Characterization of Nanoporous Low-*k* Thin Films by Small-Angle Neutron Scattering Contrast Variation

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Small-angle neutron scattering contrast variation is applied to characterization of nanoporous low-dielectric constant (low-*k*) thin films. Films are exposed to saturated solvent vapor in air, whereby the pores fill with liquid by capillary condensation. The pores are filled with mixtures of hydrogen- and deuterium-containing solvents to vary the neutron contrast with the matrix (wall). The composition of the solvent mixture is systematically varied to identify a composition that minimizes the scattered intensity (contrast match point). From the contrast match point composition, film characteristics including matrix density and homogeneity are assessed. Four spin-on low-*k* materials including a methylsilsesquioxane, an organic polymer, a xerogel, and a hydrogensilsesquioxane are characterized by the new technique. Calculated matrix mass densities are compared to independent density measurements obtained by an established specular X-ray reflectivity technique. We find no evidence of “closed pores”, defined here as pores inaccessible to the probe solvent, in any of the materials studied.

Introduction

Much of the recent developmental efforts in low-*k* dielectrics involve production of nanoporous thin films. The microelectronics industry has developed and examined dozens of possible nanoporous low-*k* materials. To understand the physical basis for mechanical, thermal, and barrier properties, thorough structural characterization is essential. Small-angle neutron scattering (SANS) is a versatile tool for characterization of properties such as mass density, homogeneity, pore volume fraction, morphology, pore size distribution, and pore connectivity. SANS data analysis is complicated by the challenges associated with the study of structurally complex materials, motivating refinement of existing techniques.

SANS contrast variation or contrast matching is an established scattering technique sensitive to a wide range of structural characteristics. Contrast variation has been successfully applied to characterize matrix properties and closed pore content in bulk nanoporous materials.[1−5] In a contrast matching experiment, pores are filled with liquids of known neutron scattering length density (SLD). 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. The solvent SLD is commonly varied by mixing hydrogen- and deuterium-containing analogues of the solvent to take advantage of the large difference in neutron scattering cross sections of hydrogen and deuterium. The variation of $I(q)$ with solvent composition may reveal the presence of inhomogeneities in matrix atomic composition and/or closed pores (defined herein as pores inaccessible to solvent). In materials without any substantial matrix inhomogeneity or closed pores, the contrast variation technique can also be used to measure the mass density of the wall (matrix). Because of its sensitivity to these critical material properties, SANS contrast variation is a valuable tool for characterization of nanoporous low-*k* materials.

SANS contrast matching has only recently been applied to low-*k* materials because of experimental difficulties associated with thin film samples. The simplest strategy to fill the pores with solvent is to immerse the thin films (on the substrate) in liquid solvent. However, the solvent mixtures usually have significant hydrogen content, resulting in a substantial amount of incoherent (background) scattering. Because the low-*k* films are usually less than 1 μm in thickness, the coherent scattering from the films (containing the structural information) is overwhelmed by the incoherent scattering from the excess solvent. In this work, a new approach is described whereby the incoherent scattering is reduced to negligible levels. If the nanoporous film is exposed to saturated solvent vapor, all accessible pores are filled with liquid solvent by capillary condensation without filling the sample cell with excess solvent. The scattered intensity is usually dominated by the coherent component, and the contrast variation technique becomes feasible.

This report describes the vapor adsorption SANS contrast variation technique and its application to the characterization of spin-on nanoporous low-*k* dielectric materials. The focus of this work is to apply SANS contrast matching to nanoporous thin films to establish its feasibility, value, and limitations as a characterization tool. We illustrate how SANS contrast variation is useful to quantify the mass density of nanoporous thin films, and we compare the measured densities to independent values from an established specular X-ray reflectivity technique. The use of SANS contrast variation to identify “closed” pores (or lack thereof) is also discussed.

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Table 1. Dielectric Constants Quoted by Supplier and Atomic Composition from Ion Scattering (according to procedure in ref 6)[a]

sample	dielectric constant	atomic composition, mole fraction[b]			
		C	H	O	Si
MSQ	2.4	0.10	0.37	0.35	0.18
polymer	2.2	0.61	0.31	0.08	0.00
HSQ	2.2	0.07	0.20	0.48	0.25
xerogel	2.2	0.14	0.33	0.34	0.19

[a] See text for explanation of uncertainties. [b] Uncertainties for all compositions are ±0.05.

Experimental Section

Materials. Certain commercial materials and equipment are identified in this paper in order to adequately specify 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 is the best available for this purpose. The low-*k* thin film samples on 0.725 mm thickness silicon substrates were obtained from International SEMATECH. The atomic composition of each sample was determined by an established ion scattering technique.[6] Measured atomic composition data and dielectric constants quoted by the suppliers are listed in Table 1. Uncertainties in atomic composition are (±0.05) mole fraction for each nucleus and represent one standard deviation from the fits to the data. Samples included a polymethylsilsesquioxane (MSQ) type, an organic polymer type, a polyhydrogensilsesquioxane (HSQ) type, and a xerogel type. All materials were spin-on type dielectrics. Toluene-h_8 and toluene-d_8 (99+ atom % d) were obtained from Sigma-Aldrich, Inc.

