%, based on the total weight of said resin and solvent.

Specific methods for application of the H-resin include spin coating, dip coating, spray coating, flow coating, screen printing and the like. 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 an H-resin film on the substrate. Any suitable means for evaporation is then

used, such as simple air drying by exposure to an ambient environment, the application of a vacuum or mild heat (≤50°C.) or during the early stages of the curing process. It should be noted that when spin coating is used, the additional drying method is minimized as the spinning drives off solvent.

Following application to the substrate, the H-resin film is cured to a crack-free insoluble coating by heating said film for a specific time at a temperature of 150°C. to 500°C., preferably 200°C. to 400°C., and more preferably 300°C. to 380°C. By "insoluble coating", it is meant a coating that is essentially not soluble in the solvent from which the H-resin was deposited to form said film or any solvent delineated above as being useful herein for the application of the H-resin. By "crack-free", it is meant a coating that does not contain any cracks visible to the human eye when examined under an optical microscope at 1000X magnification.

Any method of heating, such as the use of a convection oven, rapid thermal processing, hot plate and radiant or microwave energy may be used herein, preferably hot plates. The method used must be capable of rapidly heating the film to the desired temperature.

The duration of time that the coating is heated to cure will depend on the environment during heating, the temperature at which it is heated (soak temperature), the rate at which it is heated and the thickness of the H-resin film. At higher soak temperatures and/or higher

concentrations of oxygen in the cure environment, the cure time will be shorter. Typically, the coatings are heated from 1 second to 2 hours, preferably from 5 seconds to 30 minutes.

If the coating is not heated long enough or is heated too long at the soak temperature, then cracking will result. Essentially, there is a window of time at a given soak temperature and environment for a given coating thickness that will produce a crack free coating. At lower soak temperatures, this window is larger. As the temperature increases, this window decreases. Further as the amount of oxygen present in the environment increases, this window decreases. For example, for a film thickness of 2 μm, when the film is cured in an inert atmosphere (< 50 ppm O_2) at 320°C., the window for cure is from 2 minutes to 120 minutes. At 380°C., the window for cure is from 0.01 minute to 5 minutes.

When the coatings are not heated long enough, cracks will develop when the coatings are cooled to room temperature. It is believed that it is possible to repair/heal the cracks by further heating the coating for a sufficient period of time. When coatings are heated too long, cracks will again develop when the coatings are cooled to room temperature. However, it is not possible to subsequently repair these later cracks.

The environment in which the H-resin film is cured is typically an inert environment such as nitrogen, argon, helium or an environment containing oxygen (e.g. air). As

the oxygen content in the environment increases, the minimum time required to cure the H-resin to a crack-free coating will be reduced. Further, the window of time during which a crack-free coating will be produced will be narrowed. When heating at lower temperatures (e.g. ≤330°C.), it is preferred to have oxygen present to accelerate the cure. However, when heating at higher temperatures (e.g. ≥340°C.), it is preferred to use an inert environment.

The curing of the H-resin may take place at atmospheric, superatmospheric or subatmospheric pressures, preferably atmospheric pressure. At lower temperatures, higher pressures are used to accelerate the cure. Vacuum may be used at any temperature.

The rate at which the coatings are heated to the soak temperature plays a role to produce crack-free coatings. If the heating rate is fast, then the window of time in which a crack-free coating is produced will be longer or higher soak temperatures and/or higher coating thicknesses may be achieved without cracking. On the contrary, if the heating rate is slow, then the window of time in which a crack-free coating is produced will be shorter or lower soak temperatures and/or reduced coating thicknesses will be necessary to achieve a crack-free coating.

Thick coatings may be produced herein by forming a single thick H-resin film and thereafter curing under our controlled conditions. Thick coatings may also be produced herein by forming a thin H-resin film, thereafter curing

under our controlled conditions and then repeating the process until a desired thickness is achieved.

The first layer coatings of this invention have a thickness of at least 1.25 μm, preferably of 1.25 to 2.25 μm, and most preferably of 1.5 to 2.2 μm.

