

# MASS SPECTROMETRY OF SPIN-ON-GLASS LOW-K DIELECTRIC PRECURSORS

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## Introduction

Spin-on-glass dielectrics based on silsesquioxanes [1] (SSQ) are emerging as viable low-k interplanar dielectrics for next-generation very-large scale integrated (VLSI) circuitry.[2] The ability to spin-coat a silicon-based prepolymer onto a wafer and convert it at low temperature to silica offers several important advantages. The most important of which is the ability to planarize complex metal topography via the spin coating process thereby reducing the reliance on expensive planarization processes such as chemical-mechanical polishing.[3] A second major benefit is a lower dielectric constant ( $k \leq 3$ ) compared to silica deposited by chemical vapor deposition.[4] This allows for faster signal propagation with less power dissipation and reduced crosstalk. Finally, reflow of SSQ at high temperature, that is, the ability of the spin-on-glass to flow and find its own level during processing further enhances its ability to planarize metal topography and fill narrow gaps.

The silsesquioxane monomer is of the general form  $\text{RSi}(\text{OR}')_3$  where R is an organic substituent group, and R' is an organic leaving group. In the typical hydrolysis-condensation synthesis, this leaving group is hydrolyzed to form a monomer of the form  $\text{RSi}(\text{OH})_3$ . Upon polymerization, some, but not all, of the -OH groups react with one another to form Si-O-Si bridges and residual water. This leads to a final material that is an organic/inorganic hybrid oligomer with the chemical formula  $(\text{RSiO}_{3/2})_n$ . Being trifunctional, the silsesquioxane monomer can form a host of complex three-dimensional oligomers including fully-condensed polyhedral structures, e.g. cubes, (where all the -OH groups condense), ladder structures (where many of the -OH groups condense to form closed rings), and branched, linear structures (where no closed rings are formed). We have examined the reaction parameters for the formation of these various structural types extensively in three previous publications [5-7].

However, there is an alternative way of forming silsesquioxane monoliths. The reaction can polymerize first through the R group to form a polymeric silsesquioxane precursor:  $(\text{RSi}(\text{OR}')_3)_n$ . Then the hydrolysis-condensation reaction can be performed on this prepolymer. We have employed matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry to examine just such a polymer and have been able to make specific statements regarding the molecular structure of any given molecule in the product. In particular, accurate mass spectrometry has allowed us to count the number of residual -OH groups as a function of molecular mass and, therefore, to count the number closed rings per molecule thus quantifying the structure of the sample on an oligomer-specific basis.

## Experimental

3-methacryloxypropyltrimethoxysilane (MPTMS) was first photopolymerized through the methacrylate double bond. A solution of 1.0 g of MPTMS in 9.0 g of dichloromethane was prepared in a sealed vial with virtually no head space. The solution was exposed to sunlight at room temperature for 30 d in order to photopolymerize the MPTMS through its methacrylate group without benefit of a free radical photoinitiator. The course of the photopolymerization was monitored qualitatively by visually noting the increase in viscosity of the solution. There was little further perceptible change in the solution viscosity between 23 d and 30 d. No attempt was made to remove the inhibitor for the MPTMS.

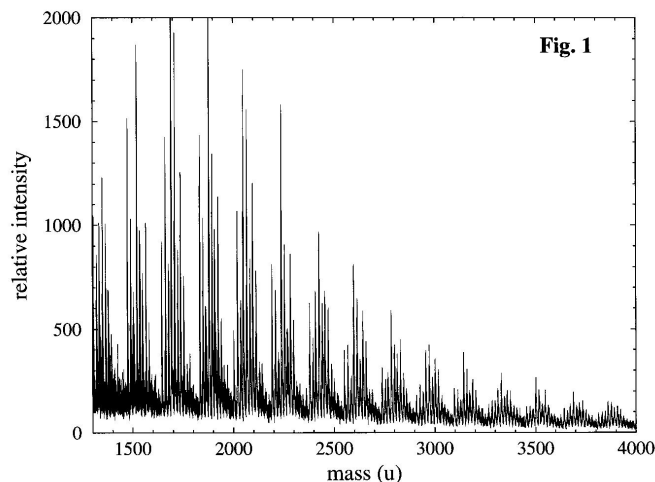
Subsequently, an aliquot of the MPTMS solution was then transferred to a solution of acetone/distilled water (1:1 mass ratio) that contained a mass fraction of 0.05 formic acid. The formic acid acted as a catalyst for the conversion by hydrolysis-condensation of the pendant  $-\text{Si}(\text{OCH}_3)_3$  groups of the MPTMS to yield the polymeric spin-on-glass precursor.

