Extended Abstracts of the 2003 International Conference on Solid State Devices and Materials, Tokyo, 2003, pp. 78-79

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Nondestructive Characterization of Pore Size Distributions in Porous Low-k Films by in-situ Spectroscopic Ellipsometry in Vapor Cell

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1. Introduction

The introduction of nanopores is a possible pathway to realize ultra-low-k dielectrics of k < 2.1 for future interconnect technology, so that reliable characterization techniques for pore structures are needed. Although gas adsorption method is widely used for characterizing pore structures of conventional porous materials, it has no sufficient sensitivity for the thin low-k films. For example, we need to destroy and peal off low-k films from the silicon substrate in order to collect sufficient sample amount for volumetric nitrogen adsorption study [1]. Baklanov and co-workers [2] recently developed the ellipsometric porosimetry (EP) in which changes in refractive index and thickness of thin low-k sample was used to obtain adsorption isotherm. As is also the case in commonly used ellipsometry, EP has a big advantage as a non-destructive technique. On the other hand, as organic vapor adsorptive, which has much less adsorption database than nitrogen, is employed for this technique, special care must be taken about it [3].

In the present work, we report results from comparative experiments among nitrogen volumetry, heptane volumetry and heptane in-situ spectroscopic ellipsometry on a porous silica low-k film from the same preparation batch in an attempt to carefully identify the effects of the differences in (1) the adsorptives and (2) the detection methods. Also, we take advantage of spectroscopic ellipsometry measurements to analyze the film optical property with multi-layer optical modeling technique when that is necessary for giving a way to much wider applicability to many low-k films.

2. Experimental

In-situ spectroscopic ellipsometry measurements in a heptane vapor cell on a piece of the periodic porous silica film with k =2.1 [4] on silicon substrate were performed by using the setup shown in Fig. 1. Also, the periodic porous silica film was pealed off from a large area of the substrate to obtain 22 milligrams of sample flakes. An automated volumetric adsorption measurement system was used to measure nitrogen and heptane isotherms.

3. Results and Discussion

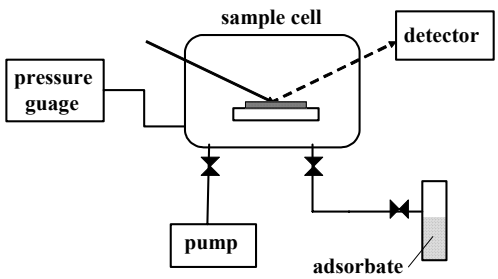

Fig. 1 Schematic daigaram of in-situ spectroscopic ellipsometry measurement setup in a vapor cell.

The periodic porous silica low-k film [4] was analyzed by volumetric adsorption of nitrogen [1] as reference and of heptane to examine the effects of the vapor adsorptive. Figure 2 shows the heptane adsorption isotherm by volumetry. Pore volume and porosity calculated from the adsorbed total volume in Fig. 2 were compared with those obtained by nitrogen adsorption in our previous work [1] as shown in Table I. In the present work, the surface tension and molar volume of liquid heptane were taken as 19.65 x 10^{-3} N m^{-1} [5], and 144.6 x 10^{-6} m^3 / mol [6], respectively. Pore volume and porosity from nitrogen and heptane volumetry showed a good agreement in Table I. Analysis of pore size distribution was carried out by using Dollimore-Heal method [7]. The statistical thickness of heptane was calculated by the BET equation [2, 3] using the constant extracted from the results shown in the inset of Fig. 2. Figure 3 compares thus obtained pore size distribution (dashed curve) with that obtained by the nitrogen volumetry (solid curve). As to the possible origins of the difference in the peak positions between the results from the two adsorptives, packing density of the adsorbates in nanopores as well as variation of surface tension in the restricted volume than from the bulk value could be responsible [8].

