

Structure and Property Characterization of Porous Low-k Dielectric Constant Thin Films using X-ray Reflectivity and Small Angle Neutron Scattering

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ABSTRACT

High-resolution X-ray reflectivity and small angle neutron scattering measurements are used as complementary techniques to characterize the structure and properties of porous thin films for use as low-k interlevel dielectric (ILD) materials. With the addition of elemental composition information, the average pore size, porosity, pore connectivity, matrix density, average film density, film thickness, coefficient of thermal expansion, and moisture uptake of porous thin films are determined. Examples from different classes of materials and two analysis methods for small angle neutron scattering data are presented and discussed.

INTRODUCTION

With decreasing feature sizes, next generation integrated circuits require materials with lower dielectric constants. A lower dielectric constant is needed to increase signal propagation speed, reduce power consumption, and to reduce crosstalk between adjacent conducting lines. One strategy to lower the dielectric constant is the incorporation of nanometer scale pores into a solid dielectric material [1,2]. The voids in the film effectively reduce the overall dielectric constant of the material. Although the introduction of voids effectively lowers the dielectric constant, other properties required for successful integration into devices including thermal, chemical, adhesive, electrical, and mechanical properties may suffer with the introduction of voids into the film. Unlike conventional fully dense dielectric materials, structural information such as the film porosity, connectivity, and pore size distribution is needed to understand and improve other critical properties of the material. Structural information as a function of processing methods and processing parameters provides materials engineers information needed to optimize these properties.

The measurement of structural and material properties of porous low-k dielectric films is challenging because the films are typically 1 μm thick and must be characterized as prepared on a silicon substrate. To date, several experimental methodologies have been developed to characterize the structure of porous low-k dielectric thin films. Gidley et al. use positronium annihilation lifetime spectroscopy to measure the average pore size and pore size distribution of porous low-k thin films [3]. Dultsev and Baklanov use ellipsometric porosimetry to also determine the average pore size and pore size distribution [4]. Wu et al. at the National Institute of Standards and Technology (NIST) use a combination of high resolution specular X-ray reflectivity (SXR) and small angle neutron scattering (SANS) to measure the average pore size, porosity, pore connectivity, matrix density, coefficient of thermal expansion, and moisture uptake of porous low-k dielectric thin films [5].

In this paper, we summarize the NIST methodology and demonstrate its application to three qualitatively different porous thin films. The analysis methods and equations needed to extract the desired information are also presented. In addition to the two-phase model used previously, we introduce another analysis formalism based upon the Porod invariant to characterize samples that cannot be analyzed using the simple two-phase model. The goal of this work is to characterize the structure and properties of porous thin films and to provide information to correlate structural information with other measured physical properties.

EXPERIMENTAL METHODOLOGY

The NIST methodology combines SXR and SANS data to characterize silica-based porous thin films. Each individual measurement technique provides several important parameters describing the porous thin film. Other critical parameters such as the film porosity and matrix density require the use of information from more than one technique. A common input necessary for each technique is the elemental composition of the film. The elemental compositions are determined through Rutherford backscattering spectroscopy (RBS) (for silicon, oxygen, and carbon) and forward recoil elastic spectroscopy (FRES) (for hydrogen). The chemical composition is needed to convert electron density to mass density for the x-ray reflectivity data and to convert neutron scattering contrast to mass density for the small angle neutron scattering data.

In the following sections, each technique will be briefly described along with the appropriate analysis formalism to demonstrate what information can be obtained using these techniques. Three samples will be used as examples. The samples are all silica-based thin films but have qualitatively different structures. The first sample, A, is an aerogel material. The second, B, is a CVD porous material and the last sample, C, is also a porous silica film. Additional details about the samples are beyond the scope of this paper. Here, we focus on the characterization methodology and the information that can be obtained using our approach.

High Resolution Specular X-ray Reflectivity

High-resolution specular X-ray reflectivity (SXR) is a powerful experimental technique to accurately measure the structure of thin films in the direction normal to the film surface. In particular, the film thickness, film quality (roughness and uniformity) and average film density can be determined with a high degree of precision. The coefficient of thermal expansion (CTE) can also be determined from measurements of the film thickness at different temperatures.

