

Subnanopore Structural Change of Time-elapsed Silica PECVD Films Elucidated by Slow Positron Annihilation and Ellipsometric Porosimetry

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To examine the effect of elapsed time on the nanoporosity, subnanoporous silica thin films, fabricated by plasma-enhanced chemical vapor deposition (PECVD), were investigated by means of low-energy positron annihilation lifetime spectroscopy and vapor-adsorption ellipsometric porosimetry. The structural change of the subnanoscaled pores was elucidated by comparison of the as deposited and 6-month-old films. It is expected that the change in the subnanoscaled pores of the present films, after exposure to air for half a year, is due to the adsorption of water molecules from air, followed by the filling up the nanoscaled pores as well as partial polycondensations between silanol groups at the silica grain boundaries of the films.

1. Introduction

Nanoporous silica films have been widely utilized as various materials for low-k dielectrics, separation membranes, and so on. In order to improve their functionality, control of nanoscaled pore structures in silica films has been extensively investigated at the molecular level. On the other hand, adequate stability of the pore structure is required to ensure the long-term usability of various devices using nanoporous silica films. Thus better understanding of the nanoscopic change of the pore structure with time is necessary to better estimate the functional lifetime. In the present work, we aimed to examine the effect of the elapsed time on the nanoporosity of silica thin films, fabricated by plasma-enhanced chemical vapor deposition (PECVD), by means of low-energy positron annihilation lifetime spectroscopy (PALS) and vapor-adsorption ellipsometric porosimetry (EP).

2. Experiments

Films with thicknesses around 450 nm were fabricated on silicon wafers at 300 °C under a pressure of 100 Pa with a RF power of 200 W using a capacitive coupled PECVD reactor with parallel plate electrodes [1, 2]. Mixtures of tetraethyl orthosilicate (TEOS, flow rate Q_{TEOS} : 5 sccm–40 sccm) and O₂ gas (flow rate Q_{O_2} : 300 sccm) were used as precursors. The deposited films were kept under atmospheric conditions in Tsukuba, Japan for 6 months, in order to examine the effect of elapsed time on the pore structures of the prepared films.

Adsorption isotherms of methanol (MeOH) at 26 °C for the present films were elucidated using a specially-designed flow-type ellipsometric porosimeter at the National Institute of Advanced Industrial Science and Technology (AIST) [3–5]. The film samples were heated to 300 °C under a dried nitrogen flow prior to the adsorption measurements so that impurities adsorbed on the film surface are

removed. In order to evaluate the adsorption isotherms, the refractive index n_o for the present films was observed as a function of flow rate ratio f_r , defined by $f_s/(f_d + f_s)$ (f_s and f_d represent the flow rates for a nitrogen gas saturated by a MeOH vapor and a dry nitrogen gas, respectively). Based on the Lorentz-Lorenz equation, $A\rho = (n^2 - 1)/(n^2 + 2)$ (A is a constant and ρ is the film density), the volume fraction occupied by the MeOH molecules V was calculated as follows,

$$V = \left[\left(\frac{n_o^2 - 1}{n_o^2 + 2} \right) - \left(\frac{n_f^2 - 1}{n_f^2 + 2} \right) \right] \left/ \left(\frac{n_a^2 - 1}{n_a^2 + 2} \right) \right. . \quad (1)$$

Here, n_f and n_a represent the refractive indices for the films at $f_r = 0$ and for the bulk MeOH ($n_{\text{MeOH}} = 1.328$) [6], respectively.

