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Variable-energy positron annihilation study of subnanopores in SiOCH-based PECVD films

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Abstract

Subnanoporosity was introduced into SiOCH-based thin films by mixing tetraethyl orthosilicate with hexamethyldisiloxane (HMDSO) in the plasma enhanced chemical vapor deposition process, and was evaluated by the variable-energy positron annihilation lifetime technique. It was found that with increasing the HMDSO fraction both porosity and pore size were enhanced, as evidenced by the decreased refractive index and increased *ortho*-positronium lifetime. The lifetimes from 2.0 to 6.8 ns suggested the tunable pore volumes within a range of 0.1–0.7 nm^3.

Keywords: Subnanopore; PECVD; Hexamethyldisiloxane; Tetraethyl orthosilicate; Thin film; Positron annihilation

1. Introduction

Introducing subnanoporosity is a key issue for the development of molecular sieving membranes (MSM) for separation with high selectivity (Nguyen et al., 2003; Raman and Brinker, 1995; Cagnon et al., 2005). MSM materials essentially require pores with *tailored size*, comparable to subnanoscale target molecules. Free space may be introduced by incorporating methyl groups in silicon oxide, providing a means of controlling subnanoporosity in the silicon-oxide-based MSM. Plasma enhanced chemical vapor deposition (PECVD) enables thin films to be synthesized from various precursors including their mixtures, and is suitable to study the effect of methyl groups on total porosity and pore size.

In this work, we fabricated SiOCH-based PECVD thin films from tetraethyl orthosilicate (TEOS) mixed with hexamethyldisiloxane (HMDSO), which contains six methyl groups ($-CH_3$). The size of subnanopores present in the prepared films was examined by measuring the lifetime of *ortho*-positronium (*o*-Ps: the spin-parallel bound state of a positron and an electron) with the variable-energy positron annihilation technique. It was found that pores in a range of 0.1–0.7 nm^3 can be introduced with the controllable total porosity by varying the precursor composition.

2. Experiments

Films were deposited on 8-in silicon wafers in a capacitive coupled PECVD reactor with parallel plate electrodes using 13.56 MHz RF at a substrate temperature of 300 °C. Mixtures of HMDSO and TEOS diluted in argon (50 sccm) and oxygen (80 sccm) with the total pressure fixed at 150 Pa were used as precursors. The HMDSO fraction in the mixture was varied from 0 to 1, while the discharge power was kept constant at 200 W.

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Thickness and refractive index of the films were measured by spectroscopic ellipsometry. The presence of voids reduces refractive index, thus it serves as a measure of film total porosity. The chemical structure of films was analyzed by Fourier transform infrared (FT-IR) spectroscopy. Positron lifetime measurements were carried out under a pressure of 10^{-6} Pa at room temperature utilizing an intense pulsed-positron beam generated with an electron linear accelerator at AIST (Suzuki et al., 1991). Multi-exponential analysis was applied to the positron lifetime data to deduce the lifetime and relative intensity of the longest-lived *o*-Ps component.

3. Results and discussion

Table 1 lists the flow rates of TEOS and HMDSO, film thickness, refractive index (n), and deposition rate. The value of $n\sim1.42$ for film A from pure TEOS is slightly lower than 1.45 for nonporous silicon oxide, possibly due to some porosity introduced into the film by the PECVD process. With increasing HMDSO fraction the refractive index decreases down to about 1.35, indicating that total porosity further increases.

Fig. 1 shows FT-IR spectra for the films prepared with different HMDSO fractions. All the films exhibit intense Si–O stretch bands peaked around 1075 cm^{-1}. These broad bands extending from 970 to 1250 cm^{-1} are generally interpreted as a superposition of three different IR absorption bands centered at 1023, 1063 and 1135 cm^{-1} (Grill, 2003). The former two bands are due to the Si–O stretching in C–Si–O bonds and Si–O–Si stretching, respectively. The 1135 cm^{-1} band is related to the Si–O–Si stretch vibration in a caged structure. The Si–O stretch bands for films C, D and E deposited from the mixtures with higher amounts of HMDSO are shifted to smaller wavenumbers in comparison with those for films A and B, suggesting that the absorption at 1023 cm^{-1} relevant to the C–Si–O structure is intensified.

The spectra for three films C, D, and E have a pronounced absorption at 1277 cm^{-1}. This specific absorption is attributable to the Si–CH_3 bending. The inset of Fig. 1 shows a plot of the intensity of the Si–CH_3 vibration (1277 cm^{-1}) relative to the Si–O vibration (1075 cm^{-1}) versus HMDSO fraction. The data clearly show that with increasing HMDSO fraction more methyl groups are introduced into the deposited films, in qualitative agreement with the red shift of the main Si–O stretch band with HMDSO fraction. This together with the results of the refractive index (Table 1) suggests that the total film porosity increases with the incorporation of the methyl groups.

It is noteworthy that films C, D, and E were prepared at much higher total flow rates of the precursors than

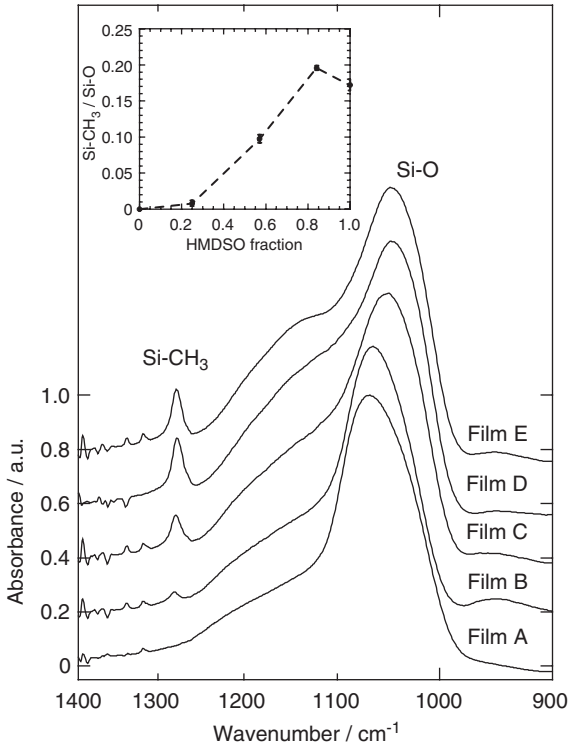

Fig. 1. FT-IR spectra of SiOCH films. The inset shows a plot of the intensity of the Si–CH_3 vibration (1277 cm^{-1}) relative to the Si–O vibration (1075 cm^{-1}) versus HMDSO fraction.

Table 1
Flow rates of TEOS (Q_{TEOS}) and HMDSO (Q_{HMDSO}), thickness (L), refractive index (n) and deposition rate (r) for SiOCH-based PECVD films

Sample	Q_{TEOS} (sccm)	Q_{HMDSO} (sccm)	L (nm)	n	r (nm/min)
A	11	0	548.9±0.8	1.421±0.004	109.8±0.2
B	11	3.7	477.2±1.3	1.395±0.003	92.1±0.3
C	11	15	513.2±1.0	1.367±0.002	135.1±0.3
D	5.6	30	667.3±1.5	1.348±0.007	148.3±0.3
E	0	30	634.1±1.0	1.355±0.001	126.8±0.2

The deposition rate was determined as the thickness divided by deposition time.