

Characterization of Pore Size Distributions in Ultralow- k Films

N. Hata^{1,2}, N. Fujii³, H. Miyoshi³, X. Li² and T. Kikkawa^{1,4}

¹MIRAI-ASRC, AIST, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

²ASRC, AIST, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

³MIRAI-ASET, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

⁴RCNS, Hiroshima University, 1-4-2 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

1. Introduction

A pore size distribution (*psd*) is one of the most crucial structural parameters of ultralow-dielectric constant (ultralow- k) films. We have demonstrated both experimentally [1,2] and theoretically [3,4] that a careful control of pore structure results in higher Young's modulus for a given k . In the present work, we propose a strategic characterization procedure for *psd*, with experimental results on periodic and disordered porous silica films produced by using a surfactant templating technique [1,2]. Uniformity of the pore sizes as is seen in a tight *psd*, the density of skeletal structure, the micropore structures, and the controllability of the *psd* are clarified with the proposed procedure.

2. Experimental

Two types of disordered porous silica films, sample A and B, were prepared by spin coating from silica precursor mixed with nonionic surfactant template HO (C₂H₄O)₁₃ (C₃H₇O)₂₀ (C₂H₄O)₁₃ H. Also, a periodic porous silica film, sample C, was prepared with cationic surfactant template C₁₂H₂₅N(CH₃)₃Cl. Details of the film preparation conditions were reported earlier [1,2]. Cu K α line $\lambda = 0.154$ nm of x-ray was used for x-ray scattering, and also reflectance measurements [5]. Volumetric physisorption analysis [6] and in-situ vapor-adsorption spectroscopic ellipsometry [6,7] were employed for adsorption / desorption isotherm measurements. From the analyses of the measurement results, pore size distributions, porosity, and skeletal density were determined.

3. Determination of *psd*, porosity and skeletal density

Figure 1 shows x-ray determined *psd* of disordered porous silica films. The sample A with a narrower *psd* shows the higher Young's modulus than the sample B, while k is

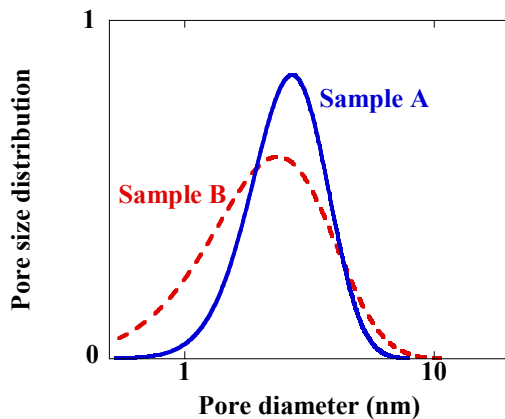


Fig. 1 Pore size distributions of disordered porous silica low- k ($k = 2.1$) films, sample A and B with $E = 5.3$ and 4.3 GPa, respectively.

comparable, consistently with the theoretical predictions [3].

Figure 2 shows adsorption / desorption isotherm of argon gas at 87 K measured for the sample A. Here, the vertical axis V is the adsorbate volume per unit weight of the film sample. It exhibits a hysteresis loop representing the existence of mesopores [8]. The relative pressure p / p_0 , the horizontal axis of Fig. 2, can be converted into the statistical thickness of argon adsorbate layer as shown in Fig. 3 by using the calibration curve, i.e., the standard adsorption isotherm of argon onto silica surface [8]. Fig. 3 is called as the ' t -plot', where t represents the statistical thickness of the adsorbate. The saturated volume (dashed line) and the near-zero intercept of the solid straight line to the vertical axis in Fig. 3 correspond to the argon amounts to fill the total pore volume (V_{pore}) and the micropore volume (V_m), respectively. The $V_{\text{pore}} = 518 \text{ cm}^3 \text{ STP g}^{-1}$ was converted into the adsorbate volume and then multiplied by the film density $\rho = 0.92 \text{ g cm}^{-3}$ determined by x-ray reflectance analysis to obtain porosity $x = 0.57$. Skeletal density ρ_{skeletal} was calculated as: $\rho_{\text{skeletal}} = \rho / (1 - x) = 2.1 \text{ g cm}^{-3}$, which is fairly close to the bulk silica density of 2.2 g cm^{-3} . On the other hand, the near-zero intercept V_m of the solid line with the vertical axis in Fig. 3 reveals that the film is nearly free from micropores, consistently with the skeletal density close to the dense bulk silica as mentioned above. Namely, the sample A has been shown to have nearly as dense skeleton as the bulk silica. It should be noted that the slope of the solid line in Fig. 3 gives a specific surface area of $620 \text{ m}^2 \text{ g}^{-1}$, comparable to the value of $670 \text{ m}^2 \text{ g}^{-1}$ obtained from the multiple layer adsorption (Brunauer-Emmett-Teller) model analysis as shown in Fig. 4.

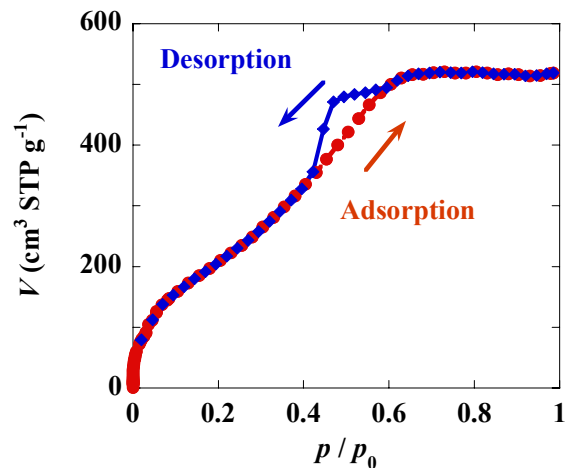


Fig. 2 Adsorption / desorption isotherm of argon molecule measured volumetrically at 87 K for the sample A in Fig. 1.