High-resolution X-ray reflectivity at the specular condition with identical incident and detector angles, θ , was measured using a θ - 2θ configuration with a fine focus copper X-ray tube as the radiation source. Typically, the reflected intensity is measured at grazing incidence angles ranging from 0.01° to 2° . The incident beam is conditioned with a four-bounce germanium [220] monochromator. The beam is further conditioned before the detector with a three-bounce germanium [220] crystal. The resulting beam has a wavelength, λ , of 1.54 \AA , a wavelength spread, $\Delta\lambda/\lambda = 1.3 \times 10^{-4}$, and an angular divergence of 12 arcsec. With a goniometer having an angular reproducibility of 0.0001° , this instrument has the precision and resolution necessary to observe interference oscillations in the reflectivity data from films up to $1.5 \text{ }\mu\text{m}$ thick.

In Figure 1, the X-ray reflectivity curve is shown for sample A plotting the logarithm of the reflected intensity (I_r/I_o) as a function of q (where $q = (4\pi/\lambda)\sin\theta$). At low q values, the X-ray

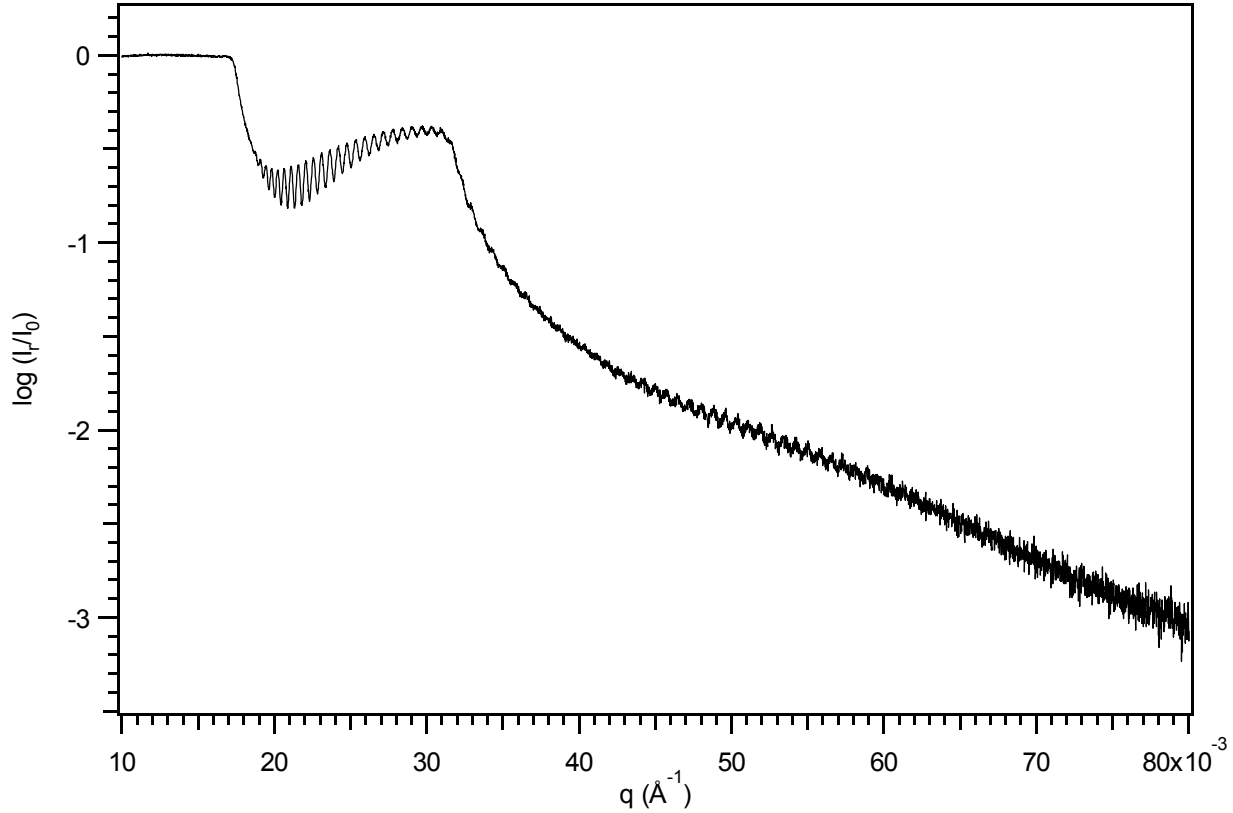


Figure 1. X-ray reflectivity data from silica-based porous thin film A presented as the logarithm of the reflected intensity vs. q where $q=(4\pi/\lambda)\sin\theta$.

beam is nearly completely reflected with a reflectivity of one. As q increases, the reflectivity dramatically drops at two separate critical angles, θ_c , the first at approximately $q=0.017 \text{ \AA}^{-1}$ and the second at approximately $q=0.03 \text{ \AA}^{-1}$. Each value of θ_c is related to the electron density of different layers in the sample. The first critical angle arises from the electron density of the porous thin film and the second critical angle arises from the silicon substrate. The oscillations that appear in the reflectivity curve between these two critical angles arise from a waveguiding region that is very sensitive to both the thickness and electron density depth profile of the film. Given the elemental composition, the average electron density of the porous thin film can be converted into an average mass density of the film. For sample A, the average mass density of the film is $0.71 \pm 0.01 \text{ g/cm}^3$. The average mass density of the film is also related to the porosity and matrix density of the film through the equation

$$\rho_{eff} = \rho_w(1 - P) \quad (1)$$

