# Structural characterization of porous low-*k* thin films prepared by different techniques using x-ray porosimetry

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Three different types of porous low-*k* dielectric films, with similar dielectric constants, are characterized using x-ray porosimetry (XRP). XRP is used to extract critical structural information, such as the average density, wall density, porosity, and pore size distribution. The materials include a plasma-enhanced-chemical-vapor-deposited carbon-doped oxide film composed of Si, C, O, and H (SiCOH) and two spin cast silsesquioxane type films—methylsilsesquioxane with a polymeric porogen (porous MSQ) and hydrogensilsesquioxane with a high boiling point solvent (porous HSQ). The porous SiCOH film displays the smallest pore sizes, while porous HSQ film has both the highest density wall material and porosity. The porous MSQ film exhibits a broad range of pores with the largest average pore size. We demonstrate that the average pore size obtained by the well-established method of neutron scattering and x-ray reflectivity is in good agreement with the XRP results. © 2004 American Institute of Physics. [DOI: 10.1063/1.1641955]

## I. INTRODUCTION

Silicon dioxide  $(SiO_2)$  has been the interlayer dielectric in the interconnect of integrated circuits. However, the dielectric constant of SiO<sub>2</sub> cannot sufficiently prevent cross talk between closely spaced copper wires in the latest generation of semiconductor devices. To address this problem, materials with lower dielectric constants (low-k) are being developed.<sup>1,2</sup> State-of-the-art nonporous low-k dielectric materials typically have k values ranging from 2.6 to 3.0, but these need to be further reduced to 2.2 or below in the next few years.<sup>3,4</sup> The most common approach for decreasing the dielectric constant is to incorporate nanometer size voids (k =1.0) into these materials. However, depending on the structural details, porosity can also adversely affect other properties crucial to chip performance, such as mechanical strength, electrical properties, and Cu diffusion into the insulator. Therefore, determining the pore size and pore size distribution (PSD) of these thin films is key to optimizing the processing conditions for implementation in the future device generations. There are several promising methodologies for characterizing pore structures,<sup>5</sup> including focused positron beam techniques,<sup>6</sup> ellipsometic porosimetry (EP),<sup>7</sup> small angle x-ray scattering (SAXS),8 and a combination of specular x-ray reflectivity (SXR), small angle neutron scattering (SANS), and ion-beam scattering.<sup>9</sup> Each of these methodologies has its inherent limitations. For examples, SANS is limited by the availability of neutron scattering facilities while both SANS and SAXS lose sensitivity for pores significantly smaller than 10 Å in diameter. At the other extreme positron beam techniques are well suited for pores smaller than 20 Å in diameter, but unfortunately require a high-vacuum environment. EP is similar to x-ray porosimetry (XRP) described herein except that it uses light, not x-rays, and monitors changes in the index of reflection. (XRP measures changes in density directly.)

Recently, we demonstrated the feasibility of XRP as a metrology to determine critical structural characteristics, such as porosity, average film density, and matrix or wall density for plasma-enhanced chemical-vapor-deposited (PECVD) low-k films with relatively small pore sizes and low porosities.<sup>10</sup> In this work, we use XRP to compare the PSD of three nanoporous low-k thin films with similar dielectric properties, but prepared by three different processing techniques and materials. We will demonstrate that XRP can perceive subtle differences in the pore structures of these otherwise similar low-k films. XRP operates on principles analogous to traditional adsorption/desorption porosimetry techniques, where the amount of a gaseous probe molecule (in this work, toluene) condensed inside the porous sample is measured as a function of its partial pressure. The partial pressure is defined here as the vapor pressure of the gas divided by the saturated or equilibrium vapor pressure. The toluene uptake is determined directly, without assumptions, from the increase of the critical angle for total x-ray reflection. Furthermore, if there are changes in film thickness upon adsorption/desorption, this can be determined precisely from the changes in the interference fringes in the SXR curves (no swelling is observed in the films presented here). The Kelvin equation<sup>11</sup> is used to describe the relationships between the partial pressure of the gas to a critical pore size for condensation. If the mechanism of pore filling is found to be inconsistent with simple capillary condensation, the Kelvin equation can be replaced with a more appropriate expression for

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converting the partial pressure for condensation into a pore size. Nevertheless, XRP provides a simple, yet powerful, way to determine PSDs within a porous thin film.

