(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 May 2003 (01.05.2003)

PCT

(10) International Publication Number
WO 03/035720 A1

(51) International Patent Classification[7]: C08G 77/12, C09D 183/04, H01L 21/312

(21) International Application Number: PCT/US02/31824

(22) International Filing Date: 4 October 2002 (04.10.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/066,261 22 October 2001 (22.10.2001) US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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— *of inventorship (Rule 4.17(iv)) for US only*

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/035720 A1

(54) Title: ETCH-STOP RESINS

(57) Abstract: Silicone resins comprising 5 to 50 mole% of ($PhSiO_{3-x)/2}(OH)_x$) units and 50 to 95 mole% ($HSiO_{(3-x)/2}(OH)_x$), where Ph is a phenyl group, x has a value of 0, 1 or 2 and wherein the cured silicone resin has a critical surface free energy of 30 dynes/cm or higher. These resins are useful as etch stop layers for organic dielectric materials having a critical surface free energy of 40 dynes/cm or higher.

ETCH-STOP RESINS

DESCRIPTION

[0001] This invention pertains to silicone resins comprising 5 to 50 mole% of $(PhSiO_{(3-x)/2}(OH)_x)$ units and 50 to 95 mole% $(HSiO_{(3-x)/2}(OH)_x)$, where Ph is a phenyl group, x has a value of 0, 1 or 2 and wherein the cured silicone resin has a critical surface free energy of 30 dynes/cm or higher. These resins are useful as etch stop layers for organic dielectric materials having a critical surface free energy of 40 dynes/cm or higher.

[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. The coatings may be formed by chemical vapor deposition or by spin-on techniques. For example, U.S. Patent No. 4,756,977 discloses the use of hydrogen silsesquioxane resins to form coatings on electronic devices.

[0003] One method for forming the integrated circuits is known as dual damascene. This method involves applying a layer of dielectric, etching the wiring pattern into the dielectric, filling the pattern with wiring metal, and repeating the process until the desired number of levels have been formed.

[0004] It has become beneficial to use at least two different materials having differing etch characteristics to produce the dielectric layer. In essence, one dielectric material serves as an etch-stop in etching of the other dielectric. It is preferred that one of the dielectric layers be an organic material while the other be an inorganic material to enhance etch selectivity between the materials. Either dielectric layer may serve as the etch-stop to the other. In oxygen-based plasmas, organic dielectrics tend to etch faster than inorganic dielectrics. In carbon fluoride based plasmas, inorganic dielectrics tend to etch faster than organic dielectrics. Sandwich structures of inorganic, organic, inorganic or organic, inorganic, organic are also useful as the dielectric layer in the integrated circuit.

[0005] PCT Patent Application No. WO 01/18861 A1 to AlliedSignal a microelectronic device having a substrate and a first dielectric layer material positioned on the substrate. A layer of a second dielectric material is positioned on the first dielectric layer and an additional

layer of the first dielectric material positioned on the second dielectric layer. The organic dielectrics are materials that contain carbon and the inorganic dielectrics are materials that are not carbon containing.

[0006] U.S. Patent No. 6,218,317 discloses the formation of methylated-oxide type hardmasks over polymeric interlayer dielectric materials having a dielectric constant of less than 3 and more preferably 2.7 or less.

[0007] When using two or more dielectric layers, it is desirable that the upper material be able to adequately coat the lower level (i.e. wet the surface). It is also desirable to have sufficient adhesion between the layers.

[0008] This invention pertains to silicone resins comprising 5 to 50 mole% of $(PhSiO_{(3-x)/2}(OH)_x)$ units and 50 to 95 mole% $(HSiO_{(3-x)/2}(OH)_x)$, where Ph is a phenyl group, x has a value of 0, 1 or 2 and wherein the cured silicone resin has a critical surface free energy of 30 dynes/cm or higher. These resins are useful as etch stop layers for organic dielectrics having a critical surface free energy of 40 dynes/cm or higher.

[0009] This invention also pertains to an integrated circuit device having a an organic dielectric layer having a critical surface free energy of 40 dynes/cm or higher and a phenylated-oxide dielectric layer having a critical surface free energy of 30 dynes/cm or higher produced from the silicone resin, wherein at least one surface of the organic dielectric layer contacts a surface of the phenylated-oxide dielectric layer.

