

## Staged Development of Modified Silicon Dioxide Films

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**Abstract.** The hydrolytic generation of SiO<sub>2</sub> films from chlorosilanes or alkoxy silanes is interrupted by incorporating labile organic groups which stop SiO<sub>2</sub> formation at a processable prepolymer stage. The monomers for the prepolymer have electron withdrawing substituents in the  $\beta$ -position. The organic groups are removed from the prepolymer at low temperature, extruding ethylene. The formation of SiO<sub>2</sub> proceeds by intramolecular condensation of the electronegative substituents which are now in a hydrolytically unstable bond with silicon and hydroxyl groups or ambient moisture. Films of the prepolymer spun onto silicon wafers are converted into uniform SiO<sub>2</sub>-rich films at temperatures between 150–400°C.

**Keywords:**  $\beta$ -chloroethylsilsequioxane,  $\beta$ -chloroethyltrichlorosilane, spin-on glass, thermal conversion, dielectric films, silicon dioxide

### Introduction

Spin-On Glasses (SOG) perform critical roles as interlayer dielectrics in current microelectronic device technology. The demand for materials with improved gap-filling and planarization properties and lower capacitance is challenging current technology. The broader definition of Spin-On Dielectric (SOD) recently accepted by the micro-electronic industry provides an opportunity for modification both on compositional and process levels compared to conventional SOGs.

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 ormosils, 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 (alkoxy silanes). 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 SiO<sub>2</sub> by sol-gel methods is the rigidity of the quaternary oxane bonded silicon (Q-group) rich matrix at intermediate stages of hydrolysis. In order for sol-gel to achieve a greater part of its potential, it would be beneficial to develop a method by which an initial skeletal framework containing a high concentration of silicon-oxygen bonds is formed, hydrolysis byproducts are removed,

the material remains processable (soluble or thermoplastic) and can subsequently be transformed to a ceramic or an ormosil with minimal formation of byproducts.

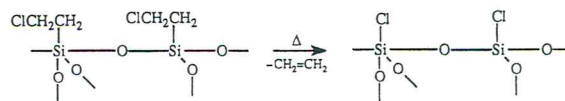
Generation of initial skeletal frameworks at appropriate molecular weights and crosslink densities to maintain processability can be conceptualized as part of a two-stage hydrolysis and condensation scheme. In the first stage, partial hydrolysis of monomers leads to prepolymers with molecular weights sufficient to account for the formation and removal of a significant portion of byproducts. In the second stage, the condensation of remaining hydrolyzeable sites proceeds, forming the ultimate ceramic. The practical problem becomes stopping the hydrolysis cleanly at the first stage before proceeding to the second. Masking a hydrolysis/condensation center is one option. The mask must be stable over a broad range of hydrolysis conditions, be removed by a mechanism that is distinct from hydrolysis, generate only low molecular weight (volatile) species and generate a site susceptible to hydrolysis or condensation.

The presence of electron withdrawing heteroatoms in alkyl side-chains bonded to silicon provide a mechanism for the cleavage of the groups from silicon. Substituents on the  $\beta$ -carbon particularly activate the Si-C bond towards cleavage. A clear example is provided by the generation of ethylene from  $\beta$ -chloroethyltrichlorosilane by base catalyzed nucleophilic elimination [1, 2]. The reaction of siloxane networks with aqueous base initiated elimination of ethylene from  $\beta$ -chloroethylsilsesquioxane with the formation of sodium silicate has been reported [3].

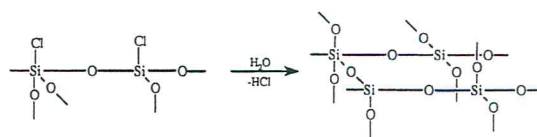


Thermally induced cleavage of these compounds can be expected to proceed by either an intermolecular or an intramolecular process that results in the formation of a direct bond between the silicon and the heteroatom and the extrusion of an olefin. The thermally induced elimination of  $\beta$ -chloroethylsilsesquioxane can be visualized as a migration of the  $\beta$ -chlorine to the silicon with the maintenance of the overall polymer architecture. Both the  $\beta$ -chloroethylsilsesquioxane and chlorosilsesquioxane at moderate molecular weights would be expected to be soluble and maintain

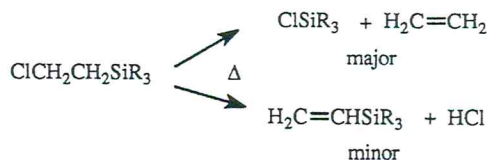
thermoplastic behavior.



