Dielectric Films for Advanced Microelectronics



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The dielectric properties of silicon dioxide (SiO₂), such as high resistivity and excellent dielectric strength, have aided the evolution of microelectronics during the past 40 years. Silica films have been successfully used over this period for both gate and interconnect applications in ultra large-scale integration (ULSI) devices. Dielectric films for gate applications need to have a higher dielectric constant, while interconnect dielectric materials need to have a lower dielectric constant, while interconnect dielectric materials need to have a lower dielectric constant, compared with SiO₂. In order to maintain the high drive current and gate capacitance required of scaled MOSFETS (metal-oxide-silicon field effect transistors). SiO₃ gate dielectrics have decreased in thickness to less than 2 nm today, with a continued effort to shrink to the thickness below 1 nm. However, SiO₄ layers thinner than 1.2 nm do not have the insulating properties required of a gate leakage current and reliability degradation. Therefore, alternative gate dielectric materials are required.

SiO₂, having been the universal dielectric material for both gate and interlayer dielectric (ILD) applications for many years, must be replaced by materials with a higher dielectric constant for gate applications and a reduced dielectric constant for interconnect applications. Replacements for silicon dioxide, such as HO₂, ZrO₂, and Al₂O₃, for introduction as high-k dielectrics (described in the central section of the book), have material properties that are quite different compared with those of traditional dense SiO₂ and these differences create many technological challenges that are the subject of intensive research. In addition, not only the development of new gate materials but also re-engineering of many technological processes is needed. For example, in the case of low-k materials (discussed in the first section of the book), active species formed during different technological processes diffuse into the pores and create severe damage. All these problems have been stimulating the development of new technological approaches, which will be dealt with in this book.

This book presents an in-depth overview of novel developments made by scientific leaders in the microelectronics community. It covers a broad range of related topics, from physical principles to design, fabrication, characterization, and application of novel dielectric films. This book is intended for postgraduate level students, PhD students and industrial researchers, to enable them to gain insight into this important area of research.

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Ps lifetimes. Plausible distributions of pores can also be determined. Depth profiling of films with PALS has proven to be an ideal way to measure the interconnection length of mesopores, allows us to search for inhomogeneities in the pore structure in low-*k* films, and is capable of exploring porosity hidden beneath dense layers, capping layers, and difusion barriers. PALS has demonstrated its usefulness in characterization of multilayer films with a complex pore structure and in investigating the evolution of pore shape and structure with porosity.

Positron researchers are continuously working to improve PALS and PAS techniques to have a broad impact in the development of future low-*k* films. While the current PALS technique is sufficient to support the microelectronics industry through the 22 nm technology node, these improvements will extend the capabilities of the technique. A reactor-based PALS nanophase characterization facility is under construction which will ultimately-have a factor of 100 higher data rate that will permit a spectrum to be acquired on a sample in 10s. In addition we are working toward implementing the capacity to study whole 300 mm wafers, reducing the spot size of the beam for improved lateral resolution, and increasing the depth range we are able to study. The impact of PALS is not limited to low-*k* dielectric films. The technique has proven to be useful in studying hardmask materials, SiN and SiC barriers, photoresists, and should be useful in exploring a wide range of porous materials and barriers.

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3.3 STRUCTURE CHARACTERIZATION OF NANOPOROUS INTERLEVEL DIELECTRIC THIN FILMS WITH X-RAY AND NEUTRON RADIATION*

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3.3.1 Introduction

The structure characterization of nanoporous interlevel dielectric (ILD) thin films is challenging because of the small sample volumes and nanometer dimensions of the pores. In this chapter, we review characterization methods for porous ILD materials using X-ray and neutron radiation sources. These methods include X-ray reflectivity (XR), small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), and X-ray porosimetry (XRP).

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POROSITY OF LOW DIELECTRIC CONSTANT MATERIALS 101

XRP, in particular, shows promise as a general laboratory characterization method that provides detailed structural information of nanoporous LLD thin films. In XRP, changes in the critical angle for total X-ray reflectance provide a sensitive measure of mass uptake of a condensate into the film. Current porosimetry absorption/desorption models can then be used to determine structure parameters such as porosity and the distribution of pore sizes. Further, XRP data can be used to determine pore structure as a function of depth in nonuniform thin films. Detailed comparisons of XRP results with those from SANS are shown and discussed.

3.3.2 Thin film density by X-ray reflectivity (XR)

High-resolution specular X-ray reflectivity (XR) is a powerful experimental technique to 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 the depth profile of density can be determined with a high degree of precision.

X-ray reflectivity measurements were performed at the specular condition with identical incident and detector angles, θ . In the examples discussed in this chapter, the equipment used was a θ - 2θ goniometer with an angular reproducibility of 0.0001°, and a fine-focus copper X-ray tube as the radiation source. 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) monochrometer. The beam is further conditioned before the detector with a three-bounce germanium (220) crystal. Conditioning of the beam with these crystals decreases the wavelength spread in comparison to instruments with collimating slits. The resulting beam has a wavelength λ of 1.5406 Å, a wavelength spread $\Delta\lambda/\lambda = 1.3 \times 10^-$, and an angular divergence of 12 arcsec. This instrument has the precision and resolution necessary to observe interference oscillations in the reflectivity data from films up to 1.5 µm thick.

