Characterization of Porous, Low-\( k \) Dielectric Thin-Films using X-ray Reflectivity

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Abstract. To reduce the RC interconnect delays and cross-talk noise associated with the sub-130 nm technology nodes, copper interconnects must be combined with low-\( k \) interlayer dielectrics (ILDs) having dielectric constants \( k \leq 2 \). In order to obtain sufficiently low dielectric constants, pores are introduced into ILD materials thereby lowering the average density of the ILD. Information concerning porous, low-\( k \) thin-films can be obtained non-destructively using grazing-incidence X-ray reflectivity (XRR) methods. Specular XRR provides information on the thickness, roughness and porosity, whilst diffuse (non-specular) XRR yields valuable information about the average pore-size, \( D \), and the pore-size distribution. In this work, we present XRR data from a spin-on, porous low-\( k \) dielectric material (MesoELK) deposited on a Si substrate. The XRR data were analyzed by fitting to simulated intensity curves using a genetic algorithm (GA). The diffuse XRR intensity curve was calculated using the distorted-wave Born approximation (DWBA) and two common models were used to describe the microstructure of porous materials, i.e. the polydispered sphere model and the random two-phase model. The resulting pore-size distribution corresponds well with that obtained from complementary methods. The assumptions and limitations of the XRR method for the non-destructive characterization of porous thin-films are discussed.

INTRODUCTION

The semiconductor industry is undergoing very significant technological changes. The established interconnect materials (Al conductors and SiO\(_2\) insulators) and processing methods that have been used for more than a decade are being replaced by Cu conductors and low-\( k \) dielectric materials. These significant changes are required because the resistance, \( R \), of the conductors and capacitance, \( C \), between adjacent conductors introduces significant RC-signal delay for sub-130 nm technology nodes. This so-called interconnect delay essentially slows chip speed and decreases performance.

A number of low-\( k \) materials are available and these fall into two general classes: 1) organosilicate (carbon doped SiO\(_2\)) materials that are deposited by chemical vapor deposition (CVD) methods and 2) organic, inorganic or hybrid materials that are deposited by spin-on methods. Generally, the second class of materials has lower intrinsic dielectric constants than materials in the first class. However, they are considered to be much more disruptive as spin-on methods have not traditionally been used to deposit interlayer dielectric (ILD) materials. To achieve very low dielectric constants \( (k \leq 2) \), pores can be introduced into materials in both classes so as to lower the average density of the ILD. The size and distribution of the pores are very important since they affect the electrical, mechanical and thermal properties of these materials. Characterization of the pores is critical to develop, optimize and monitor such low-\( k \) materials. The use of specular XRR for the characterization of porous, low-\( k \) materials has received considerable attention \[1, 2\]. The use of diffuse XRR as a method of characterizing such materials has, however, received less attention.

The objective of this work is to demonstrate that specular and diffuse X-ray reflectivity (XRR) provide valuable information about porous, low-\( k \) materials. As an example, we have measured and analyzed XRR data from an inorganic, spin-on material (MesoELK)\(^1\) deposited as a thin-film on a Si substrate.

\(^1\) MesoELK is a registered trademark of Air Products and Chemicals Inc.
THEORY

The refractive index for X-rays in a material is slightly less than unity. This gives rise to total external reflection for incidence angles that are less than some critical angle, \( \omega_c \), the magnitude of which is a few tenths of a degree and depends on the electron density of the material. The specular XRR (exit angle = incidence angle) results from coherent scattering and is sensitive to the average electron density normal to the material’s surface. As such, specular data can provide information about the density, thickness and roughness of thin-films and multilayers. The theory of specular XRR is very well established (see [3] and the references contained therein) and so will not be discussed further.

If fluctuations in the electron density parallel to the surface of a material are present (e.g. due to roughness, nanoscale particles or pores) then the incoherent, or diffuse, scattering occurs (exit angle \( \neq \) incidence angle). In the case of porous, low-\( k \) thin-films the diffuse scattering from pores usually dominates over that from roughness for angles away from the critical angle. The origin of the diffuse scattering is similar to that in conventional small angle X-ray scattering (SAXS) but employs a reflection, rather than a transmission, geometry as shown in figure 1. For this reason, the diffuse XRR technique is often referred to as grazing-incidence small angle X-ray scattering (GI-SAXS). The grazing incidence geometry means that the path length of the X-rays in thin-film samples is very much longer than in conventional SAXS. This increased path length results in a measurable scattered intensity from thin-film samples.

The theory of diffuse scattering from density fluctuations (such as nanoscale pores) in the reflection geometry is not well known, but was established several years ago by Rauscher et al. [4] who calculated the diffuse XRR intensity within the framework of the distorted-wave Born approximation (DWBA). The intensity, \( I(q) \), may be written in the form

\[
I(q) = G(\omega, \omega')T(\omega)T'(\omega')F(q) \quad (1)
\]

where \( G(\omega, \omega') \) is a geometrical term that takes into account the footprint and penetration of the incident beam, \( T(\omega) \) and \( T'(\omega') \) are the transmission factors for the incidence and exit angles, respectively. \( F(q) \) denotes the structure factor for the scattering objects, in our case pores, and is usually written as the product of two terms: 1) the scattering factor for a single object and 2) the object-object correlation function. The structure factor, therefore, embodies the structural model of the material. Here \( Q = 4\pi / \lambda \sin \theta \) denotes the magnitude of the scattering vector \( Q \) in air, \( \lambda \) is the X-ray wavelength and \( \theta \) is half the detector (scattering) angle. The quantity \( q \) denotes the magnitude of the scattering vector within the material and takes into account the effects of refraction.

