Pore Size Distributions in Nanoporous Methylsilsesquioxanes (MSSQ) Films for Low Dielectric Constant Layers

E. E. Huang,[1] M. Toney,[1] L. B. Lurio,[2*] W. Volksen,[1] C. J. Hawker,[1] J. Hedrick,[1] V. Lee,[1]
T. Magbitang,[1] D. Mecerreyes,[1] P. Brock,[1] R. D. Miller[1]
[1]IBM Almaden Research Center, 650 Harry Road, San Jose, CA, U.S.A.
[2]Massachusetts Institute of Technology, Cambridge, MA, U.S.A.
**Current address: IMMYT-Whitehead-CAT, Argonne National Laboratory, Argonne, IL, U.S.A.*

Currently, nanoporous films are of extreme interest to the chip manufacturing industry as they provide a means in which the dielectric constant, k, of an interlayer dielectric material, can be lowered through substitution of the matrix material with air (k=1.0).[1] As device dimensions decrease, this reduction in the dielectric constant represents a substantial decrease in the resistance-capacitance coupling and consequently reduces propagation delay, crosstalk noise, and power dissipation.[2]

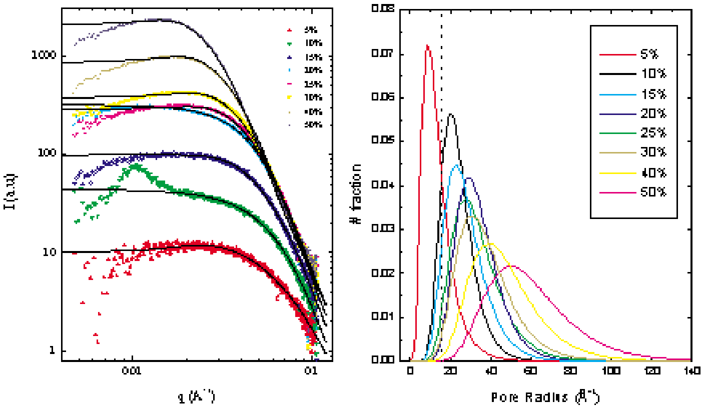

FIG. 1. Circularly averaged scattering intensity (symbols) and fits (solid lines) vs. q (left) and size distribution generated from the model fits (right).

To generate nanoporous films, we have incorporated the strategy of removing a labile component distributed in a glassy matrix, i.e., methyl silsesquioxane (MSSQ), through thermolysis.[3] The labile component, denoted as the porogen, comprises an organic , and a number of candidates are currently being studied including: poly(methyl methacrylate)-based copolymers, polycaprolactones, and polyacrylamides. The MSSQ and the organic component are dissolved in a mutual solvent, spin coated onto substrates, and annealed. Upon annealing, two processes that dictate the structure of the film occur. First, the binary-system phase separates into discrete domains corresponding to MSSQ and porogen-rich phases. Second, the MSSQ reacts by chain extension and crosslinking reactions to produce a rigid structure. If these two processes occur simultaneously, the phase separation can be limited to length scales of ~5-30 nm. Thus, by dictating the porogen/MSSQ system and the annealing conditions, films comprising the two components can be kinetically trapped into nanoscopic composites. Further annealing above the decomposition temperature of the porogen produces the porous MSSQ film.

The structures of the porous MSSQ films were examined with small-angle x-ray scattering (SAXS) at the Advanced Photon Source at Argonne National Laboratory. By using the intense x-ray beams generated from this source, the experiments could be performed directly on the ~1 mm thick films (on 80 mm Si substrates) in transmission. In contrast to real space methods, e.g., electron microscopy, the information obtained from SAXS measurements is generated from larger sampling volumes as the x-ray beam is roughly 100 x 100 mm in size. Thus, these experiments provide complementary information on a "global" scale.

The SAXS data were circularly averaged and fit to a log-normal distribution assuming a hard sphere model and applying a local monodisperse approximation[4] results are displayed in Fig. 1 for a series of films having a range of porosities that were generated. The left plot shows the circularly averaged intensity as a function of q (symbols) with their corresponding fits (solid lines). The size distributions generated from these fits are shown on the right for each porosity.

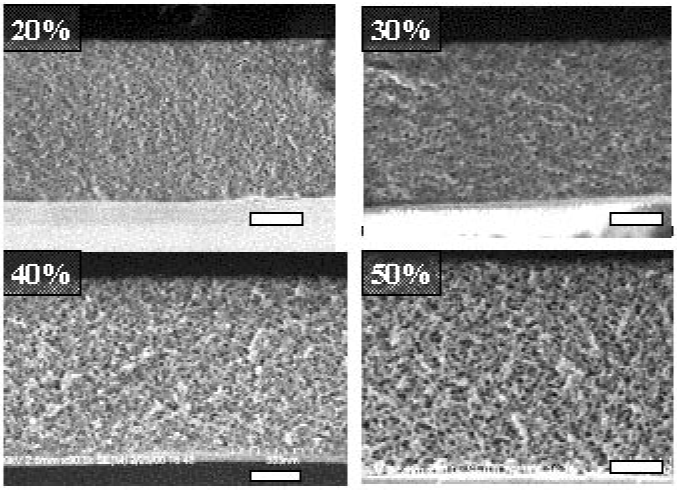

FIG. 2. Field emission scanning electron microscopy (FESEM) images obtained from a cross section of the porous MSSQ films as a function of porosity. Scale bar = 200 nm.

Consistent with field emission scanning electron microscopy (FESEM) images (Fig. 2), the pore sizes are observed to increase and the size distributions are observed to broaden with increasing porogen loading. To further these studies, we are examining the effect of porogen molecular weight, molecular weight distribution, and varying the MSSQ used in these systems.

Acknowledgments

Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. The experiments were performed on the IMMYT-Whitehead-CAT beamline 8-ID. Program funding provided by a NIST-ATP contract.

References

[1] The National Technology Roadmap for Semiconductors; Semiconductor Industry Association; San Jose, CA, 1997.

[2] W. W. Lee and P. S. Ho, MRS Bulletin **22** (10), 19 (1997).

[3] R. D. Miller, Science **286**, 421 (1999); C. V. Ngyuen, K. R. Carter, C. J. Hawker, J. L. Hedrick, R. L. Jaffe, R. D. Miller, J. F. Remenar, H.-W. Rhee, P. Rice, M. F. Toney, M. Trollsas, and D. Y. Yoon, Chem. Mater. **11**, 3080 (1999).

[4] J. S. Pedersen, Journal of Appl. Crystall. **27**, 595 (1994).