where ρ_w is the density of the matrix or wall material and P is the porosity of the film. At this point, an assumption of the matrix mass density can provide a numerical estimate of the film porosity. However, no information about the pore size can be obtained using SXR.

In addition to the average mass density of the film, the film thickness can be determined from more detailed analysis of the reflectivity data or the periodicity of the oscillations in the

reflectivity profile. The oscillations at $q > 0.03 \text{ \AA}^{-1}$ result from the destructive and constructive interference of the X-rays reflected from both the air/film interface and the film/silicon interface. The electron density depth profile of the porous thin film can be determined by fitting the reflectivity data with a model profile. A model profile is selected through the use of several layers described by their thickness, electron density, and roughness. Then, the resultant X-ray reflectivity profile is calculated using established methods [6]. The individual layer thicknesses, electron densities, and roughnesses are then numerically varied to minimize deviations between the model reflectivity calculation and the reflectivity data. However, this model profile is not certain to be a unique solution because of lost phase information. Alternatively, the thickness of the film can be independently determined from the periodicity of the reflectivity data itself. At higher q values, the oscillations in the reflectivity curve are generally free of multiple scattering contributions. A Fourier transform of the high q data enables a model free determination of the film thickness [5]. In the example in Figure 1, the film thickness is determined to be $(7610 \pm 10) \text{ \AA}$.

Small Angle Neutron Scattering

Small angle neutron scattering (SANS) is a widely used in materials science to measure the structure of materials over length scales ranging from 10 \AA to 1000 \AA [7]. This length scale matches well with the desired void structural size for porous low- k dielectric materials. Several things may be learned from the SANS data alone. First, the shape of the scattering profile provides a qualitative characterization of the structure of the film, i.e. if the pore sizes are randomly distributed or highly monodisperse. Second, the characteristic size of the pores in the film may be quantitatively determined. Finally, the pore connectivity and water uptake of the film may be determined from changes in the scattered intensity upon the immersion of the samples in the appropriate deuterated solvent [5].