In Figure 3.11, the XR curve is shown for typical porous dielectric film; plotting the logarithm of the reflected intensity (I/I_o) as a function of q (where $q = 4\pi/\lambda \sin\theta$). At low q values, the X-ray beam is completely reflected from the film surface $(I/I_o = 1)$. As q



Figure 3.11 X-ray reflectivity profile from a typical low-k film

increases, the reflectivity dramatically drops at two separate critical angles $\theta_{\rm c}$, the first at approximately q = 0.013Å⁻¹ and the second at approximately q = 0.03Å⁻¹. Each value of $\theta_{\rm c}$ is related to the electron density of different layers in the sample. The critical angle is defined as the grazing angles below which total reflectance of an X-ray beam occurs. This critical angle, $\theta_{\rm c}$ depends upon the electron density $\rho_{\rm e}$ (and thus mass density) of the film through:

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

(1)

(2)

where λ is the X-ray wavelength and r_e is the classical electron radius. In Figure 3.11, the first critical angle at $q \approx 0.019 \text{ Å}^{-1}$ arises from the electron density of the porous thin film and the second critical angle arises from the silicon substrate electron density. The oscillations that appear in the reflectivity curve between these two critical angles arise from a waveguiding mode 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. The average mass density of the film in Figure 3.11 is $0.87 \pm 0.01 \text{ g/cm}^3$, this includes contributions from both the matrix and the voids. The porosity and matrix density of the film are directly related to this average density (ρ_{wx}):

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

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 from this single XR measurement.

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 through the periodicity of the oscillations in the reflectivity profile. The oscillations beyond the critical edge of silicon ($q > 0.03 \text{ Å}^{-1}$) 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. The model profile consists of several layers described by their thickness, electron density, and roughness. In the case of the data in Figure 3.11, the reflectivity can be described by two layers corresponding to the porous film and the silicon substrate. From this electron density profile, the X-ray reflectivity profile is calculated using established methods [47]. 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 a unique solution because of lost phase information. In contrast, the thickness of the film can be uniquely determined from the periodicity of the reflectivity data. At higher *a* values, the oscillations in the reflectivity curve are generally free of multiple scattering contributions and a Fourier transform enables a model free determination of the film thickness [47]. The film thickness in Figure 3.11 is determined to be (7530 ± 10) Å, independent of the method used to extract the thickness: Fourier transform or model fitting. This sensitivity to thickness, for example, enables the measurement of the coefficient of thermal expansion (CTE) of very thin films by measuring the film thickness at different temperatures.

3.3.3 Small angle X-ray/neutron scattering

A single XR measurement of a porous dielectric film yields the average film density, but the porosity of the film cannot be determined without assuming the matrix density. This assumption can be avoided by obtaining another measurable quantity also related to both the porosity *P* and matrix density, ρ_w . One complementary experimental technique that fulfills this requirement is small-angle neutron scattering (SANS), which has been applied in transmission to thin porous dielectric films [6]. With two measurements that depend on ρ_w and *P* in different functional forms from XR and SANS, one can solve for the values of ρ_w and *P* experimentally.

SANS results provide information related to the pore size because the SANS intensity is sensitive to density fluctuation correlations. Neutron scattering is not practical in the long term for characterization of porous film due to the limited number of neutron sources. Similar to neutron scattering, small-angle X-ray scattering (SAXS) with a wavelength less than 0.1 nm can also be used to provide the same structure information. The short wavelength is needed because the X-ray energy is such that transmission experiments through silicon wafers are possible. The physics describing the scattering from SANS and SAXS is identical, but there are differences in the details. In particular, silicon is virtually transparent to neutrons and a stack of more than ten low-k films supported on silicon substrate is often used in SANS in order to increase the scattering volume and the neutron scattering signal. In contrast, X-rays have limited penetration power through silicon due to a significant absorbance and a single film is used for SAXS. The small scattering volume, weak scattering of most porous dielectrics for ILDs, and high absorbance of the silicon necessitates a high intensity X-ray source. At present, a synchrotron source is needed to obtain a large enough flux for transmission SAXS measurements with sufficient signal. Another X-ray scattering alternative is grazing incident small angle X-ray scattering (GISAXS). In a GISAXS measurement, the scattering volume can be increased by two orders of magnitude over the normal incident geometry.

3.3.4 Pore wall density and pore structure

Many of the porous films for the low-*k* application consist of a solid film with a high volume of randomly packed nanopores. A model to describe the scattered intensity from such a structure was introduced by Debye *et al.* [48] $\gamma(r) = \exp(-r/\xi)$ where ξ is the correlation length. The average dimension, or the chord length, of the pores is $\xi/(1 - P)$, and the average dimension of the wall between the pores is ξ/P . The scattering intensity based on this model is:

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

where $\Delta \rho_a$ is the neutron scattering length contrast or the electron density difference between two phases for SANS and SAXS, respectively. For porous uniform film, this value is simply the neutron scattering length or the electron density of the matrix material between the pores because the scattering length of the pores (voids) is zero. This quantity is linearly



POROSITY OF LOW DIELECTRIC CONSTANT MATERIALS 105

104 DIELECTRIC FILMS FOR ADVANCED MICROELECTRONICS

related to the mass density of the matrix and the proportionality constant can be easily determined, provided the atomic composition of the sample is known. Besides the Debye random two-phase model presented by Equation three, there are many other structure models depending on the sample morphology. This equation requires that both the SAXS or SANS intensity must on an absolute intensity scale to measure the pore structure quantitatively. Figure 3.12 shows SAXS and SANS data from a methylsilsesqioxane (MSQ)-based nanoporous film that was fitted with a polydisperse hard-sphere (PHS) model. The general shapes of these two scattering results are similar to each other whereas the intensity scales are very different; the X-ray intensity scale is more than an order of magnitude greater than that of the neutron intensity. Despite the large difference in absolute intensity between the SAXS and SANS results, the structural parameters are in relatively good agreement as shown in Table 3.1.

