



## *In situ* ellipsometry of porous low-dielectric constant films in supercritical carbon dioxide

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### ABSTRACT

This paper reports the results of *in situ* ellipsometric measurements on porous low-dielectric constant thin films being placed in a mixture of supercritical CO<sub>2</sub> and an organic solvent, intending the detection of the pores. Different low-*k* films having a dielectric constant of 2.2–3.1 were examined at pressures of 10–14 MPa and temperatures of 40–100 °C. Large changes in ellipsometric parameters were observed upon the addition of the solvent, in any condition studied, when spin-on-dielectric films that have micropores were used. Measurement conditions for films with a smaller pore size were explored and the detection of supermicropores in plasma-enhanced chemical-vapor-deposited SiOCH was succeeded.

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### 1. Introduction

Characterization of pore structure is a crucial topic in the materials science of low-dielectric constant (low-*k*) thin films. Low-*k*s having open porosity can uptake water or moisture very easily, allow the permeation of chemicals, and is not tolerant against plasma damage. A great effort has thus been made to embed isolated micro-/supermicropores [1] in the matrix [2–5]. For instance, molecular pore-stacked SiCOH (MPS) film, which is fabricated by plasma-enhanced polymerization and contains supermicropores surrounded by siloxane rings [2,3], and nano-clustering silica (NCS) which is a spin-on dielectric that has a polymer of basket-like molecules [4,5] has been developed.

There have been a very limited number of methods available for pore characterization of porous thin films executable in a non-destructive manner. Ellipsometric porosimetry (EP) is an adsorption porosimetry that uses ellipsometry to measure the degree of adsorption [6,7]. EP has a very high pore-size-distribution (PSD) resolution; however it is said that EP is not easily applicable to detecting sub-nano pores and that one measurement takes a long time [8]. Positronium annihilation lifetime spectroscopy (PALS) [9–11] has sensitivity large enough to detect atomic vacancies and is therefore ideal for evaluating closed pores, whereas its instrumentation is too complicated to allow its in-line use. The PSD resolution of PALS is not high because of the complexity of physical interactions between positronium/positron and the pore surface [12]. In addition, PALS has rather poor sensitivity for determining the open/close pore ratio, or pore connectivity. In such a measurement, a capping layer is needed to seal the open pores,

and thus the reliability of measurements depends on the quality of the capping layer [13]. Moreover, porous low-*k*s can be deteriorated during the cap formation.

The aim of this work is to provide a method for detecting the supermicro pores and for evaluating the pore connectivity of porous low-*k* thin films in an easy manner. For this purpose we propose to carry out adsorption porosimetry in a supercritical CO<sub>2</sub> fluid. Supercritical CO<sub>2</sub>, the critical point of CO<sub>2</sub> is 7.3 MPa and 31 °C [14], has the unique ability to diffuse through solids like a gas, and dissolves materials like a liquid. Diffusion flux is a product of diffusivity and density. Gases have a too-low density and liquids have a too-low diffusivity. Supercritical CO<sub>2</sub> has a moderate density between gases and liquids. The diffusion flux in supercritical CO<sub>2</sub> is thus much larger than in gases or liquids. Therefore, when supercritical CO<sub>2</sub> used as a medium for adsorption porosimetry, it is expected an adsorbate is delivered into supermicro pores easily.

In this paper, we report *in situ* ellipsometry of porous low-dielectric constant films in supercritical CO<sub>2</sub> binary solutions. The changes of ellipsometry parameters upon the addition of a probe solute were monitored. The ellipsometry was used as is in EP, because it is an easy and simple technique and it is extendable to on-site/in-line measurements.

### 2. Experimental procedure

Fig. 1 shows an experimental setup used in this work [15]. A specimen was placed in a high-pressure cell that has two optical windows. Glass having a low coefficient of thermal expansion (Pyrex™) was used as the window material to minimize the birefringence effects. Ellipsometric measurements were carried out with a usual rotating-polarizer spectroscopic ellipsometer at an

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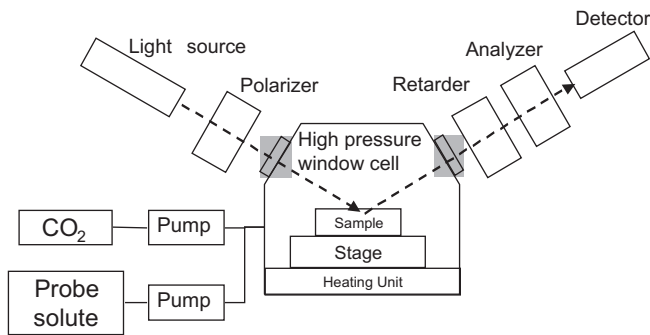


Fig. 1. Experimental setup of *in situ* ellipsometry of thin film processing in a supercritical CO<sub>2</sub> fluid.

incident angle of 70°. The birefringence calibration was carried out by comparing the measurements in air and those in pure supercritical CO<sub>2</sub>.

