Extended Abstracts of the 2005 International Conference on Solid State Devices and Materials, Kobe, 2005, pp.292-293

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Comparison of Pore Shape Models for Small Angle X-ray Scattering of a Disordered Porous Silica Low-*k* Film

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1. Introduction

Replacement of interlayer dielectrics with extremely low-dielectric-constant (low-*k*) films is one of the key issues in scaling of ultra-large-scale-integrated (ULSI) circuits. We have proposed and experimentally demonstrated the ultralow-*k* disordered mesoporous silica films synthesized by using nonionic templates [1]. In those films, the pore shape is supposed to be cylinder rather than sphere (Fig. 1). On the other hand, cross sectional transmission electron microscope observations of those films have not detected a well-defined cylindrical pore shape yet. In the present work, we carefully analyzed an experimentally obtained small angle x-ray scattering (SAXS) spectrum [2, 3] to compare it with a newly constructed SAXS simulation program for cylindrical and spherical pore shapes. From the standard deviations of the model fittings to the experimental spectrum, the cylindrical pore-shape model turned out to better fit to the experiment.

2. Experimental

SAXS measurement was made in a grazing-incedence reflection geometry with Cu Kα line of 0.154 nm in wavelength collimated and monochromated by four germanium crystals of <220> orientation and the details of the measuremnt technique were reported previously [2]. A disordered porous silica film was prepared on a crystalline silicon substrate by spin coating a mixture of acidic silica sol and nonionic surfactant template, followed by thermal annealing for template removal at 400 °C, and then by vapor treatment at 400 °C to impart hydorphobicity [1].

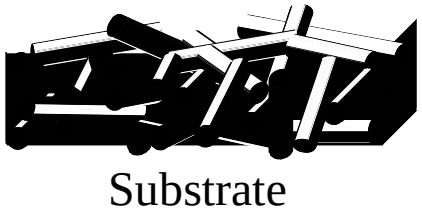

Figure 1 Schematic figure of cylindrical shape and random orientation of pores in a disordered porous silica film.

3. Simulation

A three-dimensional Fourier transformation of electron density profile corresponding to a cylindrical pore was used for calculation of SAXS spectrum:

$$\Psi(k_x x, k_y y, k_z z) = \int_{-\infty}^{\infty} \phi(x,y,z) \cdot e^{-i(k_x x + k_y y + k_z z)}\, dx\,dy\,dz \quad (1)$$

$$\phi(x,y,z) = \begin{cases} 1 & -a\sqrt{1-\frac{y^2}{b^2}} \le x \le a\sqrt{1-\frac{y^2}{b^2}}, \\ & -b \le y \le b,\ z = c \\ 0 & \text{others} \end{cases}$$

The coordinate system used in the calculation is shown in Fig. 2. Disordered orientation of the cylindrical pores was taken into account by taking average over the orientation solid-angle space. A single peaked finite breadth distribution of pore size was modeled by gamma function and SAXS intensity was calculated as:

$$|F(kx, ky, kz)|^2 = \frac{1}{\Gamma(M)}\left(\frac{M}{R_0}\right)^M \int_0^{\infty} e^{-\frac{M \cdot R}{R_0}} \cdot R^{M-1}\left(\frac{R_0}{R}\right)^2 \cdot |\Psi(k)|^2\, dR \quad (2)$$

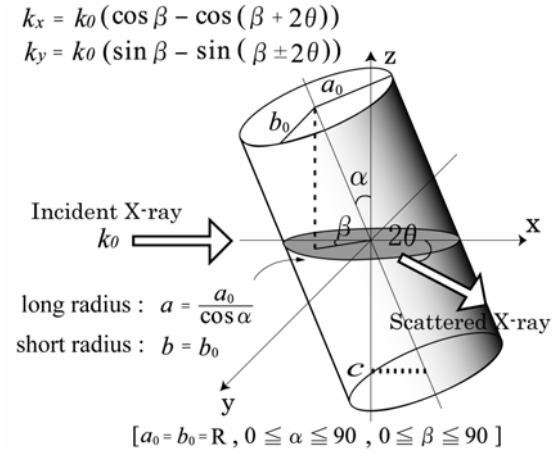

Figure 2 Coordinate system for calculation of x-ray scattering from a cylindrical pore.

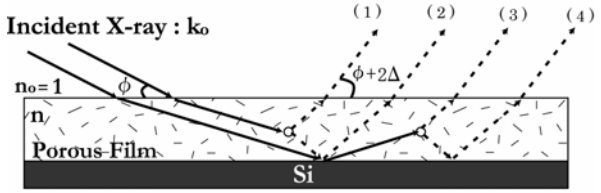

Figure 3 Schematic representation of simulation of reflection, refraction and transmission of incident and scattered x-ray at the interfaces.