Small angle neutron scattering measurements were performed on the NG1 SANS instrument at the NIST Center for Neutron Research. The porous thin film samples were placed with the beam parallel to the film surface normal. The films were stacked together (with up to 8 films) in order to enhance the scattering signal. The single crystal silicon substrates are essentially transparent to the neutron beam and the scattered intensity arises almost completely from the structure in the porous thin films. The neutron beam wavelength, λ , was 6 \AA with $\Delta\lambda/\lambda = 0.12$. The sample to detector distance was 3.6 m and the detector was offset from the beam normal by 3.5° to increase the observable range of scattering angles. The scattered intensity was collected on a 2-D detector and the data were reduced using standard data reduction methods. The scattered intensity is presented as a function of q (where $q = (4\pi/\lambda)\sin(\theta/2)$ and θ is the scattering angle) [7]. The 2-D data are circularly averaged and placed on an absolute intensity scale using pure water as a secondary standard. Figure 2 shows the circularly averaged data all three porous thin films.

The neutron scattering data can be qualitatively interpreted from the shape of the scattering curves. In q space (reciprocal space), the data at a given q value can be thought of as an observation of the sample at a particular length scale. Low q values represent larger sizes in real space and higher q values move to smaller length scales. From Figure 2, it is clear that the shapes of the scattering curves and the relative intensities of the scattering from each sample are very different. Sample A exhibits the highest scattering intensity and a monotonically decreasing