CO<sub>2</sub> was pressurized with a high-pressure pump for liquid chromatography and was supplied to the window cell. The pressure and the cell temperature were varied at 10–14 MPa and 40–100 °C. A probe solute, an organic solvent, was also pressurized and was injected to the CO<sub>2</sub> line. Changes in ellipsometric parameters,  $\Psi$  and  $\Delta$ , upon the admission of the probe solute were detected.

Table 1 lists samples used in this study. Three different plasma-enhanced chemical vapor deposition (PECVD) films and two different spin-on-dielectric (SOD) films were used. The  $k$ -values of those films ranged from 2.2 to 3.1. The pore sizes ranged from <0.5 nm to 2 nm, where the pore sizes were determined by PALS for the CVD films SOD#1 and by porosimetry SOD#2. Thermally grown SiO<sub>2</sub> was also used for comparison.

### 3. Results and discussion

Fig. 2 shows the time changes in the ellipsometric parameters upon the addition of a probe solute, acetone in this case. The pressure and temperature were 10 MPa and 50 °C and acetone was used as a probe solute. It is seen that  $\Psi$  and  $\Delta$  changed from their original values of  $\Psi_0$  and  $\Delta_0$  that were measured before the probe solute addition. A good correlation between the changes in  $\Psi$  and  $\Delta$  ( $\Psi - \Psi_0$  and  $\Delta - \Delta_0$ ) and the solute concentration was observed, i.e., the more the solute was added the larger changes occurred. In this particular case,  $\Psi - \Psi_0$  and  $\Delta - \Delta_0$  changed almost linearly against the probe solute concentration, indicating a possibility for semi-quantitative evaluation. When the concentration was decreased, both  $\Psi$  and  $\Delta$  run back to the same values as those observed during increasing. This shows that the sorption process is reversible and reproducible.

Table 1  
List of specimens used in this study.

	Thickness (nm)	Dielectric constant, $k$	Pores size (nm)
PECVD SiOCH#0 (isolated pores)	200	2.5	<0.5
PECVD SiOCH#1 (non-porogen)	120	2.7	<1.0
PECVD SiOCH#2 (non-porogen)	200	3.1	<1.0
SOD-SiOCH#1	400	2.3	1.5
SOD-SiOCH#2	150	2.2	2
t-SiO <sub>2</sub>	200	3.8	

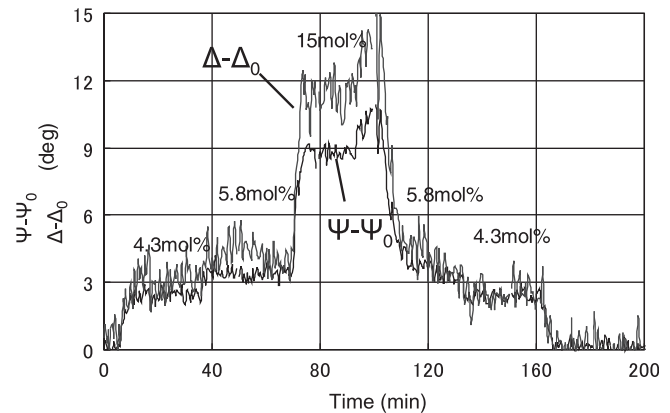


Fig. 2. Time changes in  $\Psi$  and  $\Delta$  of porous SOD#1 ( $k = 2.1$ ) as a function of acetone concentration. The pressure and temperature were fixed at 10 MPa and 50 °C.

