**Effect of heat treatment on the nanoporosity of silica PECVD films elucidated by the low-energy positron lifetime technique and ellipsometric porosimetry**

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Engineering the nanoporosity of silica thin films is important to improve the functionality of various materials for sensors, separation membranes, etc. One method to control the porosity is heat treatment of the films, which can modify the silica networks, so that the pore structure is altered at the molecular level. In this study, low-energy positron annihilation lifetime spectroscopy (PALS) and ellipsometric porosimetry (EP)[1][2] were applied to the evaluation of the nanopores in silica thin films fabricated by plasma-enhanced chemical vapor deposition (PECVD). The effect of the heat treatment on the nanoporosity was investigated.

Silica films with a thickness of 400 nm were deposited at 300°C on silicon wafers with different flow rate ratios of the oxygen and tetraethyl orthosilicate (TEOS) precursors. Refractive indices for the as-deposited silica films, a measure of the film density, decreased with increasing TEOS fraction, suggesting suppressed development of the silica networks due to the excess amount of TEOS in the precursor. PALS results showed that their pore sizes, quantified from the ortho-positronium lifetimes, increased from 0.30 nm to 0.35 nm in radius with decreasing refractive index, indicating that the pore sizes were associated with the film total porosity. The films were annealed at 550°C under a dried nitrogen flow. While the total porosity, estimated from the refractive index, was not significantly changed with the heat treatment (Fig. 1), open porosity for the annealed films was not observed by EP with methanol (Fig. 2). This means that the connected pores accessible to the methanol molecule were isolated by annealing at 550°C. Details including the positron results for the annealed films will be discussed in the presentation.

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Fig. 1 Relationship between the total porosity and the TEOS fraction for the dry silica films.

Fig. 2 Relationship between the open porosity and the TEOS fraction for the silica films.