Silicones in Coatings III

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High Density Silicon Dioxide Coatings by UV and Thermal Processing

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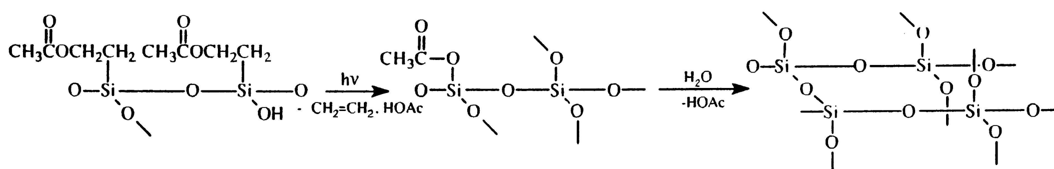
Abstract

Silsesquioxanes containing β electronegative groups are processible resins that can be applied as thin film precursors of dielectric and abrasion resistant coatings. Both UV (<215nm) and thermally driven (>280°C) cures convert the silsesquioxanes to silicon dioxide. The cure mechanism is dependent on the extrusion of ethylene with concomitant transfer of the electronegative group to silicon which then undergoes facile hydrolysis.



A minor pathway involving elimination of the protonated electronegative group can be utilized to modify the resins by organic group incorporation. The introduction of fluoride ion catalysts greatly accelerates the major pathway, lowering conversion temperatures to less than 200°C. A review of the chemistry, processing and film properties is presented.

Background

Commercial Abrasion Resistant Coatings (ARCs) show a broad elaboration of silsesquioxane or T-resin technology. Simple unmodified methylsilsesquioxane resins of controlled molecular weight and hydroxyl content were the earliest examples of abrasion resistant coatings. Current ARC technology rarely uses unmodified materials, although they retain important roles in electrical component coatings such as resistors and molding compounds as well as spin-on dielectrics (SOD) in microelectronic interlayer dielectric and planarization applications. The materials are prepared by controlled hydrolysis of alkyltrialkoxysilanes.

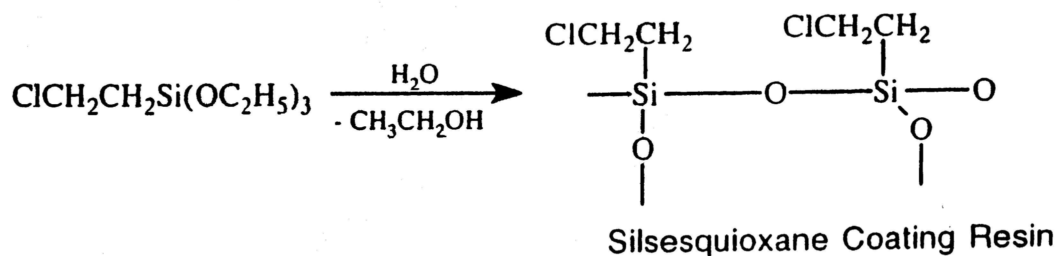
The most widely used technologies for producing high density silicon dioxide films suitable for dielectric, passivation and diffusion layers in microelectronic and optoelectronic devices usually involves plasma reaction of silane and oxygen or at atmospheric pressure, ozone and tetraethoxysilane. These process methods are incompatible with the desired future thermal budgets or product throughputs for these devices. Deposition of silicon dioxide coatings by spin-on has not

achieved broad commercial application due to physical property limitations imposed by process parameters. The spin-on glass (SOG) approach to ceramic films is an example of sol-gel processing. Sol-gel chemistry operates by generating a skeletal network of oxane bonds under low temperature conditions which ultimately develop ceramic or, as in the case of the organic modified silica (ormosil), near ceramic properties. Intrinsic in the generation of these materials is a succession of highly polar and hydrogen bond mediated reactions that are responsible for the formation of the oxane bonds and the transport and extrusion of water molecules. These processes are responsible for shrinkage and stress development. Currently, sol-gel technology entails the deposition of silicon dioxide from supersaturated solutions, usually formed by the hydrolysis of reactive precursors (alkoxysilanes). The systems are unstable, difficult to control, and usually contain byproducts (alcohols), in addition to water which must be removed from the matrix. A limiting factor during the formation of SiO2 by sol-gel methods is the rigidity of the quaternary oxane bonded silicon (Q-group) rich matrix at intermediate stages of hydrolysis.