Depending upon the type of porous material, SAXS and SANS data may not necessarily yield identical structure information from the same scattering model. The SAXS and SANS results are equivalent only under the condition that the porous material can be modeled with a two-phase structure, i.e., a void phase and a matrix phase. When the matrix is not homogenous, e.g., if hydrogen is preferentially located at the surface of the void, the contrast



Figure 3.12 (a) SANS results of a MSQ-based nanoporous film supported on silicon wafer; (b) SAXS results of the same MSQ based nanoporous film. The shape of the scattering is similar between SAXS and SANS, but the absolute magnitude of the scattering is not of the same order

Table 3.1 Structure information of a MSQ-based nanoporous film reduced from SANS and SAXS results. Result from X-ray reflectivity (XR) was used complementally to determine the structure results

SANS						SAXS				
Fitting model	Film density from XR (g/cm ³)	Wall density (g/cm ³)	Porosity (%)	Pore diameter (Å)	Fitting model	Wall density (g/cm ³)	Porosity (%)	Pore diameter (Å)		
PHS	0.965	1.568	38.4	20.3	PHS	1.48	34.6	29.6		

factors for X-rays and neutrons can change and yield different structure parameters. Hydrogen is a special case because of the very different scattering cross-section for neutrons. For this case, a three-phase model was developed to accommodate this type of structure [49]. Direct observations of a heterogeneous matrix in nanoporous films have been made with contrast match SANS [5].

For many nanoporous film applications, well-defined and ordered pores are advantageous [50]. Of particular interest has been the evolution of new mesoporous materials created using sacrificial templates since the discovery of MCM-41 [51]. (MCM-41 (Mobile Crystalline Material) is an ordered mesoporous material, displaying a honeycomb-like structure of uniform mesopores (3 nm in diameter) running through a matrix of amporphous silica.) The pore size and space group of these materials can be controlled through the choice of self-assembling template material [52] for a variety of metal oxide frameworks [53]. Slight modification of this versatile approach has been used successfully to create mesoporous films with regular packed pores [54].

To control pore orientation, methods have been developed for the directed growth of orientated mesoporous films from solution [55]. The orientation of these self-assembled nanostructured materials is similar to those observed in block copolymer films [56, 57]. Due to preferential wetting of a component of the templating agent to the free surface and/or substrate [58], film interfaces provide local orientation sites [54]. The depth of the orientation is typically determined from cross-sectional scanning electron microscopy (SEM) or transmission electron microscopy (TEM) images [59]. XR has been applied successfully to determine the depth of this surface orientation and SANS has been used to determine the packing order of the voids [60].

An alternative to transmission SAXS measurement is GISAXS. Unlike transmission SAXS, which requires a high-intensity, low-wavelength X-ray source, the GISAXS geometry, where the scattering signal is collected at the thin-film side, can increase the scattering volume by two orders of magnitude. The X-ray beam does not penetrate the silicon substrate, but is reflected from the surface. Consequently, X-rays from a typical copper source can be used for this measurement. Experimental techniques have been developed and demonstrate the capability of collecting GISAXS data within a time period less than 60s. However, the quantitative analysis of GISAXS data remains a challenge because of the difficulty in decoupling the scattering intensity from both the nanopores and the surface/ interface roughness. Before this difficulty in GISAXS data analysis is resolved, either transmission SAXS or SANS must be used for quantitative structure characterization, particularly for ordered structures.

The difficulty in obtaining access to SAXS and SANS sources for ILD porous dielectrics has led to a need for more accessible methods for the determination of both the porosity and matrix density. One potential solution to this issue is XRP.

3.3.5 X-ray porosimetry

The characterization of bulk porous materials, porosimetry, is a well-established field. Both total porosity and pore size distribution are determined by measuring the pressure dependence of liquid or gas infiltration into the porous materials [61, 62]. There are several techniques, such as gas adsorption, mercury intrusion, mass uptake, and others, capable of characterizing pores significantly smaller than 100nm. However, these methods lack the sensitivity to quantify porosity in thin porous ILD that are typically several hundred nanometers thick. The film mass is less than a few milligrams, meaning that the usual observables (i.e., pressure drop in a gas adsorption experiment or mass in an gravimetric experiment) exhibit exceedingly small changes as the pores are filled with a condensate. The porosimetry of thin ILD films requires measurement probes of condensate infusion with extraordinary sensitivity.

EP [3, 4] was developed to address this need. EP measures the refractive index and thickness of the film before and after being filled by condensate. Monitoring the amount of adsorbed condensate as a function of the partial pressure defines a physisorption iso-therm, the basic starting point for any number of analytical interpretations. However, to deduce porosity from the refractive index, approximations such as additive polarizabilities are required. This porosimetry measurement can be improved by avoiding these assumptions and approximations.