Here, R_0 and M are the radius and distribution parameters of the gamma function, respectively, as is expressed in eq. (2). The reflection, refraction, and transmission of x-ray at the top surface as well as at the interface with the substrate were taken into account as shown in Fig. 3. A simulation program to calculate SAXS spectrum was constructed.

4. Results and Discussion

The values of parameters R_0 and M defined above, and intensity factor I_0 were fitted to the experimental spectrum Figure 4 shows the experimental data points (dots) and the best fitted curve (solid line). A good agreement between experiment and simulation is observed. Solid line in Fig. 5 shows the pore size distributions corresponding to the best fitted simulation result shown in Fig. 4. The dashed line in Fig. 5 is the pore size distribution for the best fitting with the sphere model. The cylindrical pore model gives a slightly narrower pore size distribution than the spherical model in Fig. 5. Figure 6 shows the way how the standard deviation for the fitting of the experimental data with the cylindrical simulation changes when the parameters R_0 and M are varied. A systematic change in the standard deviation with R_0 and M shows that the best fitted curve can accurately be determined. The minimum standard deviation reached in the cylindrical model analysis is less than that in the spherical model as shown in the inset of Fig. 6. That suggests that the cylindrical pore-shape mode is better suited to fit to the experiment.

5. Conclusion

A SAXS spectrum of a disordered porous silica film was carefully analyzed to compare its fitting with newly developed cylindrical pore simulation program as well as with a spherical pore model. Standard deviation of the best fitting with the cylindrical pore model was shown to be lower than that with the spherical pore model, suggesting that the pore shape in the disordered porous silica film is closer to cylinder rather than sphere as is aimed in preparation method [1].

Acknowledgements

This work is partly supported by New Energy and Industrial Technology Development Organization (NEDO). Japan Science and Technology Agency (JST) is acknowledged for Cooperative System for Supporting Priority Research.

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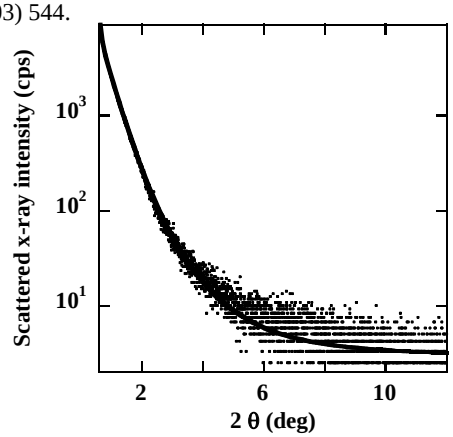

Figure 4 SAXS spectrum (dots) and best fitted simulation curve (solid line) with the cylindrical pore model.

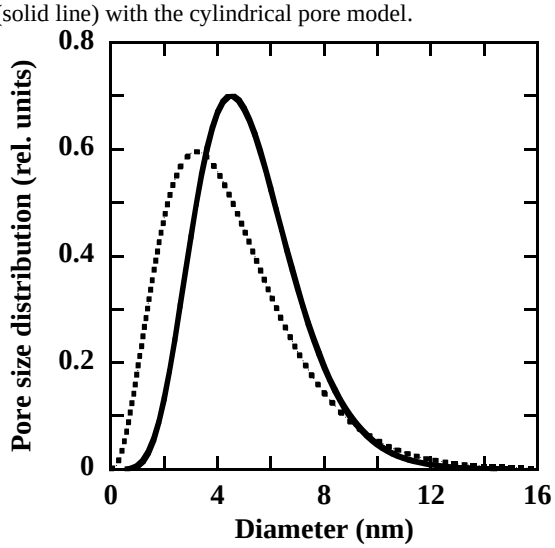

Figure 5 Pore size distributions obtained from analysis of cylindrical (solid line) and spherical (dashed line) pore models.

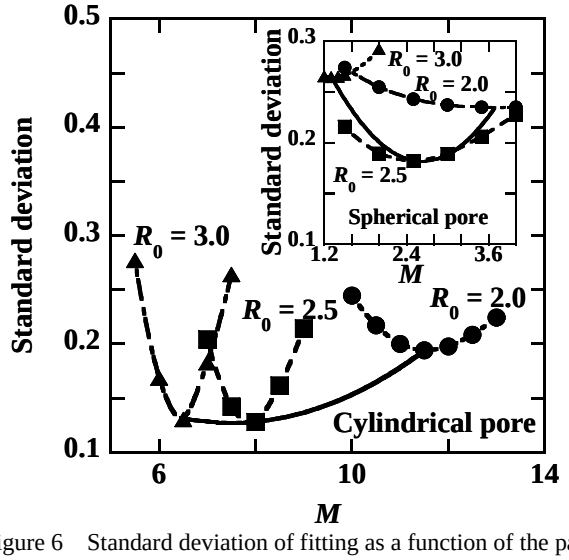

Figure 6 Standard deviation of fitting as a function of the parameter M, for three different R as parameter.