Small angle x-ray scattering for measuring pore-size distributions in porous low-κ films

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Small angle x-ray scattering for measuring pore-size distributions in porous low-κ films

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A small-angle x-ray scattering technique has been applied for characterizing pore-size distribution in porous low-κ dielectric films. The data are collected in reflection geometry using offset $\theta/2\theta$ scans for avoiding strong specular reflections from the film surface and its substrate. The effects of refraction and reflection at the film surface and interface are corrected by the distorted wave Born approximation. A Γ-distribution mode is used to determine the pore-size distribution in a film. The technique has been used to analyze porous methyl silsesquioxane films. The pore sizes were found to disperse in the range from subnanometer to several nanometers, and the results agree well with those obtained by the N_2 gas adsorption technique. © *2003 American Institute of Physics.*
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In recent years, there has been considerable interest in the research and development of low-κ dielectric materials for reducing the dielectric constants of interlayer insulators in microelectronic devices. Low-κ dielectric films are used in ultrahigh density integrated circuits to avoid a delay of signal propagation and cross talks. It has been found that an introduction of nanometer-sized pores into dielectric films reduces their dielectric constant. However, the introduction of such pores can change both chemical and physical properties of a film. In the manufacturing process of microelectronic devices, it is important to lower the film dielectric constant without significantly reducing the film properties (hardness, etc.). The structure of the pore and its size distribution are closely related to such properties of porous thin films. Several articles and letters on the characterization of pore-size distribution and porosity have been reported.[1–4]

Small angle x-ray scattering is a powerful technique for determining density fluctuations in the scale of subnanometer to 100 nm. X-ray scattering patterns can be calculated for film structures with density fluctuations by using an established scattering theory, and the observed scattering data can be analyzed quantitatively. However, the conventional small angle x-ray scattering technique using a transmission geometry is difficult, if not impossible, to use for measuring thin films on thick substrates due to weak intensities. When the film is very thin, scattering intensity is very weak. In addition, a very high fraction, if not all, of scattering x-rays are absorbed by the substrate.

We, therefore, measured small-angle x-ray scattering patterns using reflection geometry. In this case, we have to consider both reflection and refraction at the film surface and interfaces as shown in Fig. 1. Therefore, we have calculated x-ray scattering intensities for the grazing incidence geometry based on the distorted wave Born approximation (DWBA).[5]

Reflection and transmitted coefficients $R_j(\alpha)$ and $T_j(\alpha)$ of the jth layer with the incident angle α can be calculated by the Fresnel's formula. X-ray wave field $\psi_1^i(\alpha)$ in the film $(j=1)$ at the depth z is written as

$$\psi_1^i(\alpha) = T_1(\alpha) e^{ik_0(\eta_1 z + x\cos\alpha)} + T_1(\alpha) R_1(\alpha) \varphi^2 \; e^{ik_0(-\eta_1 z + x\cos\alpha)}, \tag{1}$$

where k_0 is wave vector of the incident x ray, d thickness of the film, n_0, n_1 and n_2 refractive index of the vacuum, film and substrate, respectively; φ is defined by the following equation:

$$\varphi = \exp[ik_0\eta_1 d], \quad \eta_1 = \sqrt{n_1^2 - \cos^2\alpha}. \tag{2}$$

The scattered wave can be represented by a time reversal state of the incoming wave.[6] Therefore, the scattered wave field $\psi_1^f(\beta)$ in the film with the exit angle β can be written the same way as Eq. (1) by using the time reversal state, $\tilde{R}_1^*$, $\tilde{T}_1^*$ and $\tilde{\varphi}^* = \exp[-ik_0\zeta_1^* d]$, $\zeta_1 = \sqrt{n_1^2 - \cos^2\beta}$.