In this work we have used two models developed for conventional SAXS to describe the structure of the porous, low-\( k \) material, namely:

1) Random two-phase model [5] in which one phase consists of the pores and the second phase the surrounding matrix material. This model has an exponential pore-size distribution function and is characterized by a single parameter, the correlation length, \( \xi \), which is related to the average pore-diameter, \( \langle D \rangle \), according to \( \langle D \rangle = \xi \langle 1 - P \rangle \) where \( P \) is the volume fraction of pores, i.e. the porosity.

2) Polydispersed sphere model [6]. In this model, the pores are considered to be spherical and surrounded by a matrix material. The pore-sizes follow a Gamma distribution that is characterized by two parameters. The first parameter is the mean pore-diameter, \( \langle D \rangle \), and the second is the polydispersity, \( d = \sigma^2 / \langle D \rangle \), where \( \sigma^2 \) is the variance of the distribution.

For both models, it should be noted that the porosity must be known in order to estimate the average pore-size and pore-size distribution.

EXPERIMENTAL

The experiments were performed using a Bede D1 diffractometer. Cu K\( \alpha \) radiation was produced by a
sealed tube X-ray source operated at 45 kV and 40 mA. A single, asymmetric Si(022) channel-cut crystal (CCC) together with a 100 μm slit was used to both collimate and monochromate the radiation so that only the Cu Kα1 radiation was incident upon the surface of the sample. The intensity of the incident beam was about $2 \times 10^6$ cps and the wavelength dispersion, $\Delta \lambda / \lambda$, was approximately $10^{-3}$. The angular acceptance of the detector was defined by a 100 μm slit and yielded a roughly Gaussian instrumental function with a full-width at half maximum (FWHM) of about 0.02 deg, as measured by scanning the detector through the incident beam. The background intensity was less that 0.5 cps. A second Si(022) CCC was placed before the detector when measuring the specular X-ray reflectivity, which improved the angular resolution by an order of magnitude, to approximately 0.003 deg.

The angular position of the sample, $\omega$, and detector, $2\theta$, measured with respect to the incident X-ray beam, were precisely adjusted by a goniometer with closed-loop servo system under computer control. The angular precision of both the $\omega$ and $2\theta$ axes was 0.0001 deg.

Two types of scans were performed. Specular ($\theta 2\theta$) scans measured the intensity as the detector was swept at twice the angular rate of the sample and scanned parallel to the $Q_z$-direction (perpendicular to the surface of the sample). The sample angle ranged from 0.0 deg to 1.0 deg with a step-size of 0.0005 deg. The counting-time was 5 s per data point. Radial diffuse ($2\theta$) scans, recorded the intensity as the detector swept an arc in reciprocal space with the sample angle fixed at 0.19 deg, corresponding to an angle just above the critical angle of the porous low-k thin-film. The $2\theta$-angle was varied from 0.0 deg to 6.0 deg with a step-size of 0.01 deg. The counting-time per point was 5 s leading to a measurement time of less than an hour in these experiments, though once the principle is established, production measurements could be made very much faster.

RESULTS AND DISCUSSION

Figure 3 shows the measured specular intensity from the porous, thin-film sample together with that from a Si substrate for comparison. The reflectivity curves from the porous thin-film sample display two critical angles. The smaller of these critical angles, $\omega_{c1} = 0.14$ deg, is attributed to the thin-film and the larger, $\omega_{c2} = 0.23$ deg, is due the Si substrate.

The measured specular XRR data were analyzed by fitting to a simulation using the Bede REFS software. This software employs a genetic algorithm (GA) based data-fitting procedure [7] to refine the parameters of a structural model until good agreement between measurement and simulation is obtained.

The average mass density, $\bar{\rho}$, of a porous thin-film can accurately be determined from its critical angle in a specular XRR data. From the best-fit simulation, we obtained an average mass density of $0.89 \pm 0.02$ g/cm$^3$. If the density of the matrix material, $\rho$, is known, then we can easily calculate the porosity, $P$, of the thin-film from the relationship

$$P(\%) = (1 - \bar{\rho} / \rho) \times 100 \quad (2)$$

The porosity of the thin-film was found to be 53 ± 5%. It should be noted that in the case of spin-on materials, the mass density of the matrix can usually be determined by measuring the critical angle of a thin-
film of the material deposited without pores, *i.e.* by adding no porogen during the deposition process. In the case of organosilicate materials, which often cannot be produced without some porosity, the density of the matrix must be determined by a complementary technique.

