

Condensation and cleaning of an organometallic copper compound to/from porous low-dielectric constant thin films in supercritical carbon dioxide

E. Kondoh, E. Ukai, and S. Aruga

Faculty of Engineering, University of Yamanashi, Kofu 400-8511, Japan

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* Corresponding author: e-mail kondoh@ccn.yamanashi.ac.jp, Phone/Fax +81 55 220 8778

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1 Introduction The integration of porous low-dielectric constant (low- k) thin films with the interconnects of ultra-large-scaled integrated circuits (ULSIs) is under intensive development. This is because the introduction of pores reduces the dielectric constant of the insulator and thus decreases a resistance-capacitance delay of high-frequency signals when the low- k s are used as inter-metal insulating materials. One of the key technologies in porous low- k integration is the use of supercritical fluids. A supercritical fluid is a substance with a status above its critical point. Supercritical carbon dioxide (scCO₂) possesses unique features, such as a moderate critical point (31 °C, 7.4 MPa), nano-penetration ability, zero surface tension, safeness, and solvent capability. These properties are a perfect fit for the processing of porous low- k s, from synthesis, through pore cleaning to post-dry etch repairing [1-3].

In these applications, scCO₂ is used simply as an inert medium, and chemical additives are used simultaneously. For this reason, the interaction between the additive solutes and the pores of low- k films is of crucial interest. ScCO₂ is

a dense medium; therefore, the partial pressure of a solute can reach as high as, for instance, 0.1 MPa. Such a high solute density can lead not only to its adsorption but even to liquefaction inside the pores, which does not usually occur in gas-based dry processes. Ellipsometry is a sensitive and powerful technique for the detection of sorption in porous low- k thin films. Ellipsometric studies on the sorption of gases into porous low- k s have been well documented [4]; however, few studies have been performed so far using ellipsometry in supercritical fluids.

We have developed *in-situ* ellipsometry technique in an scCO₂ ambient at elevated temperatures. In this article, we demonstrate sorption behaviour of an organometallic copper compound to porous low- k thin films. We used diisobutylmethanate-copper (Cu(dibm)₂) as a solute compound to simulate adsorption and cleaning of Cu-contamination.

2 Experimental Figure 1 shows an experimental set-up used in this study. *In-situ* measurements were carried

out using a single wavelength (633 nm) polariser rotating analyser ellipsometer. The incident angle was fixed at 70°, and the polariser transmission axis was oriented at 45° relative to the incidence plane. Organosilica-based spin-on porous low-*k* films, the equivalent of Non Clustering Silica™, were supplied by CCIC Corp. in Japan [5] and used as specimens. The porosity and pore diameter were approximately 30 % and 2 nm, respectively, and the refractive index at 633 nm was 1.30±0.00i. The thickness was 200 nm and the substrates were bare Si wafers. Thermally grown SiO₂ films, 200 nm in thickness, were used for comparison.

We used a high-pressure optical cell specially designed for our purposes. The window material used was Pyrex® glass. The effects of the cell windows and ambient were corrected by way of a usual Müller analysis [6]. Liquid CO₂ was pressurized using a plunger pump and was supplied to the cell. The pump head was cooled to approximately -4 °C to assure the liquefaction of the CO₂. The cell pressure was maintained at a target value with an automatic backpressure regulator (JASCO SCF-Bpg/M). The cell was heated with built-in cartridge heaters and the internal temperature was measured using a thermocouple. The pressures and temperatures were 8–10 MPa and 40–150 °C, respectively. Cu(dibm)₂ was dissolved in scCO₂ in a different high-pressure reservoir and was supplied to the optical cell. The amount of Cu(dibm)₂ loaded in the reservoir ranged from 0–100 mg.

The intensity of the reflected light was measured using a Si photodiode as a function of the analyser angle. Ellipsometric parameters (Ψ and Δ) were obtained by carrying out fast Fourier transformation of the light intensity data.

