Ultrahigh-sensitive and Automated Kr gas adsorption technique:A trial to characterize the porosity of thin film materials.

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The introduction of micro-pores has become a common way of obtaining ultralow-k materials over the last several years. However, no method of measuring the porosity of these materials seems to be recognized as a standard. In this study, we developed a method based on gas adsorption[1,2] that is applicable to the determination of the porosity of low-k materials. The determination of porosity using Kr adsorption has the same basis as that using N_2 adsorption, namely BET theory, Kelvin's equation and the Dollimore-Heal[3] method. We calibrated the porosity measurements for Kr adsorption based on those for N_2 adsorption using following standard samples. Namely, we adopted four kinds of powders as standard samples. Samples no.1 and 2 listed in Table I, are supplied from the Federal Institute for Material Research and Testing of Germany. Both are porous alumina, basic properties of which including BET surface area, pore-volume, pore-size distribution are measured in more than twenty separate laboratories, and certified by the above Institute. We adopted crashed quartz, no.3, as for non porous material which BET surface area was measured in 0.069 m^2/g from Kr adsorption in this study. Sample no. 4 is a meso-porous silica powder which is intentionally synthesized with controlled pore by surfactant template method. We measured both N_2 and Kr adsorption on this material in this study. Sample no.5 is a low k material synthesized using surfactant template method. In the adsorption measurement, no.5 was coated on the Si wafer, baked and cut into small pieces, about 8 mm x 50 mm square, and several pieces were used.

The Kr parameters used (density, surface tension, molar volume, etc.) were those cited in the literature[4]. The standard adsorption isotherm was measured using a sample of crushed quartz, which is considered to be a non-porous material. The volume and thickness of an adsorbed monolayer were calculated by applying a BET analysis to the standard isotherm. Kelvin's equation is

$$\ln(P/P_0) = -(2\gamma V_L/RT) \times (1/r),$$

where P is the equilibrium pressure of Kr, P_0 is the saturation pressure of Kr, γ is the surface tension, V_L is the molar volume of liquid Kr, R is the gas constant, T is the absolute temperature and r is the radius of a pore. Calculating the quantity $2\gamma V_L/RT$ from data on Kr in the literature yields a value of 1.105, whereas the reported value for N_2 is 0.4078. Using this value in the Dollimore-Heal method, we obtained the pore size distribution of mesoporous silica (no.4) shown in Fig. 1, where the squares and circles are the distributions obtained using Kr adsorption and N_2 adsorption, respectively. Then, we fitted the resultant Dollimore-Heal curve for Kr adsorption to that for N_2 adsorption with the most similar pore size distribution, and obtained the curve indicated by the triangles, Kr fit, in the same figure. As a result, it was found that the value of $2\gamma V_L/RT$ had to be adjusted to 0.42. In the remainder of this study, we used this value in determining the pore size distributions of other samples.

Figure 2 shows the pore size distributions obtained for the five samples listed in Table I. The vertical axis is pore volume in arbitrary units. Clearly, our Kr adsorption technique can detect the differences among these samples. And quantitatively, the most probable pore radii of Samples 1 and 2 are in fairly good agreement with the values in Table I obtained by the N_2 adsorption technique. Our results indicate that the porous silica film Sample no.5 has pores with a radius of less than 1 nm.

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Table I Standard samples

No.	material	most probable pore radius(nm)	
		N_2 method	Kr method
1	porous alumina	3.2	3.2
2	porous alumina	2.4	2.6
3	nonporous silica	not detected	not detected
4	mesoporous silica	1.4	1.4**

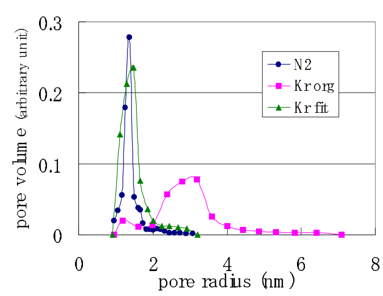

Fig.1 Curve fitting for Kr adsorption to N_2

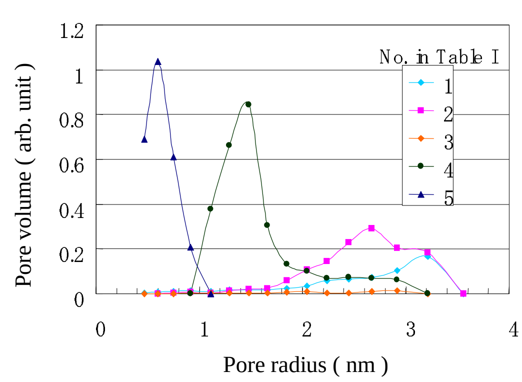

Fig.2 Pore size distribution

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