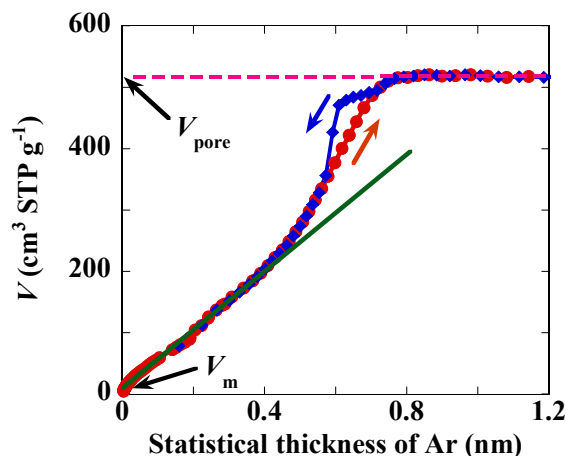


Fig. 3 The adsorbate volume plotted against the statistical thickness of Ar onto silica surface. The slope of the solid straight line corresponds to the specific pore surface area, and the horizontal dashed line corresponds to the total pore volume.

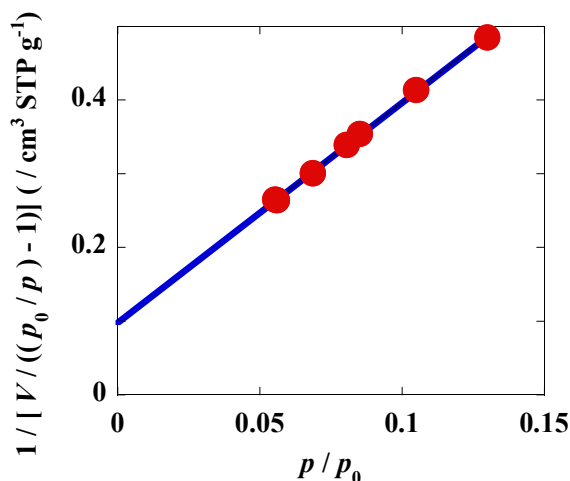


Fig. 4 Multilayer adsorption (Brunauer-Emmett-Teller) model analysis of the sample A. The slope and intercept with the vertical axis of the solid straight line are used to obtain the specific pore surface area.

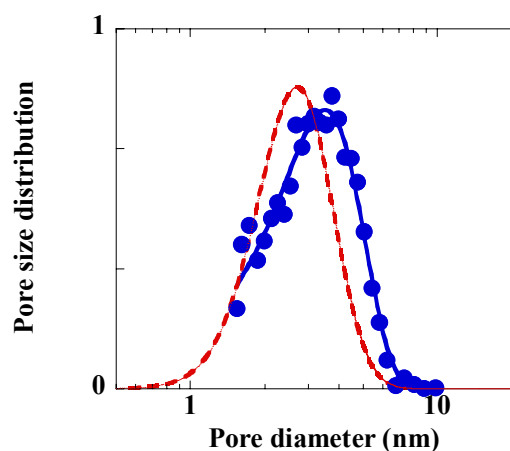


Fig. 5 Comparison of *psd*'s determined by x-ray (dashed line) and volumetric physisorption (solid line with dots) analyses. Minor difference in the distributions originates from different physical principles of the measurements.

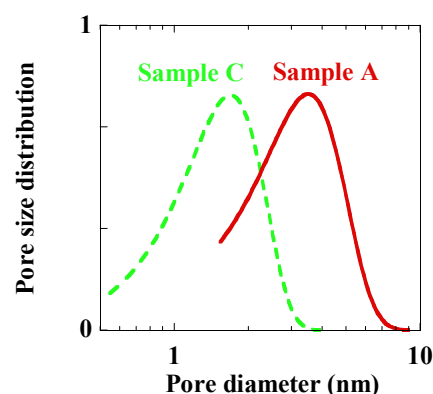


Fig. 6 *Psds* of two typical porous silica films prepared with surfactant templates with different molecular sizes: sample A (solid line) with HO (C₂H₄O)₁₃ (C₃H₇O)₂₀ (C₂H₄O)₁₃ H, while sample C (dashed line) with C₁₂H₂₅N(CH₃)₃Cl.

4. Effects of analysis techniques and templates on *psd*

The adsorption isotherm in Fig. 2 was analyzed by considering capillary condensation of adsorbate into the mesopores to obtain *psd* [6-8]. The result is shown in Fig. 5 together with that determined by the x-ray analysis. The distributions are not completely identical because of the different physical mechanisms of measurements: The physisorption reflects the adsorbate capillary condensation, while the x-ray scattering reflects the electron density fluctuation. Figure 6 compares the *psd* of sample A with that of sample C. In relation to the earlier result [7] which showed that the pore size can minutely be controlled by varying the alkyl chain length of the surfactant molecule, the present result in Fig. 6 evidences that the pore size can be controlled over the wide range by selecting surfactant molecular sizes.

5. Conclusion

A systematic procedure to characterize *psd* of ultralow-*k* films was proposed. It has then been demonstrated that pore size uniformity, skeletal density, and pore size controllability of ultralow-*k* porous silica films prepared by surfactant templating technique can quantitatively be examined by the proposed procedure.

Acknowledgments

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