## **II. EXPERIMENTAL PROCEDURE**

Three classes of low-k materials prepared through different techniques are used for this study. The first class of material is a hydrogensilsesqioxane (HSQ) porous film prepared by evaporation of a high boiling point solvent after gelation of the HSQ resin.<sup>3</sup> The second is a methylsilsesquioxane (MSQ) porous film generated through a templated vitrification of low molecular mass siloxane oligomers.<sup>12</sup> The third material is deposited by PECVD from a mixture precursor of an organic (the porogen) and tetramethylcyclotetrasiloxane.<sup>4</sup> This will be referred to as porous SiCOH. The dielectric constants of the porous HSQ, porous MSQ, and porous SiCOH films are all similar, approximately 2.20, 1.85, and 2.05, respectively. In light of the similar dielectric properties, we compare the pore structures in these films since the latter also affects other critical properties.

SXR measurements at grazing incident angles monitor the critical angle for total external x-ray reflectance, and thus changes in electron density of the film as toluene adsorbs/ desorbs into/out of the pores.<sup>13</sup> The x-ray source is a finely focused copper  $K\alpha$  radiation ( $\lambda = 1.54$  Å) with highresolution optics described elsewhere.9 The films are mounted in the reflectometer and first evacuated at 175 °C for 2 h before cooling to room temperature. Then reflectivity is collected at room temperature to determine the critical angle of the sample in a vacuum. Next, the sample temperature increases to 125 °C and a stream of air saturated with toluene at 20 °C is passed over the film. This air is saturated by slowly bubbling through liquid toluene at  $(20\pm0.1)$  °C.<sup>14</sup> When the sample temperature is also at 20 °C, the toluene environment around the sample is fully condensing, i.e., the partial pressure  $P/P_0$  is 1.0. Here, P is the actual vapor pressure while  $P_0$  is the equilibrium vapor pressure. Heating the sample increases  $P_0$  which effectively decreases  $P/P_0$ . By heating the sample to 125 °C (and keeping the purge air saturated with toluene at 20 °C),  $P/P_0$  is effectively reduced to zero. The toluene adsorption/desorption curves are then collected by changing the sample temperature between 125 °C and 25 °C. After each temperature change, 30 min is allowed for equilibration before the reflectivity measurement. Here, we compare the results from XRP to those obtained through the SANS/SXR techniques described elsewhere.<sup>9</sup> The SANS measurements are done on the NG1 beamline at the National Institute of Standards and Technology Center for Neutron Research. Like XRP, the SANS under a vacuum also determines an average pore size for the film.

#### **III. RESULTS AND DISCUSSION**

Figure 1 shows experimental SXR data for the different porous low-*k* films both under a vacuum and in the toluene-saturated environment. The data are presented as the logarithm of the reflectivity (defined as  $I_{\text{reflected}}/I_{\text{incident}}$ ) as a function of q ( $q = (4 \pi/\lambda) \sin \theta$ ). As the incident angle  $\theta$  in-



FIG. 1. SXR curves of porous HSQ, porous MSQ, and porous SiCOH thin films. The curves are offset for clarity. The standard uncertainty in  $\log(I_{\text{reflected}}/I_{\text{incident}})$  is less than the linewidth.