Chemistry

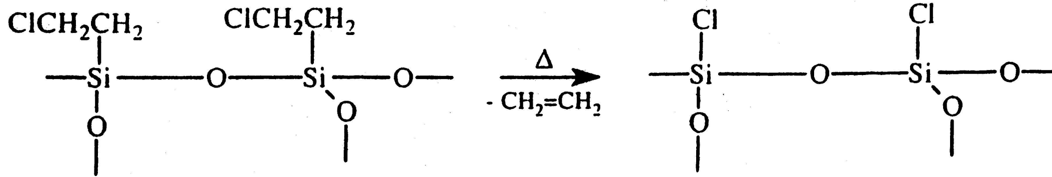
Masked hydrolysis/condensation centers is one option for controlling the deposition of silicon dioxide. The mask must be stable over a broad range of hydrolysis conditions, be removed by a mechanism that is distinct from hydrolysis, generating only low molecular weight (volatile) species and resin sites susceptible to hydrolysis and condensation. We have previously reported an approach to SOG materials based on "hydrolysis in stages:" using β-chloroethyl-silsequioxanes and related resins as silica precursors.[1,2]

First Stage Hydrolysis



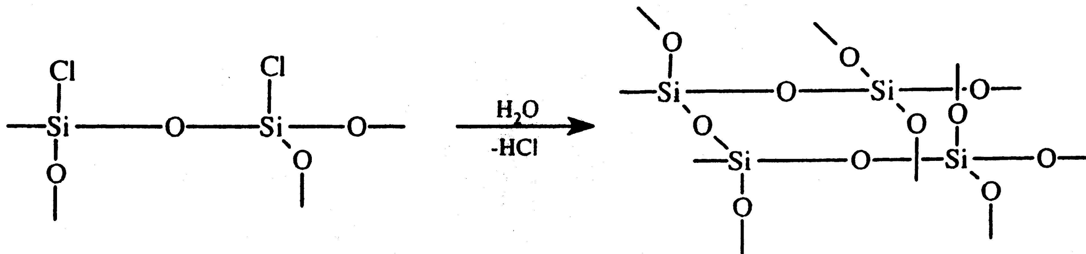
Silsesquioxane Coating Resin

Demasking



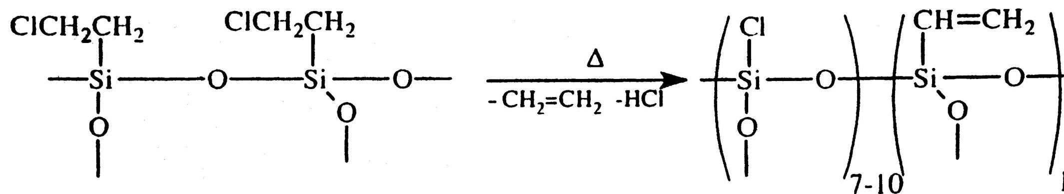
Silsesquioxane Coating Resin

Second Stage Hydrolysis — Silica Formation



Generation of initial skeletal frameworks at appropriate molecular weights and crosslink densities to maintain processabitity can be conceptualized as part of a two-stage hydrolysis and condensation scheme. In the first stage, partial hydrolysis of OE monomers leads to prepolymers with molecular weights sufficient to account for the formation and removal of a significant portion of byproducts. The prepolymers are stable, soluble and retain a significant number of hydroxyl or silanol groups. In the second stage, the mask is is removed from the resin and the condensation of remaining hydrolyzable sites proceeds, forming the ultimate ceramic.

Under UV conditions the demasking is quite clean, resulting in pure silica[3]. Under thermal process conditions, the demasking or elimination step is not always clean due to a minor reaction pathway which ultimately results in the incorporation of low levels of carbon.



The thermal process can be altered to give essentially pure silicon dioxide by incorporation of fluoride ion catalysts such as tetrabutyammonium fluoride.[4] The catalyst also lowers the temperature requirements for thermal conversion.

Silsesquioxane Properties

Silsesquioxane Synthesis

The β-substituted ethylsilsesquioxane prepolymers were prepared either by direct hydrolysis of β-substituted ethyltrichlorosilane or the β-substituted ethyltriethoxysilane. Examples of the two methods follow.