XRP is very similar to EP, but the film density is directly measured from the critical angle, provided the film composition is known [63]. Exposing the film to a partial pressure of condensable vapors changes the film density profile and potentially the film thickness, both of which are measured independently with XR. The change in film density can be directly related to the amount of adsorbed condensate, and thus porosity, if the density of the condensed fluid is known or assumed to be bulk-like. XRP directly measures the average prorosity, average film density, and average wall density of the material separating the pores. The average pore size and pore size distribution from the physisorption isotherm can be determined using existing porosity resize distribution. The depth resolution is typically within a few nanometers.

Porosimetry fundamentals

Traditional forms of adsorption porosimetry rely upon weight gain due to the surface adsorption and/or condensation of vapor inside the porous media. The current status of the porosimetry field can be found in a number of texts [61, 62, 64]. Today, the most common form of porosimetry is the nitrogen physisorption isotherm and serves as a useful model for porosimetry concepts. In these experiments, the porous sample, usually a powder, is sealed in a vessel of fixed volume, evacuated, and cooled to liquid N₂ temperatures. The sample vessel is then dosed with a fixed volume of pure N₂ gas. The fixed volume of the

POROSITY OF LOW DIELECTRIC CONSTANT MATERIALS 107

vessel combined with the known volume of gas defines the pressure. However, at low dosing pressures some of the N₂ condenses on the surface of the sample, resulting in a reduction of the 'predicted' partial pressure that can be measured with an accurate pressure transducer. By knowing the initial and final dosing pressures in the fixed volumes, the amount of adsorbed N₂ onto the pore surfaces can be calculated.

At higher partial pressures, after a few monolayers of the gas adsorb onto the pore walls, N_2 begins to condense inside the smallest pores, even though the vapor pressure in the system may be less than the liquid equilibrium vapor pressure. Zsigmondy [65] was the first to illustrate this effect and describe the process, using concepts originally proposed by Thompson (Lord Kelvin), as capillary condensation [66]. The classic Kelvin equation relates the critical radius for this capillary condensation r_e , to the partial pressure P_0 , liquid surface tension γ , and molar volume V_m through:

$$r_{\rm c} = \frac{2V_m\gamma}{-RT} \frac{1}{\ln\left(P/P_0\right)} \tag{4}$$

where *T* is the temperature and *R* is the universal gas constant. This relationship demonstrates that the critical pore size for capillary condensation increases with the partial pressure, until the equilibrium vapor pressure of liquid N₂ is achieved and r_c approaches infinity; the vapor spontaneously condenses. In the porosimetry apparatus, capillary condensation leads to a noticeable pressure drop that can also be converted into the amount of adsorbed vapor. A more detailed description of these physiosorption isotherms can be found elsewhere [61, 62, 64].

These measurements become exceedingly difficult in thin, low-k dielectric films where there is limited sample mass. A typical low-k dielectric film is approximately 500 nm thick, with an average density of 1g/cm³ and a porosity of approximately 50% by volume. This means that on a 76.2 mm (3 in) diameter wafer there will be approximately 1 × 10⁻³ cm³ of pore volume on top of several grams of Si. Traditional porosimetry techniques lack the sensitivity to register the pressure, mass, or calorimetric changes that occur when condensing such a small amount of vapor; metrologies with higher sensitivity are needed to quantify the porosity in thin low-k dielectric films. It is also desirable that the characterization be *in situ*, on the supporting Si wafer. This obviates sample damage and the errors that result from scraping large quantities of low-k material off multiple wafers, and further retains the possibility of on-line or process control checks in the fabrication or industrial lab settings.

X-ray porosimetry fundamentals

XRP combines specular XR measurements with capillary condensation where the needed sensitivity to mass uptake comes from the accuracy of thin-film density measurements with XR. If the environment surrounding the film is gradually enriched with an organic vapor, such as toluene, the vapor will condense in the pores with the radii commensurate with the critical radii for capillary condensation. This condensation increases the density of the sample. Recall earlier estimates that the density of a low-k film is of the order of 1 g/cm³, diven that most condensed organic vapors also have densities of the order of 1 g/cm³, complete

condensation leads to a significant (i.e., of the order of 50%) change in the total film density. This offers a very effective mechanism to monitor the vapor uptake as a function of partial pressure and obtaining physisorption isotherms.

All the above discussions have been focused on the characterization of blank or unpatterned porous ILD films. Upon plasma processing for pattern etching or photoresist ashing the porous structure will often be modified, in most cases densification at the film surface occurs. For some cases, a limited and controlled densification at the sidewall of the patterns is desirable since it may facilitate the deposition of barrier layer on the sidewall. This points to the need of additional metrology to quantify the extent of sidewall densification. Work is in progress to develop metrology to address this type of porous structure measurement need.