creases, the x-rays first penetrate the film at a critical angle  $\theta_c$ , at which point the reflected intensity drops sharply. The square of this critical angle is proportional to average electron density of the thin film through the equation,  $\theta_c$  $=\lambda (\rho_e r_e/\pi)^{0.5}$ , which can then be used to calculate the average mass density from the atomic composition. Here  $\rho_{e}$ is the electron density and  $r_e$  is the classical radius of an electron. For these films, the atomic composition is determined experimentally via ion beam scattering, through a combination of the Rutherford backscattering, forward scattering, and forward recoil scattering techniques.<sup>15</sup> The comparison of the reflectivity curves under a vacuum in Fig. 1 shows that the critical angle for total reflection occurs at lower angles (lower q) for the films with lower k, qualitatively indicating that the density of porous thin film decreases with the dielectric constant. It is also clear that the critical angle shifts to a higher q in the presence of the saturated toluene vapor. Capillary condensation of the toluene inside the accessible pores results in an appreciable increase of the density. A larger difference between critical angles of the vacuum and the toluene-saturated curves indicates a greater uptake of toluene, and thus a greater porosity. From these two curves, one can calculate the total amount of toluene adsorbed, the total porosity P, and the density of the material separating the pores  $\rho_{\rm wall}$ .<sup>10</sup> However,  $\rho_{\rm wall}$  calculated by this method is an average of the wall material plus any unfilled pores, i.e., pores too small or inaccessible to a toluene molecule. The porosities obtained by this method for the porous HSQ, porous MSQ, and porous SiCOH films are 46%, 34%, and 31%, respectively. The corresponding wall densities of the porous HSQ, porous MSQ, and porous SiCOH films are 1.83 g/cm<sup>3</sup>, 1.35 g/cm<sup>3</sup>, and 1.31 g/cm<sup>3</sup>, respectively. Notice that the porous HSQ film has the highest porosity, yet its dielectric constant is the largest because of its high wall density. It is also interesting that the porous MSQ and porous SiCOH films have similar average densities, wall densities, and atomic compositions, despite the fact

TABLE I. Atomic composition, dielectic constant (k), and structural characteristics of porous low-k thin films prepared through different techniques. The relative standard uncertainties of the atomic composition,  $q_c^2$ , density, porosity, and pore radius  $\pm 2\%$ , 0.05 Å<sup>-2</sup>, 0.05 g/cm<sup>3</sup>, 1%, and 1 Å, respectively.

	Atomic composition (Si:O:C:H) (%)		$q_c^2$ (E-4) (Å <sup>-1</sup> )	Average density (g/cm <sup>3</sup> )	Wall density (g/cm <sup>3</sup> )	Porosity (%)	Pore radius (Å)	
Samples		k					XRP	SANS
Porous HSQ	25:48:7:20	2.20	4.25	0.98	1.83	46	13	9
Porous MSQ	15:25:19:41	1.85	3.95	0.89	1.35	34	15	10
Porous SiCOH	10:20:28:42	2.05	4.04	0.91	1.31	31	5	3

they are prepared from very different techniques. The elemental composition and detailed structural characteristics of the samples are summarized in Table I.

The sensitivity and resolution of SXR are sufficient to reveal subtle differences between the three films as the toluene atmosphere gradually varies from  $P/P_0 = 0$  (vacuum) to  $P/P_0 = 1$  (saturated) and toluene progressively adsorbs into the pores. The toluene uptakes determined from the critical angle are plotted as a function of the relative partial pressure in Fig. 2. The adsorption isotherm for the porous SiCOH film displays a prominent uptake at low partial pressures that quickly levels off. There is no hysteresis between the adsorption and desorption branches. This is characteristic of filling micropores, i.e., pores less than 2 nm in diameter,<sup>16</sup> indicating that the PECVD process generates a large population of small pores. In comparison, the porous MSQ films adsorb over a broad range of larger partial pressures. There is also a pronounced hysteresis between the adsorption and desorption pathways for the porous MSQ film, indicating a larger distribution of mesopores. This indicates that the porogen in the PECVD film forms smaller domains than the spin-cast MSQ film, leading to smaller pores in the porous SiCOH film. This is striking because the porous SiCOH and MSQ films are otherwise similar in terms of their atomic composition, total porosity, and wall densities; the primary difference is in their PSDs.