[0010] This invention pertains to silicone resins comprising 5 to 50 mole % of $(PhSiO_{(3-x)/2}(OH)_x)$ units and 50 to 95 mole % $(HSiO_{(3-x)/2}(OH)_x)$ units based on the total amount of silicon containing units in the resin, where Ph is a phenyl group, x has a value of 0, 1 or 2.

[0011] The silicone resins contain 5 to 50 mole % of $(PhSiO_{(3-x)/2}(OH)_x)$ units, alternatively 25 to 50 mole %, alternatively 30 to 45 mole %. Higher amounts of $(PhSiO_{(3-x)/2}(OH)_x)$ in the silicone resin results in higher amounts of carbon in the phenylated dielectric layer. This reduces the etch selectivity between the phenylated-oxide dielectric layer and the organic dielectric layer. Additionally, higher amounts of carbon in the final

film contributes to lower adhesion of the phenylated-oxide dielectric layer to the organic dielectric layer.

[0012] For the silicone resin to have utility as a dielectric layer in combination with an organic dielectric layer it is desirable to have a critical surface free energy of 30 dynes/cm or higher in cured silicone resin. For every 1 mole % increase in $(PhSiO_{(3-x)/2}(OH)_x)$ in the silicone resin it is theorized that the critical surface free energy in the cured resin increases 0.31 dyne/cm. Thus, higher amounts of $(PhSiO_{(3-x)/2}(OH)_x)$ units in the silicone resin are desirable however, it has been found that as the amount of $(PhSiO_{(3-x)/2}(OH)_x)$ units increase the adhesion of the cured silicone resin to the organic dielectric layer decreases. It is preferred that the cured silicone resin have a critical surface free energy in the range of 35 to 60 dynes/cm, more preferably 35 to 45 dynes/cm.

[0013] The structure of the silicone resin is not specifically limited. The silicone resin may be essentially fully condensed or may be only partially condensed. When the silicone resin is partially condensed less than 40 mole % of the units in the silicone resin should contain Si-OH groups. Higher amounts of these units can result in instability in the resin and the formation of gels. Typically 6 to 38 mole % of the units in the silicone resin contain Si-OH groups.

[0014] The silicon resin has a weight average molecular weight (Mw) in the range of 500 to 400,000 and preferably in the range of 500 to 100,000, alternatively 700 to 10,000.

Silicone resins useful herein may be exemplified by, but not limited to

$(PhSiO_{3/2})_a(HSiO_{3/2})_d$

$(PhSiO_{3/2})_a(PhSiO_{2/2}(OH))_b(HSiO_{3/2})_d$

$(PhSiO_{3/2})_a(PhSiO_{2/2}(OH))_b(HSiO_{3/2})_d(HSiO_{2/2}(OH)_e$

$(PhSiO_{3/2})_a(HSiO_{3/2})_d(HSiO_{2/2}(OH)_e$

$(PhSiO_{3/2})_a(PhSiO2/2(OH))_b(PhSiO_{1/2}(OH)_2)_c(HSiO_{3/2})_d$

$(PhSiO_{3/2})_a(PhSiO_{2/2}(OH))_b(PhSiO_{1/2}(OH)_2)_c(HSiO_{3/2})_d(HSiO_{2/2}(OH)_e$

where $a > 0$, $b \geq 0$, $c \geq 0$, $d > 0$, $e \geq 0$, $0.05 \leq a+b+c \leq 0.5$, $0.5 \leq d+e \leq 0.95$ and $b+c+e \leq 0.4$.

[0015] The resins may be produced by methods known in the art. For example, the resins may be produced by the hydrolysis and condensation of a mixture of a phenyl trialkoxy and

hydrogen trialkoxy silane as set forth in U.S. Patent No. 5,762,697 to Sakamoto et al. Alternatively they may be produced by the hydrolysis and condensation of a phenyl trichlorosilane and hydrogen trichlorosilane as set forth in U.S. Patent No. 6,281285 to Becker et al. and U.S. Patent No. 5,010,159 to Bank et al.

[0016] The silicone resin is typically produced in the presence of a solvent. Any suitable organic or silicone solvent that does not contain a functional group which may participate in the reaction may be used in producing the silicone resin. The solvent is generally used in an amount of 40 to 98 weight percent based on the total weight of solvent and silane reactants, alternatively 70 to 90 weight percent. The reaction may be carried out as a dual phase or single-phase system.