Low-energy PALS using a ^{22}Na -based pulsed positron beam at AIST [1, 7] was performed with a positron incident energy E of 5 keV at room temperature in vacuum. A multi-exponential analysis was applied to the recorded lifetime data with 4 million counts to deduce the average lifetimes τ of the long-lived *ortho*-positronium (*o*-Ps). The pore radius r [nm] is determined from the obtained τ [ns] based on the following equation [8, 9],

$$\tau = 0.5 \left[1 - \frac{r}{r + 0.1656} + \frac{1}{2\pi} \sin \left(\frac{2\pi r}{r + 0.1656} \right) \right]^{-1} \quad (2)$$

3. Results and discussion

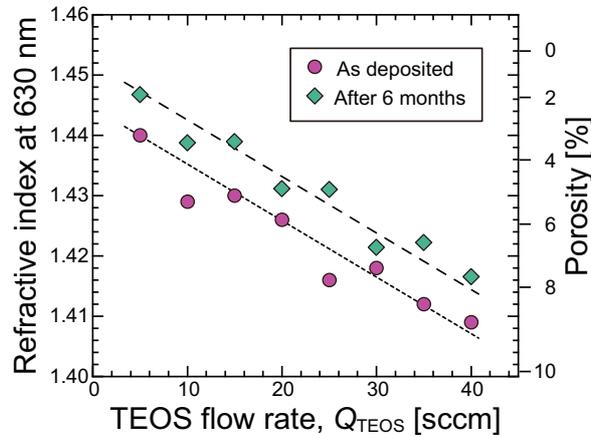


Fig. 1 Variation of the refractive indices at 630 nm for the PECVD silica films as deposited and after 6 months. The data were measured under a dried nitrogen gas flow. The lines are drawn for clarification.

The variation of the refractive indices at 630 nm n_f under a dry condition for the films as deposited and after 6 months is shown as a function of TEOS flow rate Q_{TEOS} in Fig. 1. On the right axis, the total porosity V_T is shown, which was calculated from n_f based on the following equation,

$$V_T = \left[\left(\frac{n_{\text{silica}}^2 - 1}{n_{\text{silica}}^2 + 2} \right) - \left(\frac{n_f^2 - 1}{n_f^2 + 2} \right) \right] \left/ \left(\frac{n_{\text{silica}}^2 - 1}{n_{\text{silica}}^2 + 2} \right) \right. , \quad (3)$$

where n_{silica} is the refractive index for bulk silica (assumed as 1.457 [10] for this work). For the as-deposited films, n_f decreased with increasing Q_{TEOS} , indicating that the film total porosity V_T is

increased. This is probably due to suppressed development of the silica networks originating from the excess amount of TEOS in the precursor, leading to an enhanced extension of silica grain boundaries during the film fabrication [11]. For the films after 6 months n_f is slightly shifted to higher values, corresponding to a reduction of V_T by $\sim 1.7\%$, while the film thicknesses around 450 nm were unchanged.

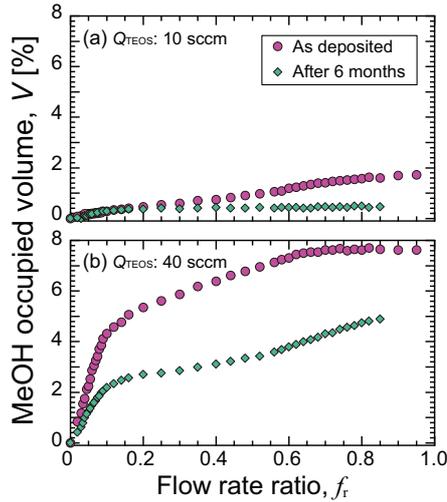


Fig. 2 MeOH adsorption isotherms at 26 °C for the present films as deposited and after 6 months. The data are obtained for the films deposited with $Q_{\text{TEOS}} = 10$ sccm (a) and $Q_{\text{TEOS}} = 40$ sccm (b).

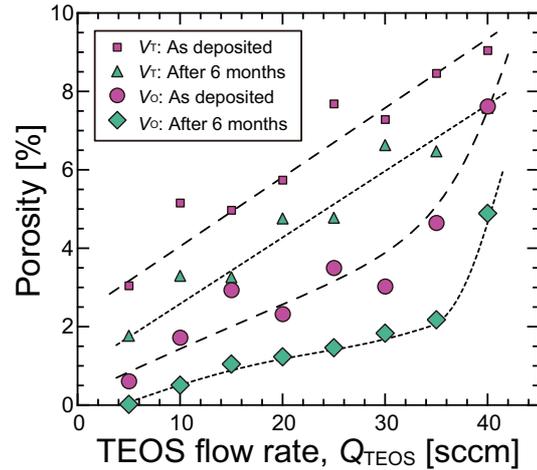


Fig. 3 Variation of the total and open porosities V_T and V_O for the present films as deposited and after 6 months as a function of TEOS flow rate Q_{TEOS} . The lines are drawn for clarification.

