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# Adsorption in-situ Spectroscopic Ellipsometry Analysis of Disordered Porous Silica Low-*k* Films

Xianying Li[1], Nobutoshi Fujii[2], Nobuhiro Hata*[1,3] and Takamaro Kikkawa[3,4]

[1]ASRC, AIST, 16-1 Onogawa, Tsukuba, Ibaraki 305-8568, Japan
[2]MIRAI-ASET, 16-1 Onogawa, Tsukuba, Ibaraki 305-8568, Japan
[3] MIRAI-ASRC, AIST, 16-1 Onogawa, Tsukuba, Ibaraki 305-8568, Japan
[4]RCNS, Hiroshima U., 1-4-2, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan
*E-mail: n.hata@aist.go.jp; Tel: +81-29-8615422

## 1. Introduction

The replacement of non-porous low-dielectric-constant (low-*k*) films in Cu/low-*k* interconnects in ultra-large-scale-integrated (ULSI) circuits with porous low-*k* (ultralow-*k*) materials has been investigated. Issues in the materials development are characterization and analysis of pore diameter, pore structure and pore skeletal structure. In the present work, we report the results from adsorption in-situ spectroscopic ellipsometry analyses [1] of a series of ultralow-*k* disordered mesoporous silica films synthesized by using nonionic templates [2], to discuss the capability of the measurement technique to sensitively monitor the variations in pore-size distributions controlled by concentration and size of the template molecules.

## 2. Experimental

Figure 1 shows the experimental setup for the adsorption in-situ spectroellipsometric measurements, which is similar to what we reported earlier [1]. In short, the sample cell is equipped with optical windows, sample stage with temperature control, vapor inlet and outlet ports and vapor pressure monitor. Adsorbed amount was monitored by a change in sepctroellipsometrically obtained optical properties of the porous film sample as a function of vapor pressure to obtain adsorption / desorption isotherms. N-heptane was employed as the adsorptive.

The disordered porous silica films were prepared by spin coating the mixtures of acidic silica sol and nonionic surfactant templates as schematically shown in Fig. 2 in comparison with periodic porous silica films [2]. Three nonionic surfactants were used for increasing the molecular weight as template, P45 ($EO_{13}(PO)_{20}EO_{13}$), P64, and P84. On the other hand, with P45, the template concentration $C_t$ was varied from (a) 1, (b) 1/3, (c) 1/4.5, to (d) 1/6 times of the template to silica precursor molar ratio described in ref. [2]. Post-spin-coating thermal annealing as well as vapor treatment with 1,3,5,7-tetramethylcyclotetrasiloxane were employed to remove the template to obtain porous silica films with a high hydrophobicity.

## 3. Result and Discussion

The inset of Fig. 3 shows adsorption / desorption isotherms for the disordered porous silica films prepared using the template molecule P45 of four different template concentrations. The horizontal axis is the heptane vapor

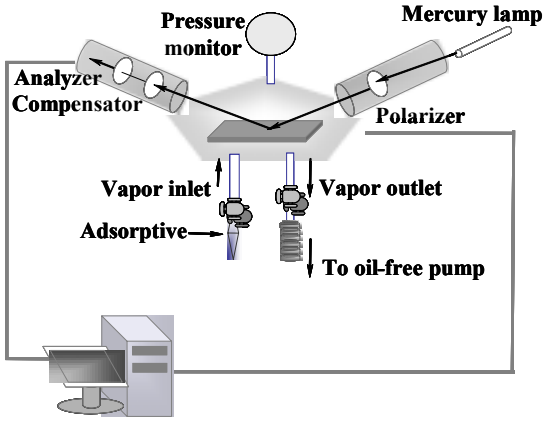


Fig.1 Schematic diagram of the mesurement setup

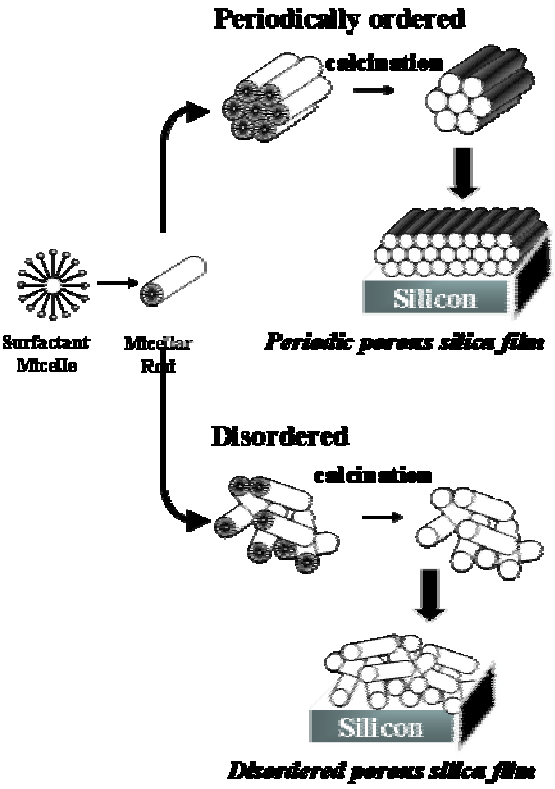


Fig. 2 Schematic diagram of preparation of disordered or periodically ordered porous silica films [2].