Silsesquioxane from halosilane. β-chloroethyltrichlorosilane (25.0g, 0.126M) was added dropwise to 250 mL of deionized water at a temperature of 0-5°. Upon completion of the addition, 200 mL of dichloromethane was added to the reaction mixture and stirred for 10 minutes, in order to extract the polymeric reaction products. The organic phase was separated and retained. The mixture was then filtered to remove a small amount of particulates. After evaporation of the solvent, the recovered silsesquioxane prepolymer was dried overnight under high vacuum to yield a clear resin in an amount of 10.65 g (73% of theory). The β-chloroethylsilsesquioxane (BCESQ) was determined to have a number average molecular weight (Mn) of 750-1250 and a weight average molecular weight (Mw) of 1200-1600. NMR indicated an approximate ratio of 1 hydroxyl group for every 3 silicon-atoms.

Silsesquioxane from alkoxysilane. Water (1.17g, 0.065 mol) was added dropwise to a solution of β-chloroethyltriethoxysilane (4.0g, 0.216 mol) in methanol (2.07g, 0.065 mol). Four drops of 0.01 M HCl were added. The reaction mixture immediately became more viscous. Solvent was allowed to evaporate over a period of four days. The polymeric reaction product, β-chloroethyl-silsesquioxane, was a dense clear hard resin that was slightly soluble in tetrahydrofuran. The 2-chloroethylsilsequioxane was determined to have a number average molecular weight (Mn) of 4500-4700 and a weight average molecular weight (Mw) of 9000-11,000.

monomer	Mn	Mw	Yield
$ClCH_2CH_2SiCl_3$	780	1320	73%
$BrCH_2CH_2SiCl_3$	1200	2870	78%
$ClCH_2CHClSiCl_3$	340	620	26%
$ClCH_2CH_2Si(OC_2H_5)_3$	4600	10,400	>90%
$CH_3COOCH_2CH_2SiCl_3$	~2000	~4000	

The silsesquioxanes form stable solutions in moderately polar solvents such as diglyme, methylene chloride, tetrahydrofuran and methoxypropanol.

β-Chloroethylsilsesquioxane (BCESQ) in methoxpropanol

concentration:	15%
density:	0.96g/cc
viscosity:	4 cSt.
flashpoint:	35°C

Thin film preparation

Thin films in these studies were prepared by spin coating (2000 rpm) on silicon (100) waters, UV grade quartz or sodium chloride. The films are subsequently converted by thermal or UV methods to high density silicon dioxide films.

Properties of the solvent-free β-Chloroethylsilsesquioxane films
film thickness ~2000Å
refractive index: 1.51
density: 1.45g/cc
UV absorbance, max.: 200(vs), 230, 285nm

Uncatalyzed thermal conversion

Thermal conversion of resins begins at temperatures as low as 180°C, but does not proceed at significant rates until temperatures of 300°C. Minimal carbon incorporation is achieved by cure at 350°-450°C in presence of air. Humidity is considered to be an essential element in reaching maximum film

densities. Bulk mass loss is 52%, resulting in ceramic films about one-half the thickness of as-cast BCESQ.

Properties of ceramic films prepared by thermal conversion of β-Chloroethylsilsesquioxane (BCESQ) at 450°C for 2 hours in air.

density: 1.88 (~85% of thermally grown oxide)
roughness, rms: 0.39 nm
dielectric constant: 3.2-4.1
composition: 30% Si, 50% O, 8% C, 6% H, <1% Cl (none detected)

UV conversion

UV conversions of resins have been effected with low pressure mercury lamps (184.9 nm), zinc lamps (213.9nm) and ArF lasers (193nm). The results previously reported eliminated possible ozone or thermal induced cure processes. Insults from ArF lasers indicate that the reaction is completed at an integrated fluence of ~100J/cm^2. Dielectric properties are optimized by heating films to 250° after UV exposure.

Properties of ceramic films prepared by UV conversion of β-Chloroethylsilsesquioxane (BCESQ)

refractive index: 1.44
density: 1.71
dielectric constant: 3.2-3.6
composition: SiO_2 (C, Cl non-detected, 9-10 at% H)
UV absorbance max: none >190nm

Catalyzed thermal conversion

The low temperature conversion of resins can be facilitated by the addition of a fluoride ion catalyst such as tetrabutylammonium fluoride. The reaction begins at temperatures less than 200°C and leads to carbon-free silicon dioxide. Experimental protocols have been cure for 2.5 hours at 190°C followed by 1.5 hours at 350°C.