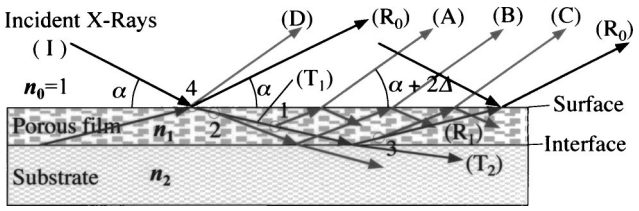

FIG. 1. Scattering processes for porous films with grazing incidence geometry. (R_0) Specular reflection, (A), (B), and (C) scattering in the film, (D) scattering at the surface.

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The scattering cross section by the scatterer potential $V(r)$ with number density N in the film can be calculated by the transition from the initial state to the scattered state. If the scatterer is distributed randomly in the film and the frequently oscillated thickness fringes are ignored, the cross section can be written as

$$\frac{d\sigma(\alpha,\beta)}{d\Omega}=\frac{1}{16\pi^2}|\langle\tilde{\psi}_1^f(\beta)|V|\psi_1^i(\alpha)\rangle|^2$$

$$=N\left[\begin{array}{l}|\tilde{T}_1T_1|^2|F(q^+)|^2\dfrac{1-e^{-2k_0\,\mathrm{Im}(\eta_1+\zeta_1)d}}{2k_0\,\mathrm{Im}(\eta_1+\zeta_1)}+|\tilde{T}_1\tilde{R}_1T_1|^2\\ \times|F(q^-)|^2e^{-4k_0\,\mathrm{Im}\,\zeta_1 d}\dfrac{1-e^{-2k_0\,\mathrm{Im}(\eta_1-\zeta_1)d}}{2k_0\,\mathrm{Im}(\eta_1-\zeta_1)}\\ +|\tilde{T}_1T_1R_1|^2|F(q^-)|^2e^{-4k_0\,\mathrm{Im}\,\eta_1 d}\\ \times\dfrac{1-e^{-2k_0\,\mathrm{Im}(\zeta_1-\eta_1)d}}{2k_0\,\mathrm{Im}(\zeta_1-\eta_1)}+|\tilde{T}_1\tilde{R}_1T_1R_1|^2|F(q^+)|^2\\ \times e^{-4k_0\,\mathrm{Im}(\zeta_1+\eta_1)d}\dfrac{e^{2k_0\,\mathrm{Im}(\eta_1+\zeta_1)d}-1}{2k_0\,\mathrm{Im}(\eta_1+\zeta_1)}\end{array}\right] \tag{3}$$

$$F(q)=\frac{1}{4\pi}\int_{\text{scatterer}}\exp[i\mathbf{q}\cdot\mathbf{r}]V(\mathbf{r})d\mathbf{r} \tag{4}$$

$$\left.\begin{array}{l}q^+=k_0\sqrt{\mathrm{Re}[\eta_1+\zeta_1]^2+(\cos\alpha-\cos\beta)^2}\\ q^-=k_0\sqrt{\mathrm{Re}[\eta_1-\zeta_1]^2+(\cos\alpha-\cos\beta)^2}\end{array}\right\}. \tag{5}$$

For calculating the form factor $F(q)$ of the scatterer, we have employed a Γ-distribution mode for the pores in the film

$$|F(q;R_0,M)|^2=\frac{1}{\Gamma(M)}\left(\frac{M}{R_0}\right)^M\int_0^\infty e^{-M\cdot R/R_0}\times R^{-1+M}\left(\frac{R_0}{R}\right)^3|r_e\rho\overline{f}(q)\Omega^{FT}(q,R)|^2dR, \tag{6}$$

where r_e is the classical radius of electron, ρ the number density of the atoms and $\overline{f}(q)$ average atomic scattering factor of the film material

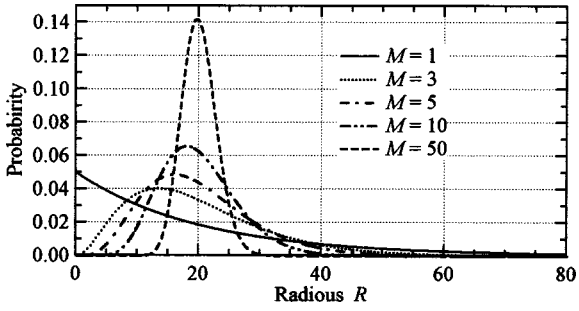

FIG. 2. The shape of Γ-distribution for average value $R_0=20$ for various shape parameter M.