[0017] Useful organic solvents may be exemplified by, but not limited to, saturated aliphatics such as n-pentane, hexane, n-heptane, and isooctane; cycloaliphatics such as cyclopentane and cyclohexane; aromatics such as benzene, toluene, xylene, mesitylene; ethers such as tetrahydrofuran, dioxane, ethylene glycol diethyl ether, ethylene glycol dimethyl ether; ketones such as methylisobutyl ketone (MIBK) and cyclohexanone; halogen substituted alkanes such as trichloroethane; halogenated aromatics such as bromobenzene and chlorobenzene; esters such as isobutyl isobutyrate and propyl propronate. Useful silicone solvents may be exemplified by, but not limited to cyclic siloxanes such as octamethylcyclotetrasiloxane, and decamethylcyclopentasiloxane. A single solvent may be used or a mixture of solvents may be used.

[0018] The reaction to produce the silicone resin can be carried out at any temperature so long as it does not cause significant gellation or cause curing of the silicone resin. Typically the reaction is carried out at a temperature in the range of 5 °C to 150 °C, with ambient temperature suggested.

[0019] The time to form the silicone resin is dependent upon a number of factors such as the temperature, the type and amount of silane reactants, and the amount of catalyst, if present. Typically the reaction time is from several minutes to several hours. One skilled in the art will be able to readily determine the time necessary to complete the reaction.

[0020] Following completion of the reaction the catalyst may be optionally removed. Methods for removing the catalyst are well know in the art and would include neutralization, stripping or water washing or combinations thereof. The catalyst may negatively impact the shelf life of the silicone resin especially when in solution thus its removal is suggested.

[0021] In the process for making the silicone resin, after the reaction is complete, volatiles may be removed from the silicone resin solution under reduced pressure. Such volatiles include alcohol by-products, excess water, catalyst, hydrochloric acid (chlorosilane routes) and solvents. Methods for removing volatiles are known in the art and include, for example, distillation.

[0022] Following the reaction to produce the silicone resin a number of optional steps may be carried out to obtain the silicone resin in the desired form. For example, the silicone resin may be recovered in solid form by removing the solvent. The method of solvent removal is not critical and numerous methods are well known in the art (e.g. distillation under heat and/or vacuum). Once the silicone resin is recovered in a solid form, the resin can be optionally re-dissolved in the same or another solvent for a particular use. Alternatively, if a different solvent, other than the solvent used in the reaction, is desired for the final product, a solvent exchange may be done by adding a secondary solvent and removing the first solvent through distillation, for example. Additionally, the resin concentration in solvent can be adjusted by removing some of the solvent or adding additional amounts of solvent.

[0023] This invention also pertains to forming a dielectric material in an integrated circuit device wherein the dielectric material is comprised of at least one layer of an organic dielectric having a critical surface free energy of at least 40 dynes/cm and a second phenylated-oxide dielectric layer produced from the silicone resin of this invention and having a critical surface free energy of at least 30 dynes/cm.

[0024] The benefit of this "dual layer" dielectric material is that one dielectric layer is able to serve as an etch stop layer for the other. Good surface wetting can be achieved by the use of a phenylated-oxide inorganic layer having a critical surface free energy of at least 30 dynes/cm with an organic dielectric having a critical surface free energy of at least 40 dynes/cm. By having good surface wetting one is able to achieve an essentially uniform coating of one material over the other.

[0025] The organic dielectric layer may be produced by methods known in the art, using materials known in the art. One suitable organic dielectric material is SiLK™ manufactured by Dow Chemical Co. This material produces a dielectric layer having a critical surface free energy of 53 dynes/cm. SiLK™ may be processed using conventional spin coating techniques and equipment.

[0026] The silicon resin may be used to prepare a phenylated-oxide dielectric layer by

(I) coating a semiconductor substrate with a silicone resin comprising 5 to 50 mole% of ($PhSiO_{(3-x)/2}(OH)_x$) units and 50 to 95 mole% ($HSiO_{(3-x)/2}(OH)_x$), where Ph is a phenyl group, x has a value of 0, 1 or 2 and

(II) heating the coated semiconductor substrate at a temperature sufficient to cure the silicone resin and produce a phenylated-oxide dielectric layer.