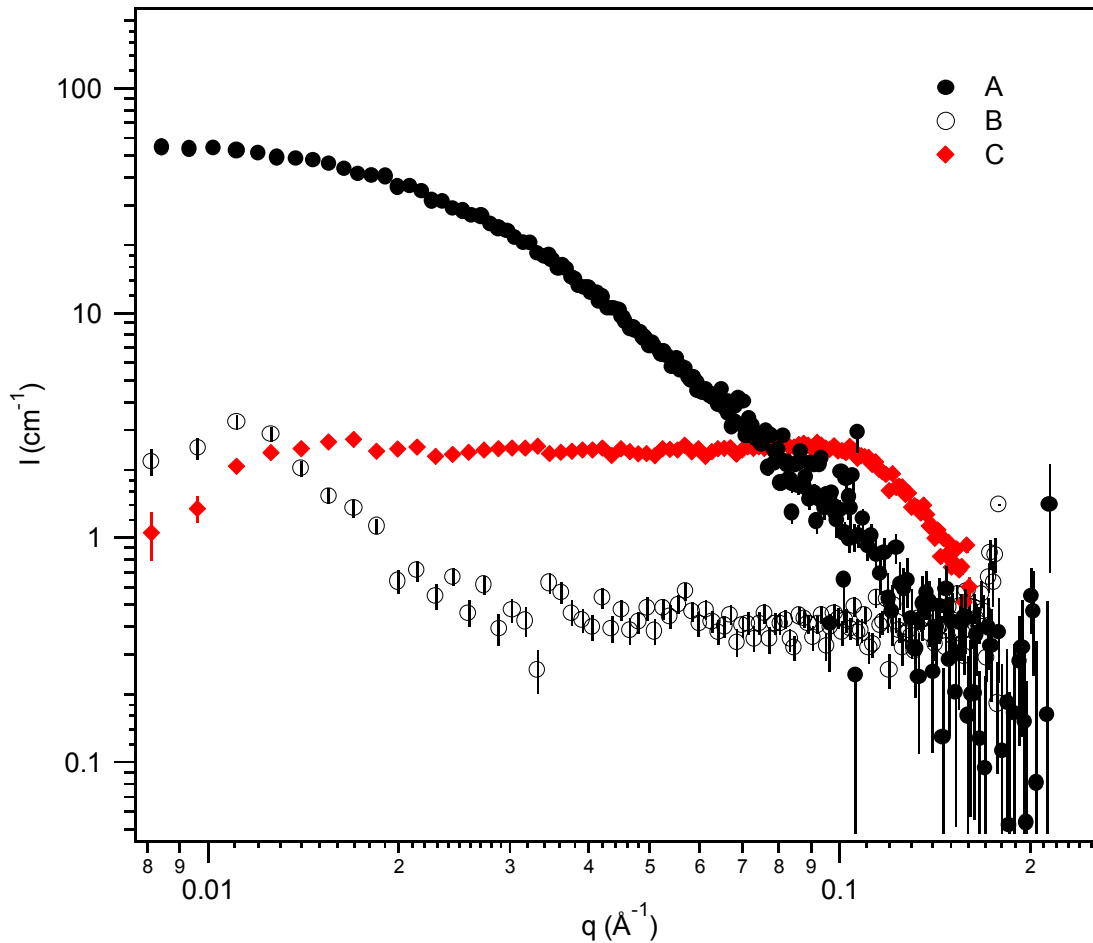


Figure 2. Representative SANS data from three qualitatively different silica-based porous thin films. The absolute intensity is shown as a function of q where $q = (4\pi/\lambda)\sin(\theta/2)$. Sample A is an aerogel material, sample B is a CVD prepared material, and sample C is a porous silica sample.

scattering profile with q . This suggests that sample A has structural features over all observed length scales and is indeed well characterized by the random two-phase model of Debye to be described later [8]. In contrast, sample B has a very low scattering intensity suggesting the presence of fewer scattering sites. There are features at low q values, indicating some heterogeneities at larger length scales, but the scattering intensity at $q > 0.03 \text{ \AA}^{-1}$ arises primarily from inelastic or background scattering. Sample C is intermediate to A and B in terms of scattering power, but has an interesting scattering profile. The intensity is almost flat over q ranging from 0.02 \AA^{-1} to 0.1 \AA^{-1} . This indicates that the film appears homogeneous over the breadth of these length scales. At $q > 0.1 \text{ \AA}^{-1}$, the scattered intensity drops very sharply with a power law dependence very close to q^{-4} . This scaling power of the intensity with q is important and was first described by Porod [9]. Porod demonstrated that the scattered intensity of two-phase systems with infinitely sharp interfaces must decrease as q^{-4} at length scales (real space) that are both smaller than the average size and curvature of the domains. The power law generally reflects the requirement that at larger q values, the scattering arises from the total

interfacial boundary. Sample C is an interesting sample with nearly homogeneous structure until the Porod region where the interface between the pore and the matrix material is very sharp.

To quantitatively analyze the SANS data, a suitable scattering model must be chosen to describe the data. Thus far, three different analysis methods have been used and/or developed to analyze porous thin film samples, a simple two-phase model, a three-phase model, and a Porod model. The two-phase model and the Porod model will be presented here. The three-phase model is derived from the two-phase model and is the focus of an accompanying paper [10].

Two-phase analysis using the Debye model

The two-phase model is the simplest model to describe a high porosity material. In this model, there are only two phases, the pores and the matrix material. Additionally, the matrix material is assumed to be homogenous. Debye developed the formalism describing the scattering that arises from a random two-phase structure [8]. The density correlation function describing the structure is assumed to be $\gamma(r) = \exp(-r/\xi)$, where ξ is the correlation length. The average chord length of the pores is then given by the equation $l_c = \xi/(1-P)$. The SANS intensity is given by the equation

$$I(q) = \frac{8\pi P(1-P)\Delta\rho_n^2 \xi^3}{(1+q^2\xi^2)^2} \quad (2)$$

where $\Delta\rho_n$ is the neutron scattering contrast and is determined by the elemental composition of the solid matrix material and is linearly dependent upon ρ_w . The correlation length, ξ , and the scattered intensity at $q=0$, can be determined by linearly fitting SANS data plotted as $1/I^{1/2}$ vs. q . At this point in the analysis, only the correlation length is quantitatively determined. For the case of sample A, the correlation length is found to be $(25.3 \pm 0.5) \text{ \AA}$.

To determine the film porosity, P , and the matrix mass density, we must use additional information from SXR. Given $I(0)$ and ξ , equation (2) becomes a function only of ρ_w and P . From the SXR formalism, equation (1) is also a function of ρ_w and P . With two equations and two unknowns, ρ_w and P , we can solve for these two quantities for the porous thin film. For sample A, we find that porosity is $(56 \pm 1)\%$ by volume, the matrix mass density is $(1.63 \pm 0.05) \text{ g/cm}^3$, and the average chord length of the pore is $(57.5 \pm 0.5) \text{ \AA}$.

