# Nanoporous Ultra-Low Dielectric Constant Materials

The next generation of interlayer dielectric materials for microelectronics must have an ultra-low dielectric constant of less than 2.0 to meet the *National Technology Roadmap for Semiconductors* [1]. In addition, the material must have excellent thermal stability and mechanical properties [2, 3]. One route is to introduce nanometer sized pores into a material with an initially low dielectric constant ($k \approx 2$ to $3$). The presence of the pores lowers the dielectric constant of the nanoporous film as the dielectric constant of air is 1.0. One class of materials that is receiving significant attention is based on poly(methylsilsesquioxane) (PMSSQ) which has a dielectric constant between 2.7 and 2.8 (lower than conventional $SiO_2$) and good thermal stability up to 500 °C [4, 5]. The dielectric constant is a function of the level of porosity and detailed knowledge of the morphology is required for implementation in electronic packaging.

A schematic of the synthesis process is shown in Fig. 1. The materials are based on an inorganic matrix of PMSSQ containing a porogen (i.e., a labile pore generating material) based on a poly(methylmethacrylate) copolymer (coPMMA) as a template for creating the pores [6, 7]. A film is prepared by dissolving the PMSSQ matrix precursor material and the coPMMA porogen in a common solvent and spin casting onto a silicon substrate.

The film is then slowly ramped up in temperature to 450 °C. During this temperature ramp, the matrix film fully cures by about 225 °C, resulting in microphase separation of the coPMMA polymer. Above about 350 °C the coPMMA polymer degrades leaving nanometer sized pores. Neutron scattering was used with a deuterated coPMMA polymer to understand the morphological development of the films during the cure. The use of the deuterated porogen provides contrast for neutron scattering in the hybrid (polymer containing) system that is not available with x-ray scattering.

*In situ* studies of the curing process by small angle neutron scattering (SANS) were performed. To provide sufficient scattering signal, four or more samples on Si wafers were stacked to increase the scattering volume.

Figure 2 shows a set of SANS data from a PMSSQ thin film containing 20 % molecular fraction of porogen at various cure temperatures. The scattered intensity varies as a function of curing temperature due to morphology changes occurring in the sample. For the as-spun materials there is a shoulder at high $q$ from which a radius of gyration ($R_g$) of 12 Å was obtained by Guinier analysis. After heat treatment at 225 °C the shoulder in $I(q)$ becomes more pronounced and shifts to about $q = 0.06$ Å$^{-1}$. The shift to smaller $q$ indicates a coarsening of the microphase separated porogen domain structure. A radius of gyration of $R_g = 23$ Å for the domains was obtained for the cured materials. The scattering curves do not change significantly between 225 °C and 300 °C, indicating that the morphology remains fixed until the degradation of the polymer at 450 °C. The dramatic
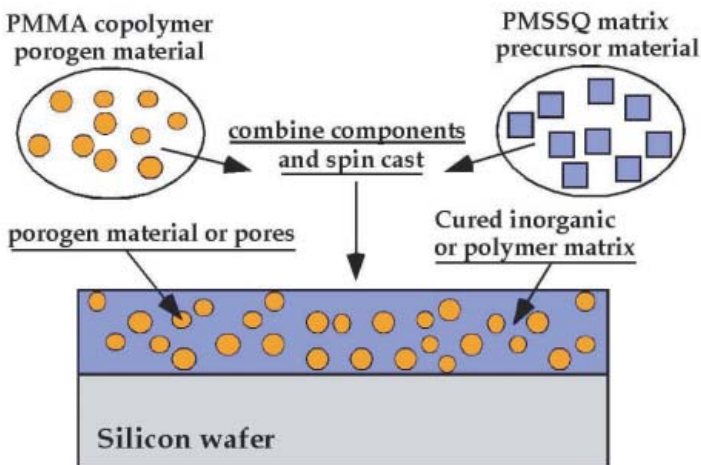


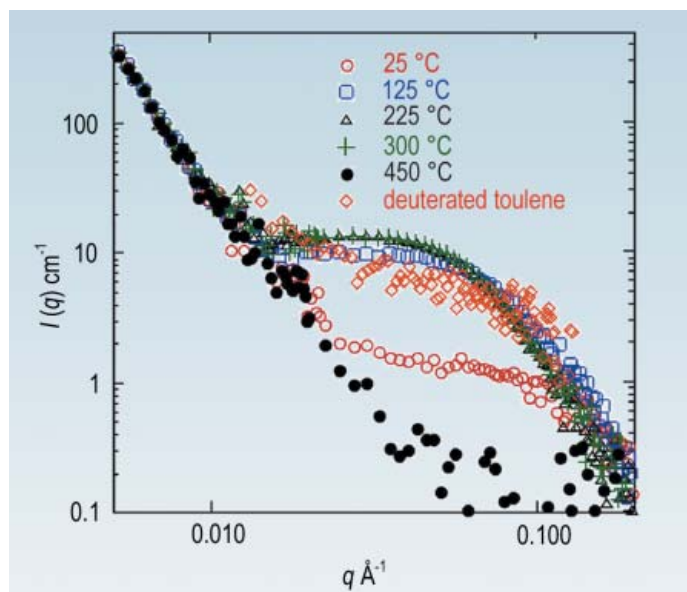FIGURE 1. Schematic showing the generation of nanoporous PMSSQ films.



