A Three-phase Model for the Structure of Porous Thin Films Determined by X-ray Reflectivity and Small-Angle Neutron Scattering

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ABSTRACT

A methodology to characterize nanoporous thin films based on a novel combination of high-resolution specular x-ray reflectivity and small-angle neutron scattering has been advanced to accommodate heterogeneities within the material surrounding nanoscale voids. More specifically, the average pore size, pore connectivity, film thickness, wall or matrix density, coefficient of thermal expansion, and moisture uptake of nanoporous thin films with non-homogeneous solid matrices can be measured. The measurements can be performed directly on films up to 1.5 μ m thick while supported on silicon substrates. This method has been successfully applied to a wide range of industrially developed materials for use as low-k interlayer dielectrics.

INTRODUCTION

Porous materials with nanoscale voids are leading candidates for next-generation low dielectric constant or low-k thin films to be used as an interlayer dielectric (ILD) materials. The introduction of voids in the material can effectively lower the dielectric constant, k, of the base material. For example, when the film porosity approaches 75% by volume, the dielectric constant of silica, nominally about 4, can be reduced to about 2.0 and below [1]. A low dielectric constant for ILD is needed to decrease the energy needed to propagate a signal and to decrease crosstalk between adjacent conductors. Many techniques have been established to characterize the performance properties for interlevel dielectric thin films [2]. However, few techniques are able to measure the structural properties of porous films ~1 μ m thick supported on silicon substrates. Recently, Gidley et al. used positronium annihilation lifetime spectroscopy to measure void sizes and distributions [3]. Baklanov et al. use ellipsometric porosimetry to also measure void sizes and distributions [4]. Wu et al. [5] have demonstrated that the average void size, porosity, film density, coefficient of thermal expansion, connectivity among voids and moisture uptake can be measured using a combination of high resolution specular x-ray reflectivity [6-8] (SXR) and small angle neutron scattering [9] (SANS) techniques.

In the use of SXR and SANS to characterize nanoporous thin films, an underlying hypothesis of this methodology is the homogeneity of the material surrounding the voids. It invokes a simple two-phase model in which the material around the voids is assumed to be homogeneous. The only heterogeneity in the film comes from the voids. For many materials from different sources, the two-phase methodology has been successfully applied. However, there exist samples where the SANS intensities are too high for any two-phase material given its measured elemental

composition. As a result, the two-phase model results in unrealistically high values for the density of the material surrounding the voids. To ensure more reasonable values, a new three-phase model methodology is developed here that is capable of dealing with deficiencies in the two-phase methodology. The underlying principles for both the three phase and the two-phase methodology [5] are identical; they both rely on the complementary nature of the results from SANS and SXR. The difference lies in the model used to interpret the SANS results. Consequently, the results on CTE, film thickness, and the electron density are unchanged with regard to the specific methodology used because these quantities are determined solely from SXR data.

The rest of this manuscript will be arranged as follows. The fundamentals of SANS, SXR and the two-phase methodology will be briefly reviewed, the shortcoming of the two-phase model will then be discussed and followed by outlining the rationale for introducing three-phase model. An example of the application of the three-phase model will be provided at the end of the manuscript.

TWO-PHASE METHODOLOGY

The novelty of our approach to characterizing porous thin films is two fold: the use of a new high-resolution x-ray reflectometer to accurately characterize films up to 1.5 µm thick and the use of complementary data obtained from both SXR and SANS as a set of simultaneous equations to quantitatively determine structural parameters of porous thin films. In the two-phase method [5], we used the simplest description of a porous material; a two-phase model where one phase is comprised of the voids and the other is comprised of the connecting material. The connecting material (the pore wall material) is assumed to be uniform in composition and in density. With this assumption, the average density of the film can be parameterized with two unknowns, the porosity, P, and the wall density, ρ_w . These two variables cannot be independently determined from either SXR or SANS data alone. By using both techniques and solving simultaneous equations, specific to each technique and involving these two variables, the values of the unknowns can be determined. In order to perform this analysis, we must also know the chemical composition of the film. The chemical compositions were determined using a combination of Rutherford back scattering (RBS) (for silicon, oxygen, and carbon) and forward recoil elastic scattering (FRES) (for hydrogen). The film composition is used to convert electron density to mass density in the SXR data analysis and to determine the scattering contrast between the connecting material and pores in the SANS analysis. In addition to P and ρ_w another parameter, the correlation length, ξ , is determined from the SANS data. These three parameters are widely used to characterize two-phase materials. Most of the low k ILD films analyzed by us are well characterized using the two-phase model.

Many of the ILD samples, however, are found to contain a significant amount of hydrogen atoms. Hydrogen represents a special case in neutron scattering because the neutron scattering length, b_H , of hydrogen is negative. As a result, the spatial distribution of hydrogen has a major impact on the observed SANS intensity. The three-phase model is developed to help interpret the inhomogeneous distribution of hydrogen with the thin film.

THREE-PHASE METHODOLOGY

For a two-phase system, the neutron scattering contrast, η^2 , can be expressed as

$$\eta^2 \propto P(1-P)(\rho_w \sum (n_i b_i / m_i))^2$$
 (1).