The pore connectivity and moisture uptake of the film can also be determined using the Debye formalism. The samples are placed into quartz cells and immersed in either deuterated toluene (d-toluene) or deuterated water (D2O). The d-toluene solvent is chosen because it readily wets the samples provided to us thus far. If either of the deuterated solvents penetrates open and interconnected pores, the absolute value of the scattered intensity changes because of the large contrast change in $\Delta\rho_n^2$ from air or vacuum in the pores to a deuterated material. If all the pores within a sample were filled, the entire scattered intensity would increase by roughly a factor of 18.3. If the increase in scattered intensity is less than 18.3, then only a fraction of the pores are filled with the solvent. In a similar manner, the moisture uptake of D2O may also be determined. In this methodology, pore connectivity represents the fraction of pores that are interconnected and accessible to a solvent at the outside surface. The details of this approach may be found in an earlier publication [5].

Porod invariant analysis

Although many of the samples are well described by the Debye two-phase model, several samples exhibit SANS profiles that cannot be analyzed in this framework. To address these samples, the Porod invariant analysis developed to describe small angle scattering from a two-phase system is applied to determine the average pore size of the porous low-k dielectric thin film. To apply this method, the sample must be a two-phase system with sharp interfacial boundaries. The scattering curve must decrease as q^{-4} as predicted using Porod's law. To extract the characteristic length scale of the pores, the average chord length in the pore structure, we use the Porod invariant of the scattered intensity given by

$$Q_{\text{exp}}^* = \int_0^{\infty} q^2 I(q) dq \quad (3).$$

Conceptually, the Porod invariant relates the experimental intensity to the average mean square of the scattering length fluctuations [9]. The measured invariant can be used to directly determine the average chord length, l_c , through the relationship [9]

$$l_c = \frac{\pi}{Q_{\text{exp}}^*} \int_0^{\infty} q I(q) dq \quad (4).$$

An important advantage of this procedure is that the average chord length of the materials can be determined without reference to an absolute intensity. This procedure is applied to sample C shown in Figure 2. For this scattering curve, the intensity drops off at $q > 0.1 \text{ \AA}^{-1}$ values as q^{-4} . This power law indicates that the interface between the pores and the matrix material is sharp and the integrals in equation (3) and (4) converge. The average chord length for sample C is determined to be $(20.8 \pm 0.5) \text{ \AA}$. It should be noted that since the Porod limit is reached, the data are extrapolated to high enough q values to ensure convergence of the integral in equation (3). This is necessary in this case because the scattered intensity cannot be measured at high enough q values because the observed length scale reaches the size of constituent atoms.

To determine the porosity of the film using this formalism, we use the theoretical definition of the invariant given by the following equation

$$Q_{\text{th}}^* = 2\pi^2 \Delta\rho_N^2 P(1-P) \quad (5).$$

As in the Debye two-phase model, there are two equations, equation (2) and equation (5), which are functions of ρ_w and P (given the elemental composition). In this case, Q_{th}^* is replaced with Q_{exp}^* . We implicitly assume that the structure of the thin film is well described by only two homogeneous phases, the pores and the matrix material, and that the interface between the pores and the matrix is very sharp. Using equations (2) and (5), the porosity and matrix density of sample C are found to be $(64 \pm 1)\%$ by volume and $(2.19 \pm 0.05) \text{ g/cm}^3$, respectively.

SUMMARY

We have demonstrated that the complementary use of high-resolution specular x-ray reflectivity and small angle neutron scattering is a powerful method for the characterization of

the structure and properties of porous thin films for use as low-k dielectric materials. These techniques are able to measure porous thin films up to 1 μm thick as prepared on silicon substrates. In addition to the measurement of film porosity, thickness, roughness, coefficient of thermal expansion, average film density, average pore size, and pore connectivity, this methodology uniquely provides the matrix wall density. Two different frameworks are applied to specific porous thin film SANS data to obtain important structural information, the average chord length, of the films. The data obtained from these methods and others can be used to correlate structural properties to processing method and conditions as well as other important material properties other than dielectric constant.

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