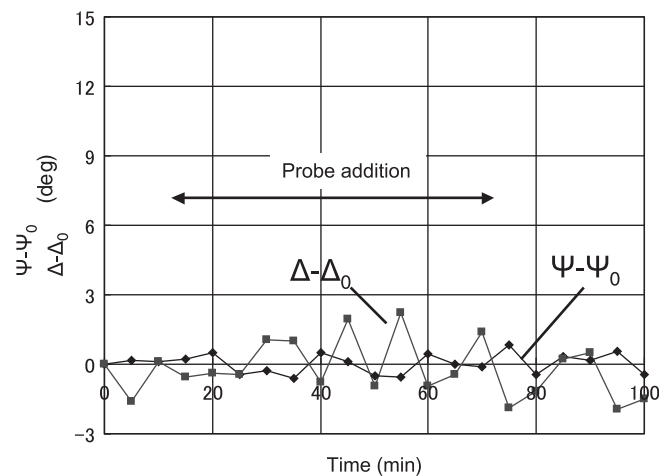


Fig. 3. Time changes in  $\Psi$  and  $\Delta$  of thermally grown SiO<sub>2</sub> upon the addition of methanol at a concentration of 4.3 mol%. The pressure and temperature were fixed at 10 MPa and 50 °C.

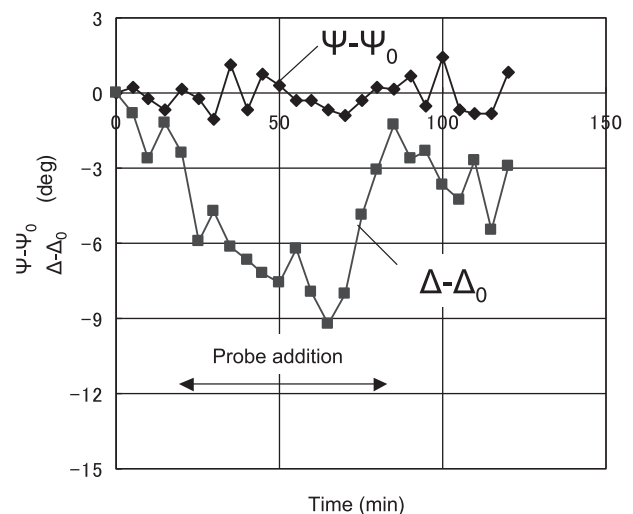
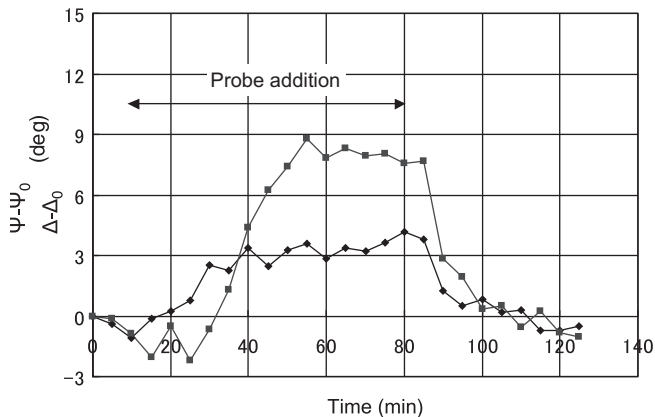
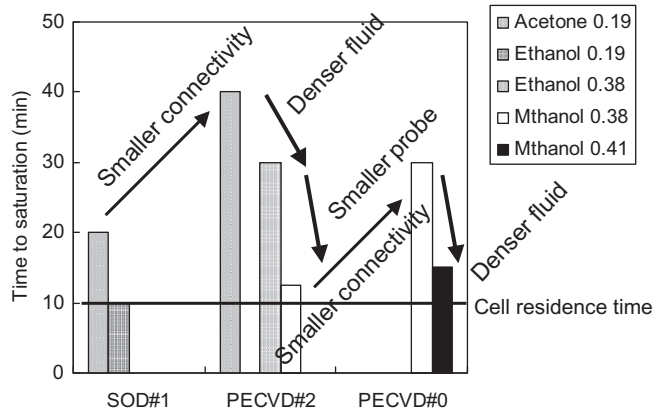


Fig. 4. Time changes in  $\Psi$  and  $\Delta$  of porous PECVD#1 ( $k = 3.1$ ) upon the addition of acetone at a concentration of 4.3 mol%. The pressure and temperature were fixed at 10 MPa and 100 °C.



**Fig. 5.** Time changes in  $\Psi$  and  $\Delta$  of porous PECVD#0 ( $k = 2.5$ ) upon the addition of methanol at a concentration of 4.3 mol%. The pressure and temperature were fixed at 14 MPa and 50 °C.