Figure 2 shows typical adsorption isotherms of MeOH observed at 26 °C for the films as deposited and after 6 months, fabricated with $Q_{\text{TEOS}} = 10$ sccm and 40 sccm. For the as-deposited films significant adsorptions are observed, and the observed MeOH occupied volume V is increased with increasing f_r , indicating that those films have amounts of open pores, accessible to the MeOH molecules. The V values in the high flow rate region of $f_r \sim 0.9$ are associated with the respective film open porosity V_O [12]. V_O for the as-deposited film with $Q_{\text{TEOS}} = 40$ sccm is significantly higher than for that with $Q_{\text{TEOS}} = 10$ sccm. For the films after 6 months the respective V_O values are decreased from those for the as-deposited films.

Figure 3 shows the variation of V_O for the films as deposited and after 6 months as a function of Q_{TEOS} . In the figure the respective total porosities V_T , estimated from n_f as in Fig. 1, are plotted for comparison. V_O for the as-deposited films is gradually increased from 0.5 % to 8 % with increasing Q_{TEOS} , indicating that the open porosity, detected by MeOH molecules, is also enhanced as V_T is increased with increasing Q_{TEOS} . This indicates that a higher TEOS fraction in the precursor effectively enhances the formation of more open pores. For the films after 6 months V_O at each Q_{TEOS} is decreased, especially the reduction in V_O somewhat becomes larger at higher Q_{TEOS} .

Figure 4 shows typical PALS data for the films as deposited and after 6 months, prepared with $Q_{\text{TEOS}} = 10$ sccm and 40 sccm, obtained at $E = 5$ keV (a mean implantation depth of about 240 nm with $\rho = 2.2$ g/cm³). For all the films a long-lived component due to the annihilations of *o*-Ps in the nanoscaled pores is observed. For the films with $Q_{\text{TEOS}} = 10$ sccm the long-lived lifetime is obviously shortened after 6 months, while that for the film deposited with $Q_{\text{TEOS}} = 40$ sccm is only slightly changed.

Figure 5 shows a plot of the analyzed average lifetimes of *o*-Ps τ versus Q_{TEOS} obtained from the

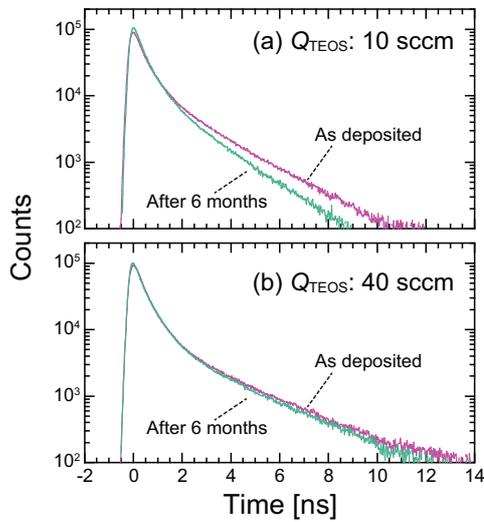


Fig. 4 PALS data at a positron incident energy E of 5 keV observed for the present films as deposited and after 6 months, fabricated at $Q_{\text{TEOS}} = 10$ sccm (a) and 40 sccm (b), respectively.