Fitting X-ray reflectivity data. A complete analysis of X-ray reflectivity data requires modeling the reduced data using well-established models and procedures. The equations needed to model specular reflectivity data are straightforward [47, 66, 67]. The basic procedure involves constructing a model electron density depth profile consistent with well-known scattering length density parameters for the material or materials of interest, solving a recursion formula for the expected X-ray reflectivity data, then iterating the model profile until a satisfactory fit is obtained with the experimental reflectivity curve. The greatest limitation in the analysis of X-ray reflectivity data is the need for a model profile to fit to the data. There are many different software packages available to fit X-ray reflectivity data

For XRP, it is often sufficient to measure only the critical angle of the sample because changes in the amount of adsorption are proportional to the changes in the sample electron density. For more detailed analysis, it may become necessary to perform full data fits of the XRP reflectivity curves for situations, for example, where the film swell or the pore size distribution is depth dependent. The following sections show how the X-ray reflectivity data can be used to determine important information about the structure of nanoporous thin films.

Interpretation of XRP data. In this section, we illustrate how to interpret and analyze XRP with films from three different classes of porous low-k dielectric material. The films are characterized in terms of critical structural information, such as the average film density, average wall material density, porosity, and the pore size distribution. By way of introduction, the first class of material is a hydrogensilsesqioxane (HSO) film prepared by the evaporation of a high-boiling-point solvent after gelling the HSQ resin [69]. The second is a MSQ film generated through a templated vitrification of low molecular mass siloxane oligomers [70]. The third material is deposited by plasma enhanced chemical vapor deposition (PECVD) from a mixture of an organic precursor (the porogen) and tetramethylcyclotetrasiloxane [71]. This last film will be referred to as porous SiCOH. The reported dielectric constants of the porous HSQ, MSQ, and SiCOH films are 2.20, 1.85 and 2.05, respectively. In light of the nominally similar dielectric constants, we compare and contrast the pore structures in these films because the structure also affects other critical properties such as the mechanical properties of the film. XRP is able to perceive differences in the pore structures of these otherwise similar low-k films. Later, the characteristics of the porous films obtain from XRP are also compared with similar data obtained through scattering, specifically SANS/XR techniques [5, 69, 72].

Figure 3.13 displays experimental XR data for the three porous low-k films both under vacuum and in the presence toluene-saturated air. The square of this critical angle is pro-



POROSITY OF LOW DIELECTRIC CONSTANT MATERIALS

109



Figure 3.13 SXR curves of (A) porous HSQ, (B) porous MSQ, and (C) porous SiCOH thin films. The curves are offset for clarity. The standard uncertainty in $\log(UI_0)$ is less than the line width. (Reprinted from *Journal of Applied Physics* **95**(5) 2355 (2004) with permission from the American Institute of Physics)

portional to average electron density of the thin film, as discussed previously through Equation (1), which is then used to calculate the average mass density from the atomic composition. For these films the elemental composition is determined experimentally via ion beam scattering, using the combination of the Rutherford backscattering, forward scattering and forward recoil scattering techniques discussed elsewhere [69, 73].

Comparing the reflectivity curves under vacuum in Figure 3.13 shows that q_c occurs at 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 q_c shifts to 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 q_c 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, thus the total porosity P, as well as the density of the wall material ρ_{wall} separating the pores [63]. P and ρ_{wail} can be determined from two simple experiments: reflectivity under dry (evacuated) and toluene saturated environments. This leads to two equations based on a simple rule of mixtures:

$$\rho_{dry} = (1 - P) \rho_{wall} \tag{5}$$

$$\rho_{\text{sat}} = P \rho_{\text{liquid}} + (1 - P) \rho_{\text{wall}} \tag{6}$$

In addition to *P* and ρ_{wall} , ρ_{dry} is the total average density of the dry (evacuated) film, ρ_{su} is the average density of the film in the presence of the saturated vapor, and ρ_{tiquid} is the density of the condensed liquid. ρ_{dry} and ρ_{su} are defined by the Q_2^2 values of the reflectivity experiments in the dry and vapor saturated environments, respectively, while ρ_{tiquid} is assumed to be bulk-like for this calculation. The elemental composition of the low-k film, the elemental composition of the toluene condensate, and Equation (1) are used to convert the electron densities into mass densities. Knowing ρ_{dry} and ρ_{sult} leaves two equations that can be solved for the remaining two unknowns, *P* and ρ_{sult} .

108

It should be noted that Equations (5) and (6) do not account for pores that may be inaccessible to the condensing vapor; such porosity is folded into the average wall density of the material. Pores might not be accessible if they are isolated, unconnected to the surface, too small to accommodate the vapor molecules, or excluded because of an unfavorable surface energy. Our experience with a broad range of low-k dielectric materials indicates that toluene is able to access most pores, especially if the matrix (wall) material exhibits swelling in the presence of toluene. Toluene has low polarity and wets most low-k materials, which also have low polarity (i.e., low dielectric constant). Notable exceptions, however, include highly fluorinated materials that the toluene will not wet or penetrate the wall material. Solvent vapors other than toluene may be used if pore accessibility becomes an issue.

Equations (5) and (6) do not account for swelling of the low-k film by the condensate. XRP is well suited to address swelling because the XR data also provide an accurate measure of film thickness. Using toluene vapor, we rarely see evidence of film swelling greater than 1% in thickness for most nonorganic low-k materials. However, this is not the case for polymeric samples that can swell appreciably. In some respects, a small amount of film swelling helps the XRP measurement. If the condensate can gently swell the film, it is reasonable to assume that all pores are accessible because swelling shows that the condensate can diffuse through the wall material and is not dependent upon connected channels to the surface. In the presence of swelling, Equation (6) should be modified such that the porosity is given by:

$$P = \frac{\rho_{\text{sat}} t_{\text{sat}} - \rho_{\text{dry}} t_{\text{dry}}}{\rho_{\text{liquid}} t_{\text{dry}}} - \frac{t_{\text{sat}} - t_{\text{dry}}}{t_{\text{dry}}}$$

(7)

where t_{dry} and t_{ext} are the film thickness values of the dry and swollen films. This equation assumes that the volume of liquid toluene is conserved (rule of mixtures) upon absorption into the film and the wall material. Once P is determined, Equation (5) can be used to extract ρ_{wall} for the dry material.