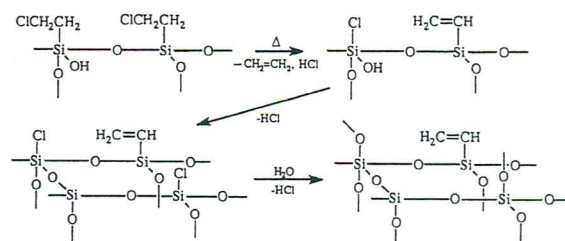
Subsequent hydrolysis would then be anticipated to yield high molecular weight crosslinked structures.



The requirement for water to promote the cross-linking can be reduced by incorporating hydroxyls (silanol) in the polymer. Finally, it is important to note that the elimination of hydrogen chloride competes with ethylene extrusion as described by Davidson et al. [4, 5].



Thus a reaction cascade for  $\beta$ -substituted silanes leading to  $\text{SiO}_2$ -rich structures can be depicted as follows.



In this study, the synthesis and characterization of a variety of silsesquioxane and modified silsesquioxane prepolymers are reported. Preliminary experiments on the thermal conversion of  $\beta$ -substituted silsesquioxane prepolymers to  $\text{SiO}_2$ -rich films are also reported.



## Experimental

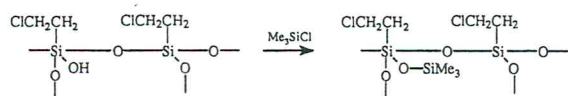
### Precursor Synthesis

The  $\beta$ -substituted halosilanes were synthesized by the catalyzed addition of hydrogen halides to the vinylchlorosilane by published methods. The  $\alpha$ ,  $\beta$ -substituted halosilanes were synthesized by the direct addition of halogens to the corresponding vinylsilanes [6]. Ethoxysilanes were prepared by reaction of the halosilanes with triethylorthoformate.

### Silsesquioxane Synthesis

The  $\beta$ -haloethylsilsesquioxane prepolymers were prepared either by direct hydrolysis of the  $\beta$ -haloethyltrichlorosilane or the  $\beta$ -haloethyltrimethoxysilane. Examples of the two methods follow.

**Silsesquioxane from Halosilane.**  $\beta$ -chloroethyltrichlorosilane (25.0 g, 0.126 mole) 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 mixture was then filtered to remove a small amount of particulates. The organic phase was separated and retained. The aqueous phase was extracted with three additional 100 mL portions of dichloromethane. The washes were combined with the original dichloromethane extract, stirred over sodium sulfate for one hour and then filtered. 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  $\beta$ -chloroethylsilsesquioxane, with reference without correction to polystyrene standards, was determined to have a number average molecular weight (Mn) of 780 and a weight average molecular weight (Mw) of 1320. Residual silanol groups in the silsesquioxane prepolymer were apparent in the infrared spectrum and could be quantified by NMR after reaction with trimethylchlorosilane.



Following derivitization, the silanol absorption ( $\sim 3400 \text{ cm}^{-1}$ ) was absent. The ratio of trimethylsilyl to  $\beta$ -chloroethyl groups was determined by  $^1\text{H}$  NMR to be 1 : 3. Thus if each silicon contains one  $\beta$ -chloroethyl group, approximately every third silicon retains a silanol.

### Modified silsesquioxanes.

Monomer 1	Monomer 2 (mole%)	Mn*	Mw*	Yield
$\text{ClCH}_2\text{CH}_2\text{SiCl}_3$	—	780	1320	73%
$\text{BrCH}_2\text{CH}_2\text{SiCl}_3$		1200	2870	78%
$\text{ClCH}_2\text{CHClSiCl}_3$		340	620	26%
$\text{ClCH}_2\text{CH}_2\text{SiCl}_3$	$(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ (5%)	1580	2580	$\sim 75\%$
$\text{ClCH}_2\text{CH}_2\text{SiCl}_3$	$\text{HSiCl}_3$ (25%)	780	1530	77%

\*Molecular weights reported are GPC values using a polystyrene reference without correction.