P again is the porosity or the volume fraction of the voids, and b_i , n_i and m_i denote the neutron scattering length, the number fraction and the atomic weight of element i, respectively. The summation in equation (1) is over all the elements present in samples. The observed SANS intensity dictates the magnitude of η^2 and the SXR data determine the value of the product $\rho_w(1-P)$. In samples with significant amount of hydrogen, the observed SANS intensity (and hence η^2) can only be accounted for with an unrealistic value of ρ_w . For example, a sample with the following composition by number, Si (16%), O (26%), C (19%) and H (39%) was measured and SXR results indicated that the film density was (0.72 ± 0.01) g/cm³. Using a combination of SANS and SXR data, the calculated value of ρ_w was (3.30 ± 0.2) g/cm³, a value higher than that of quartz and thus an unrealistic one. The corresponding porosity was (78 ± 1.5) %. This high wall density value can be regarded as a definitive sign that the hydrogen atoms are not uniformly distributed within the wall or matrix material. In the two-phase methodology, the overall density of the matrix material was forced to adopt a high value in order to provide sufficient scattering contrast between the matrix material and the wall and compensate for the inhomogeneous distribution of hydrogen.

The three-phase model is developed as a reasonable model to represent the heterogeneous distribution of hydrogen in the porous thin film. Since it is unphysical to have all the hydrogen atoms to form a phase or clusters by themselves, we assume that all the hydrogen and carbon atoms exist as hydrocarbons and are segregated from the silicon and oxygen atoms. The nanoporous thin film mentioned above is then assumed to be comprised of three phases, the hydrocarbon phase (phase 1), the silicon and oxygen or silica phase (phase 2) and the voids (phase 3). The corresponding contrast factor of the three phase material can be expressed as

$$\eta^{2} \propto \Phi_{1}(1-\Phi_{1})(B_{2}-B_{3})^{2} + \Phi_{2}(1-\Phi_{2})(B_{3}-B_{1})^{2} + \Phi_{3}(1-\Phi_{3})(B_{1}-B_{2})^{2}$$
(2)

where Φ_j stands for the volume fraction occupied by phase j [10]. By definition, Φ_3 is equal to P, the porosity of the film. B_j is the neuron scattering length of phase i and is defined as $\rho_j \Sigma (n_i b_i / w_i)$ where ρ_j is the mass density of phase j and the summation is over all the elements existed in phase j. Also by definition, B₃, the neutron scattering length of voids, is zero. Within the above equation there are a total of five unknowns and they are Φ_1 , Φ_2 , Φ_3 , ρ_1 , and ρ_2 . There are two obvious constraints or relations for these unknowns and they are;

$$\Sigma \Phi_i = 1 \tag{3}$$

for the sum of all three volume fractions to be unity, and

$$\Phi_1 \rho_1 / \Phi_2 \rho_2 = (n_c m_c + n_H m_H) / (n_{Si} m_{Si} + n_o m_o)$$
(4)

where the mass ratio between phases 1 and 2 is equal to the ratio of the total mass of the constituents. At this point, there are still three unknowns and the SXR data provide an additional relation or constraint for these unknowns. More explicitly,

$$Q_c^2 \propto (\Phi_1 \rho_1 + \Phi_2 \rho_2) / (\Phi_1 + \Phi_2)$$
 (5).

Where Q_c^2 stands for the critical angle expressed in the Fourier space measured by SXR, and the right hand side of the above equation is, by definition, the matrix material or the wall density. The SANS data provide a measure of η^2 of the equation (2), but there is still a need for one more experimental measurement of some of the five variables. In this work, we instead assume that the density of hydrocarbon phase, ρ_1 , to be unity. This is believed to be a reasonable assumption because the bulk density of many hydrocarbons is close to one.

The sample mentioned above was reanalyzed using the three-phase model and the matrix density was found to be (1.71 ± 0.05) g/cm³, a value close to that of a thermally grown silicon oxide and its porosity was (58 ± 1.5) %. This example does not necessarily prove that the matrix material surrounding the voids is indeed made of two phases, a hydrocarbon phase and a silica phase. This result does provide strong evidence that the matrix is not a homogeneous one-phase material. The three-phase model discussed here is the simplest extension of the two phase model and its application shall be limited to cases where the two-phase methodology fails to provide physically meaningful results.

In addition to all six Φ_i and ρ_i parameters, three correlation lengths, ξ_i , one for each phase i, are needed to fully characterize a three-phase system. It is noteworthy that there is only one correlation length for a two-phase system and its value can be deduced directly from the SANS data using Debye, Porod, or other analysis schemes [11]. For a three-phase system, all three correlation lengths manifest themselves in the SANS results via a relation similar to that of equation (2). Each correlation length is weighted by the neutron scattering contrast factor of that particular phase. Conveniently, the neutron contrast factor of hydrocarbons, especially for those with a 1:2 carbon to hydrogen ratio, is nearly zero because the scattering length of hydrogen is -3.74×10^{-13} cm and 6.65×10^{-13} cm for carbon. Accordingly, the measured correlation length in our example can be treated as if the system is a two-phase system with a silicon-oxygen phase and a voids-hydrocarbon phase. The chord length of each phase can be deduced with the two-phase scheme [11].

After their structural parameters being determined with the three-phase scheme, the pore connectivity and moisture uptake can be determined using the methodology developed for two-phase system. The pore connectivity and moisture uptake were measured by conducting SANS measurement on samples immersed respectively in either a deuterated organic solvent or in deuterated water. Organic solvents with low interfacial tension can readily fill interconnected pores having a passage to the exterior surface to cause a scattering contrast change. Deuterated toluene has been used for all of the samples tested because it spreads readily on surfaces of those samples. Once the pores are filled, the scattering contrast changes dramatically depending on the neutron scattering length of the solvent used. The percentage of the pores filled by solvent or water can be determined from the difference in SANS intensities between thin films before and after immersion.

CONCLUSION

A combination of SXR and SANS data from some nanoporous thin films indicate that the matrix material surrounding the voids is not homogeneous and that hydrogen within the film must be segregated in some way. By assuming that of all the hydrogen and carbon are segregated into a phase with a mass density of unity, a three-phase methodology has been developed and applied successfully to samples that previously could not be described with a simple two-phase model.

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