Specular X-ray reflectivity (SXR). SXR measurements were obtained from a high-resolution reflectometer capable of characterizing films up to 1.5 μm thick. Data were collected with the grazing incident angle equal to the detector angle (specular condition), and the reflected intensity was recorded as a function of angle. The film thickness, surface roughness, and electron density profile were deduced using computer modeling to fit the experimental SXR data. Unless otherwise stated, measured thicknesses were assumed to have an uncertainty of (±20 Å) (1 standard deviation).

Small-Angle Neutron Scattering (SANS). SANS measurements were conducted at the National Institute of Standards and Technology (NIST) Center for Cold Neutron Research 8 m facility.[7,8] A sample to detector distance of 384 cm was employed. The neutron wavelength was $\lambda = (6 \text{ or } 9)$ Å with a spread of $\Delta\lambda/\lambda = 0.12$. Data processing was conducted on a μVAX 4000 computer with the software provided by the Center for Neutron Research at NIST.[9] The number of counts was corrected for detector sensitivity, background scattering, and empty cell effects. Absolute scattering intensities were calculated by use of a silica standard and the experimental values for sample transmissions. The resulting data sets were circularly averaged to yield absolute scattered intensity I as a function of scattering vector, $q = 4\pi \sin \theta/\lambda$. Fits of the scattering data were made by a least-squares fit, giving an average and a standard deviation to the fit. The relative uncertainties reported are 1 standard deviation. Total combined uncertainties from all external sources are not reported, as comparisons are made with data obtained under the same conditions. In cases where the limits are smaller than the plotted symbols, the limits are left out for clarity.

The experimental setup is shown schematically in Figure 1. Samples on Si wafers were cut into circular disks of approximately 2 cm diameter, larger than the neutron beam diameter of 1.27 cm. SANS measurements were conducted on stacks of 6−10 films to increase the scattered intensity. Films were cut from the same wafer to ensure identical physical characteristics. The film stack was placed inside a custom-built flow-through stainless steel scattering cell equipped with quartz windows. The cell was made leak-tight by compression of the quartz windows against solvent-resistant rubber O-rings. The flow-through assembly was placed under vacuum during SANS experiments to eliminate scattering from air and to permit removal of an unnecessary optical component from the beam path. The samples remained at approximately atmospheric pressure during experiments, and vapor flow through the cell was verified by use of an exit bubbler.

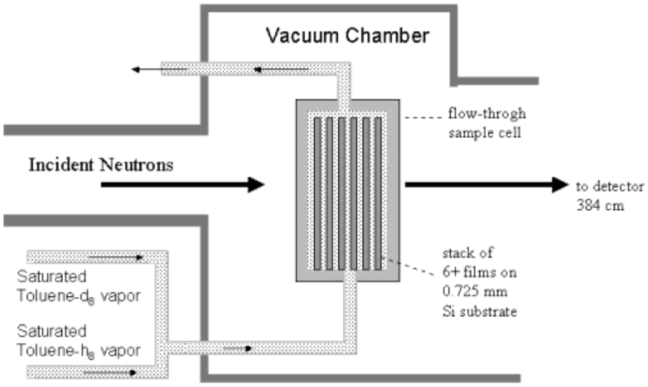

Figure 1. Schematic diagram of flow-through apparatus for SANS contrast variation experiments. The H/D solvent vapor mixture is continuously delivered to the sample cell using syringe pumps or mass flow controllers.

The solvent vapor was delivered to the samples by use of two syringe pumps with adjustable flow rates. The syringe pumps were equipped with two 100 cm^3 syringes filled with hydrogen-containing solvent and deuterium-containing solvent. Syringes contained 1−2 cm^3 of solvent liquid in equilibrium with a comparatively large volume of saturated vapor. The effluent from the two syringes was combined, giving a saturated solvent vapor mixture, the composition of which could be controlled by adjusting the flow rates of the two pumps.

Results and Discussion

SANS Measurements under Vacuum. Before contrast variation experiments were conducted, scattered intensity $I(q)$ was first measured for all samples under vacuum (Figure 2). (For data where the error bars are the same size as the symbols or smaller, error bars have been omitted for clarity.) Both neutron and X-ray[10−13] scattering can provide estimates of pore size and/or spacing in low-*k* materials provided the contrast between the matrix and pores is sufficient and the pores are large enough to be accessible to the technique (pore diameter greater than about 1 nm, generally speaking). For all of the materials in this study including the MSQ sample, contrast between the pores and matrix resulted in strong coherent scattering. Our results contradict a claim made elsewhere that SANS is inappropriate for study of MSQ dielectrics due to insufficient contrast between pore and matrix scattering length densities.[10] The MSQ type dielectric (Figure 2A) and the xerogel (Figure 2B) exhibited scattering typical of randomly structured two-phase materials. Scattering data for these samples could be fit

