Nanopore structure relevant to the D$_2$O permeation into silica thin films as studied by secondary ion mass spectrometry, ellipsometric porosimetry and positron annihilation

S Yoshimoto$^{1,3}$, K Ito$^2$, H Hosomi$^1$, T Nakamura$^1$ and M Takeda$^1$

$^1$Toray Research Center, Inc., Otsu, Shiga 520–8567, Japan
$^2$National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305–8565, Japan
$^3$Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, Hiroshima 739–8527, Japan
E-mail: Shigeru.Yoshimoto@trc.toray.co.jp

Abstract. Subnanoscopic pore structure relevant to the water permeation for two types of silica thin films, fabricated by plasma-enhanced chemical vapor deposition (PECVD) and thermal oxidation (TO), were examined by means of dynamic secondary ion mass spectrometry (D-SIMS), vapor-adsorption ellipsometric porosimetry (EP), and low-energy positron annihilation spectroscopy (PALS). The D$^-$ secondary ion intensity for the PECVD film, observed using D-SIMS, was much higher than for the TO film, indicative of the higher permeance of D$_2$O molecules in the matrix of the PECVD film. The results from PALS and EP suggest that this is ascribed to the larger pores and the higher open porosity of the PECVD film as compared to the TO film.

1. Introduction
Silica thin film has been widely utilized as the top coating layer of various materials in the nanotechnology fields, such as the barrier layer of the display for electronic devices and the active layer of separation membranes. Better understanding of molecular permeation in silica films is necessary to develop innovative materials. In this work we examine the pore structure relevant to the water permeation for two types of silica thin films by means of dynamic secondary ion mass spectrometry (D-SIMS), vapor-adsorption ellipsometric porosimetry (EP), and low-energy positron annihilation spectroscopy (PALS).

2. Experimental
2.1. Sample preparation
Two types of silicon oxide films were prepared through a plasma-enhanced chemical vapor deposition (PECVD) and a thermal oxidation (TO), respectively. The PECVD film was fabricated on a silicon wafer at 400 °C from a mixture of tetraethyl orthosilicate (TEOS) and O$_3$ diluted in a helium gas. The TO film was grown on a silicon wafer at 950 °C in a mixture of H$_2$ and O$_2$ gas sources. The thickness, the refractive index and the density for the obtained films are listed in table 1. FT-IR spectra for both films are shown in figure 1, and the enhanced IR absorption over 3000 cm$^{-1}$ to 3800 cm$^{-1}$ for the PECVD film is attributable to the stretching vibration of OH groups [1], indicating that hydrophilic terminal silanols are introduced more into the silicon oxide network of the PECVD film. For depth profiling of D$^-$ ions
Table 1. Thickness $L$, refractive index $n_{630}$ at a wavelength of 630 nm and density $\rho$ for the present films.

|       | $L^a$ [nm] | $n_{630}^b$ | $\rho^b$ [g/cm$^3$] |
|-------|------------|-------------|---------------------|
| PECVD | 90.0       | 1.427       | 2.10                |
| TO    | 99.4       | 1.456       | 2.29                |

$^a$Determined by spectroscopic ellipsometry.
$^b$Determined by x-ray reflectometry.

due to D$_2$O permeated from the film surface, both the films were exposed to deuterium oxide (D$_2$O: 99.9 %, Wako Japan) vapor at 70 °C for 3 hours in a thermostat chamber.

2.2. Dynamic secondary ion mass spectrometry (D-SIMS)
D-SIMS was conducted at 25 °C in a ultra high vacuum chamber (2.7 x 10$^{-8}$ Pa) using a 50 nA, 3 keV Cs$^+$ primary ion beam incident at 60° with respect to the sample normal, and the actual sputtered area was 300 x 600 μm$^2$. In the measurement, negative secondary ions including D$^{-}$ were detected for the present films exposed to D$_2$O vapor. Charge neutralization was induced through 0.5 keV electron beam irradiation to the vicinity of the sputtered area. The depth scale was obtained by calibrating the retention time at the film-substrate interface to the respective film thicknesses.

2.3. Ellipsometric porosimetry
Adsorption isotherms of water and methanol (MeOH) at 26 °C for the present films were elucidated using the specially-designed flow-type ellipsometric porosimeter at AIST [2]. Prior to the adsorption measurements, the samples were heated at 300 °C under a nitrogen gas flow to remove impurities adsorbed on the film surface. Ellipsometric parameters ($\Delta$, $\Psi$) with various wavelengths $\lambda$ were measured with varying the flow rate ratio $f_r$, proportional to the adsorbate concentration. The flow rate ratio $f_r$ is defined by $f_s/(f_d + f_s)$, where $f_s$ and $f_d$ represent the flow rates for a nitrogen gas saturated by the adsorbate vapor and a dry nitrogen gas, respectively. The observed parameters ($\Delta$, $\Psi$) were analyzed based on an ambient-film-substrate three-layers model under the assumption of the Cauchy equation [3], describing the refractive index $n$ as a function of $\lambda$. In order to obtain the isotherms, the overall refractive index $n_o$ at $\lambda = 630$ nm upon successive adsorption of the adsorbates were elucidated as a function of $f_r$.