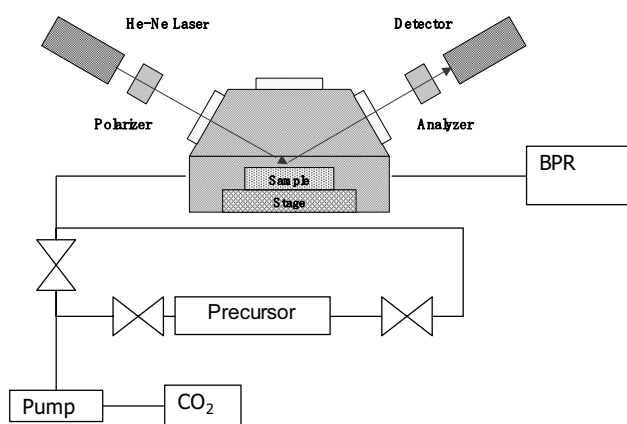


Figure 1 Apparatus used in this work. BPR stands for back-pressure regulator.

3 Results and discussion

3.1 Changes in Ψ and Δ over time Figure 2 shows the changes in Ψ and Δ over time, recorded on a 200 nm-thick dense SiO₂ film. The pressure and temperature were 10 MPa and 50 °C, respectively. In the time ranges where solid symbols are used, scCO₂ was made to flow through the reservoir, thus supplying Cu(dibm)₂ to the ambient area.

In the same sense, open symbols indicate that scCO₂ was supplied directly through a bypass line without detouring through the reservoir. Practically no changes in Ψ and Δ were seen upon the addition of Cu(dibm)₂.

A significant fluctuation, however, occurred at the initial moment of Cu(dibm)₂ addition. A careful analysis revealed that this was due to the scattering of light and the resulting decrease in light intensity. ScCO₂ is a dense and compressive fluid; it thus easily causes density inhomogeneity. This results in the ‘hazing’ of the scCO₂ when a small pressure or temperature fluctuation occurs. In the present case a small pressure difference between the cell and reservoir was thought to lead to such a fluctuation. Therefore, the data at 20–25 min is not very reliable.

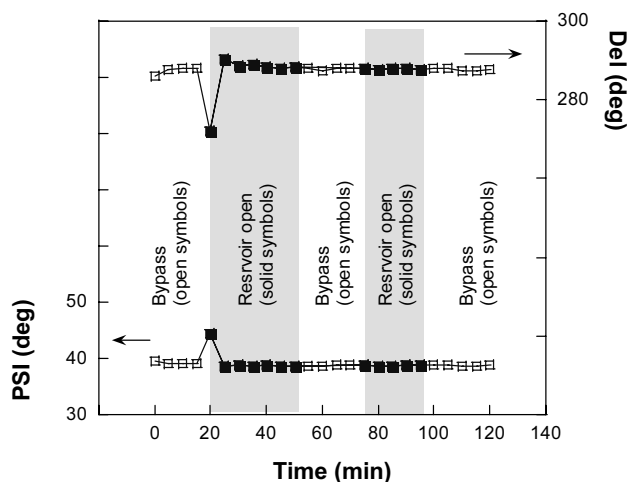


Figure 2 Changes in Ψ and Δ over time for a 200 nm-thick thermally grown SiO₂. Solid symbols indicate that Cu(dibm)₂ was applied, and open symbols show the time ranges within which Cu(dibm)₂ was intentionally not applied.

Figure 3 shows changes in Ψ and Δ over time for a 200 nm-thick porous low-*k* thin film. The temperature was 150 °C and the pressure was 10 MPa. The meaning of the open and solid symbols is the same as in Figure 2. During the supply of 50 mg of Cu(dibm)₂ to the optical cell, Δ increased gradually and saturated at values higher than its initial value by about 20°. Δ decreased when the valves of the reservoir were closed and the bypass valve was opened. Ψ behaved in the opposite manner, instead showing a decrease of 20° upon the addition of Cu(dibm)₂ (dosing) and an increase when fresh scCO₂ was supplied (purging). Obviously these changes occurred due to adsorption and desorption, or condensation and cleaning, of Cu(dibm)₂ in porous low-*k* films, as observed in vacuum sorption processes [4].