The MALDI-TOF mass spectrometry was performed using sinapinic acid as the matrix with chloroform as the solvent. Cationization occurred due to adventitious sodium. The mass ratio of matrix to analyte used was in the range of 10:1 to 5:1. The targets were prepared by electrospraying at a potential of 5 kV the analyte+matrix solution onto stainless steel target plates.

This resulted in uniform target spots giving good signal at all locations on the plate. The mass spectrometer was used in reflectron mode with delayed extraction at an extraction potential of 25 kV.

## Results

**Figure 1** shows the center portion of a mass spectrum for a typical synthesis. The estimated relative standard uncertainty, defined as the signal-to-noise ratio divided by four, ranges from 3 for the major peaks to 0.5 for the minor peaks of interest. **Figure 2** shows the region around one oligomer of the polymer (where an oligomer is defined as having a given number of silicon atoms,  $n$ ). In the case shown  $n=8$ . For each peak shown  $n$  is constant but the number of lost methyl groups from hydrolysis,  $p$ , varies as does the number of lost water molecules from the subsequent condensation reaction,  $t$ . The loss of a methyl group is given by the reaction  $-\text{SiOCH}_3 \rightarrow \text{SiOH}$ , for a net mass loss of 14 u. The loss of a water molecule is given by  $2(-\text{SiOH}) \rightarrow -\text{SiOSi} + \text{H}_2\text{O}$ , for a mass loss of 18 u. For each loss of water a closed ring is formed *intramolecularly*. In **Figure 2** the peak at the extreme left is identified as  $n:p:t = 8:24:6$  for a mass of 1643 u. (This groups extends to about mass 1649 u due to isotopes.) For  $n=8$  the maximum value for  $p$  is 24 (3x8 methyl groups per oligomer) and the maximum value for  $t$  is 12 (24/2 possible intramolecular condensations). This indicates that this oligomer is fully hydrolyzed but only half condensed. Working to the right the next cluster of isotopes is 8:24:5, and the one to the right of that is two overlapping clusters, 8:23:5 and 8:24:4. In this way the each oligomer in the spectrum can be identified. As we move to the right both the extent of hydrolysis and the extent of condensation decrease.



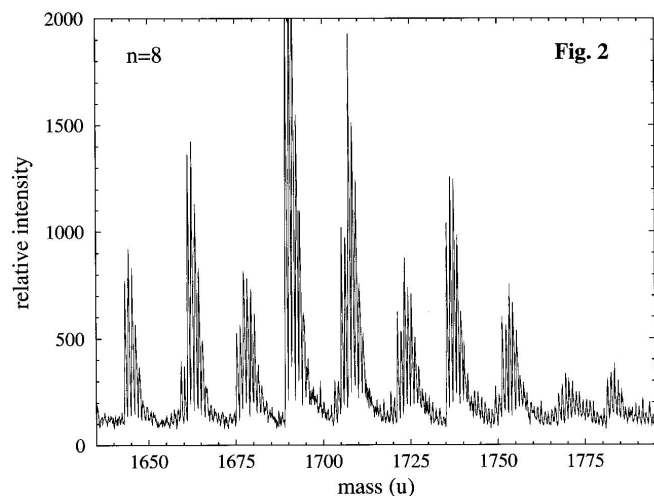
**Figure 1.** The central portion of the full mass spectrum of propyl methacrylate silsesquioxane. Estimated standard uncertainty of the peak position from calibration and repeatability studies is 0.2 u, and the estimated relative standard uncertainty in overall signal intensity from repeatability studies is 15 %.

