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## Variable-energy Positron Study of Nanopore Structure in Hydrocarbon–Siliconoxide Hybrid PECVD Films

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### Abstract

Nanopore formation upon heat treatment of hydrocarbon-siliconoxide hybrid films was investigated by means of the variable-energy positron annihilation  $\gamma$ -ray and lifetime techniques. The films were prepared using plasma enhanced chemical vapor deposition (PECVD), and nanoscopic pores in the films were developed through the decomposition of a sacrificial hydrocarbonous porogen by annealing the films at temperatures up to 600 °C. As a result of the positron annihilation  $\gamma$ -ray measurements, the line-shape  $S$  parameter increases with increasing annealing temperature from 150 °C to 400 °C, while it reduces with further increasing temperature. This suggests that more positronium annihilate with carbonous elements remaining on the wall of pores formed at temperatures up to 400 °C. The lifetime measurements revealed the nanopore sizes in the range from 0.2 nm<sup>3</sup> to 2.0 nm<sup>3</sup>. With increasing the pore size the film refractive index reduced from 1.44 to 1.29. The variable-energy positron techniques were demonstrated to be useful to examine the nanoporosity evolution for porous PECVD films.

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**Keywords:** positron annihilation, positronium, plasma enhanced chemical vapor deposition, tetraethyl orthosilicate, porosity

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### 1. Introduction

A key issue for developing various functional materials such as gas sensors[1], separation membranes[2], and insulators for next generation semiconductor devices[3] is manufacturing silicon oxide films with engineered nanopores. In the present work, silicon-oxide-backboned porous films were prepared through the decomposition of a sacrificial porogen, unstable organic phase intentionally introduced into the films to generate pores by pyrolysis. The nanopore formation upon heat treatment and the resultant porous structure were investigated by means of the variable-energy positron annihilation techniques.

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## 2. Experimental

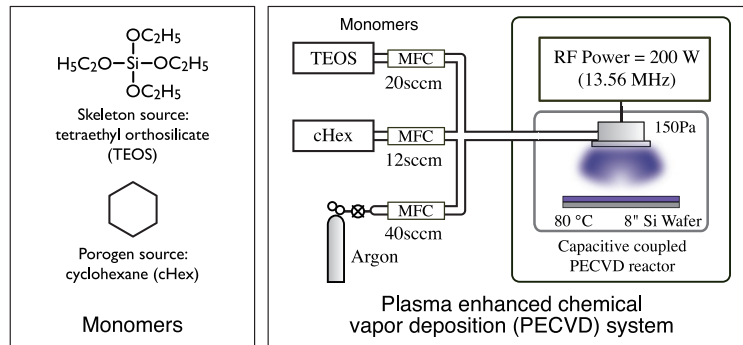


Figure 1: Monomers and PECVD system.

Films containing a hydrocarbonous porogen were deposited on 8-inch silicon wafers at 80 °C in a capacitive-coupled plasma enhanced chemical vapor deposition (PECVD) reactor with parallel plate electrodes[4, 5]. Mixtures of tetraethyl orthosilicate (TEOS) and cyclohexane diluted in argon were used as precursors. The deposition was carried out with respective flow rates of 20 sccm and 12 sccm for TEOS and cyclohexane under a pressure of 150 Pa with 200 W RF power. The obtained films were prebaked at 150 °C under a flow of TEOS vapor, followed by thermal annealing at various temperatures from 150 °C to 600 °C under a dried nitrogen atmosphere. The thicknesses of the prepared films were about 600 nm to 900 nm, determined by spectroscopic ellipsometry. The apparatus and the deposition conditions are shown in Figure 1.

The chemical structure of the obtained films was analyzed by Fourier transform infrared (FT-IR) spectroscopy. In order to obtain the film porosity as a function of annealing temperature, heptane adsorption isotherms at 26 °C were observed by means of ellipsometric porosimetry. Positron annihilation  $\gamma$ -ray energy spectra were measured by using a  $^{22}\text{Na}$ -source-based magnetically-guided beam[6] at various positron incident energies  $E_{\text{in}}$  from 0 to 20 keV. The line-shape  $S$  parameter, a measure of Doppler broadening of annihilation radiation, was determined as the ratio of the counts appearing in the central region (510.3 keV–511.7 keV) to the total counts of the 511-keV annihilation photo peak (506.8 keV–515.2 keV). Positron lifetime measurements were carried out at  $E_{\text{in}} = 4$  keV by utilizing an intense pulsed-positron beam generated with an electron linear accelerator[7]. A multi-exponential analysis was applied to the recorded positron lifetime data to deduce a hole radius  $r$  [nm] from the longest-lived positronium (Ps) lifetime component  $\tau$  [ns] based on the following equation[8, 9],

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

The hole volume  $V$  in  $\text{nm}^3$  was calculated from  $V = \frac{4}{3}\pi r^3$ .