At low partial pressures, the adsorption process in both spin-on-glass (SOG) films (porous HSQ and MSQ films) is



FIG. 2. Adsorption/desorption isotherms for porous HSQ, porous MSQ, and porous SiCOH films. The lines are smooth fits using the sum of a sigmoidal and a log-normal function, for porous HSQ, and porous MSQ, and a Gaussian and a sigmoidal function, for the adsorption and the desorption curves of porous SiCOH, respectively.

gradual at first, but increases steeply at intermediate partial pressures due to capillary condensation in the mesopores. After these mesopores are filled, the adsorption isotherms level off. Note that capillary condensation and evaporation do not take place at the same partial pressures, i.e., there is an appreciable hysteresis. The hysteresis loop in the MSQ film is highly asymmetric (broad on adsorption, narrow on desorption), suggesting that pore connectivity (network) effects are important.<sup>17</sup> If larger pores can only be accessed through neighboring or interconnected narrow pores, the larger pores are not free to desorb at the relative pressure corresponding to their critical capillary radius. The smaller pores block the desorption of the larger pores in a manner that has been described as the ink-bottle effect in the porosimetry literature.<sup>11</sup> The result is a simultaneous draining of both the small and large mesopores at a partial pressure corresponding to the critical radius of the smaller pores, and hence the sharp drop in the desorption curve in Fig. 2.

From the adsorption/desorption isotherms, we have already qualitatively arrived at the pore structures schematics displayed in Fig. 3. The PECVD process creates the smallest pores, in very large quantities. The lack of a hysteresis loop confirms that the dimensions of pores are on the order of a few toluene molecules. These pores, as well as all the films studied here, are apparently interconnected since toluene freely diffuses into and out of the structures. The total porosity is, however, greater in the HSQ material as indicated by the largest toluene uptake. The pores in the porous HSQ, generated by the evaporation of a high boiling point solvent, are larger than the pores of the PECVD material. Like the pores in porous SiCOH, those in the porous HSQ are fairly uniform in their size distribution as indicated by the symmetric and relatively narrow hysteresis loop. This is in contrast to the MSQ film with its very broad pore size distribution and the largest average pore size (despite the lower porosity in comparison to the HSQ film). As discussed above, the sharp desorption branch of the MSQ film in contrast to the broad adsorption pathway indicates that pore blocking effects are significant.

This qualitative description can be quantified by using the Kelvin equation<sup>11</sup> to convert the partial pressures in Fig. 2 into pore sizes, thereby establishing a PSD. Again, we emphasize that the use of the Kelvin equation here is for demonstration purposes. The Kelvin equation,  $r_c$  $= -2V_m\gamma/[RT \times \ln(P/P_0)]$  gives the critical pore size for capillary condensation, where  $\gamma$  is the liquid surface tension,  $V_m$  is the molar volume of the liquid, P is the vapor pressure, and  $P_0$  is the equilibrium vapor pressure at temperature T. The desorption branch is generally used to calculate the

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FIG. 3. Proposed structures of the pores in the porous HSQ, porous MSQ, and porous SiCOH films.

PSD, as shown in Fig. 4. The average pore radii in the porous HSQ, porous MSQ, and porous SiCOH films are approximately 13 Å, 15 Å, and 5 Å, respectively. However, the desorption branch of the MSQ film implies a narrow PSD. It is important to realize that this represents the minimum or constricting pore and that the true distribution is larger; therefore, both the adsorption and desorption branches need to be considered.

SANS data also provide a measure of an average pore size that can be compared to the XRP data. Figure 5 displays the SANS data fit with the Debye model<sup>18</sup> to extract an average pore size. In general, an increase in the scattering intensity corresponds to increase in the pore size and porosity. The porous SiCOH film shows weaker scattering than either of the porous SOG films, consistent with the smaller pore size and low porosity. The highest scattering intensity in the porous MSQ film is also consistent with the greatest population of larger pores. For the porous HSQ and porous MSQ films, fits with the Debye model give average pore radii of 9 Å and 10 Å, respectively, comparable to the pore sizes obtained by XRP in spite of the concerns regarding the application of the Kelvin equation to such small pores. The Debye model fit to the scattering data for the porous SiCOH, yields a pore radius of approximately 3 Å. However, these pores are too small for the application of the Debye model given its requirement of a distinct boundary between the pore and the dense material. This respects the fact that XRP is superior than SANS in characterizing small pore porosity.