The porosities obtained by this method (no swelling, using Equations 5 and 6) for the porous HSQ, MSQ, and SiCOH films are $(46 \pm 1)\%$, $(34 \pm 1)\%$, and $(31 \pm 1)\%$, respectively. (Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure; in no case does such identification imply recommendations by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for this purpose.)

The resulting wall densities of the porous HSQ, MSQ, and SiCOH films are $(1.83 \pm .05)$ g/cm³, $(1.35 \pm .05)$ g/cm³ and $(1.31 \pm .05)$ g/cm³, respectively. Notice that the porous HSQ film has the highest porosity, yet its dielectric constant is the largest. This apparent contradiction is resolved through the observation that the porous HSQ film also has highest wall density. It is also interesting that the porous MSQ and SiCOH films have similar average densities, wall densities, and atomic compositions, despite the fact they are prepared from very different techniques. The elemental composition, detailed structural characteristics, and standard uncertainties in the pore characteristics of the samples are summarized in Table 3.2.

The sensitivity and resolution of XR are sufficient to reveal subtle differences between the three films as the toluene atmosphere gradually varies from $P/P_0 = 0$ (dry air) to $P/P_0 = 1$ (toluene saturated) and toluene progressively infiltrates the pores. In terms of the

POROSITY OF LOW DIELECTRIC CONSTANT MATERIALS 111

Table 3.2 A summary of the atomic compositions, dielectric constants k, and structural characteristics of different porous low-k films. The relative standard uncertainties of the atomic compositions Q_c^2 , densities, porosities and pore radii are $\pm 2\%$, 0.05 Å⁻², 0.05 g/cm³, 1%, and 1 Å, respectively

Porous Film	Atomic composition (Si:O:C:H)	k	Q_{c}^{2} (×10 ⁻⁴ Å ⁻¹)	$ ho_{ m dry}$ (g/cm ³)	$ ho_{ m wall}$ (g/cm ³)	P (%)	Pore radius (Å)	
							XRP	SANS
HSQ	25:48:7:20	2.20	4.25	0.98	1.83	46	13	9
MSQ	15:25:19:41	1.85	3.95	0.89	1.35	34	15	10
SiCOH	10:20:28:42	2.05	4.04	0.91	1.31	31	5	3



Figure 3.14 Critical angle changes for the porous HSQ sample as P/P0 increases systematically from 0 (dry air) to 1 (toluene saturated air). Condensation of the toluene inside the pores results in an appreciable and measurable change in q_c^2 . Reprinted from X-ray Reflectivity as a Metrology to Charaterize Pores in Low-k Dielectric Films in ACS Symposium Series 874: Polymers for Microelectronics and Nanoelectronics. Published 2004 American Chemical Society

reflectivity data, Figure 3.14 illustrates these changes in the porous HSQ film in the region of the q_e . By assuming that the mass density of adsorbed toluene is the same as the bulk fluid, the increase in q_c^2 above the vacuum level can be used to calculate the amount of toluene adsorbed into the film as a function of the relative partial pressure. These data are presented as physisorption isotherms in Figure 3.15.

In Figure 3.15, the porous SiCOH film shows a prominent uptake at low partial pressures that quickly levels off. There is also no hysteresis between the adsorption and desorption branches. This is characteristic of filling micropores (pores less than 2nm diameter) [6], 62, 64, 74], indicating that the PECVD process generates a large population of small pores. In comparison, the porous MSQ film continues to 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, consistent with the filling of larger mesopores. This indicates that the porogen in the PECVD film forms smaller domains than the spin-cast

110

112

DIELECTRIC FILMS FOR ADVANCED MICROELECTRONICS



Figure 3.15 Physisorption isotherms for the porous (A) HSQ, (B) MSQ, and (C) SiCOH films. The lines are smooth fits using the cumulative sum of a sigmoidal and a log-normal function for porous HSQ and MSQ films, and the sum of a Gaussian and a sigmoidal function for porous SiCOH, film. (Reprinted from *Journal of Applied Physics* 95(5) 2355 (2004) with permission from the American Institute of Physics)

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 pore size distributions (PSDs).

At low partial pressures, the adsorption process in both spin-on-glass (SOG) films (porous HSQ and MSQ films) is 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 [75]. If larger pores can be accessed only through neighboring or interconnected narrow pores, the condensate in the larger pores is not free to desorb at the relative pressure corresponding to their critical capillary radius. The smaller pores block the desorption of the solvent from the larger pores in a manner that has been described as the 'ink-bottle' effect [61, 76]. 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. Hence, the sharper drop in the desorption curve compared with the adsorption barch in Figure 3.15.