The chemical composition and molecular structure of the insoluble coating produced herein is not fully understood. However, it is believed that the composition is different from insoluble coatings produced using known cure methods based on the unique properties (thickness, crack-free, etc.) that are achieved using our claimed cure process.

The second layer of our multi-layer coating of this invention is comprised of silicon dioxide produced by deposition (i.e. CVD, PECVD, etc.) of a silicon-containing material having a thickness of at least 100 nm to 2 μm, preferably at least 170 nm, more preferably at least 200 nm and most preferably at least 300 nm.

The method of applying the second layer is not critical and such coatings are applied by any chemical vapor deposition technique such as thermal chemical vapor deposition (TCVD), photochemical vapor deposition, plasma enhanced chemical vapor deposition (PECVD), electron cyclotron resonance (ECR) and jet vapor deposition. It is also conveniently 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. Methods for producing silicon dioxide layers by CVD are more completely described in U.S. Patent 4,981,724.

For example, in thermal chemical vapor deposition, the coating is deposited by passing a stream of the desired precursor gas over a heated substrate. When the precursor gas contacts the hot surface, it reacts and deposits the coating. Substrate temperatures in the range of 25°C. to 1,000°C. are sufficient to form these coatings in several minutes to several hours, depending on the precursor gas and the thickness of the coating. Reactive metals can also be used in such a process to facilitate deposition.

In PECVD techniques, a precursor gas is reacted by passing it through a plasma field. Reactive species are formed and focused at the substrate where they readily adhere. The advantage of a PECVD process over a thermal CVD process is that in the former, lower substrate and processing temperatures are used, i.e., 25°C. to 600°C.

Plasma used in a PECVD process can be energy derived from electric discharges, electromagnetic fields in the radio-frequency or microwave range, lasers or particle beams. In most plasma deposition processes, it is preferred to use radio frequency (i.e., 10 kHz to 10^2 MHz) or microwave energy (i.e., 0.1-10 GHz or 10^9 Hz) at moderate power densities (i.e., 0.1-5 watts/cm^2). The frequency, power and

pressure are tailored to the precursor gas and equipment being used.

To produce a silicon dioxide layer, there is typically reacted a silicon-containing precursor gas and a source of oxygen. Precursor gases that are used to produce the silicon dioxide layer include silane; alkylsilanes such as dimethylsilane and trimethylsilane; alkoxysilanes such as orthosilicates such as tetraethylorthosilicate (TEOS); halosilanes such as trichlorosilane; silacyclobutanes and others.

Sources of oxygen include air, oxygen, ozone, nitrous oxide, nitric oxide and the like.

Other materials such as carrier gases of helium or argon; dopants such as phosphine or borane; halogens or any other material that would add desirable properties to the second layer may be present.

It has been found that when a layer of silicon dioxide having a thickness of at least 100 nm is deposited over the claimed H-resin coating that our multi-layer coatings are stable to subsequent thermal processing.

EXPERIMENTAL PROCEDURE:

A hydrogen silsesquioxane resin (H-resin) composition comprising 40 wt% H-resin $(HSiO_{3/2})_n$ was prepared according to U.S. Patent 3,615,272 having a number average molecular weight of between 9,800 and 13,900, dissolved in a low molecular weight polydimethylsiloxane, was used in the following examples.

Several 10.2 cm (4 inch) sample wafers were coated with said H-resin using a Headway™ spin coater at 2000 rpm for 40 seconds. The wafers used for the experiments were either bare wafers or wafers having a 100 nm layer of PECVD silicon dioxide ("SiO_2").

The cure system used consisted of a hotplate, a culture petri dish, a modified glass funnel with nitrogen inlets and an infrared temperature reader. The hotplate was first preheated to a temperature of 20°C. to 30°C. higher than the temperature listed in Table 1. Then, the spun wafer was introduced in the petri dish by lifting up the glass funnel during which time the nitrogen flow was 2-3 times that used during the cure process. The surface of the wafer was heated to the desired temperature (typically requiring 30 to 50 seconds), the nitrogen flow was reduced and the wafer was heated for the desired time at the temperature (reported in Table 1). When the coating was cured in air, the above cure process was used except that the nitrogen purge was not used.

