X-ray Reflectivity Porosimetry for the Characterization of Porous Low-k Dielectric Constant Thin Films

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Abstract. X-ray reflectivity porosimetry is a highly sensitive measurement method used to quantify the capillary condensation of a solvent vapor inside porous low-k dielectric films on a silicon substrate. As the partial pressure of the solvent environment over the film increases, capillary condensation occurs in progressively larger pores. This results in an appreciable increase in the electron density of the film. By monitoring the changes in the critical angle for total X-ray reflectance, one can directly calculate the average electron density, and therefore the solvent uptake. By invoking traditional porosimetry absorption/desorption procedures, characteristics such as porosity and the distribution of pore sizes can be extracted.

INTRODUCTION

Increased miniaturization of the integrated chip has largely been responsible for the rapid advances in semiconductor device performance, driving the industry's growth over the past decade. Soon the minimum feature size in a typical IC device will be well below 100 nm. At these dimensions, interlayers with extremely low dielectric constants (k) are imperative to reduce cross-talk and increase device speed. State-of-the-art non-porous silicon based low-k dielectric materials have k values on the order of 2.7. However, k needs to be further reduced to keep pace with the demand for increased miniaturization. There are a number of potential material systems for these next generation low-k dielectrics, including organosilsesquioxane resins, sol-gel based silicate materials, CVD silica, and entirely polymeric resins. However, it is not yet evident as to which material(s) will ultimately prevail. Nevertheless, decreasing k beyond current values requires generating large-scale porosity; lower dielectric constant materials are not feasible with fully dense materials.

The demand of increased porosity in reduced dimensions creates many difficulties. To generate extensive porosity in sub-100 nm films and features one must have exacting control over the pore generation process. The first step towards achieving this control, even before addressing materials issues, is to be able to accurately characterize the physical pore structure (porosity, pore size, pore distribution). While there are several mature porosimetry techniques (gas adsorption, mercury intrusion, quartz crystal microbalances, etc.) capable of characterizing pores significantly smaller than 100 nm, most methods do not have sufficient sensitivity for these porous low-k films. The sample mass in a 100 nm thick film is exceedingly small and the usual observables (i.e., pressure in a gas adsorption experiment or mass in a quartz crystal microbalance) exhibit extremely small changes as the pores are condensed or filled. Thin films require a porosimetry technique with extraordinary sensitivity. Currently, there are few experimental techniques for the on-wafer characterization of pore structure. They include positronium annihilation lifetime spectroscopy (PALS) [1], ellipsometric porosimetry (EP) [2], and a combination of x-ray reflectivity (XR) [3] and small angle neutron scattering (SANS) [4, 5].

POROSIMETRY

Here, we describe an X-ray reflectivity method to characterize pores (both porosity and size distribution) in sub-100 nm films. The experiments are similar to

traditional gas adsorption techniques where the partial pressure P of a given vapor is increased until condensation occurs inside the smallest pores via capillary condensation. Further increasing P increases the critical radius for capillary condensation r_c, progressively filling the larger pores with liquid. There are several possible relations to relate r_c to P, the simplest being the Kelvin equation:

$$r_c = \frac{2V_m\gamma}{-RT}\frac{1}{\ln(P/P_o)} \qquad (1)$$

where γ is the liquid surface tension, V_m is the molar volume of the liquid, P is the partial pressure, and P_o is the equilibrium vapor pressure over a flat liquid surface at temperature T. By knowing the amount of toluene condensed in the sample as a function of P/Po, one can calculate a pore size distribution from Eq. (1). This is the starting point for most porosimetry methods, like the traditional gas adsorption techniques where the amount of condensed vapor is inferred from the pressure drop of a fixed volume of gas as the molecules leave the vapor phase and form a liquid. However, the pressure drop upon adsorption is so small in these thin films that the common methods of porosimetry are no longer feasible.