## 3. Results and discussion

Figure 2 shows a typical FT-IR spectrum for the PECVD film before annealing. The distinct absorption peak around  $1100 \text{ cm}^{-1}$  is due to silicon oxide network. Incorporation of a hydrocarbonous component into the prebaked film is confirmed by the absorption peak over  $2800 \text{ cm}^{-1}$  to  $3000 \text{ cm}^{-1}$  due to the CH stretching vibration. Figure 3 shows the variation of the CH absorption peak (Figure 3(a)) and its intensity (Figure 3(b)) on the annealing temperature, respectively. As we can see, the intensity gradually decreases with increasing temperature up to 500 °C. Above 500 °C it goes to almost zero, suggesting that the hydrocarbonous porogen are mostly decomposed.

Figure 4 shows the variation of the film porosity, determined from heptane adsorption isotherms at 26 °C, as a function of annealing temperature. Clearly the film porosity gradually increases with increasing temperature from 150 °C, and then it approaches a constant value of 35% above 500 °C. Comparison of this variation with the FT-IR

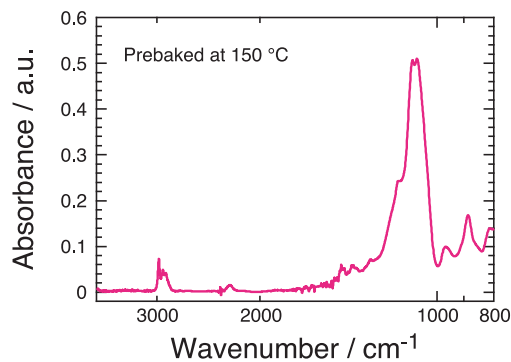


Figure 2: Typical FT-IR spectrum for the PECVD film prebaked at 150 °C.

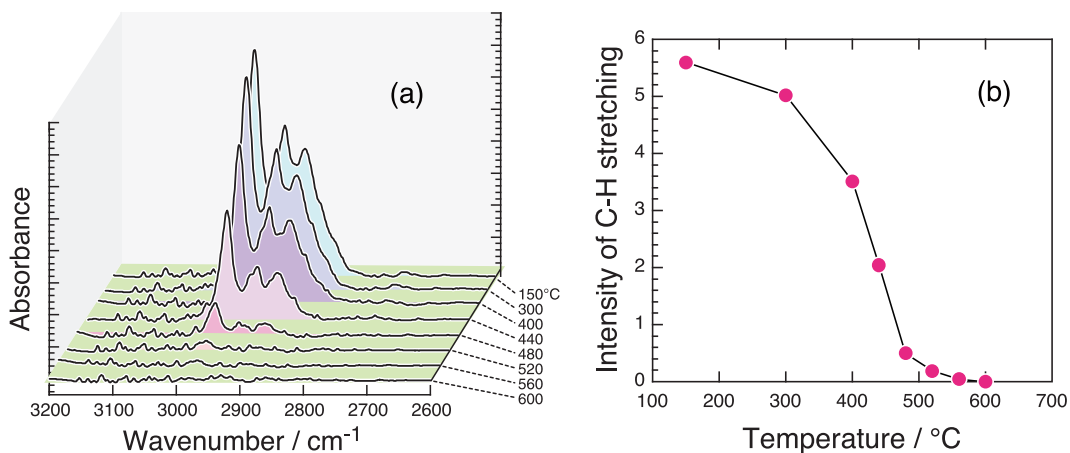


Figure 3: (a) Absorption peaks of CH at various annealing temperatures. (b) Annealing temperature dependence of the CH absorption peak intensity.

result in Figure 3(b) indicates that the porosity is remarkably developed from 300 °C to 500 °C as most porogen is decomposed in that temperature range.