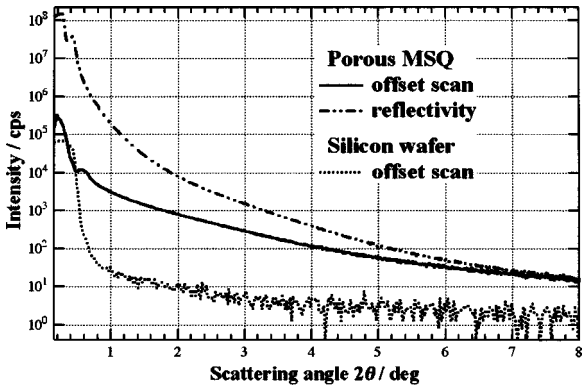

FIG. 3. Diffuse scattering pattern obtained by offset scan and reflectivity curves for a porous MSQ film. Offset scan pattern for a bare silicon wafer is also shown for the comparison.

$$\Omega^{FT}(q,R)=\frac{4\pi R^3}{(qR)^3}[\sin(qR)-(qR)\cos(qR)] \tag{7}$$

is the form factor of the sphere with radius R. R_0 is the average radius. Γ-distribution is suitable for representing non-negative radius distribution, because it is a distribution for the positive numerals. In addition, its shape is able to change flexibly by varying the shape parameter M ($1/\sqrt{M}$ is the normalized variance) as shown in Fig. 2.

X-ray scattering measurements for porous structures were made using a Rigaku ATX diffractometer[7] and a rotating anode x-ray generator operated at 50 kV and 300 mA. Parallel and monochromatic Cu $K\alpha$ radiation obtained by a parabolic graded multilayer mirror[8] was used. The sample position was slightly shifted with the angle $\Delta=0.1°$ from the symmetric $\theta/2\theta$ position (offset scan) to avoid strong specular reflection. This offset angle was selected for obtaining enough separation from the specular reflection. It depends on the resolution of the measuring system.

The observed reflectivity and small-angle scattering curves for spin-on coated porous methyl silsesquioxane (MSQ) film are shown in Fig. 3. It should be noted that the intensity of specular reflection (reflectivity) is much higher than that of scattering obtained by the offset scan. However, the intensity of offset scan data for the MSQ film is still much higher than that from a bare silicon wafer. This shows that the scattering from the pore is clearly detected.

We compared three spin-on MSQ films 1, 2, and 3 having different dielectric constants by the present technique. The densities of these films are listed in Table I; they are estimated by the critical angles of the x-ray total reflection.[1] We can see a clear relation between the dielectric constant and the film densities as expected. The lower the film density, the lower the dielectric constant.

The pore size distributions in the films were determined by comparing experimental and calculated offset-scan curves, and by optimizing R_0 and M in Eq. (6) by least-

TABLE I. Densities and dielectric constants for the three MSQ films.