[0027] The semiconductor substrate may contain an organic dielectric layer, over which the phenylated-oxide dielectric layer is formed. Alternatively the phenylated-oxide dielectric layer may be formed first and the organic dielectric layer is then formed over the phenylated-oxide dielectric layer.

[0028] The silicone resin is typically applied to the substrate as a solvent dispersion. Solvents that may be used include any agent or mixture of agents that will dissolve or disperse the silicon resin to form an essentially homogeneous liquid mixture. The solvent is typically a single solvent or mixture of solvents that are used in the reaction to produce the silicone resin, described above. Suggested solvents are propylene glycol methyl ether acetate, cyclohexanone, γ-butyrolacetone, methyl isobutyl ketone, methyl propyl ketone, mesitylene, and silicones.

[0029] The amount of solvent is not particularly limited but is typically present in an amount of 40 to 99.5 % by weight, alternatively 60 to 99.5 % based on the weight of silicone resin and solvent.

[0030] Specific methods for application of the silicone resin to the substrate include, but are not limited to, spin-coating, dip-coating, spay-coating, flow-coating, screen-printing and others. The suggested method for application is spin-coating.

[0031] When a solvent is used the solvent is removed from the coated substrate following application. Any suitable means for removal may be used such as drying, the application of a vacuum and/or the application of heat (i.e. such as passing a coated wafer over hot plates). When spin coating is used, the additional drying method is minimized since the spinning drives off most of the solvent.

[0032] Following application to the substrate, the coated substrate is heated at a temperature to cure the silicone resin. A cured silicone resin is essentially insoluble in a solvent which may be used for it application to the substrate. Typically the coated substrate

is heated to a temperature in the range of 100 °C to 600 °C to cure the silicone resin, with 100°C to 450°C suggested.

[0033] The atmosphere used during the curing of the resin is not particularly limited. Useful atmosphere include oxygen containing atmospheres such as air and inert atmospheres such as nitrogen, and argon. By "inert" it is meant that the environment contain less than 50 ppm and preferably less than 10 ppm of oxygen. The pressure at which the curing and removal steps are carried out is not critical. The curing is typically carried out at atmospheric pressure however, sub or super atmospheric pressures may work also.

[0034] Any method of heating may be used to cure the silicone resin. For example, the substrate may be placed in a quartz tube furnace, convection oven, rapid thermal processing or allowed to stand on hot plates. Furnaces are commonly used in the industry to produce cured resin films on integrated circuits.

[0035] The layers of dielectric materials may be produced in any order. For example, a layer of organic dielectric may be produced on a semiconductor substrate and thereafter a layer of inorganic dielectric may be formed thereon. Alternatively, a layer of inorganic dielectric may be produced on the semiconductor substrate and thereafter a layer of organic dielectric may be produced thereon. Additionally, sandwich structures or multiple layers may be formed. For example, a layer of organic dielectric may be produced on the substrate followed by a layer of inorganic dielectric, followed by another layer of organic dielectric.

[0036] The following non-limiting examples are provided so that one skilled in the art may more readily understand the invention. In the following examples, Ph represents phenyl, Me represents methyl, T represent the unit $SiO_{3/2}$ (i.e. $T^{Ph} = PhSiO_{3/2}$).

[0037] Critical surface free energy (surface energy) was measured using contact angle based on a process under ASTM D 724.

[0038] Adhesion was measured using a stud pull procedure.

EXAMPLES

Example 1.

[0039] To ethylene glycol dimethyl ether (EGDME) was added the corresponding alkoxysilanes in the amounts given in the table 1. The solution of EGDME and alkoxysilane was stirred for several minutes, following which deionized water containing 100 ppm nitric acid catalyst was added. The mixture was vigorously stirred at room temperature for 4 days. After stirring propylene glycol methyl ether acetate (PGMEA) was added. The original solvent (ethylene glycol dimethyl ether), residual water, alcohol by-products and residual nitric acid were removed from the solution by rotary evaporation, leaving the resin product (10 wt.%) in propylene glycol methyl ether acetate solution.

Example 2.