**Silsesquioxane from Alkoxysilane.** Water (1.17 g, 0.065 mol) was added dropwise to a solution of  $\beta$ -chloroethyltrimethoxysilane (4.0 g in, 0.216 mol) in methanol (2.07 g, 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,  $\beta$ -chloroethylsilsesquioxane, was a dense clear hard resin that was slightly soluble in tetrahydrofuran. The  $\beta$ -chloroethylsilsesquioxane was determined to have a number average molecular weight (Mn) of 4600 and a weight average molecular weight (Mw) of 10,400.

### Conversion of Silsesquioxanes to Ceramic Films

**Thermal Processing of Silsesquioxane.** A  $\beta$ -chloroethylsilsesquioxane prepared by the halosilane method was prepared as a 15% solution in diglyme. The coating solution was applied by conventional spin-casting techniques onto 75 mm wafers, by spinning at 2000 rpm to yield a coating of 2000 Å in thickness. The wafers were heated to a temperature of 450°C in air, assuring that relative humidity was greater than 10%, for four hours. After this thermal processing, the silicon wafers contained an  $\text{SiO}_2$ -rich ceramic layer in a uniform featureless film that was 1100 Å thick. The resulting ceramic film was analyzed by Rutherford Backscattering Spectroscopy (RBS) measurements and was found to contain (atom basis) 30% Si, 50% O, 8% C, 6% H, <1% Cl. X-ray reflectivity studies indicated

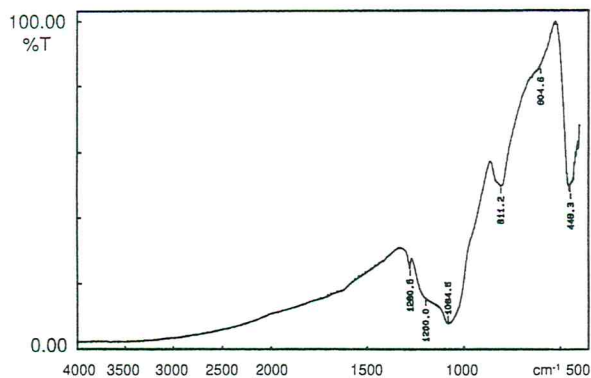
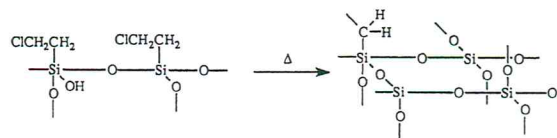


Figure 4.  $\beta$ -chloroethylsilsequioxane—infrared.

accurate for films to as thin as tens of nanometers [8]. An attempt was made to characterize the state of the carbon in the thermally processed films. Calculations suggest that a two carbon unit is bound to approximately 1 out of 8 silicons, but the RBS technique is insensitive to bonding and does not indicate whether the carbon is vinylic or saturated. Separately, bulk  $\beta$ -chloroethylsilsequioxane was processed at  $380^\circ$  to form a yellow-orange powder. The powder was examined by diffuse reflectance infrared spectroscopy (DRIFT) and as a mull in nujol. Strong absorptions were observed at 2975, 1411 and  $1280\text{ cm}^{-1}$ , Fig. 4. The spectrum was consistent with amorphous silicon dioxide with free and hydrogen bonded silanols. However, the absorption at  $1280\text{ cm}^{-1}$ , presumably a silicon-carbon vibration, is unusual since it is at least at  $5\text{ cm}^{-1}$  higher frequency than any previously reported for silicon-carbon. The spectrum indicated the absence of absorption patterns usually associated with vinylic carbon or ethylene bridged silicon. Solid-state NMR studies are planned to determine the exact form of carbon in these films. Above  $600^\circ$  the films turn black, although they retain integrity up to  $1000^\circ$ . These films have not been studied.

## Conclusions

$\beta$ -substituted silsesquioxanes are a new class of precursors for  $\text{SiO}_2$ -rich films. Thermal conversion results in films which incorporate a thermally stable form of carbon.



$\beta$ -substituted silsesquioxanes offer a new process and compositional approach for spin-on dielectrics.

## Acknowledgment

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## Note

1. The unit molecular weight was calculated as 118.60 for a trimeric unit with 1 hydroxyl group.

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