	Density (g/cm^3)	Dielectric constant κ
1	1.17	2.54
2	1.10	2.43
3	1.00	2.28

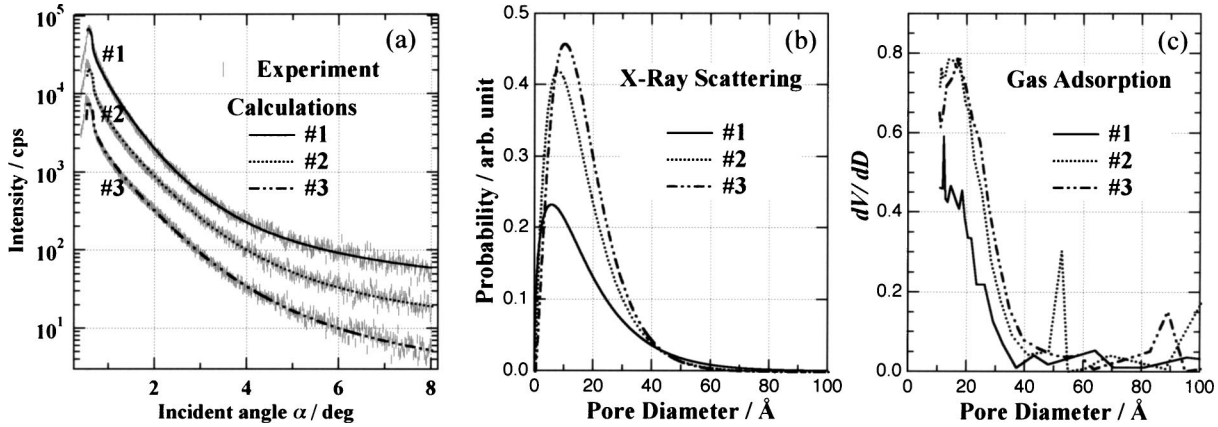

FIG. 4. (a) Experimental and calculated x-ray small-angle scattering patterns for the three porous MSQ films. Pore-size distribution of the films obtained by (b) x-ray scattering and (c) N_2 gas adsorption technique.

squares analysis. The observed and calculated scattering patterns and the resultant pore-size distributions by using the optimized parameters are shown in Fig. 4. The pore-size distributions are normalized by the x-ray scattering intensities. The higher scattering intensity indicates higher porosity. In the same figure, we also show the pore-size distributions obtained by N_2 gas adsorption technique. Extremely small pores (diameter $D<1$ nm) could not be analyzed by the latter technique, because the Kelvin equation is not applicable for such small pores. A reasonable agreement between these two techniques was obtained in the region of $D>1$ nm.

Diffuse scattering from the film surface (indicated by (D) in Fig. 1) sometimes interferes with the scattering by the pores in the film. In such a case, we have to estimate the contribution of the former. It can be also calculated based on the DWBA,[6,9] whereas the parameters of surface roughness σ, ξ, and h are known; they are rms roughness, lateral correlation length and Hurst parameter, respectively. In order to estimate these parameters, we have measured rocking scan patterns at several 2θ positions in addition to the offset scan. From these data, we could estimate not only the pore parameters but also surface roughness parameters. Typical examples are shown in Fig. 5. We could see the contribution of the surface scattering was dominant only at the regions of very low incident and exit angles.

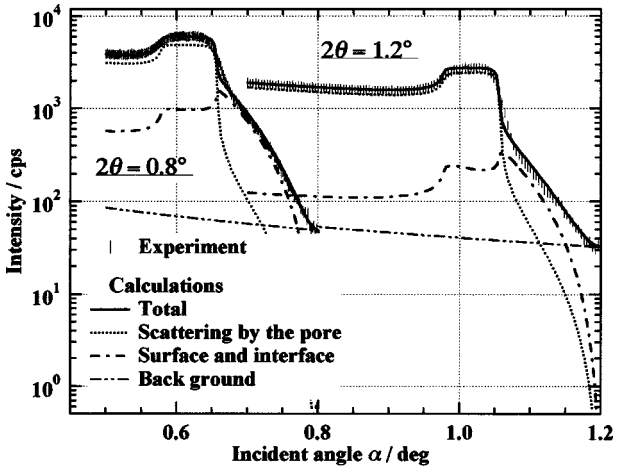

FIG. 5. Rocking scan pattern at $2\theta=0.8°$ and 1.2°. The contributions from the pore and surface diffuse scattering are compared.

In summary, a small-angle x-ray scattering has been applied for determining pore-size distribution in porous low-κ films. For the purpose of rapid and nondestructive analysis, we have used reflection mode measurement and calculated x-ray scattering intensities taking account of refraction and reflection at the surface and interface based on the DWBA. The results were well in accord with that from the gas adsorption technique.

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