In the case of water, the actual relative humidity was adapted for the parameter instead of $f_r$. Based on the Lorentz–Lorenz equation, $A_p = (n^2 - 1)/(n^2 + 2)$ ($A$ is a constant and $\rho$ is the density), the specific amounts of the adsorbate in a film are assumed to be proportional to the volume fraction occupied by the adsorbate molecules $V$, quantified by the following equation

$$V = \left| \left( \frac{n_f^2 - 1}{n_f^2 + 2} \right) - \left( \frac{n_d^2 - 1}{n_d^2 + 2} \right) \right| \left( \frac{n_o^2 - 1}{n_o^2 + 2} \right).$$

(1)

Here, $n_f$ and $n_d$ were fixed to the refractive indices for the corresponding films with $f_r = 0$ and for the bulk adsorbates (water: 1.331 and MeOH: 1.328). By using this equation with the measured $n_o$, the adsorption isotherms for the present films were obtained as the variation of $V$ as a function of $f_r$. 

![Figure 1. FT-IR spectra for the present films.](image)
2.4. Low-energy positron annihilation lifetime spectroscopy
Positron lifetime measurements were carried out by utilizing a $^{22}\text{Na}$-based pulsed-positron beam system (Fuji-Imvac, Japan). The measurements were performed at room temperature in vacuum. For each measurement 5 million counts of the annihilation events were accumulated. A multi-exponential analysis was applied to the recorded lifetime data to deduce the long-lived ortho-positronium ($o$-Ps) lifetime $\tau$. The pore radius $r$ [nm] was estimated from the obtained $\tau$ [ns] based on the following equation [4, 5],

$$
\tau = 0.5 \left[ 1 - \frac{r}{r + 0.166} + \frac{1}{2\pi} \sin \left( \frac{2\pi r}{r + 0.166} \right) \right]^{-1}.
$$

3. Results and discussion
Figure 2 shows the depth profile of the $D^-$ intensities for the PECVD and TO films, exposed to $D_2O$ vapor. The $D^-$ intensity for the PECVD film is almost constant throughout the film, while that for the TO film slightly decreases from the near surface to shallow depths, and becomes constant deeper than $\sim 30$ nm with a value which is about $10^3$ times lower than for the PECVD film. This indicates that in comparison with the TO film a larger amount of $D_2O$ molecules are homogeneously distributed inside the film after the exposure to $D_2O$ vapor, and $D$ atoms remaining even in a high vacuum were detected by the D-SIMS measurements. On the other hand, the gradual decrease in $D^-$ intensity for the TO film suggests a transitional state of $D_2O$ permeation from the film surface into bulk. Based on the profile for the TO film, the diffusion coefficient is estimated to be of the order of $10^{-20}$ m$^2$/s, comparable to the value of water in the bulk silica at $60^\circ C$ ($3.1 \times 10^{-20}$ m$^2$/s) [6].

Figure 3 shows the adsorption isotherms of water and MeOH for the two films. Whereas both the isotherms for the TO film show little amount of the adsorption, those for the PECVD film increase with increasing relative humidity and flow rate ratio, where $V$ at the higher concentration of water and MeOH approach, respectively, 8.0 % and 1.6 %, defined as the total adsorption on the pores ($V_t$). This illustrates that a significant amount of open porosity is formed in the PECVD film. From this result, the higher $D^-$ intensity for the PECVD film in figure 2 can be ascribed to the larger surface area in comparison with the TO film, on which more $D_2O$ adsorbs, possibly followed by the substitution of hydrogens at the pore surface by deuteriums.

The difference in $V_t$ for water and MeOH adsorbed on the PECVD film suggests that the subnanoscaled pores, connected to the film surface, somewhat influences the diffusion of those adsorbates.
in the film. In order to evaluate pore sizes for the films, PALS spectra were observed at an incident positron energy $E$ of 1.5 keV (figure 4), in which the long-lived $o$-Ps component is observable for both the films. The mean pore radius $r_p$ for the PECVD film estimated from the $o$-Ps lifetimes $\tau$ with equation (2) is 0.32 nm (table 2). Based on the respective van der Waals radii for water ($r_{\text{water}} = 0.14$ nm) and MeOH ($r_{\text{MeOH}} = 0.21$ nm) [7], the mean radius is larger in the order of $r_p > r_{\text{MeOH}} > r_{\text{water}}$. Thus we can reasonably expect that the diffusion of MeOH molecules is inhibited more than that of water due to the bottlenecking pores, belonging to the smaller region of the pore size distribution, which leads to the reduced $V_t$ for the MeOH adsorption in comparison with the water adsorption.

4. Summary
Subnanoscopic pore structure relevant to the molecular permeation for two kinds of the silica thin films was examined by means of D-SIMS, EP, and PALS. The D$^-$ secondary ion intensity, originating from D$_2$O, for the PECVD film was much higher than for the TO film, indicative of the higher permeance of D$_2$O molecules in the former silica film. In light of the results from EP and PALS, it was demonstrated that significant amounts of open porosity in the subnanoscopic range are formed in the PECVD film and that bottlenecking pores with a radius smaller than \( \sim 0.3 \) nm may partly prevent MeOH from diffusing into interconnected pores in the film.

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