[0040] Ethylene glycol dimethyl ether (EGDME), phenyltrichlorosilane and trichlorosilane were added into a flask reactor in the amounts shown in Table 2. The solution was cooled to 10-12°C, while maintaining the solution under a nitrogen atmosphere. In a separate flask EGDME and water were combined in the amounts shown in Table 2. The water/EGDME solution was added to the chlorosilane/EGDME over the time shown in Table 2. After the addition the solution was allowed to warm to 20°C and stirred for the time shown in Table 2 (Bodying time) to body the formed resin. 200 grams of propylene glycol methyl ether acetate (PGMEA) was added to the solution. Using a rotary evaporator at 40°C, the solution was concentrated to approximately 21 weight % resin content to remove the EGDME solvent. To the resin solution was then added 30 g of ethanol to the solution and the flask contents rotary evaporated to remove the ethanol and residual water and hydrochloric acid. The solution was then diluted to 10 weight % resin by addition of PGMEA. Example 2-2 was carried out in PGMEA instead of EGDME.

Table 1

Example	$HSi(OEt)_3$ (grams)	$PhSi(OMe)_3$ (grams)	Water (grams)	EGDME (grams)	Molecular Weight Mw(Mn)	SiOH level (mole%)	Target Composition*	Actual Composition*
1-1	100.00	40.23	43.82	370.00	1976 (951)	15.7	$T^{Ph}_{0.25}T^{H}_{0.75}$	$T^{H}_{0.71}T^{H,OH}_{0.07}T^{Ph}_{0.13}T^{Ph,OH}_{0.09}T^{Ph,(OH)2}_{0.01}$
1-2	55.00	66.38	36.15	380.00	804 (601)	38.22	$T^{Ph}_{0.50}T^{H}_{0.50}$	$T^{H}_{0.46}T^{H,OH}_{0.16}T^{Ph}_{0.13}T^{Ph,OH}_{0.23}T^{Ph,(OH)2}_{0.02}$
1-3	130.00	22.41	48.83	356.00	2944 (1171)	17.1	$T^{Ph}_{0.125}T^{H}_{0.875}$	$T^{H}_{0.77}T^{H,OH}_{0.12}T^{Ph}_{0.04}T^{Ph,OH}_{0.05}T^{Ph,(OH)2}_{0.01}$
1-4	160.00	4.95	53.94	350.00	9188 (2137)	14.3	$T^{Ph}_{0.025}T^{H}_{0.975}$	$T^{H}_{0.86}T^{H,OH}_{0.14}T^{Ph}_{0.00}T^{Ph,OH}_{0.01}$

*Ratio given in molar values.

Table 2

Example No.	$PhSiCl_3$ (g)	$HSiCl_3$ (g)	EGDME 1 (g)	EGDME 2 (g)	Water (g)	Addition Time, hr	Bodying Time, hr	Target Composition*	Actual Composition*
2-1	40	63	316	80	23	0.75	2.00	$T^{Ph}_{0.25}T^{H}_{0.75}$	$T^{Ph,OH}_{0.07}T^{Ph}_{0.23}T^{H}_{0.72}$
2-2	42	81	PGMEA 304	PGMEA 615	30	2	0.75	$T^{Ph}_{0.25}T^{H}_{0.75}$	$T^{Ph,OH}_{0.08}T^{Ph}_{0.17}T^{H}_{0.75}$
2-3	81	52	617	121	30	1	1.5	$T^{Ph}_{0.50}T^{H}_{0.50}$	$T^{Ph,(OH)2}_{0.07}T^{Ph,OH}_{0.25}T^{Ph}_{0.22}T^{H}_{0.46}$
2-4	61	69	612	120	30	1.5	3,5	$T^{Ph}_{0.36}T^{H}_{0.64}$	$T^{Ph,(OH)2}_{0.02}T^{Ph,OH}_{0.135}T^{Ph}_{0.2}T^{H}_{0.64}$
2-5	54	74	613	120	30	1.5	3.5	$T^{Ph}_{0.32}T^{H}_{0.68}$	$T^{Ph,(OH)2}_{0.04}T^{Ph,OH}_{0.14}T^{Ph}_{0.16}T^{H}_{0.67}$

Comparative Example 1.

