

X-ray Reflectivity as a Metrology to Characterize Pore Size Distributions in Low-K Dielectric Films

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INTRODUCTION

Increased miniaturization of the integrated chip has largely been responsible for the rapid and continued advances in semiconductor device performance, driving the industry's growth over the past decade. By the year 2003, the minimum feature size in a typical device will drop below the 100 nm level. At these dimensions, interlayers with extremely low dielectric constants (K) are imperative to reduce cross talk and increase device speed. Solutions exist for dielectrics with $K \approx 2.7$, primarily through organosilsesquioxane (SSQ) resins, but to decrease K further requires pore generating additives or porogens. An organic porogen will phase separate from the spin-on resin during application and decomposes at elevated temperatures, thereby inducing large-scale porosity. However, in sub-100 nm films the generation of such porosity requires exacting control. The first step to achieve this understanding, and the focus of this presentation, is to develop high-resolution metrologies that characterize the pores (both porosity and size distribution) in sub-100 nm films. This is crucial to help the materials and process engineers to rationally design the viable and effective low-K dielectric solutions.

METHOD

Specular X-ray reflectivity has been widely used to characterize the thickness, electron density profile, and roughness of low-K dielectric films deposited directly onto Si wafers [1-3]. When a beam of X-rays is impinging on a film at grazing incident angles, all of the X-rays are reflected from the surface. As the incident angle is increased, eventually a critical angle is reached where the X-rays penetrate the sample surface. The critical angle θ_c at which this occurs is proportional to the density of the film through:

$$\theta_c = \lambda(\rho_e r_e / \pi)^{0.5} \quad (1)$$

where λ is the wavelength, r_e is the classical electron radius, and ρ_e is the electron density. By measuring changes in the critical angle of a low-K dielectric film, eq.(1) allows us to track changes in the film density.

To extract a distribution of pore sizes in the film, we couple X-ray reflectivity measurements with the mechanism of capillary condensation. According to the Kelvin equation, at a given partial pressure there is a critical radius at which a solvent will spontaneously condense inside a pore. This critical radius is described by:

$$r_k = \frac{V_m \gamma}{-2RT \ln(P/P_o)} \quad (2)$$

where γ is the surface tension of the liquid, V_m is the molar volume, P is the partial pressure of the liquid vapor, and P_o is the equilibrium partial pressure of the liquid over a flat surface at temperature T . As indicated by eq.(2), this critical radius increases as the partial pressure increases. By slowly increasing the vapor pressure of an organic solvent, such as toluene, over a low-K dielectric film, one can induce capillary condensation of the solvent into progressively larger pores. The X-ray scattering length difference between an empty and toluene filled void is enormous, meaning that the changes in θ_c accurately reflect density changes from the adsorbed toluene. It is then trivial to determine the pore size distribution from the mass of toluene adsorbed as a function of r_k . In the case of toluene, it is easy to access pore radii ranging from (2 - 250) Å by simply varying either P or T in eq. (2).

RESULTS AND DISCUSSION

Fig. 1 demonstrates the changes in X-ray reflectivity curves that arise from the P/P_o variations in a typical low-K dielectric film. In this case the variations reflect heating the substrate, i.e., variations of P_o , T , γ , and V_m , while P is held constant at the P_o for 20 °C. The reflectivity is presented as $\log(R)$, where R is the ratio of the reflected and incident intensities, as a function of q ($q = 4\pi \sin(\theta)/\lambda$).

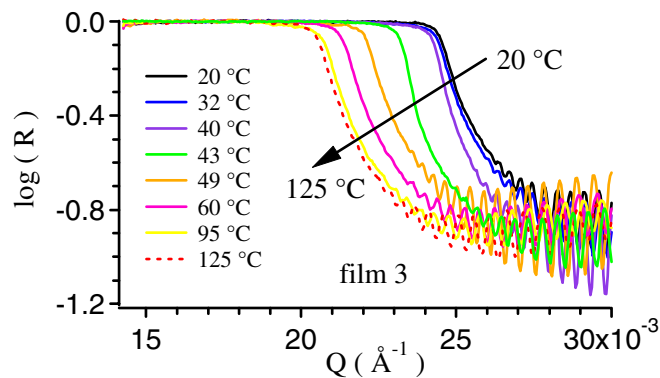


Figure 1. Thermally induced changes in the critical angle of the X-ray reflectivity as toluene condenses in the pores of a typical low-k dielectric film. At 20 °C toluene is fully condensed in the pores and at 125 °C the pores are completely empty. The standard uncertainty in determining the critical angle is 5%.

At low angles all of the X-rays are reflected ($\log(R) = 0$) while at high angles Kessig fringes appear due to interference from the two surfaces of the film. At an intermediate angle there is a sharp transition as the X-rays penetrate the film at θ_c , defined by the wave vector where $R = 0.5$. The θ_c variations define the film density, and thus toluene uptake, as described by eq. (1).

