

PORE SIZE DISTRIBUTIONS IN LOW-K DIELECTRIC THIN FILMS FROM SANS POROSIMETRY

Ronald C. Hedden,* Hae-Jeong Lee, Christopher L. Soles, and Barry J. Bauer

Polymers Division
National Institute of Standards and Technology
Gaithersburg, MD, 20899

*current address:
Dept. of Materials Science and Engineering
Penn State University
University Park, PA 16802

Introduction

The microelectronics industry is testing a wide variety of porous low-dielectric constant ("low-k") materials for future use in integrated circuits¹ To understand low-k thin film properties, a quantitative analysis of pore size distribution is vital. A new approach has been developed based on a small angle neutron scattering (SANS) porosimetry technique. The new technique quantifies pore size distribution (PSD) and reveals subtle material characteristics inaccessible to other measurement techniques.

The new approach to pore size determination combines the established science of capillary porosimetry with a powerful analytical technique, SANS. Capillary porosimetry is an established experimental technique applicable to determination of PSDs. The porous material is exposed to the vapor of a "probe solvent," and pores fill with liquid solvent by capillary condensation. An adsorption isotherm is constructed by measuring solvent uptake as a function of partial pressure. In general, filling of the pores with solvent is size-dependent; the smallest pores fill first as solvent partial pressure is increased. While optical or gravimetric techniques may be employed to measure solvent uptake, specular X-ray reflectivity (SXR) has proven to be a sensitive and accurate measurement method.

Experimental*

Materials: The porous thin film low-k dielectric sample on a silicon substrate was obtained from International SEMATECH. The atomic composition of the sample was determined by an established ion scattering technique.² Measured film atomic composition was (0.18 Si, 0.35 O, 0.10 C, 0.37 H) by mole fraction. Standard uncertainties in atomic composition are (± 0.05) by mole fraction, representing one standard deviation based on the goodness of typical fits to the data. Toluene-*h*₈ and toluene-*d*₈ (99+ atom % d) were obtained from Sigma-Aldrich, Inc.

Specular X-ray reflectivity (SXR): SXR data were obtained using a custom built high-resolution reflectometer capable of characterizing films up to 1.5 μm thick. The film thickness, surface roughness, and electron density profile were deduced using a computer modeling routine (mlayer). Overall pore volume fraction and solvent uptake were deduced from the calculated electron densities. Standard uncertainties in pore volume fractions are estimated to be (± 0.014) and represent one standard deviation based on the goodness of typical fits to the SXR data. SXR porosimetry was conducted by one of two methods. In the "pressure variation" method (PV), a stream of saturated toluene in dry air (at constant partial pressure P_0) from a bubbler held at 25 $^{\circ}\text{C}$ was combined with a second stream of pure air to control solvent partial pressure. The solvent partial pressure was increased in increments from $P/P_0 = 0.0$ (pure air) to $P/P_0 = 1.0$ (saturated toluene) by controlling the flow rates of the air and saturated toluene streams. In the "temperature variation" (TV) method, a stream of saturated toluene vapor from a bubbler held at 30 $^{\circ}\text{C}$ was passed through the sample chamber and P/P_0 was varied by changing the sample temperature, effectively changing P_0 inside the pores. The sample temperature was varied from 30 $^{\circ}\text{C}$ to 125 $^{\circ}\text{C}$. In data analysis, a value of P equal to the vapor pressure of toluene at

30 $^{\circ}\text{C}$ was assumed. Temperatures were in the range ± 0.2 based on repeated observations.

Small-angle neutron scattering (SANS): SANS measurements were conducted at the National Institute of Standards and Technology Center for Neutron Research 8 m facility.^{3,4} A sample to detector distance of 384 cm was employed. The neutron wavelength was $\lambda = (6 \text{ or } 9) \text{ \AA}$ with a spread of $\Delta\lambda/\lambda = 0.12$. Data processing is described elsewhere.⁵ A stack of 10 films was placed inside a custom-built flow-through stainless steel scattering cell equipped with quartz windows.

SANS porosimetry experiments were conducted using a "contrast match" toluene mixture. The composition of the contrast match toluene mixture was determined to be (0.22 toluene-*d*₈, 0.78 toluene-*h*₈) by mole fraction.⁵ In a fashion similar to the SXR porosimetry experiments, the solvent partial pressure P/P_0 could be varied by either PV or TV techniques. Fits of the scattering data were made by a least squares fit, giving relative uncertainties reported of one standard deviation, based on the goodness of the fit. In cases where the limits are smaller than the plotted symbols, the limits are left out for clarity.