Following cure, the petri dish containing the wafer and the funnel were removed from the hotplate surface and cooled rapidly. The nitrogen flow was maintained until the coating surface temperature was below 30°C.

A coating of silicon dioxide was then applied to the wafers by PECVD using 10% SiH_4 in He plus N_2O. The wafer temperature during deposition was 350°C. and the pressure was 400 kPa (3000 Torr).

Results and specific processing conditions are shown in Table 1.

The wafers having thereon a silicon dioxide coating of 170 nm were not produced in a clean room and the coatings contained particles. The cracking was minor and limited to those areas around the particles. Therefore. it is believed that multi-layer coatings wherein the silicon dioxide coatings had a thickness of at least 100 nm will be thermally stable.

Table 1

Cure Condition			Coating Thickness (μm)	SiO_2 Liner Thickness (nm)	Cap Thickness (nm)	Thermal Processing (Cracked? Y/N)			
Temp (C)	Time (min)	Atmosphere				Cure Cycle		450 °C Annealing	
						1	4	N_2	O_2
350	0.33	N_2	1.906	100	300	N	N	N	N
350	0.42	N_2	1.916	100	300	N	N	N	N
350	0.5	N_2	1.901	100	300	N	N	N	N
350	0.75	N_2	1.926	100	300	N	N	N	N
350	1	N_2	1.922	100	300	N	N	N	-
350	0.5	Air	1.521	100	300	N	N	N	-
350	1	Air	1.502	100	300	N	N	N	-
350	2	Air	1.522	100	300	N	N	N	-
250	1.5	Air	1.537	100	300	N	N	N	N
250	2	Air	1.502	100	300	N	N	N	N
250	1.5	Air	1.966	100	300	N	N	-	-
250	1.5	Air	2.023	100	300	N	N	-	-
250	2	Air	1.986	100	300	N	N	-	-
360	1	N_2	1.963	100	1000	N	N	N	-

360	1	N_2	1.877	100	1000	N	N	N	-
360	1	N_2	1.916	100	1000	N	N	N	-
360	1	N_2	2.035	100	1000	N	N	N	-
340	2	N_2	1.987	100	1000	N	N	N	-
340	2	N_2	2.007	100	1000	N	N	N	-
340	2	N_2	2.056	100	1000	N	N	N	-
340	2	N_2	1.947	100	1000	N	N	N	-
320	2	N_2	1.971	100	1000	N	N	N	-
320	3	N_2	2.009	100	1000	N	N	N	-
350	0.33	N_2	1.955	100	none	N	N	Y	-
350	1	N_2	1.922	100	none	N	N	Y	-
250	2	Air	1.986	100	none	N	N	Y	-
350	2	Air	1.522	100	none	N	N	Y	-
340	2	N_2	1.987	100	170	N	N	Y	-
340	2	N_2	2.007	100	170	N	N	Y	-
360	1	N_2	1.963	100	170	N	N	Y	-
360	1	N_2	1.877	100	170	N	N	Y	-

"-" means that the data is unavailable.

Claims

1. A method of producing a multi-layer coating comprising

applying a fillerless composition comprising hydrogen silsesquioxane resin onto a substrate to form a film having a thickness of 1.25μm to 2.25μm;

heating the film at a temperature of 150°C. to 500°C. in an inert or oxygen containing environment for a time sufficient to produce an insoluble coating free of cracks having a thickness of 1.25μm to 2.25μm;

depositing a layer of silicon dioxide having a thickness of at least 100 nm over the insoluble coating.

2. The method as claimed in claim 1 wherein the fillerless composition also contains a solvent and the solvent is removed to form the film.

3. The method as claimed in claim 2 wherein the fillerless composition contains from 50 to 80 wt% solvent.

4. The method as claimed in claim 1 wherein the insoluble coating has a thickness of 1.5μm to 2.2μm.

5. The method as claimed in claim 1 wherein silicon dioxide is deposited by chemical vapor deposition.

6. The method as claimed in claim 1 wherein the silicon dioxide has a thickness of 300 nm to 2μm.

7. The method as claimed in claim 1 wherein the electronic substrate has a layer of primary passivation thereon having a thickness of 30 nm to 300 nm.