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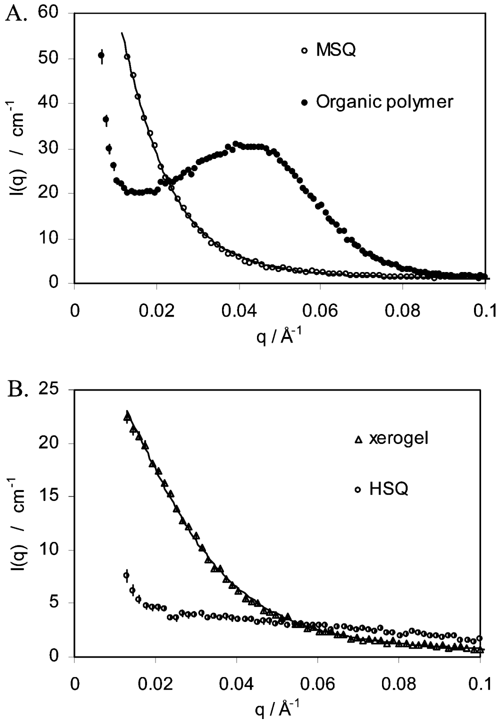

Figure 2. Scattered intensity for all samples in a vacuum. For the MSQ and xerogel samples, lines are fits to the DAB expression (eq 1).

reasonably to the Debye–Anderson–Brumberger (DAB) expression:[14]

$$I(q) = \frac{8\pi\phi_0(1-\phi_0)(\rho_m\sigma_m - \rho_s\sigma_s)^2\xi^3}{(1+\xi^2q^2)^2} \tag{1}$$

In eq 1, ϕ_0 is the volume fraction of pores, ξ is the correlation length in cm, ρ_m and ρ_s are the mass densities of the film matrix (wall) and the solvent in g cm^{-3}, and σ_m and σ_s are the total neutron scattering lengths per unit mass of the matrix and the solvent in cm g^{-1}. Lines in Figure 2 are best fits to eq 1. The best fit to the scattering data for the MSQ sample gave a correlation length of $\xi = 44.4 \pm 0.2$ Å, and the best fit for the xerogel sample gave $\xi = 26.7 \pm 0.2$ Å. (Unless otherwise specified, uncertainties in fitted parameters are 1 standard deviation based on the quality of the fits and do not reflect the total combined uncertainty, as measurements were made under similar conditions.) The correlation length can be visualized as a “grain size” for the material averaged over both phases.

The data from the HSQ (Figure 2B) and organic polymer (Figure 2A) films were not analyzed in the context of any scattering models. The scattering from the HSQ film suggested a random morphology, but fits to eq 1 did not satisfactorily represent the data due to an upturn in the scattered intensity $I(q)$ at low q. The organic polymer type dielectric had a prominent peak in the scattering, characteristic of an ordered pore structure, and an upturn in scattered intensity at low q. The peak maximum is located at approximately $q_{max} = 0.045$. Application of Bragg’s law gives an order-of-magnitude estimate of the pore spacing of $d = 2\pi/q_{max} \approx 140$ Å.

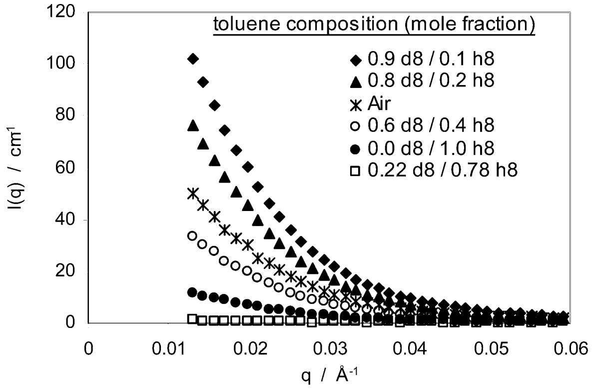

Figure 3. Contrast variation with the MSQ dielectric using toluene-h_8 and toluene-d_8 mixtures. When the pores are filled with solvent of the contrast match point composition, the scattered intensity approaches zero over all q.

SANS Contrast Variation by Solvent Vapor Adsorption. Contrast variation was conducted by filling the pores with mixtures of toluene-h_8 and toluene-d_8 by vapor adsorption. Two streams containing saturated toluene-h_8 and toluene-d_8 vapor in dry air were combined and passed through the flow-through SANS sample cell (Figure 1). The composition of the vapor was adjusted by controlling the relative flow rates of the toluene-h_8 and toluene-h_8 streams. This procedure assumes that the saturated vapor pressures of the two solvents are the same, so that the composition of the vapor is given directly by the ratio of the flow rates. This is a reasonable assumption for toluene-h_8 and toluene-d_8 under the conditions of temperature and pressure employed in this study. The procedure also assumes that neither solvent preferentially adsorbs in the pores so that the composition of the liquid in the pores is the same as that in the vapor.