In closing, Fig. 6 illustrates the ability of XRP to vertically resolve the density profile through the thickness of the film as a function of the partial pressure. This is a distinct

advantage of XRP over other low-k porosimetry techniques. Figure 6(a) shows a series of reflectivity data for the porous HSQ sample as a function of increasing toluene vapor pressure. As toluene condenses progressively into larger pores, the critical angle visibly shifts to higher angles [or higher qin the reciprocal space of Fig. 6(a) as a consequence of the increased average film density. The reflectivity data are fit using a least-squares fitting algorithm<sup>19</sup> to extract the real space physical density profiles in Fig. 6(b). These density profiles are presented in terms of  $q_c^2$ , which in units of Å<sup>-2</sup> is a scattering length density proportional to the physical density (see the previous definitions of q and  $\theta_c$ ). On the horizontal axis 0 Å is defined to be the free surface of the low-kfilm. Moving into the film, there is a step increase of  $q_c^2$  from 0 (air) to some value between (0.42 and 0.62)  $\times 10^{-3}$  Å<sup>-2</sup> reflecting the low-k film density. Another step increase of  $q_c^2$ to a value of approximately  $1.04 \times 10^{-3}$  Å<sup>-2</sup> is encountered beyond 7200 Å, indicating the Si substrate.

There are two features in Fig. 6(b) worth mentioning. First, the density increase from toluene condensation occurs uniformly throughout the film thickness. We do not observe preferential condensation near either the free surface or buried interface, which would arise if there were a difference in the pore size in these regions; the pore size distribution appears to be uniform throughout the film. SXR is capable of detecting such a heterogeneous adsorption if it were to exist. Second, we do not observe a pronounced swelling of the film upon saturating it with toluene. It is trivial to extract this type of information with Å level sensitivity from the reflectivity data. In fact, Fig. 6(b) actually indicates a slight contraction of the film as the partial pressure increase. While at first this



FIG. 4. PSDs from desorption curve fits in Fig. 2 of porous HSQ, porous MSQ, and porous SiCOH films.



FIG. 5. SANS data of porous HSQ, porous MSQ, and porous SiCOH films.

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FIG. 6. (a) SXR curves of porous HSQ film collected at varying partial pressure. The curves are offset for clarity. The standard uncertainty in  $\log(I_{\text{reflected}}/I_{\text{incident}})$  is less than the linewidth. (b) Corresponding density depthe profiles through the depth of the film determined from the best fit to the SXR data in (a).

may seem counterintuitive, it is vital to realize that *sample* temperature is changed here to vary the partial pressure;  $P/P_0=1$  occurs at 20 °C while  $P/P_0=0$  occurs at 125 °C. In this respect, the contraction on going from dry to toluene saturated air is a thermal contraction. Although the data are not shown here, the increase in the thickness of porous HSQ film in a vacuum and under saturated toluene at constant temperature (room temperature) is approximately 1%. Therefore, expansion and contraction in film thickness arise from heating and cooling between 20 °C and 125 °C.

# **IV. CONCLUSION**

In summary, we have applied XRP to measure pore characteristics, i.e., porosity, average film density, wall density, average pore size, and pore size distribution in porous low-k thin films prepared by different formulation processes. The x-ray technique is nondestructive and capable of characterizing thin films directly on a Si wafer, and sensitive enough to perceive subtle structural differences between the different films. XRP has the potential as a valuable experimental tool to provide the semiconductor industry with structural information for developing low-k dielectric materials and optimizing their processing conditions.

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