It is well known that the Laplace pressure across a curved liquid-air interface (i.e., meniscus) shifts the equilibrium vapor pressure to lower values, causing sub-equilibrium vapors to condense inside small pores. Eq. (1) assumes that the pressure difference across the radius of curvature is the only driving force for condensation of toluene inside a pore. However this ignores the possibility of other effects such as preferential wetting, interactions between the toluene and the substrate, increases in the viscosity of the toluene absorbed into pores or channels that approach several macromolecular diameters [6], or even the possibility of spinodal evaporation/condensation [7]. It has been shown that ignoring these effect by using the Kelvin equation, especially in pores smaller than 20 nm, can lead to errors in the pore size of 100 % or more [7-9]. It is beyond the scope of this text to address which analysis is most appropriate for interpreting the adsorption/desorption isotherms; to a large extent this depends upon the details of the low-k material, adsorbate, and pore structure. Rather, we demonstrate that X-ray reflectivity can be used as a highly sensitive method to generate the adsorption/desorption isotherms to be analyzed by Eq. (1) or more sophisticated data interpretation schemes.

In Eq. (1) one of two thermodynamic parameters, either T or P, can be used to vary the critical radius for capillary condensation. Isothermally one can effect changes of r_c by adjusting the toluene concentration in the atmosphere. Experimentally this is achieved by mixing feed streams of dry and toluene-saturated air in various ratios. Analytically this isothermal method is attractive since both γ and V_m are held constant. However, the experimental set-up for isothermal mixing is elaborate because accurate mass flow control valves are required. It is easier to flow a room temperature stream of toluene-saturated air over the sample and vary film temperature. When the film is at room temperature, the vapor will condense and toluene should fill all the voids. Heating the sample increases the equilibrium vapor pressure P_o of the condensed toluene, causing P/P_o, and therefore r_c, to decrease. However, this non-isothermal approach is complicated by the fact that both γ and V_m are a function of temperature.

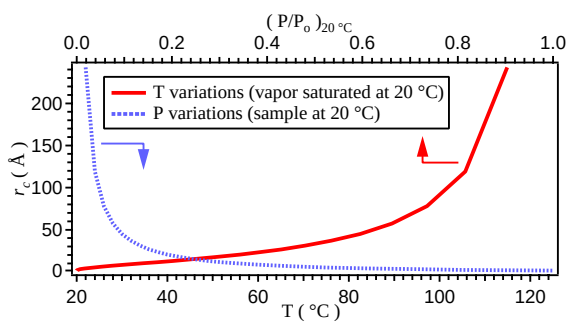

FIGURE 1. In the Kelvin equation, r_c can be varied two ways. r_c values from approximately (1 to 250) Å can be obtained by mixing ratios of dry and toluene saturated air at 20 °C. Likewise, a comparable range of pore sizes can be achieved by flowing air saturated in toluene at 20 °C across the sample and heating the film between 20 °C and 125 °C.

Thermodynamically, it is immaterial whether T or P is used to probe the range of critical pore sizes. The only relevant variables in the Kelvin equation, in addition to the radius of curvature, are $_g$ and V_m and it should be possible to correct for the T variations of these parameters. In principle, the pore size distribution should not depend upon the combination of T and P used to probe a particular critical pore size. For example, suppose that two porosimetry experiments are performed: one utilizing traditional P variations where the toluene vapor concentration is varied while the film is isothermally held at 20 °C and another where toluene vapor saturated at 20 °C flows across the samples while the film is heated from 20 °C to elevated temperatures. In this scenario, for each value of r_c at a given P/P_o (under the isothermal conditions) there should be an equivalent rc at a temperature above 20 °C. Graphically this is depicted in Figure 1. The vertical axis indicates the critical

radius r_c while the upper and lower horizontal axes denote the P and T variations, respectively. The solid line shows how r_c varies isothermally with P/Po (upper horizontal axis) while the dotted line depicts the non-isothermal variations (lower horizontal axis) for air saturated with toluene at 20 °C. In this simple model of the Kelvin equation it should be possible to compare the non-isothermal adsorption/desorption data with the isothermal data through the equality of rc, which yields:

$$\left(\frac{P}{P_o}\right)_{20°C} = \left(\frac{P}{P_o}\right)_T^{\left(\frac{\gamma_{20°C} V_{m,20°C} T}{\gamma_T V_T 293}\right)} \qquad (2)$$

In the following we present both T and P variation data, with the P variations presented as 20 °C isothermal data through the use of Eq. (2).