pressure normalized to its saturated vapor pressure at the measurement temperature of 298 K. The vertical axis is the adsorbed volume of heptane which was calculated according to eq. (1) of Ref. [1]. The isotherms for the $C_t = 1$ and $C_t = 1 / 3$ show hysteresis loops corresponding to irreversibility of adsorption-desorption behavior in mesopores. The normalized vapor pressures corresponding to the inflection points of the isotherms differed slightly between the results for $C_t = 1$ and $C_t = 1 / 3$, reflecting a difference in pore size distributions. With further decrease of template concentration $C_t$ the inflection point moved to lower vapor pressure and the hysteresis loop narrowed and finally vanished at $C_t = 1 / 6$ as is seen in the inset of Fig. 3. It should be noted that the adsorption / desorption isotherms obtained by the present technique essentially coincide with those from well-established volumetric argon physisorption measurement, a result of which for the sample $C_t = 1$ is shown in Fig. 4. The higher $p / p_0$ corresponding to the inflection point for Ar than for heptane correctly reflects the differences of molecular volume and surface tension.

The adsorption / desorption isotherms in the inset of Fig. 3 were analyzed by the Dollimore-Heal (DH) method [3] using the c parameter value, which was determined by the Brunauer-Emmet-Teller (BET) plot, to obtain pore size distributions [1]. The result from the desorption branch for the four samples are shown in Fig. 3. A trend of the pore size shrinkage with decrease of template concentration $C_t$ is clearly seen in Fig. 3.

Figure 5 shows pore size distributions from desorption branches of the adsorption / desorption isotherms (inset of Fig. 5) of disordered porous silica films prepared using the three templates of different sizes. The molar ratio of the template to the silica precursor was kept constant for the preparation of the films. The adsorbed volume as well as the pore size varied reflecting the difference in molecular sizes of the templates.

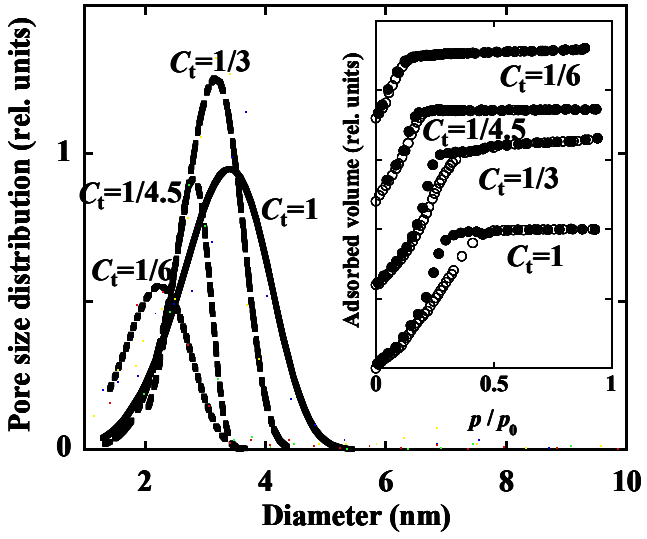


Fig.3 Adsorption / desorption isotherms (inset) and pore size distributions of disordered porous silica films prepared with varied P45 template concentrations.

## 3. Conclusion

A nondestructive technique of adsorption *in-situ* spectroscopic ellipsometry for analyzing the pore size distributions was applied to the disordered porous low-*k* films. The result revealed that this measurement technique can detect the variations in peak position and width of pore size distributions of disordered porous silica films that are controlled by the molecular size and concentration of nonionic templates.

## Acknowledgments

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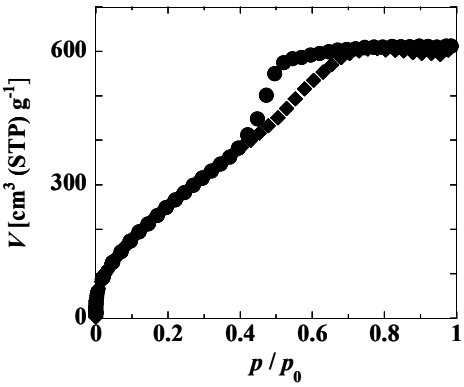


Fig. 4 Argon adsorption / desorption isotherm of disordered porous silica film with $C_t = 1$.

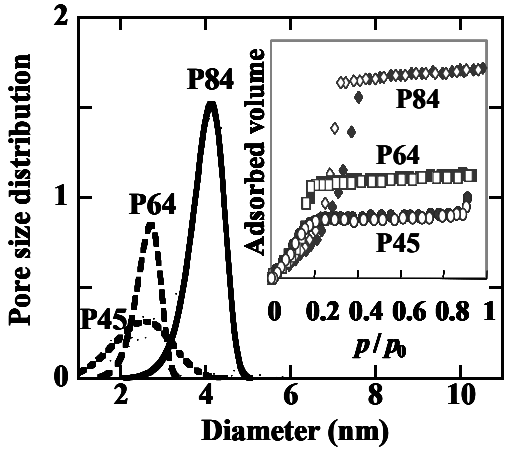


Fig.5 Isotherms (inset) and pore size distributions of disordered porous silica films prepared with templates P45, P64, P84.