Properties of ceramic films prepared by thermal conversion of β-Acetoxyethylsilsesquioxane (BAESQ) w/ 5% tetrabutylammonium fluoride

roughness, rms: 0.35 nm
composition: 43.6% Si, 53.1% O, 0.9% C, 0.9% H, 1.5% F

Conclusion

Beta-substituted silsesquioxanes offer a new approach to uniform high density silicon dioxide films. Simple synthetic methods allow preparation of films with a range of crosslink densities and organic modification. Catalyzed and catalyzed thermal processing and UV laser and lamp cures allow the fabrication of silicon dioxide films for optical, dielectric and abrasion resistant coatings.

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2. Q. Pan, G. Gonzalez, R. Composto, W. Wallace, B. Arkles, L. Figge, D. Berry, Thin Solid Films, *345*, 244, 1999.

3. J. Sharma, D. Berry, R. Composto, H. Dai, J. Mater. Res., 14, 990, 1999

4. K. Ezbiansky, B. Arkles, R. Composto, D. Berry, in "Chemical Process. of Dielectrics, Insulators and Electron. Ceram., MRS Symp Series.", 2000 (in press).

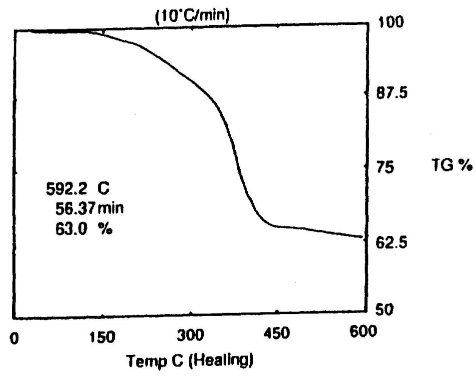

Figure 1. β-chloroethylsilsesquioxane—TGA in argon.

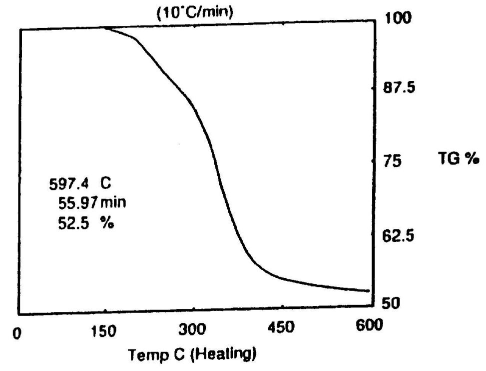

Figure 2. β-chloroethylsilsesquioxane—TGA in air.

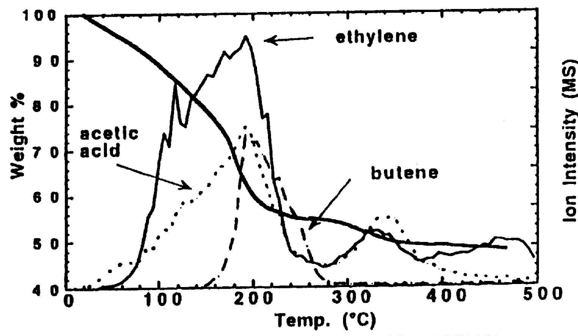

Figure 3: TGA/MS of BAE resin with 5% TBAF.

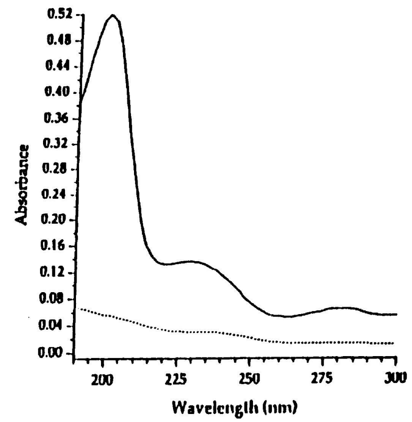

FIG. 4. Ultraviolet absorption spectrum taken before (solid line) and after (dotted line) irradiation by 193 nm laser with integrated fluence = 284 ± 28 J/cm^2.