[0041] Concentrated hydrochloric acid (37 percent in water), octylsodium sulfate and toluene (1) in the amounts given in Table 3 were combined. The solution was stirrer at 1200 rpm at 20°C to mix the two phases. Into a separate flask were added toluene (2), trichlorosilane and methyltrichlorosilane in the amounts given in Table 3. The mixture of chlorosilanes and toluene were combined over 4 hours while maintaining vigorous stirring. The resulting resin was bodied for a minimum of 4 hours at 20°C. The stirrer was then stopped and the phases allowed to separate. The concentrated hydrochloric acid phase was removed and discarded. The organic phase was washed 8 times with 1L portions of deionized water. This was continued until a pH of 4 was achieved. The organic phase was transferred to a flask and concentrated to 30 weight percent resin using a rotary evaporator. Toluene was added to the resin solution to decrease the resin concentration to 20 weight percent. To the solution was then added ethanol at a level of 10 weight percent of the total solution weight. The resin was again concentrated with a rotary evaporator to 30 weight percent in order to remove the ethanol and any residual water and hydrochloric acid. The solution was diluted with toluene to 20 weight percent resin.

[0042] The resin was purified by fractionation of the resin by adding acetonitrile to the toluene/resin solution. Typically three resin fractions could be isolated by adding acetonitrile to attain a 0.65 ratio of solution/acetonitrile to precipitate the high molecular weight fraction; a 0.13 ratio to precipitate the middle fraction (40-45 percent of the material), with the final solution containing the low molecular weight material. The middle fraction was used for evaluation purposes and had an average molecular weight of 40,000 as measured by 3D light scattering GPC.

[0043] These materials were dissolved in cyclohexanone for thin film studies at solids concentrations of 7.5 to 10 wt%.

Comparative Example 2.

[0044] Resins were prepared using the same procedure as in Example 1 except that $Me(OMe)_3$ was used in place of $Ph(OMe)_3$. The amounts or reactants and resins produced are in Table 4.

Table 3

Example No.	$MeSiCl_3$ (g)	$HSiCl_3$ (g)	HCl (g)	OSS** (g)	Toluene 1	Toluene 2	Target Composition*
C1-1	149	406	1422	10	3910	700	$T^{Me}_{0.25}T^{H}_{0.75}$
C1-2	299	271	1422	10	3910	700	$T^{Me}_{0.50}T^{H}_{0.50}$

** OSS = Octyl Sodium Sulfate

Table 4

Example	$HSi(OEt)_3$ (grams)	$MeSi(OMe)_3$ (grams)	Water (grams)	EGDME (grams)	Target Composition*
C2-1	30.42	40.23	13.82	100.00	$T^{Me}_{0.25}T^{H}_{0.75}$
C2-2	20.21	16.9	13.92	100	$T^{Me}_{0.50}T^{H}_{0.50}$

Example 4.

[0045] Samples from Examples 1 and 2 were diluted in PGMEA to a concentration of 1 to 3 wt%, filtered and spin-coated onto silicon wafers. The spin rates were selected in the range of 2000 to 5000 RPM to achieve as-spun thickness in the range of 250 angstroms. The coated wafers were heated in a rapid thermal processor in a nitrogen atmosphere at 250°C for two minutes to produce the phenylated-oxide coating. Results are given Table 4.

[0046] A second phenylated-oxide layer was produced over the first using the same procedures as above. Results of the film quality (film on film) are given in Table 1.

Table 5

Example Material	Film Quality (Si Wafer)	Surface Energy 250°C Cure	Dk	Adhesion	Film Quality (film on film)
1-1	no dewets	34	3.06	43.9	dewets
1-2	small pores	41	3.01	13.4	small pores
1-3	no dewets	31	3.04	65.3	dewets
1-4	no dewets	31	3.09	59.8	dewets
2-1	no dewets	37.1	--	47.3	no dewets
2-2	no dewets	40.1	3.32	43.9	no dewets
2-3	no dewets	40.8	3.10	4.4	no dewets
2-4	no dewets	37	3.35	60.6	no dewets
2-5	no dewets	35.5	3.38	59.1	no dewets

Comparative Example 3.

[0047] Samples from Comparative Examples 1 and 2 were diluted in PGMEA to a concentration of 1 to 3 wt %, filtered and spin-coated onto silicon wafers. The spin rates were selected in the range of 2000 to 5000 RPM to achieve as-spun thickness in the range of 250 angstroms. The coated wafers were heated in a rapid thermal processor in a nitrogen atmosphere at 250°C for two minutes to produce a methylated-oxide coating. Results are given Table 6.