EXPERIMENTAL

X-ray reflectivity can be used to monitor the increase in the electron density that occurs when toluene condenses in the porous thin film. When a beam of X-rays is incident onto a smooth surface at a shallow or grazing angle, total reflection occurs and X-rays do not penetrate the film. As the angle of incidence increases, a critical angle is encountered at which point the X-rays begin to penetrate the film. This critical angle, θc, is related to the electron density re through:

$$\theta_c = \lambda(\rho_e r_e / \pi)^{0.5} \qquad (3)$$

where λ is the X-ray wavelength and r_e is the classical electron radius. While the absolute pressure or mass changes as toluene condenses into a thin, low-k dielectric film may be very small, the change in the film's electron or mass density is significant. Therefore, θc is very a sensitive indicator of the amount of toluene condensed in the film.

High-resolution x-ray reflectivity at the specular condition (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. The incident and reflected beams are both passed through germanium [220] monochromators. The resulting beam has a wavelength, λ, of 1.54 Å, a wavelength spread, $\Delta\lambda/\lambda = 1.3\times10^{-4}$, 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 1.4 µm thick. The reflectivity data are plotted as a function of q ($q = (4\pi/\lambda)\sin\theta$).

RESULTS AND DISCUSSION

To demonstrate the sensitivity X-ray porosimetry, Figure 2 displays a series of reflectivity curves as a function of the toluene partial pressure for a typical hydridosilsesquioxane (HSQ) low-k dielectric film. Each reflectivity curve (as shown) requires approximately 15 min to collect, and we have allowed 30 min between partial pressure jumps for the film to equilibrate. We have verified that 30 min is more than sufficient (by a factor of about 3) for the film to come to equilibration for a largest possible pressure jump, i.e., from P/Po = 0 to P/Po = 1.0. Returning to Figure 2, at low angles all of the incident X-rays are reflected such that $R = I_{incident}/I_{reflected} = 1$, or log (R) = 0. Then at the critical wave vector, the X-rays penetrate the film and the

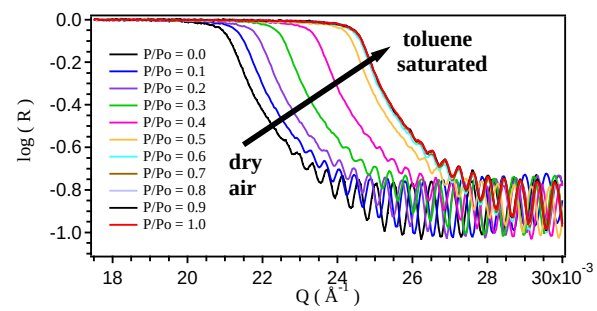

Figure 2. X-ray reflectivity curves as a function of the toluene partial pressure for a porous HSQ low-k dielectric film. As the toluene partial pressure increases, the critical angle for total reflection also increases (moves to higher Q) in response to the toluene condensing in progressively larger pores. The standard uncertainty in log(R) is less than the line width

reflectivity drops significantly. It is evident that this critical point shifts to higher wave vectors (higher angles) as the environment becomes saturated with toluene. Qualitatively, at low partial pressures, there is a moderate increase of θc for increments of P/P_o of 0.1. Then, at moderate values of P/P_o, the same partial pressure increments lead to much larger changes of θc, indicating a larger volume of pores being filled at these intermediate pressures. Finally, at high P/P_o values the changes in qc for equal increments of P/P_o become very small, indicating that few additional pores are filled at the highest partial pressures. As we

shall see below, the nature of these increments contains detailed information about the pore size distributions.