Proper contrast variation experiments require avoiding h–d exchange reactions between the sample and the solvent. If the sample is partially deuterated by exposure to deuterated solvent, then the solvent scattering length density is altered and the accuracy of the measurement is compromised. Toluene-h_8 and toluene-d_8 were used as probe solvents for all experiments in this report. Because toluene does not have acidic protons/deuterons under the conditions employed in these experiments, the risk of h–d exchange between solvent and sample is minimized. The absence of measurable h–d exchange was further verified by exposing selected samples to pure toluene-d_8, followed by a dry nitrogen gas purge. The scattered intensity of all samples returned to the original level following the purge, indicating that the scattering length densities of the samples were not affected and the composition of the samples was therefore not altered.

Contrast Variation Data. Figure 3 shows contrast variation scattering data for the MSQ film. The composition of the solvent vapor was varied incrementally from 1.00 mole fraction toluene-d_8 to 1.00 mole fraction toluene-h_8, changing the scattering length density of the liquid in the pores. As the mole fraction of toluene-h_8 increased, the scattered intensity passed through a minimum near 0.2 toluene-d_8/0.8 toluene-h_8. At this point, little coherent scattered intensity remained over all q. As the mole fraction toluene-h_8 was increased to 1.00, the scattered intensity increased again as the liquid composition deviated from the match point. The SANS data for the xerogel sample followed a similar trend (Figure 4). The scattered intensity for the xerogel also passed through a minimum near 0.2 toluene-d_8/0.8 toluene-h_8, at which point little residual scattering was observed.

In contrast, the organic polymer film and the HSQ film behaved differently during contrast variation. Figure 5 shows the contrast variation SANS data for the organic

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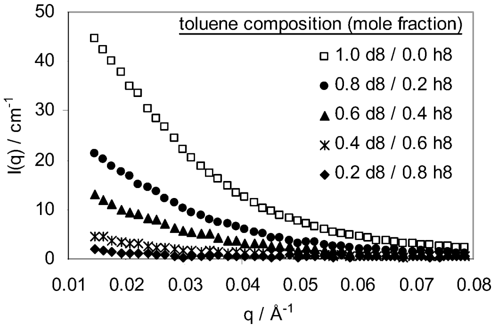

Figure 4. Contrast variation with the xerogel dielectric using toluene-h_8 and toluene-d_8 mixtures.

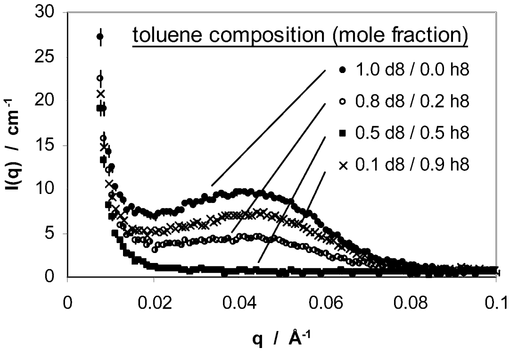

Figure 5. Contrast variation with the organic polymer dielectric using toluene-h_8 and toluene-d_8 mixtures. Contrast variation changes the intensity of the peak due to ordered pores, but the low-*q* scattering upturn was present for all solvent compositions.

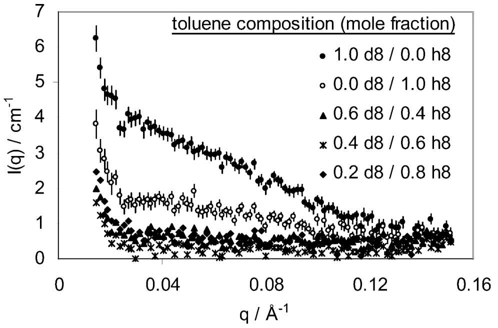

Figure 6. Contrast variation with the HSQ dielectric using toluene-h_8 and toluene-d_8 mixtures.

polymer dielectric. The broad peak in the scattering disappears near a solvent composition of (0.5 toluene-h_8/0.5 toluene-d_8) by mole fraction. However, the strong upturn in the scattering observed at low-*q* is present over all values of solvent composition. There is no solvent composition at which the low-*q* scattering is eliminated, although there is some variation in the scattered intensity in this region. Similar results were obtained for the HSQ material (Figure 6). (In Figure 6, error bars are omitted for clarity on data sets near the contrast match point composition but were similar to those shown for the other data sets.) This sample has a weak upturn at low-*q* that could not be eliminated by contrast variation. If one considers only the data at $q > 0.04$, this sample has a match point of about (0.6 toluene-h_8, 0.4 toluene-d_8).