Typical toluene adsorption curves are displayed in Fig. 2 for three low-K dielectric films. The films are all based on SSQ resins with varying amounts of the porogen additive. Films 1 and 2 consist of identical SSQ resins formulated with 1 % and 30 % by mass of the porogen respectively.

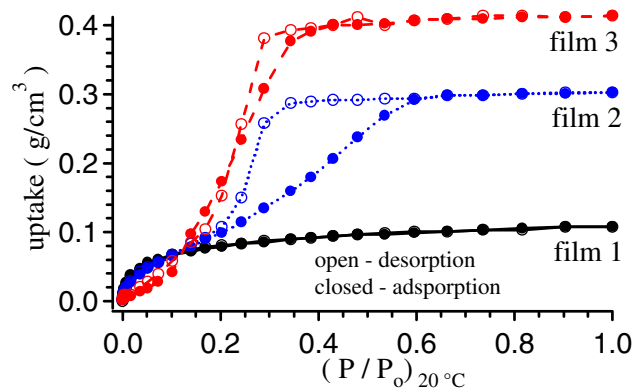


Figure 2. The uptake reflects the capillary condensation of toluene in three different low-K dielectric films. Mass uptake at low partial pressures reflects condensation in small pores while uptake at high pressures indicates larger pores. The film differences are described in the text. The standard uncertainty in the uptake values are 5%.

Film 3 is comprised of a slightly different SSQ resin, also formulated with a large amount of porogen. The shape of the adsorption curves contains detailed information about the pores. In comparing films 1 and 2, both show a small, but strong toluene uptake at low P/P_o as the

smallest pores are filled. In film 1, further increasing P/P_0 does not lead to increased uptake, indicating that larger pores are not present. However, films 2 and 3 show a very strong toluene uptake at higher P/P_0 indicating larger pores. This is consistent with large amounts of porogen in films 2 and 3. It is also worth noting that there is a hysteresis between the adsorption and desorption curves in film 2. The hysteresis will arise if there is a strong distribution of pores sizes such that the desorption from a large pore is blocked by a pathway through a smaller pore that has yet to reach its critical radius.

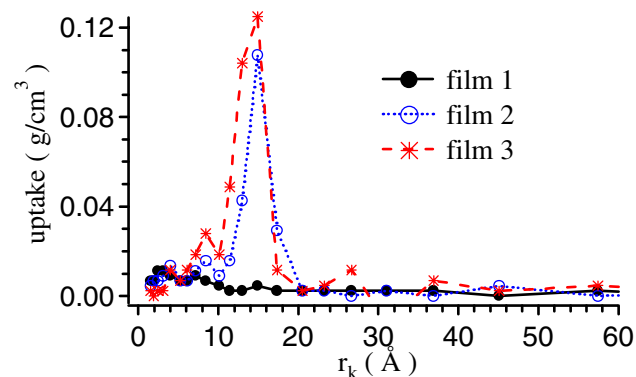


Figure 3. Qualitative pore size distributions for films 1, 2, and 3 derived from the uptake curves in Fig. 2. The population of large pores in films 2 and 3 represent porosity induced by the porogen.

Finally, the pore size distribution is determined by taking the derivative of the adsorption curves after converting the P/P_0 axis to r_k (eq. (2)). This is shown in Fig. 3 where the increment of the mass uptake is displayed as a function of r_k . As expected, all films show a minor population of voids near a critical radius (2 -5) Å. These relatively small voids represent the native porosity of the SSQ resin.

However, films 2 and 3 also display a large population of voids with radii ranging from (10 – 20) Å. These larger voids are a direct consequence of the added porogen. In principal, it is possible to use Fig. 3 and the density of the solvent to extract the total porosity of the film. Of course, such a calculation would be predicated on the assumption that toluene can access all of the pores, i.e., there are no closed or inaccessible pores.

The pore size distributions in Fig. 3 should be considered qualitative at this time as we have yet to accurately assess the standard uncertainty. From the mass uptake alone, this uncertainty is estimated to be 5 %. However, this does not account for situations such as inaccessible pores or wetting of the toluene of onto the pore surfaces. These possibilities, which would affect the calculations, are not taken into account with the current analysis. A more complete analysis is in progress.

CONCLUSIONS

We demonstrate that specular X-ray reflectivity can be coupled with the mechanism of capillary condensation to map out pore size distributions in low-K dielectric films. The measurements can be implemented on most X-ray diffractometers (with only minor modification) and therefore accessible to most laboratories. Additionally, the metrology is compatible with a Si substrate and therefore suitable for on-wafer characterizations.

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