Results and Discussion

Contrast Match SANS. The first stage of neutron porosimetry is a "contrast match point" determination. The pores are filled with solvent mixtures of variable neutron scattering length density (SLD). The solvent SLD is varied by mixing hydrogen and deuterium containing analogs of the solvent. The scattered intensity $I(q)$ from the solvent-filled porous material depends on the difference in SLD or "contrast" between the solvent and the matrix. The solvent SLD is varied systematically, and the scattered intensity $I(q)$ is measured at each composition. If the material is homogeneous in atomic composition and all of the pores fill with solvent, a contrast match solvent composition exists for which $I(q)$ becomes zero over all q . If the material has inhomogeneities in its atomic composition, or if some of the pores are not filled by solvent ("closed pores"), a contrast match point will not be observed. SANS porosimetry is more applicable to samples with a true contrast match point.

Figure 1 shows the SANS from the film with $P/P_0 = 1$, under which conditions all of the accessible pores are filled with solvent. At a composition of 22 mole % toluene-*d*₈, the scattering is reduced to a low level suggesting that all of the pores are filled without any "closed" pores being present. This contrast matched composition is used in the neutron porosimetry.

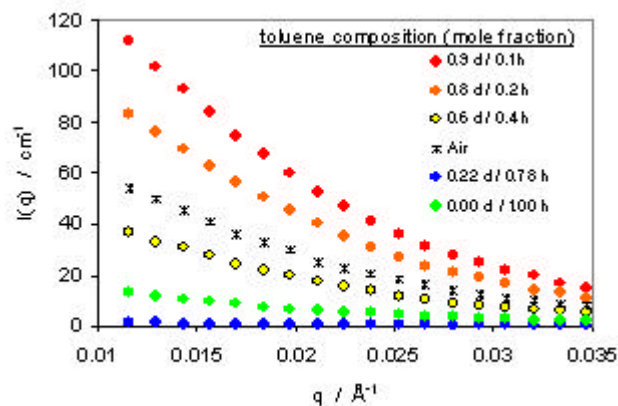


Figure 1. Contrast variation using toluene-*h*₈ and toluene-*d*₈ mixtures. When the pores are filled with solvent of the contrast match point composition, the scattered intensity approaches zero over all q .

Neutron Porosimetry. The second stage of the measurements is porosimetry using solvent vapor of the contrast match composition. SANS data are collected as the partial pressure of the probe solvent is increased (sorption) and decreased (desorption). When pores fill with the contrast match liquid, their SLD matches the sample matrix, so the SANS measurement yields the size of only the "empty" pores. Thus, as solvent partial pressure is increased, pore size is measured for sub-populations of pores of increasingly large size. The film used in this study has a random two-phase morphology that could be well represented by a fit to the Debye-Anderson-Brumberger expression.⁶

* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

Official contribution of the National Institute of Standards and Technology; not subject to copyright in the United States.

$$I(q) = \frac{8p f_0 (1-f_0) (r_m s_m - r_s s_s)^2 x^3}{(1+x^2 q^2)^2}$$

ϕ_0 is the volume fraction of pores, ξ is the correlation length, ρ_m and ρ_s are the mass densities of the film matrix (wall) and the solvent, and σ_m and σ_s are the total neutron scattering lengths per unit mass of the matrix and the solvent. The best fit to the scattering data for the film under vacuum (empty pores) gave a correlation length of $\xi = (44.4 \pm 0.2) \text{ \AA}$. The correlation length is a composite phase size for the material including both pore and matrix phases. For a randomly structured two-phase porous material, the average pore size is most easily expressed as an average chord length, $l_c = \xi / (1-\phi_0)$.

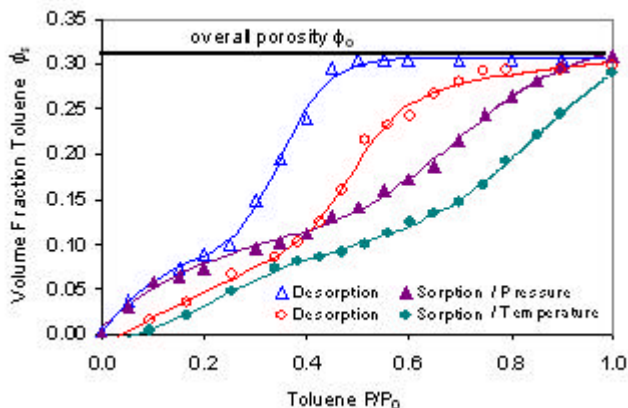


Figure 2. Solvent adsorption data measured by x-ray reflectivity. Porosimetry is conducted by two methods: under isothermal conditions while varying partial pressure in a carrier gas (green, black), or in a saturated solvent atmosphere while varying sample temperature (red, blue).