## Discussion

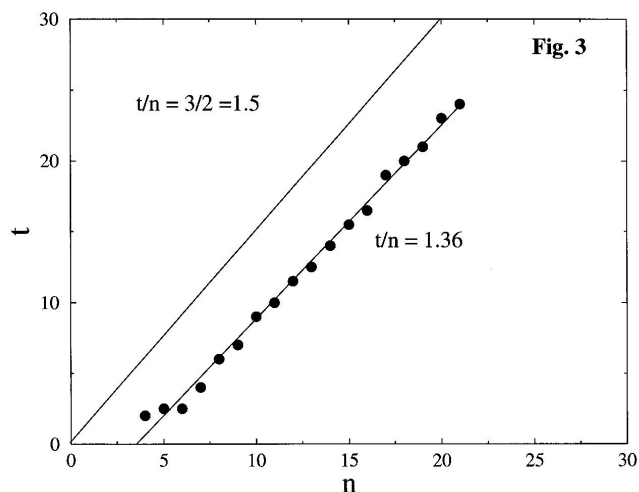
For this material the extent of hydrolysis remains high but the degree of condensation is always somewhat lower than the maximum possible. This is likely due to topological constraints on the molecule disallowing any structure where complete condensation is possible. There are also other trends apparent in the data. **Figure 3** is a plot of the greatest number of closed loops in a given oligomer (equal to the number of lost water molecules,  $t$ ) versus the number of repeat units in the molecule (equivalent to the number of silicon atoms in the molecule,  $n$ ). The greatest number of closed loops is simply the farthest left peak for any given oligomer as shown in **Figure 2**. (In all cases this corresponded to an oligomer that was also fully hydrolyzed, that is  $p=p_{\text{max}}$ .) The estimated standard uncertainty for the number of closed loops in **Figure 3** is one. The solid line in **Figure 3** has a slope of 3/2 and indicates where the points would lie if the analyte consisted of fully-condensed polyhedra. If the structure were highly branched with no closed loops ( $t=0$  for each  $n$ ) each of these points would lie on the abscissa (which is a line having a slope and intercept each identically equal to zero). Instead the points lie in

between these extremes with a slope of 1.36 indicating a mixed structure having some closed loops but also retaining a large number of silanol groups. This slope is the key to determining the topological nature of the analyte.

The upturn in the data of **Figure 3** at small  $n$  is likely due to the direct hydrolysis-condensation of residual monomer that has not reacted through the propyl methacrylate R group. These points have a slope of  $t/n = 1/2$  indicative of this type of reaction as described in our previous work [5-7].



**Figure 2.** A single-repeat-unit detail of the full mass spectrum shown in Figure 1 for the oligomers having 8 repeat units (i.e. 8 silicon atoms). The distance between peaks in this single major cluster is either 18 u indicative of the intramolecular loss of water, or 14 u indicating the hydrolysis of a methyl group.



**Figure 3.** A plot of  $t$  vs.  $n$  for the spectrum shown in Figure 1. Uncertainty of  $\pm 1$  for  $t$  applies to each point on the graph.

### Conclusions

MALDI-TOF mass spectrometry has been shown to be an effective method to determine the degree-of-intramolecular-condensation of polymeric silsesquioxanes. It has been shown that both the degree of hydrolysis and the degree of condensation can be measured on an oligomer-by-oligomer basis. Broadly considered, these results point to a means to understand reactivity and gelation in silsesquioxanes and in condensation-reaction systems in general.

### References

- (1) Baney, R.H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.*, **1995**, *95*, 1409.
- (2) Loboda, M.J.; Grove, C.M.; Schneider, R.F. *J. Electrochem. Soc.*, **1998**, *145*, 2861.
- (3) Wallace, W.E.; Wu, W.L.; Carpio, R.A. *Thin Solid Films*, **1996**, *280*, 37.
- (4) Patrick, W.J.; Guthrie, W.I.; Standley, C.I. *J. Electrochem. Soc.*, **1991**, *138*, 1778.
- (5) Wallace, W.E.; Guttman, C.M.; Antonucci, J.M. *J. Am. Soc. Mass Spectrom.* **1998**, *10*, 224.
- (6) Wallace, W.E.; Guttman, C.M.; Antonucci, J.M. *Polymer* **2000**, *41*, 2219.
- (7) Wallace, W.E.; Guttman, C.M.; Antonucci, J.M. *ACS Polym. Preprints*, **2000**, *41(1)*, 633.