By comparing the general shape of the adsorption/desorption isotherms for the three different films, one can qualitatively arrive at the schematic pore structures depicted in Figure 3.16. The PECVD process creates the smallest pores, in very large quantities. The lack of a hysteresis loop confirms that the dimensions of pores are of 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 total toluene uptake in Figure 3.15. The pores in HSQ are also clearly larger than the PECVD material's pores. 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



POROSITY OF LOW DIELECTRIC CONSTANT MATERIALS

Figure 3.16 Schematic pore structures for the porous HSQ, MSQ, and SiCOH films. (Reprinted from *Journal of Applied Physics* 95(5) 2355 (2004) with permission from the American Institute of Physics)



Figure 3.17 Approximate pore size distributions from the smooth fits through the physisorption isotherms in Figure 3.16, using Equation (4) to convert P/P_0 into a pore size. The distributions from the adsorption branch (solid lines) can be significantly broader and shifted to larger pore sizes than the corresponding desorption branch, especially in those materials (such as the MSQ film) with a large distribution of mesopore sizes

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 using equation to convert the partial pressures for capillary condensation in Figure 3.15 into pore radii. Plotting the relative toluene uptake as a function of the pore size establishes the pore size distribution (PSD). To illustrate this procedure we use the simplest example of the Kelvin equation (Equation 4) to convert P/P_0 into a critical radius for capillary condensation. However, we acknowledge that alternative expressions to Equation (4) are probably more appropriate. The Kelvin equation lacks terms that account for interactions of the condensate with the pore surfaces and is not well suited for situations where the pore size approaches the dimensions of the condensate molecule. Nevertheless, Figure 3.17 shows the resulting pore size distribution, with the total areas beneath the curve scaled to a value consistent with the total *P* for each film as reported in Table 3.2. It should be noted that the symbols in Figure 3.17 are not measured data; they are generated from the smooth fits in described in the capiton of



Figure 3.15. Generally, we find that the increments of P/P_0 in experimental data of Figure 3.15 are not sufficiently fine for a point-by-point differentiation when using a Kelvin equation to generate Figure 3.17; significantly smoother and reasonable distributions are obtained by transforming the arbitrary fit function. As long as the empirical fit accurately parameterizes the physisorption data, this is a reasonable procedure.

In the literature, it is traditional to use the desorption branch of the physisorption isotherm to report the PSDs. The average pore radii in the porous HSQ, MSQ, and SiCOH films taken from the desorption curves in Figure 3.17 are approximately 13, 15, and 5Å, respectively. However, this average is biased towards the minimum or constricting pore in regard to the ink-bottle effect; a more complete interpretation of the pore structure always results from analyzing both the adsorption and desorption branches. For example, in Figure 3.17 notice that there is a relatively large difference between adsorption and desorption was approximately 15Å, the desorption branch leads to an approximate average pore radius of 27Å. By contrast, the discrepancy is much less for the HSQ film (-13Å on desorption and 16Å on absorption) and nearly the same (no discrepancy) for the SiCOH film. This is consistent with the previous discussion of the isotherms in Figure 3.15 and the schematic pore structures in Figure 3.16.

3.3.6 Comparison of small-angle scattering and X-ray porosimetry

SANS is also capable of quantifying the average pore size in these low-k dielectric films, providing a useful comparison for the XRP data. The SANS measurements discussed herein were performed on the NGI beam line at the National Institute of Standards and Technology Center for Neutron Research. SANS is collected with the sample under vacuum, like the XRP, and shown in Figure 3.18. These scattering curves can be fit with the Debye model (Equation 3) [48] to extract an average pore size. An increase in the scattering intensity corresponds to increase in the pore size and/or porosity. In Figure 3.18, the porous SiCOH



Figure 3.18 SANS data for the porous HSQ (circles), MSQ (diamonds), and SiCOH (triangles) films under vacuum. (Reprinted from *Journal of Applied Physics* 95(5) 2355 (2004) with permission from the American Institute of Physics)

POROSITY OF LOW DIELECTRIC CONSTANT MATERIALS 115

film shows noticeably weaker scattering than either of the porous SOG films, consistent with the smaller pore size and lower porosity. The greatest scattering intensities occur in the porous MSQ film, which is also consistent with the largest population of larger pores. For the porous HSQ and MSQ films, the Debye model gives reliable fits with average pore radii of 9 and 10 Å, respectively. The radii are comparable to the XRP pore sizes reported in Table 3.2. However, the SANS intensities in the porous SiCOH film are too low to reliably apply the Debye model; the scattering is not strong from this low porosity film. If the Debye model were applied the resulting pore radius would be approximately 3 Å. This result is unphysical in light of the implicit assumption in the Debye model that there is a distinct interface between the pore and the wall material; 3Å is comparable to a single atomic radius, meaning that the model is not appropriate. Nevertheless, there is reasonably good agreement between the SANS and XRP data for the higher-porosity HSQ and MSQ film. However, we must also mention that there are examples, not reported here, where the SANS and XRP data do not yield consistent data. Recall the discussion above of the oversimplifications of the Kelvin equation; this was chosen as the simplest case example for demonstration. Likewise, analysis of the SANS data with the Debye model suffers from the two-phase approximation where the matrix or wall material is considered to be homogeneous. To a large extent, the agreement between SANS and XRP will depend on the consistency of the models chosen to analyze the pore size distributions.