Table 6

Target Composition	Example No.	Cure Temperature (°C/2 minutes hot plate)	Surface Energy (dyne/cm)	Film Quality
$T^{Me}_{0.25}T^{H}_{0.75}$	C2-1	100	25.5	Dewets
$T^{Me}_{0.25}T^{H}_{0.75}$	C2-1	150	29.5	Dewets
$T^{Me}_{0.50}T^{H}_{0.50}$	C2-2	150	29.9	Dewets
$T^{Me}_{0.50}T^{H}_{0.50}$	C2-2	250	26	Dewets
$T^{Me}_{0.25}T^{H}_{0.75}$	C1-1	250	24.9	Dewets
$T^{Me}_{0.25}T^{H}_{0.75}$	C1-1	350	25.9	Dewets
$T^{Me}_{0.50}T^{H}_{0.50}$	C1-2	250	27.3	Dewets

CLAIMS

1. A silicone resin comprising 5 to 50 mole % of $(PhSiO_{(3-x)/2}(OH)_x)$ units and 50 to 95 mole % $(HSiO_{(3-x)/2}(OH)_x)$ units based on the total amount of silicon containing units in the resin, where Ph is a phenyl group and x has a value of 0, 1 or 2.

2. The silicone resin as claimed in claim 1 wherein there is 25 to 50 mole % of $(PhSiO_{(3-x)/2}(OH)_x)$ units and 50 to 75 mole % $(HSiO_{(3-x)/2}(OH)_x)$ units in the silicone resin.

3. The silicone resin as claimed in claims 1 or 2 wherein less than 40 mole% of the units in the silicone resin contain Si-OH groups.

4. A solution comprising

(I) a silicone resin comprising 5 to 50 mole % of $(PhSiO_{(3-x)/2}(OH)_x)$ units and 50 to 95 mole % $(HSiO_{(3-x)/2}(OH)_x)$ units based on the total amount of silicon containing units in the resin, where Ph is a phenyl group and x has a value of 0, 1 or 2.

(II) 40 to 99.5 wt% of a solvent based pm the weight of (I) and (II).

5. The solution as claimed in claim 5 wherein the solvent is chose from propylene glycol methyl ether acetate, cyclohexanone, γ-butyrolacetone, methyl isobutyl ketone, methyl propyl ketone, mesitylene, silicones.

6. A phenylated-oxide dielectric having a critical surface free energy of at least 30 dynes/cm.

7. A method of producing a phenylated-oxide dielectric comprising

(I) applying silicone resin comprising 5 to 50 mole % of $(PhSiO_{(3-x)/2}(OH)_x)$ units and 50 to 95 mole % $(HSiO_{(3-x)/2}(OH)_x)$ units based on the total amount of silicon containing units in the resin, where Ph is a phenyl group and x has a value of 0, 1 or 2 to a substrate,

(II) heating the coated substrate to a temperature in the range of 100°C to 450°C to cure the silicone resin.

8. The method as claimed in claim 7 wherein there is 25 to 50 mole % of $(PhSiO_{(3-x)/2}(OH)_x)$ units and 50 to 75 mole % $(HSiO_{(3-x)/2}(OH)_x)$ units in the silicone resin.

9. The method as claimed in claim 7 wherein less than 40 mole% of the units in the silicone resin contain Si-OH groups.

10. An integrated circuit comprising a dielectric material wherein the dielectric material comprises

(A) at least one organic dielectric layer having a critical surface free energy of at least 40 dynes/cm and

(B) at least one phenylated-oxide dielectric layer having a critical surface free energy of at least 30 dynes/cm.

11. The integrated circuit as claimed in claim 20 wherein the phenylated-oxide dielectric layer is applied over the organic dielectric layer.

12. The integrated circuit as claimed in claim 20 wherein the organic dielectric layer is applied over the phenylated-oxide dielectric layer.

INTERNATIONAL SEARCH REPORT

national Application No
PCT/US 02/31824

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G77/12 C09D183/04 H01L21/312

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 C08G C09D H01L C08L

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)

WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 281 285 B1 (BECKER ET AL) 28 August 2001 (2001-08-28) claim 20	1
A	EP 0 419 076 A (DOW CORNING) 27 March 1991 (1991-03-27) page 5, line 5 - line 10	1
A	US 5 169 909 A (OKAWA) 8 December 1992 (1992-12-08) example 3	1

☐ 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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 February 2003	28/02/2003

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	Lentz, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

[redacted]ational Application No
PCT/US 02/31824

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