To extract the critical angle, we fit the reflectivity data using a least-squares recursive multi-layer fitting algorithm [10]. Specifically we model the low-k dielectric film as a single layer of uniform density (through the film thickness) on top of a thick Si wafer. As the partial pressure increases, we assume that the density increase from condensing toluene is uniform throughout the film, i.e., the average density of the film increases. This average density comes from the fitting algorithm in terms of Qc2. By examining Eq. (3), one can see that qc2, or it's reciprocal space analog, Qc2, is directly proportional to the electron (and thus mass) density of the film. For more details regarding the experimental protocol, refer to a recent publication on the technique [11].

The premise of X-ray porosimetry is analogous to ellipsometric porosimetry (EP) [2], which also utilizes the capillary condensation of organic vapors to map out adsorption/desorption isotherms. However, EP tracks condensation/evaporation through changes in porous films index of refraction, not the electron density. EP assumes that the optical polarizablilities of the adsorbate and adsorbent are additive, which is not immediately evident. It remains to be seen if this affects the data from low-k films where the condensed organic liquid is confined to nanometer-sized pores. Confinement is known to affect deviations from bulk-like behavior in many physical properties, bringing the additivity issue into question. However, the number electrons per atom do not change upon confinement. The values of Qc2 provide a more direct measure of the toluene uptake.

Effects of varying P or T

Examples of the adsorption/desorption isotherms are shown in Figure 3. In this representation Qc2 is plotted as a function of the partial P/P_o. Clearly there are pronounced changes in Qc2 as toluene condenses in the porous HSQ film. Specifically there are two sets of adsorption/desorption isotherms corresponding to the isothermal P (squares) and T (circles) variations respectively. The open symbols denote the adsorption branch of the isotherm while the closed symbols indicate the desorption branch. The non-isothermal T variations have been transformed into their equivalent 20 °C isotherms through Eq. (2). This allows direct comparison of true isothermal P/Po variations to their T variation counterpart.

There are several striking features in Figure 3. First, the T and P variation methods are not equivalent. This indicates that the assumptions behind the Kelvin equation are not entirely appropriate. Factors like heats of adsorption or deviations from the bulk physical properties for the condensed toluene could be significant. However, the reason for this failure has yet to be identified and could vary from sample to sample. The pore size distributions calculated from Eq. (1) are also not unique and depend on the measurement protocol. Currently, we are working on trying to understand the differences between these T and P variation data sets.

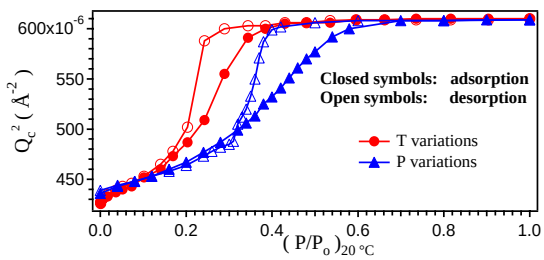

Figure 3. Adsorption/desorption curves generated by the T (circles) and P (triangles) variation techniques (see text). The two techniques do not produce identical isotherms, indicating that adsorption is not temperature invariant. The standard uncertainty in Qc2 is comparable to the size of the data markers.

SUMMARY

We demonstrate that X-ray reflectivity is a powerful tool for extracting porosity information from highly porous, ultra-thin low-k dielectric films. As the partial pressure of an organic solvent is increased, capillary condensation occurs and this results in a marked increase in the critical angle for total X-ray reflectance. Tracking this critical angle as a function of the partial pressure generates thin film adsorption/desorption isotherms that are traditionally analyzed in porosimetry. If the atomic composition of the film is known, it is possible to calculate the absolute porosity from the total toluene uptake. If a reliable adsorption/desorption models exists, one can extract pore size distributions from the isotherms. This is shown through the application of the Kelvin equation and capillary condensation.

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