As illustrated by the data for the four samples studied here, there are two general outcomes of the contrast variation experiment: a true "contrast match point" may or may not be observed. A true contrast match point is reached when the coherent part of $I(q)$ is equal to zero over all *q*. The contrast match condition indicates that the solvent SLD is identical to the matrix SLD, such that there is no contrast between the matrix and the solvent-filled pores throughout the sample. In this case, one can conclude that the sample matrix has essentially homogeneous atomic composition. If there were significant inhomogeneities in the matrix on a nanometer or larger length scale, measurable coherent scattering would be observed at all solvent compositions. The existence of a true match point also verifies that all pores are open (accessible) to toluene. If "closed" pores were present that could not be filled with toluene, a true match point would not be observed. This indicates that for the MSQ and xerogel samples, which show negligible scattering at their contrast match points, none of the pores are "closed" (inaccessible) to toluene. This observation does not necessarily mean that all of the pores are connected to the surface, however. It is quite possible that the solvent is slightly soluble in the matrix, so even pores that are completely isolated from the surface (surrounded by matrix on all sides) might be filled by the solvent.

The other general case occurs when a contrast match condition is not observed, as for the organic polymer and HSQ samples. One or more minima may be observed in $I(q)$ as solvent SLD is varied, but $I(q)$ cannot reach zero over all *q* at any given solvent composition. The lack of a true contrast match point indicates that either the matrix material is inhomogeneous and/or some of the pores are inaccessible to solvent ("closed"). In either of these situations it is not possible to reach a state of uniform SLD throughout the entire system by filling pores with solvent. In some cases, as with the organic polymer and HSQ films in this study, a pseudo match point may exist where a minimal amount of residual scattering remains over a certain portion of the *q*-range but substantial scattered intensity is observed over a different *q*-range. In other cases, the scattered intensity may be nonzero over all *q* for all solvent compositions.

When no true match point is found, quantitative analysis of the scattering data is usually complicated,[15] permitting only qualitative conclusions. There is no rigorous way to discern whether closed pores, matrix inhomogeneities, or both may be present. However, it is sometimes possible to make qualitative arguments in favor of one or the other. For example, for the organic polymer sample, the low-*q* upturn is due to variations in scattering length density on a much larger length scale than the size of the ordered pores. The residual scattering near the pseudo match point composition of (0.5 toluene-h_8/0.5 toluene-d_8) resembles the scattering from a random two-phase material as described by eq 1. Therefore, a fit of eq 1 can be used to estimate a size scale for the inhomogeneities. Figure 7 shows a fit of eq 1 to the residual scattering, from which a correlation length ξ of about 250 Å was found. In this case, the low-*q* upturn was attributed to matrix inhomogeneities rather than closed pores. The existence of a population of closed pores of large size in this sample is physically unlikely given the fact that the small ordered pores responsible for the peak in $I(q)$ are readily accessible to the solvent. The possibility of substrate scattering was ruled out by checking scattering from the blank substrate over the same *q* range.

By this logic, for both the HSQ and organic polymer films, no conclusive evidence of "closed pores" was found with toluene as probe solvent nor with any of the samples in this study. However, it is quite possible that had a different probe solvent been used, some of the pores may not have filled. The authors suggest that when the probe

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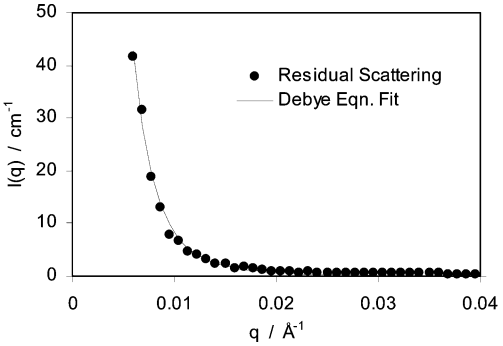

Figure 7. Fit of the DAB expression (eq 1) to the residual scattering at the pseudo match point for the organic polymer dielectric.

solvent is slightly soluble in the matrix material, all of the pores are able to fill with liquid, whether they are directly accessible from the film–atmosphere interface or not. Thus, the SANS contrast variation technique is not necessarily a straightforward means by which to quantify pore interconnectivity.

Calculation of Matrix Mass Density from SANS. For a material with a true contrast match point, the matrix mass density can be quantified. Calculation of matrix density requires an accurate determination of the contrast match point composition and independent information about the matrix atomic composition. For a porous material of homogeneous atomic composition, regardless of sample morphology, the scattered intensity is proportional to the contrast between the matrix and the solvent squared

$$I(q) \propto (\rho_\mathrm{m}\sigma_\mathrm{m} - \rho_\mathrm{s}\sigma_\mathrm{s})^2 \tag{2}$$