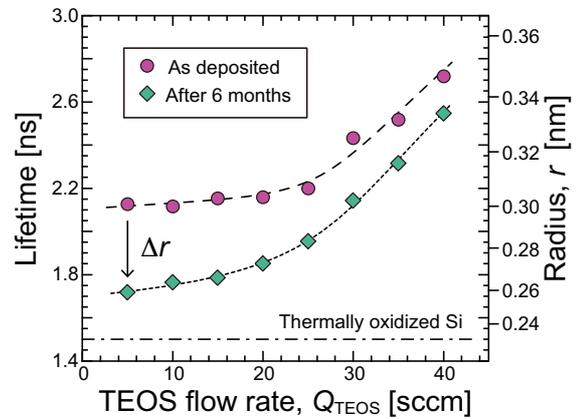


Fig. 5 Variation of the o -Ps lifetime τ and pore radius r estimated from τ for the present films as deposited and after 6 months as a function of Q_{TEOS} . The broken and dotted lines are drawn for clarification. The dash-dot line represents the value for thermally oxidized Si.

analysis of the PALS data in Fig. 4, where the o -Ps lifetime for thermally oxidized Si is indicated by the dash-dot line at ~ 1.5 ns [4] for comparison. On the right-hand axis the pore radius r calculated from τ based on Eq. (2) is also shown. The obtained τ values for the as-deposited films range from 2.1 ns to 2.7 ns, which correspond to pore radii from 0.31 nm to 0.35 nm. The pore size significantly increases with increasing Q_{TEOS} , indicating that the pores existing in the as-deposited films are in the subnanometer-scaled range, larger than the MeOH molecule with a van der Waals radius of 0.21 nm [13]. As for the time-elapsed films, the pore sizes are significantly decreased from those for the respective as-deposited films, resulting in pore sizes in the range from 0.27 nm up to 0.34 nm in

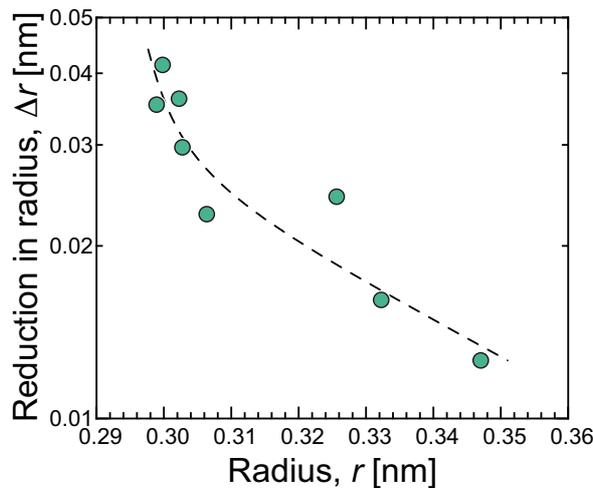


Fig. 6 Variation of the reduction in radius Δr between the present films as deposited and after 6 months as a function of radius r for the as-deposited films. The line is drawn for clarification.

radius. In Fig. 6, the variation of the reduction in radius Δr is shown as a function of r for the as-deposited films. Δr is considerably decreased with increasing r , indicating that the effect of the elapsed time on the pore size change is stronger for the films with smaller pores.

For the films after 6 months, the average pore size r , the total and open porosities (V_T and V_O) were decreased, while the film thicknesses were little influenced. In light of the fact that V_T and V_O were obtained for the films as deposited at 300 °C, we expect that these results may be ascribed to the adsorption of water molecules from air, followed by the filling up of the nanoscaled pores as well as partial polycondensations between silanol groups at silica grain boundaries of the present films. In addition to this, the PALS results suggested that this nanoscopic structural change is more affected for the films with smaller pores as evident in Fig. 6. It was demonstrated that the nanoscaled pore structure of the as-deposited silica PECVD films were significantly influenced by exposure of the films to air even in ambient conditions.

4. Summary

The effect of elapsed time on the nanoporosity of silica thin films, fabricated by PECVD, has been examined by means of low-energy PALS and EP. For the as-deposited films, V_T , estimated from the refractive index, V_O from EP, and r from PALS increased with increasing TEOS flow rate Q_{TEOS} of the precursor, probably due to the suppressed development of the silica networks. For the films measured after 6 months, V_T , V_O , and r were decreased at each Q_{TEOS} . It is expected that the change in the nanoporosity of the 6-month-old silica PECVD films is due to the adsorption of water molecules from air, followed by the filling up the nanoscaled pores as well as partial polycondensations between silanol groups at the silica grain boundaries.

Acknowledgment

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