Interference (Kiessig) fringes are clearly visible in the specular XRR data from the porous sample. The period of these fringes is, to a very good approximation, independent of material parameters and is equal to $\Delta\omega = \lambda / 2t$ where $t$ is the thickness of the thin-film. From the best-fit simulation, the thickness of the thin-film was determined to be $531.1 \pm 0.1$ nm.

![Diffuse X-ray reflectivity data (2θ-scan) from a porous low-k dielectric thin-film sample as a function of the incidence angle, $\omega$, and scattering angle, $2\theta$. Darker corresponds to more intensity scattered from the sample.](image)

The large angular range corresponds to scattering from small objects – the pores within the thin-film.

Omote *et al.* [8] have recently described using longitudinal diffuse (offset $\theta/2\theta$) scans to estimate the pore-size distributions in several porous, low-$k$ films. The radial diffuse ($2\theta$) scans used in this work may, however, offer two important advantages:

1) They provide the ability to study the variation in pore-size distribution as a function of depth into the thin-film
2) They allow parallel data collection over a range of $2\theta$ angles using a position sensitive detector (PSD), which reduces measurement time

At incidence angles below the critical angle $\omega_c$, the diffuse intensity is concentrated to a fairly narrow angular region around the specular reflection. The reason for this is that the X-rays do not penetrate into the thin-film and the diffuse reflectivity is dominated by scattering from the surface roughness.

As the incidence angle is increased just beyond the first critical angle, the X-rays penetrate into the thin-film but are totally reflected by the Si substrate. This creates a standing wavefield within the thin-film and the diffuse intensity extends over several degrees $2\theta$. The two sharp peaks present in both curves at very small angles of incidence, $\omega < 0.5$ deg, are, from left to right, caused by the incident and specularly reflected beams.

In order to estimate size distribution of the pores within the sample, the diffuse XRR was measured. Figure 4 shows the measured radial diffuse intensity from the porous, low-$k$ sample extending from 0.0 deg to 6.0 deg in $2\theta$. The sample angle was adjusted such that $\omega = 0.19$ deg during the measurement. For comparison, the same scan was performed on a bare Si substrate and these data are shown for comparison. The two sharp peaks present in both curves at very small angles of incidence, $\omega < 0.5$ deg, are, from left to right, caused by the incident and specularly reflected beams.

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Figure 5 shows an iso-intensity map that was produced from a series of radial diffuse scans measured as the incidence angle, $\omega$, was increased from 0.07 to 0.54 deg in steps of 0.014 deg. Variations in the pore-size distribution with depth would result in changes in the diffuse intensity distribution with increasing $\omega$. As significant changes are not present in the map, we can conclude that there is no appreciable
variation in the pore-size distribution as a function of depth within the porous, low-k sample. The diagonal streak in the map is the specular scatter and the broad, diffuse “hump” centered around \( \omega \approx 0.175 \) deg results from a maximum in the transmitted amplitude when the incidence angle of the scattered radiation is equal to the critical angle of the thin-film (Yoneda wing [3]).

FIGURE 6. Longitudinal diffuse XRR data from a MesoELK thin-film (thin, dashed line) deposited on a Si wafer. The best-fit simulation using the polydispersed sphere model is also shown (thick, solid line). The 2\( \theta \)-scan was performed with the incidence angle, \( \omega = 0.19 \) deg, just beyond the critical angle of the thin-film. The inset shows the estimated pore-size distribution function.

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The diffuse XRR data was fitted to a simulation assuming both the random two-phase model and the polydispersed sphere model to describe the structure of the thin-film using a GA-based data-fitting procedure [7]. Figure 6 shows the measured diffuse XRR from the sample together with the best-fit simulation, which was obtained using the polydispersed sphere model. Experimental data outside of the range \( Q \lesssim 0.4 \) \( \text{nm}^{-1} \) were excluded from the data-fitting procedure. The best-fit simulation yielded an average pore-size of \( \langle D \rangle = 3.0 \pm 0.3 \) nm and a polydispersity equal to \( d = 0.7 \). The polydispersity value is rather large, which indicates that the distribution of pore-sizes is broad. We found that \( \langle D \rangle \) and \( d \) were somewhat correlated parameters and so as to reduce the effect of this correlation, the polydispersity was only allowed to take discrete values in steps of 0.1.

The results obtained from fitting the diffuse XRR from the sample are consistent with those obtained from similar samples using small angle neutron scattering (SANS). These measurements gave a broad pore-size distribution with an average pore-size of 20-30 Å [9].

CONCLUSIONS

Using an example MesoELK film deposited on a Si substrate, we have demonstrated that specular and diffuse XRR can provide valuable information about structure of porous, low-k materials. The specular XRR intensity yields the average density of the film and, if the matrix density is known, the porosity, \( P \). The thickness and surface/interface roughness of the film can also be obtained from such measurements. Once the porosity is known, the average pore-size, \( \langle D \rangle \), and pore-size distribution can be estimated by fitting the measured diffuse XRR intensity distribution to a simulation based on a model of the material’s pore structure. Since XRR methods are both non-contacting and non-destructive they have the potential to be routinely used in semiconductor laboratories and fabs.

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REFERENCES