X-ray Reflectivity Porosimetry. If the volume fraction of the solvent in the film is also measured as a function of partial pressure, then average pore size and pore volume fraction are simultaneously known. XRP allows such measurement with high precision, and is a powerful complement to SANS porosimetry. Further information about the pore filling process was obtained by use of SXR to measure the uptake of solvent in the film as a function of P/P_0 . Recently, SXR has emerged as a quantitative analytical technique for analysis of pore and matrix characteristics in low- k dielectrics. SXR porosimetry has been applied to measure film thickness, pore volume fraction, matrix mass density, coefficient of thermal expansion, and solvent/moisture uptake in low- k dielectrics.

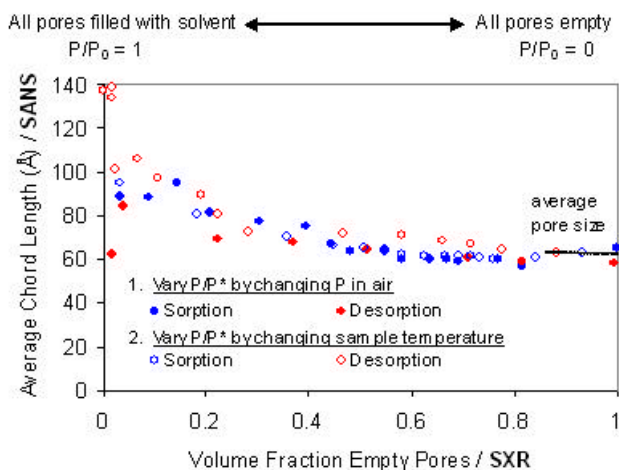


Figure 3. Average chord length from SANS porosimetry plotted vs. volume fraction empty pores from x-ray reflectivity. The scattering data contain size information related to the average size of only the empty portion of the pores.

A simple physical model frequently chosen to analyze adsorption data is the classical Kelvin equation.⁷ While this procedure provides a means to rapidly convert adsorption data to a size distribution, reliance on the Kelvin equation imposes major limitations on the accuracy of the measurement. From the point of view of data interpretation, the adsorption hysteresis exhibited by most mesoporous materials introduces serious ambiguities. Figure 2 shows four curves representing data taken by adsorption and desorption by both the PV and TV methods. The data curves clearly do not coincide, and application of the Kelvin equation to this data would result in four different pore size distributions.

Combination of Neutron and X-ray Results. Figure 3 shows combined results from both techniques: pore size from SANS is plotted vs. empty pore volume fraction from SXR. The data are essentially unaffected by hysteresis phenomena within the limits of uncertainty of the experiment. When all pores are empty, the SANS measurement gives the average pore size for the entire distribution. As pores are filled, the upper end of the pore size distribution is probed because only the larger pores are empty and contribute to $I(q)$ from SANS. For the sample shown in figure 3, the average pore size is about 60 \AA , but the sample contains some pores of 80 \AA or larger. By using capillary porosimetry to isolate the scattering from the largest pores, subpopulations of large pores within a low- k material can be readily identified, provided their concentration is high enough to make a measurable change in the scattering.

Conclusions

Capillary porosimetry experiments combined with in-situ SANS measurements reveal quantitative information about pore size and the pore filling process in nanoporous thin films. SANS porosimetry is conducted with a "contrast match" solvent mixture that fills all accessible pores via capillary condensation. The method is most applicable to materials with homogeneous matrix atomic composition. SANS measurements provide a more quantitative and less ambiguous approach to PSD compared to analysis of adsorption data by the Kelvin equation.

Acknowledgements

We thank International Sematech for providing the samples and for financial support, and the Office for Microelectronics Programs at the National Institute of Standards and Technology for financial support. We thank Derek Ho and Charles Glinka (NCNR) for maintaining the 8 m SANS equipment. Dr. Hedden acknowledges the support of a National Research Council / NIST postdoctoral fellowship.

References

1. Maex, K.; Baklanov, M.R.; Shamiryan, D.; Lacopi, F.; Brongersma, S.H.; Yanovitskaya, Z.S. *Journal of Applied Physics* **2003**, *93*(11), 8793-8841.
2. Composto, R.J.; Walters, R.M.; Genzer, J. *Mat. Sci. Eng. R* **2002**, *38*, 107-180.
3. Hammouda, B.; Krueger, S.; Glinka, C.J. *J Res. Natl. Inst. Stan.* **1993**, *98*, 31-46.
4. Prask, H.J.; Rowe, J.M.; Rush, J.J.; Schroeder, I.G. *J. Res. Natl. Inst. Stan.* **1993**, *98*, 1-13.
5. "Characterization of Nanoporous Thin Films by Neutron Contrast Variation." Hedden, R.C.; Lee, H.-J.; Bauer, B.J. Accepted by *Langmuir* 10/03.
6. Debye, P.; Anderson, H.R.; Brumberger, H. *Journal of Applied Physics* **1957**, *28*, 679.
7. Gregg, S.J.; Sing, K.S.W. *Adsorption, Surface Area and Porosity*, Second Ed.; Academic Press: London, 1982.