The total scattering length per unit mass is defined by

$$\sigma = \sum c_i b_i / \sum_i c_i (m_i/N_\mathrm{A}) \tag{3}$$

In eq 3, c_i is the local molar concentration of a given nucleus in g cm^{-3}, b_i is the scattering length of the nucleus in cm, m_i is its molar mass in g mol^{-1}, and N_A is Avogadro's number. The quantity $\rho_s\sigma_s$ is the solvent scattering length density (SLD). In a contrast match experiment, as the composition of liquid in the pores is changed, a plot of $I(q)$ vs solvent SLD at any arbitrary value of q will have a parabolic shape if the matrix is homogeneous. The value of the solvent SLD at the minimum of the parabola corresponds to the match point where the contrast factor of the matrix is the same as that of the solvent. Alternately, $I(q)$ may be plotted vs solvent composition, since the solvent SLD is related linearly to the mole fraction of the deuterated species provided the volumes of the h-containing and d-containing solvents are additive

$$\text{solvent SLD} = x_\mathrm{D}\mathrm{SLD}_\mathrm{D} - x_\mathrm{H}\mathrm{SLD}_\mathrm{H} \tag{4}$$

In eq 4, x_D is the mole fraction of the deuterium-containing solvent and ($x_H = 1 - x_D$) is the mole fraction of the hydrogen-containing probe solvent in the contrast match solvent mixture. SLD$_D$ and SLD$_H$ are the scattering length densities of the deuterium-containing and hydrogen-containing solvents in their respective pure liquid states.

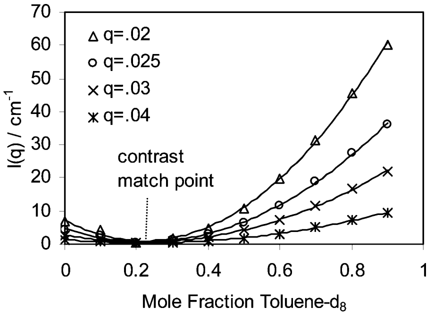

Figure 8. Determination of the contrast match point for the MSQ dielectric. Scattered intensity at a given value of q is plotted vs solvent composition. The match point is q-independent for this sample.

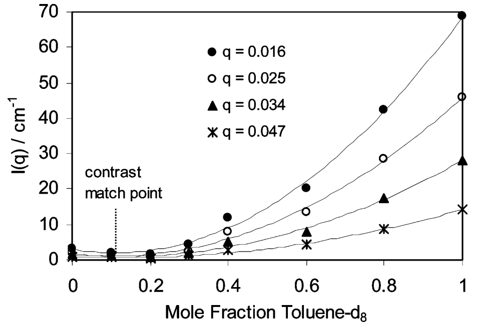

Figure 9. Determination of the contrast match point for the xerogel dielectric.

The MSQ and the xerogel are materials that effectively have a true contrast match point at which the scattered intensity approaches zero over all q. The quantitative determination of the match point composition is achieved by plotting $I(q)$ vs solvent composition at constant q and fitting the data to a parabola. Figure 8 shows $I(q)$ vs mole fraction toluene-d_8 for the MSQ dielectric. Several plots were made for different values of q to demonstrate that the minimum in the scattered intensity was q-independent. By fitting a second-order polynomial to the data in Figure 8, a match point of (0.22 ± 0.02) toluene-d_8/(0.78 ± 0.02) toluene-h_8 by mole fraction was calculated for the MSQ material. The calculated match point corresponds to a solvent SLD of (2.00 ± 0.11) × 10^{10} cm^{-2}. Figure 9 shows a similar analysis for the xerogel sample, from which a contrast match point of (0.14 ± 0.02) toluene-d_8/(0.86 ± 0.02) toluene-h_8 was calculated, giving a solvent SLD of (1.60 ± 0.11) × 10^{10} cm^{-2}. With these calculations, the mass density of the probe solvent inside the nanometer-sized pores was assumed to be the same as its bulk density.

If the sample matrix is homogeneous, the matrix SLD can be taken as equal to the solvent SLD at the match point. The identification of the contrast match point permits evaluation of the matrix mass density if the atomic composition of the film is known. The mass density is given by

$$\rho_\mathrm{m} = \frac{\mathrm{SLD}_\mathrm{match}}{N_\mathrm{A}\sum b_i x_i}\sum m_i x_i \tag{5}$$

In eq 5, ρ_m is the mass density of the matrix in g cm^{-3}, b_i is the scattering length of nucleus i in cm, x_i is its mole fraction in the sample in the dry state (determined by ion scattering herein), m_i is the molar mass of the nucleus expressed in g mol^{-1}, N_A is Avogadro's number, and SLD$_\mathrm{match}$ is expressed in cm^{-2}. SLD$_\mathrm{match}$ is calculated from the composition of the solvent at the contrast match point according to eq 4. For the MSQ sample, the calculated matrix density from the match point was 1.97 ± 0.11 g cm^{-3}. The calculated density of the xerogel sample was 1.37 ± 0.07 g cm^{-3}.