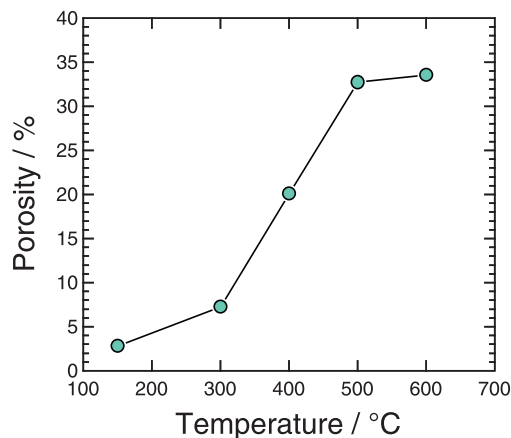


Figure 4: Variation of the film porosity for the PECVD films as a function of annealing temperature.

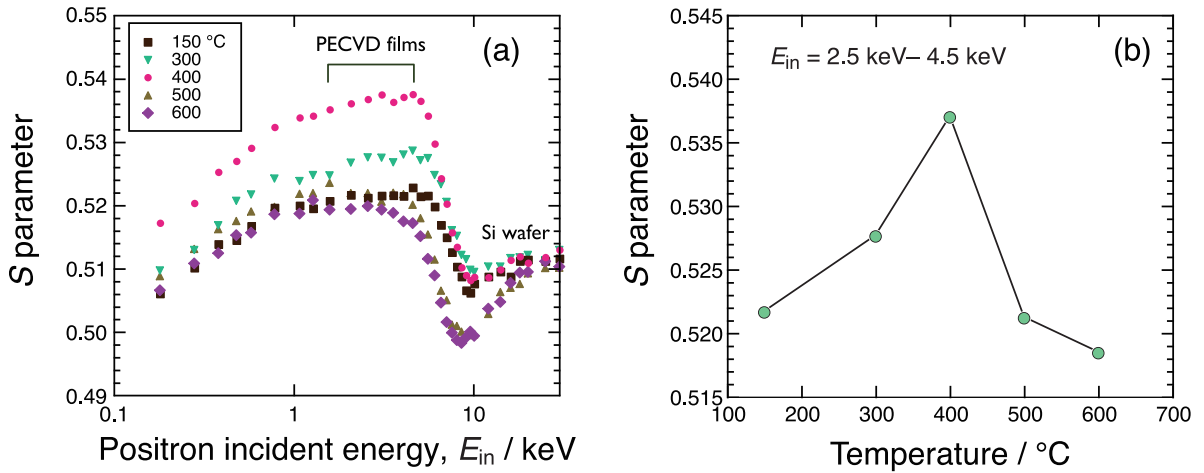


Figure 5: (a) Positron incident energy  $E_{in}$  dependence of  $S$  parameter for the PECVD films annealed at different temperatures. (b) Plot of averaged  $S$  obtained at  $2.5 \text{ keV} \lesssim E_{in} \lesssim 4.5 \text{ keV}$  vs. annealing temperature.

Figure 5(a) shows the variations of the line-shape  $S$  parameter for the PECVD films as a function of positron incident energy  $E_{in}$  ( $S$ - $E$  curve). The  $E_{in}$  dependence of  $S$  is divided roughly into four stages, namely, (1)  $E_{in} \lesssim 2.5 \text{ keV}$ , (2)  $2.5 \text{ keV} \lesssim E_{in} \lesssim 4.5 \text{ keV}$ , (3)  $4.5 \text{ keV} \lesssim E_{in} \lesssim 15 \text{ keV}$ , and (4)  $15 \text{ keV} \lesssim E_{in}$ . These stages are reasonably ascribed to the annihilation of positrons (1) in the film subsurface region, (2) in the film, (3) in the interface region between the film and the silicon substrate, and (4) in the silicon substrate, respectively. In Figure 5(b), the variation of the averaged  $S$  parameter obtained at  $2.5 \text{ keV} \lesssim E_{in} \lesssim 4.5 \text{ keV}$  (stage 2) is shown as a function of annealing temperature.  $S$  increases with increasing temperature from 150 °C to 400 °C, and it reduces with further increasing temperature. It is known that the annihilation of positrons with electrons belonging to carbonous constituents provides