FIGURE 2. SANS data taken during cure of a nanoporous PMSSQ thin film.

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decrease in intensity of the SANS curve at 450 °C is due to a loss of neutron scattering length density contrast because of the degradation of the porogen and the formation of pores in the film.

To provide neutron contrast between the pores and the matrix, the fully cured sample was exposed to deuterated toluene. These data are also shown in Fig. 2. The scattering is largely recovered after exposure to deuterated toluene, indicating that the porous structure is maintained with no collapse after degradation of the polymer.

Figure 3 shows a set of neutron reflectivity profiles and scattering length density (SLD) profiles of a nanoporous PMSSQ thin film prepared with 20 % molecular fraction of porogen and deposited on a silicon substrate. The film was exposed to deuterated toluene liquid and vapor to examine solvent swelling. The film thickness is observed to increase upon exposure to both liquid and vapor. A higher porosity is observed in a 50 Å region next to the silicon surface. This is probably due to porogen surface segregation at the substrate interface and is in agreement with results from transmission electron microscopy.

## References

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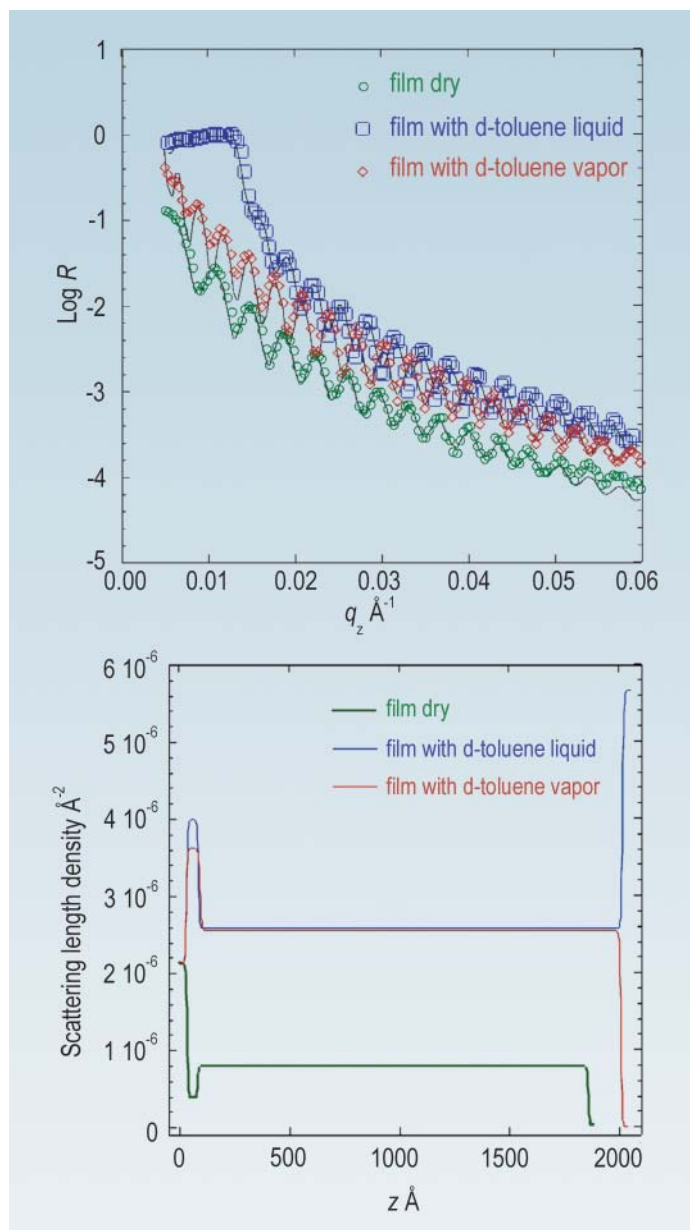
**FIGURE 3. Above, neutron reflectivity data (symbols) and best fit (lines) calculated from the scattering length density profiles shown below for a nanoporous PMSSQ thin film under various conditions.**