When the cell was purged, Ψ and Δ did not recover to their initial values but saturated at a lower value for Ψ and a higher value for Δ , as seen in Fig. 3. We speculate that this is due to the effect of system contamination as discussed later in this paper. When the dosing and purging of

Cu(dibm)₂ were repeated, Ψ and Δ increased and saturated at similar values as in the first cycle.

When a higher amount of Cu(dibm)₂ (100 mg) was used for dosing, the increase in Δ and the decrease in Ψ were both greater than those observed with 50 mg. During purging, Δ decreased and Ψ increased, as in the case of 50 mg, but to a much lesser degree. This may suggest a physical limitation in cleaning a highly adsorbing film. The maximum and minimum values of Ψ and Δ during the purge of the second cycle were the same as those of the first cycle, exhibiting the reversible nature of sorption.

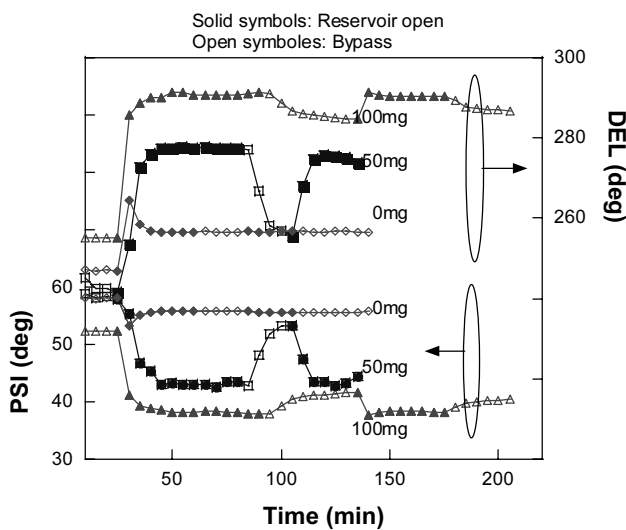


Figure 3 *In-situ* measured changes in Ψ and Δ over time for a 200nm-thick porous low- k thin film. In the time ranges where solid symbols were used, scCO₂ was made to flow through the reservoir and thus Cu(dibm)₂ was applied.

3.2 Effects of system contamination An increase in Δ and a concurrent decrease in Ψ were seen even when dosing was intentionally not carried out. This is shown in the data set for 0 mg in Fig. 4. In this run, no Cu(dibm)₂ was loaded into the reservoir, and the experimental procedure was carried out in the same manner as in the other two cases. At the beginning of the first cycle of dosing/purging, changes in Ψ and Δ were similar to those described above, but they occurred to a much lesser degree. However, changing ceased immediately and both Ψ and Δ maintained a constant value whether scCO₂ flowed through the reservoir line (solid symbols) or the bypass line (open symbols).

A possible explanation that accounts for this behaviour is residual Cu(dibm)₂ in the reservoir. The residual Cu(dibm)₂ adsorbs to the low- k film, resulting in a quick decrease/increase of Ψ/Δ , even if Cu(dibm)₂ was intentionally not loaded in the reservoir. Once the cell was contaminated, the Cu(dibm)₂ that remained in the cell during purging was thought to give Ψ and Δ values, hereafter referred to as “base lines”, different from the initial values. Such a

strong “contamination” effect suggests a strong interaction between Cu(dibm)₂ and the interior of the pores.

Indeed, when 50 mg of Cu(dibm)₂ was used, the minimum values of Δ and the maximum values of Ψ stabilized at the base lines during purging. The initial values of Ψ and Δ were different from those of the other two data sets and were close to the base lines.

3.3 Model analysis Figure 4 shows Ψ - Δ trajectories of the experimental data sets for 50 mg and 100 mg. The experimental data are compared with the Δ - Ψ values obtained using single-layer film models. The dashed lines trace (Ψ , Δ) points as a function of refractive index, n , for different film thicknesses. The refractive index of scCO₂ used for the calculations was 1.02 at 10 MPa and 150 °C, which was preliminarily determined in our laboratory. In our analyses, the pores are assumed as already being filled with scCO₂ before Cu(dibm)₂ dosing. It is noted that the change in the refractive index is approximately 0.005 even if all of the vacant pores are filled with scCO₂.