In contrast to the volumetric detection, the ellipsometric detection has a big advantage of thousands of times higher sensitivity. On the other hand, we need to take into account the surface / interface roughness layer and depth profile of refractive index in the optical modeling used to analyze the ellipsometric spectra. Also, the validity of effective medium approximation which is used to calculate

the adsorbed amount from the refractive index needs to be confirmed. For the sample studied in this work, we employed a two-layer optical model (inset of Fig. 4) for spectral analysis to improve the fitting to obtain the adsorption isotherm shown in Fig. 4. It was then analyzed in the same manner as the volumetrically obtained heptane

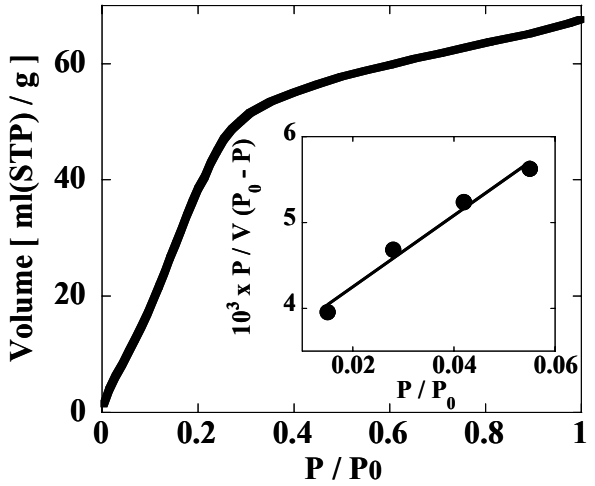

Fig. 2 Adsorption isotherm of heptane measured volumetrically. The horizontal scale p / p_0 denotes the heptane pressure p normalized by the saturated vapor pressure of heptane p_0. Inset is the BET plot.

Table 1 Summary of pore volume and porosity

adsorptive	pore volume	porosity
nitrogen	468 mm^3 /g	38 %
heptane	435 mm^3 / g	35 %

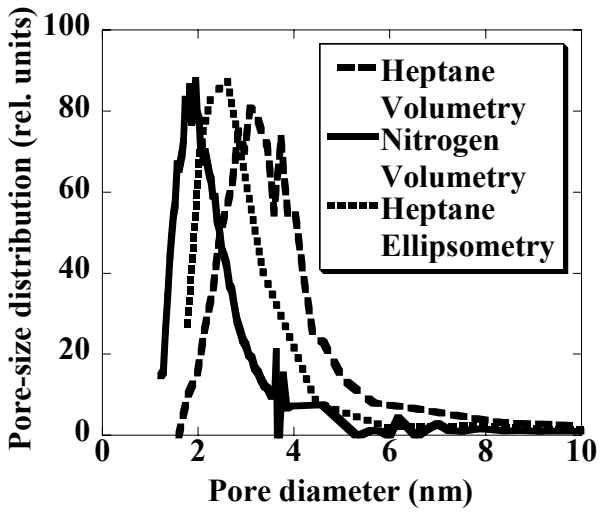

Fig. 3 Comparison of pore size distributions of the periodic porous silica low-k films determined by nitrogen and heptane volumetry (solid and dashed lines) and heptane in-situ spectroscopic ellipsometry (dotted line).

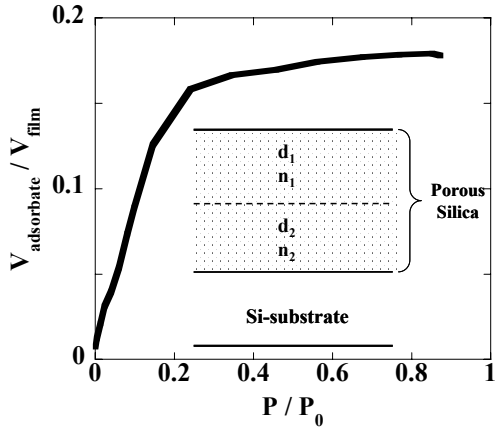

Fig. 4 Heptane adsorption isotherm measured by in-situ spectroscopic ellipsometry. Inset is a schematic of the two-layer optical model employed in the analysis.

adsorption isotherm to get the pore size distribution shown by the dotted curve in Fig. 3. The origin of the slight difference from the volumetric result needs to be carefully identified.

4. Conclusions

We performed highly sensitive and powerful pore characterization of a porous low-k film by in-situ spectroscopic ellipsometry in heptane vapor cell and compared the results with those from heptane and nitrogen volumetry measurements. We conclude that both the database of (1) vapor adsorptive and of (2) ellipsometric detection modeling needs to be accumulated for reliable metrology of porous low-k films.

Acknowledgements

This work was supported by NEDO. JST is acknowledged for the Cooperative System for Supporting Priority Research.

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