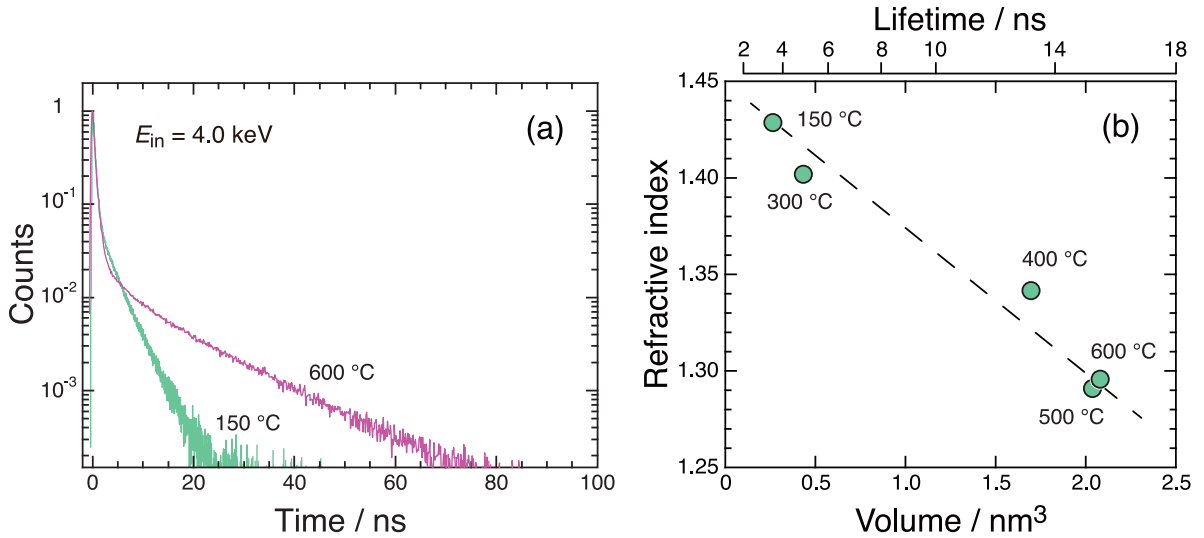


Figure 6: (a) Background subtracted positron lifetime data for the PECVD films annealed at different temperatures. The films were capped with 30-nm-thick nonporous silica. (b) Plot of the film refractive index vs. hole volume calculated from the Ps lifetime based on Eq. (1). On the upper axis shown is the Ps lifetime. The values in the figure represent the annealing temperatures. The refractive indices were determined by spectroscopic ellipsometry.

a higher  $S$  value than that with oxygen groups[10], while *para*-Ps self-annihilating in larger pores also enhances a  $S$  value. The variation of  $S$  suggests that more positronium tend to annihilate with carbonous elements remaining on the wall of pores formed by the porogen decomposition at temperatures up to 400 °C. Above 500 °C, the lower  $S$  reveals that most positrons annihilate with oxygen atoms. This is due to the complete elimination of the porogen.

Figure 6(a) shows the positron lifetime data obtained at  $E_{in} = 4.0$  keV for the prebaked and annealed films. The lifetime data for the film annealed at 600 °C has a pronounced longer-lifetime component. This suggests that larger holes are introduced as a result of the decomposition of the hydrocarbonous porogen by the annealing. Figure 6(b) shows the plot of the film refractive index vs. hole volume calculated from the Ps lifetime based on Eq. (1). As displayed in this figure, the hole volume increases from 0.2 nm<sup>3</sup> to 2.0 nm<sup>3</sup> with increasing the annealing temperature up to 600 °C, and the film refractive index well correlates with the hole volume in the range of 1.29 to 1.44. The obtained results indicate that the larger pores are formed with decomposing of the larger amount of the porogen, and the film refractive index decreases with increasing the size of the nanoholes, formed concurrently with the development of the porosity.

#### 4. Conclusion

We have investigated nanopore formation upon heat treatment of hydrocarbon-siliconoxide hybrid PECVD films by means of the variable-energy positron annihilation  $\gamma$ -ray and lifetime techniques. The variations of the IR absorption intensity for the hydrocarbonous porogen and the film porosity on the annealing temperature showed that most porogen is decomposed at temperatures from 300 °C to 500 °C, and accordingly the porosity is remarkably developed as the porogen decreased. From the results on the positron annihilation  $\gamma$ -ray measurements, the highest  $S$  was found for the film annealed at 400 °C, indicating that more positronium annihilate with carbonous elements remaining on the pore wall as the film porosity is evolved. The nanopore sizes in the range from 0.2 nm<sup>3</sup> to 2.0 nm<sup>3</sup>, obtained from the Ps lifetimes, were found to be correlated with the film refractive index from 1.44 to 1.29. The variable-energy positron techniques were demonstrated to be useful to examine the nanoporosity evolution of porous PECVD films.

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