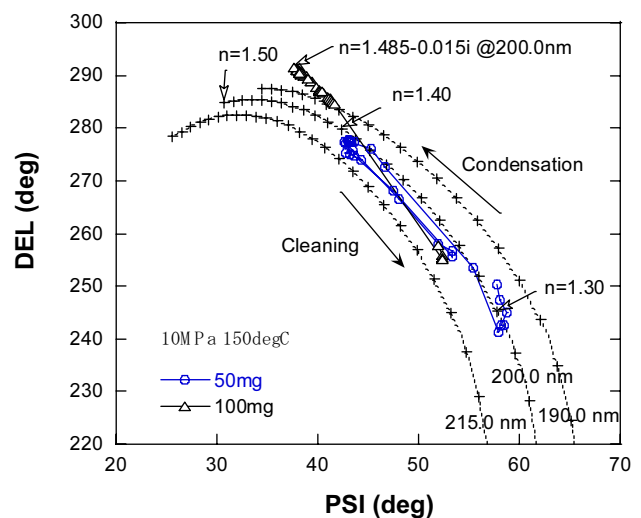


Figure 4 *In-situ* measured changes in Ψ and Δ over time for a 200 nm-thick porous low- k thin film. In the time ranges where solid symbols were used, scCO₂ was made to flow through the reservoir and thus Cu(dibm)₂ was applied.

The experimental data for 50 mg start at around (Ψ , Δ)=(58, 245), which corresponds to approximately (n , t)=(1.30, 200), where t is the film thickness. When scCO₂ was dosed with Cu(dibm)₂, (Ψ , Δ) moved upward and to the left, tracing the dashed line of $t=200$ nm. This shows only the refractive index change and no significant “swelling” (volumetric increase in thickness) occurred upon sorption. (If the film swelled, presumably it did so at the beginning of the first cycle, as suggested from the initial behaviour of Ψ and Δ . This is an interesting topic, but is not discussed here in detail due to the lack of data.)

During the purging with scCO₂, the experimental data retraces the trajectory, but slightly to the left of the 200 nm

gray line. This may indicate that the film swelling became significant at that point or that the deposition of some other substance occurred. Interestingly, the second cycle traced exactly the same line as this inner trajectory.

The data set for 100 mg exhibited a very different behavior. Its trajectory deviated immediately from the $t=200$ nm line and traced the same line, which did not follow the behaviour of a single-layer transparent dielectric film (gray lines). The reason for this is not clear at present. The (Ψ, Δ) point at the end of the 100 mg trajectory was $(n, t)=(1.52, 177)$, which may suggest that significant film shrinkage occurred. On the other hand, assuming that the film thickness was kept at 200 nm, the apparent refractive index at this point is estimated at $n=1.485-0.015i$, which indicates that the film is absorbing. The latter is not surprising, because $\text{Cu}(\text{dibm})_2$ absorbs red light [7]. Multi-layer adsorption or liquid-like condensation at the top of surface may account for this.

4 Conclusion We have developed an *in-situ* ellipsometry technique for use in supercritical carbon dioxide (scCO_2) fluids. Because scCO_2 is a dense and compressive medium, we found it important to suppress temperature and pressure fluctuations in the optical cell. The sorption behaviour of $\text{Cu}(\text{dibm})_2$ into porous low- k thin films was studied as a model case for the contamination and cleaning of pores. Reversible adsorption/desorption was observed

when the amount of $\text{Cu}(\text{dibm})_2$ loaded was low. During the sorption cycle, the Ψ - Δ trajectory traced almost a constant film thickness curve, which indicates a simple increase/decrease in the refractive index. When a larger amount of $\text{Cu}(\text{dibm})_2$ was used, less sorption reversibility was observed and the corresponding Ψ - Δ trajectory deviated from the constant-thickness curve.

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