**Fig. 6.** The behaviors of the time-to-saturation as functions of proving conditions.

Another aspect that one can understand from this figure it that the changes in  $\Psi$  and  $\Delta$  reached steady state in several minutes after the concentration change. The exponential time constant (time-to-saturation, TTS, hereafter) was almost about 4 min for the case of Fig. 1. This time was almost consistent with the fluid residence time in the cell. Indeed, when the flowrate (liquid CO<sub>2</sub> conversion) was decreased from 2 to 1 ml/min, the TTS increased to about 7 min, which is almost doubled. This indicates the adsorption process itself is fast and that our method can provide a quick way for characterizing pore structures.

When a thermally grown SiO<sub>2</sub> film was used instead for comparison, we observed no changes in  $\Psi$  and  $\Delta$  (Fig. 3), which means our observation on porous low- $k$  thin films represent the information of the pore structure.

Fig. 4 shows the time changes in  $\Psi$  and  $\Delta$  for PECVD#1 ( $k = 3.1$ ) of which pore size was less than 1 nm. The pressure and temperature were 10 MPa and 100 °C and acetone was used as a probe solute. Besides the sign of the change, a similar behavior as in Fig. 2 is clear, which suggests that extremely small pores were detected by our method. The TTS was longer, about 30 min in this case, showing that this film showed slower penetration of the supercritical CO<sub>2</sub> solution than the SOD film. Therefore TTS can be used as a measure of the permeability of supercritical CO<sub>2</sub> solutions.

However, under the same conditions as the experiment shown in Fig. 4, we did not observe no changes in  $\Psi$  and  $\Delta$  when PECVD#0 film ( $k = 2.5$ ) was used as a specimen. The recorded time changes of  $\Psi$  and  $\Delta$  were almost the same as the case of thermally grown SiO<sub>2</sub>. We then increased the pressure and employed methanol as a probe solute. The reason for this is as follows. A supercritical fluid is a density-tunable medium. The density varies greatly as functions of pressure and temperature. Increasing the density can thus increase diffusion flux, because the diffusion flux is a product of diffusivity and density as previously described. In this experiment, we increased the fluid pressure to 14 MPa. Along with this, the probe solute was changed to methanol of which molecular size is smaller than acetone. Fig. 5 shows the time changes in  $\Psi$  and  $\Delta$  under these modified conditions. We can now clearly see large changes; however, the TTS became longer even than the experiment shown in Fig. 4.

Fig. 6 summarizes the TTS for different low- $k$  films as functions of the kind of solvent and the fluid density. The TTS became longer as the pore size decreases (the pore sizes were SOD#1 > PECVD#2 > PECVD#0 in the order). Either densification of the fluid or the use of smaller molecules resulted in the decrease of the TTS (see PECVD#2 and PECVD#0).

Finally, the results of all the measurements carried out in this work are summarized in Table 2. Plus signs (+) indicate that the changes in  $\Psi$  and  $\Delta$  are observed and minus signs (–) indicate that the changes were not observed. From the experiments using acetone, it is understood that temperature lowering was needed for detecting smaller pores. The use of a probe solute that has a smaller molecular size was found preferable to detect the smaller pores.

#### 4. Conclusion

We conducted *in situ* ellipsometric study of different porous low- $k$  films placed in supercritical CO<sub>2</sub> solutions. We confirmed changes in the ellipsometric parameters upon the addition of probe solutes. These changes originated from the permeation of the supercritical CO<sub>2</sub> solutions, because no changes were observed on a dense thermally grown SiO<sub>2</sub>. The SOD films showed quick permeation of the solution, and PECVD showed a slower permeation. The time-to-saturation (TTS) was found to be a good measure of the permeability of the CO<sub>2</sub> solutions.

**Table 2**

Summary of experimental results of this study. Plus (+) and minus (–) indicate that the appearance or non-appearance of changes in ellipsometric parameters, respectively.  $d$  is pore size.

Probe	Temperature (°C)	PECVD#0 $k = 2.5$ $d < 0.5$	PECVD#1 $k = 2.7$ $d < 1$	PECVD#2 $k = 3.1$ $d < 1$	SOD#1 $k = 2.3$ $d = 1.5$	SOD#2 $k = 2.2$ $d = 2$	t-SiO <sub>2</sub>
Ethanol	100	–	–	+	+	+	–
Acetone	100	–	–	–	+	+	–
	50	–	+	+	+	–	–
	40	–	+	+	+	–	–
Methanol	50	+	+	+	–	–	–

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