For samples without a true contrast match point, one can sometimes calculate an apparent contrast match point

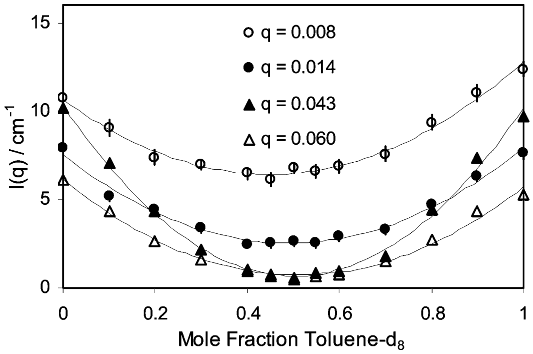

Figure 10. Determination of the contrast match point for the organic polymer dielectric.

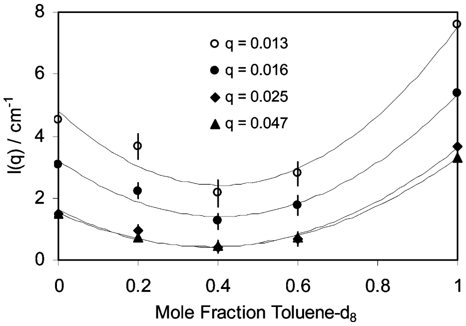

Figure 11. Determination of the contrast match point for the HSQ dielectric.

using the solvent composition at which the minimum scattered intensity is observed. For example, if a low-q upturn is observed as for the HSQ and organic polymer films in this study, an apparent contrast match point can be determined at higher values of q, from which approximate matrix mass densities can be calculated. Values for the matrix mass density calculated in this way ignore the underlying physical origin of the scattering. The volume fraction of any compositional inhomogeneities or closed pores and the nature of their spatial distribution in the samples are unknowns. In the absence of detailed knowledge of how the SLD and atomic composition vary throughout the sample, such calculations are only approximate. However, we compute the results for the organic polymer and HSQ films here as an exercise. For the organic polymer film, considering only data above $q = 0.02$, an apparent match point of approximately (0.5 toluene-h_8, 0.5 toluene-d_8) is observed (Figure 10). This match point corresponds to a matrix scattering length density of about 3.3×10^{10} cm^{-2}. By use of atomic composition data from ion scattering, the calculated matrix mass density is about 1.46 g cm^{-3}. Following a similar procedure for the HSQ sample (Figure 11), considering data above $q = 0.04$, the calculated match point of approximately (0.6 toluene-h_8, 0.4 toluene-d_8) gives a matrix SLD of about 2.9×10^{10} cm^{-2} and a matrix mass density of about 2.12 g cm^{-3}. These values may be close to the average matrix mass density if the inhomogeneities occupy a small volume fraction of the sample. However, in the absence of independent information about the nature of the inhomogeneities, these densities can only be considered approximations.

Matrix Mass Density: Comparison of SANS and X-ray Reflectivity. To supplement data from SANS contrast variation, an established specular X-ray reflectivity (SXR) technique was applied to measure sample thickness, pore volume fraction (porosity), and matrix mass density.[16,17] Porosity ϕ_0 and matrix mass density ρ_m were determined by a solvent uptake experiment that requires independent information about matrix atomic composition. Fits to the SXR data provide a critical angle θ_c, below which total external reflection occurs. The angle θ_c is related to the bulk electron density in the films

$$\rho_{el} = \pi\theta_c^{\,2}/\lambda^2 r_e \tag{6}$$

In eq 6, λ is the X-ray wavelength (1.54 Å) and r_e is the radius of an electron, taken as 2.82×10^{-5} Å. The film electron density in a vacuum (empty pores) is compared to its electron density in a saturated solvent atmosphere (liquid-filled pores). The increase in the film electron density upon filling the pores is proportional to the total number of solvent molecules in the film. The number of solvent molecules per unit volume in the film is given by

$$\frac{\text{solvent molecules}}{\text{volume}} = \left(\frac{\rho_{el}^{\ s} - \rho_{el}^{\ vac}}{n_{el}}\right) \tag{7}$$

In eq 7, $\rho_{el}^{\ s}$ is the electron density of the film when filled with solvent, $\rho_{el}^{\ vac}$ is the electron density of the film in a vacuum, and n_{el} is the number of electrons per solvent molecule. If the mass density of the solvent inside the pores is assumed to be the same as its bulk density ρ_s, then the volume fraction of the solvent in the film is given by

$$\phi_s = \left(\frac{\rho_{el}^{\ s} - \rho_{el}^{\ vac}}{n_{el}}\right)\left(\frac{M_s}{\rho_s}\right) \tag{8}$$

where M_s is the molar mass of the solvent. If all the pores are assumed to be filled with solvent, then the volume fraction of solvent ϕ_s is equated to the sample porosity ϕ_0. The standard uncertainty in reported pore volume fractions was estimated as (±0.014) for all samples and represents 1 standard deviation based on typical fits to the data.