XRP is a very sensitive form of porosimetry, especially for those materials with very small pores or low porosity supported on thick substrate. This is illustrated with the porous SiCOH film where SANS is unable to reveal the porosity in this film because the pores are too small, below the sensitivity of the technique. However, in Figure 3.13 there is still a very significant change in the raw XRP data as toluene condenses inside the pores.

One distinct advantage of XRP over other forms of porosimetry, including the ellispometric porosimetry technique, is the potential to vertically depth profile the density (and therefore porosity) through the thickness of the film. Recall that the reflectivity data can be fit using a multilayer model. In the preceding examples, the low-k films were modeled with a single layer of uniform density, both under vacuum and in the presence of toluene. However, Figure 3.19 shows an example of a low-k dielectric film that has a multilayer structure, with different porosities in the different layers. Figure 3.19(a) shows the reflectivity data for this film both under vacuum and in the toluene-saturated environment. The general shape of the reflectivity curves is noticeably different from the preceding examples. In addition to the high-frequency interference fringes that indicate the total film thickness. there are also lower frequency oscillations in the data as roughly indicated the lines and arrows. The low-frequency oscillations are due to a mutlilayer structure. Fitting the reflectivity data requires three distinct layers for the low-k film, as shown in Figure 3.19(b). The electron density of the layers as a function of distance into the film (starting from the free surface) is plotted in terms of Q_c^2 . Near the free surface (layer 1) the density is noticeably larger than the rest of the low-k film, the consequence of a plasma treatment to the surface. The density appears lowest (layer 3) near the Si substrate (the physical origin of the lower density in layer 3 is not understood).

When this multilayer film is exposed to the toluene environment, two effects become obvious. First, the density increases in all three layers of the low-k film as toluene condenses in the individual pores. Second, the total film thickness swells by approximately 4.4%, meaning that Equation (7) most be used to extract the porosities. What may be less obvious is that each of the three layers in the low-k film absorbs different amounts of toluene.

114

116

DIELECTRIC FILMS FOR ADVANCED MICROELECTRONICS



Figure 3.19 XRP data for a low-k film comprised of three distinct layers: (a) reflectivity data for the (A) dry and (B) toluene saturated films, revealing both a high-frequency periodicity due to the total film thickness and low-frequency oscillations due to the thinner individual layers; (b) real-space scattering length density profiles a function of distance into the film, revealing the thickness and density of the individual layers

Qualitatively, Figure 3.19(b) shows that layer 2 takes in the most toluene while layer 1 picks up the least. Equation (7) can be used to calculate the porosities in layers 1, 2, and 3 as approximately 13, 21, and 16%, respectively. Despite the lower overall electron density in layer 3, the greatest porosity is found in layer 2. This is because the wall densities are also greater in layer 2, offsetting the porosity effect in terms of the average film density.

3.3.7 Conclusions

The structure characterization of nanoporous interlevel dielectric (ILD) thin films is challenging because of the small sample volumes and nanometer dimensions of the pores. There are few characterization methods for porous ILD materials including PALS, EP, and those utilizing X-ray and neutron radiation sources such as X-ray reflectivity (XR), small angle X-ray scattering (SAXS), small angle neutron scattering (SANS), and X-ray porosimetry (XRP). XRP, in particular, shows promise as a general laboratory characterization method

POROSITY OF LOW DIELECTRIC CONSTANT MATERIALS 117

that provides detailed structural information of nanoporous ILD thin films. In XRP, changes in the critical angle for total X-ray reflectance provide a sensitive measure of mass uptake of a condensate into the film. Current porosimetry absorption/desorption models can then be used to determine structure parameters such as porosity and the distribution of pore sizes. Further, XRP data can be used to determine pore structure as a function of depth in nonuniform thin films.

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3.4 ELLIPSOMETRIC POROSIMETRY

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3.4.1 Introduction

In ellipsometric porosimetry, the porosity evaluation is nondestructive and based on analysis of dielectric function that makes the results very suitable for microelectronics [77, 82]. The measurement of effective pore size and porosity is based on penetration and condensation of organic vapor in the pores and allows prediction of behavior of the porous materials during different technological processes including interaction of porous dielectric films with etch, strip, cleaning chemistries, chemical vapor deposition (CVD), etc. Additional advantage of EP is the possibility of evaluation of other properties important for integration such as mechanical properties, hydrophobicity, diffusion barrier, etc.

3.4.2 Fundamentals of ellipsometric porosimetry

The effective dielectric constant k_p of a two-component system depends on dielectric constants of the components k_1 and k_2 and their relative fractions V and (1 - V) (Clausius-Mossotti equation):

$$\frac{k_{\rm p}-1}{k_{\rm p}+2} = \sum_i \frac{4\pi N_i}{3\varepsilon_0} \alpha_i = V \frac{k_1-1}{k_1+2} + (1-V) \frac{k_2-1}{k_2+2} \tag{1}$$

In the case of porous materials one of the components is air $(k_1 = 1)$ and

$$\frac{k_{\rm p}-1}{k_{\rm w}+2} = (1-V)\frac{k_{\rm s}-1}{k_{\rm w}+2} \tag{2}$$

In these equations V is the relative pore volume (V_{pore}/V_{nim}) , $k_2 = k_s$ is dielectric constant of the film skeleton. N_i and ε_0 are number of molecules per volume unit (density) and