Independent measurement of the atomic composition of the matrix material permits calculation of the matrix mass density. The bulk density of the film (including pores) is given by

$$\rho_{bulk} = \rho_{el}^{\ vac}\left(\frac{\sum_{i=\mathrm{C,H,O,Si,...}} x_i M_i}{\sum_{i=\mathrm{C,H,O,Si,...}} x_i n_{el,i}}\right) \tag{9}$$

In eq 9, x_i is the mole fraction of nucleus i in the matrix, M_i is the molar mass of nucleus i, and $n_{el,i}$ is the number of electrons in nucleus i. Sums are taken over all nuclei present in the matrix. By use of the porosity calculated from the solvent sorption experiment, the matrix mass density (not including pores) is given by

$$\rho_m = \frac{\rho_{bulk}}{1 - \phi_0} \tag{10}$$

Measured parameters are summarized in Table 2. The measured mass densities for the samples are reasonably close to the values determined by SANS contrast variation, differing by about 25% at most. Comparing SXR and SANS

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(16) Lee, H. J.; Lin, E. K.; Wang, H.; Wu, W. L.; Chen, W.; Moyer, E. S. *Chem. Mater.* **2002**, *14*, 1845−1852.

(17) Wu, W. L.; Wallace, W. E.; Lin, E. K.; Lynn, G. W.; Glinka, C. J.; Ryan, E. T.; Ho, H. M. *J. Appl. Phys.* **2000**, *87*, 1193−1200.

Table 2. Calculated Thickness, Porosity, and Matrix Mass Density for All Samples from SXR, and Matrix Mass Density from SANS Contrast Variation[a]

	thickness,[b] Å			matrix mass density/g cm^{-3}	
sample	air	saturated toluene	porosity ϕ_0	SXR	SANS[c]
MSQ	10360	10440	0.309	1.58 ± 0.09	1.97 ± 0.11
polymer	11480	12110	0.437	1.31 ± 0.09	1.46
HSQ	7180	7270	0.429	1.76 ± 0.12	2.09
xerogel	8080	8000	0.614	1.57 ± 0.16	1.37 ± 0.07

[a] See text for explanation of uncertainties. [b] Uncertainties for all thicknesses are ±20 Å. [c] SANS matrix mass densities for polymer and HSQ samples are approximations.

results, the SANS mass densities are slightly higher for three of the four materials. All of the values are physically reasonable for the respective materials. For the MSQ and xerogel samples, there is no basis to prefer the results from either SANS or SXR. For the HSQ and organic polymer samples, the approximate densities from SANS are reasonably close to the more reliable SXR values (which are not affected by matrix inhomogeneities).

The SXR results also yield valuable information about film swelling. For SANS contrast variation experiments, it is desirable to select a probe solvent that acts noninvasively and does not deform the matrix of the nanoporous film or distort the pore structure. Judging by the SXR thickness data, toluene was a suitable choice of probe solvent for the MSQ, HSQ, and xerogel samples, which changed in thickness by about 1% or less upon exposure to saturated toluene vapor. Toluene was a marginal choice of solvent for the organic polymer film, which swelled by about 5%. However, the swelling should not affect the qualitative conclusions drawn in this report regarding the nature of this material.

Comment on an Earlier Study. The xerogel sample in this study is the same material as the sample characterized in ref 17. However, the present study employed an improved approach to SXR data analysis, and different values for sample thickness and matrix density are reported here. Matrix density and porosity were previously computed by a different method whereby zero-angle SANS intensity was used to estimate pore volume fraction using the DAB equation (eq 1 in this paper). Due to the uncertainty associated with extrapolation of scattered intensity to zero angle, the previous method is less precise than the X-ray sorption method used in this report. In ref 17, the authors also concluded that the material had substantial closed pore content based on a different interpretation of a solvent sorption experiment using toluene-d_8. This conclusion was also drawn based on extrapolation of scattering data to zero angle, while the present study employs an improved analytical method using the full SANS q range, an improved SXR modeling routine, and multiple data sets. The SANS contrast variation experiments show definitively that all of the pores are in fact accessible to toluene. On the basis of the observation of a true SANS contrast match point for this sample, the previous claims of closed pore content cannot be justified. The values reported here for the xerogel properties therefore supersede those previously reported.

Summary

Characterization of nanoporous thin films by SANS contrast variation is possible by a vapor adsorption technique using a mixture of saturated hydrogen- and deuterium-containing solvent vapors in a carrier gas. If a true contrast match point is found, the matrix can be assumed to be homogeneous in atomic composition. For materials with homogeneous matrix, the matrix mass density can be found if atomic composition is known. If no contrast match point is observed, then significant matrix inhomogeneities and/or “closed pores” may be present. For materials with homogeneous matrix atomic composition, the matrix mass density can be calculated. Matrix densities for the four low-*k* materials studied here were approximately consistent with independent measurements from X-ray reflectivity. A limitation of the SANS contrast variation technique is that it can provide only qualitative information about the structure of materials of inhomogeneous matrix composition.

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