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Positron annihilation studies of mesoporous silica films using a slow positron beam

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Abstract

Positron annihilation lifetime spectra were measured for mesoporous silica films, which were synthesized using triblock copolymer ($EO_{106}PO_{70}EO_{106}$) as a structure-directing agent. Different positron lifetime spectra for the deposited and calcined films indicated the formation of meso-structure after calcination, which was confirmed by Fourier transform infrared (FTIR) spectra and field emission-scanning electron microscopy (FE-SEM) observation. Open porosity or pore interconnectivity of a silica film might be evaluated by a two-dimensional positron annihilation lifetime spectrum of an uncapped film. Pore sizes and their distributions in the silica films were found to be affected by thermal treatments.

Keywords: Positron annihilation; Mesoporous film; Slow positron beam

1. Introduction

Characterization of the pore structures of mesoporous materials is extremely important, since they can be applied for separation, catalysis, encapsulation, chemical sensing, and low-dielectric (low-*k*) and optical coatings due to their well-defined pores with narrow distributions, high surface areas, unusual stability and process-ability. A few kinds of methods, such as gas adsorption porosimetry, ellipsometric porosimetry (EP), small angle neutron scattering (SANS), small angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and positron annihilation spectroscopy (PAS), etc. were used to characterize the pore structures [1].

Recently, PAS was widely used to characterize microporous and mesoporous materials [2–11], since pore size and its distribution can be derived from the *ortho*-positronium (*o*-Ps, a triplet state of a positron–electron atom) lifetime and its distribution in materials [2,4], and PAS based on a variable-energy pulsed slow positron beam can be well used to measure the depth-profile of defect properties in thin films. The intrinsic

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lifetime of *o*-Ps is 142 ns in a vacuum. However, its lifetime in a pore can be shortened to a few to a few tens nanoseconds depending on the pore size. The effective radius can be calculated from the *o*-Ps ''pick-off'' annihilation lifetime according to the semi-empirical quantum-mechanical Tao–Eldrup model [12–14] as well as the extended models by Shantarovich [15], Goworek et al. [16,17], Gidley et al. [3,4] and Ito et al. [18].

In the present work, positron annihilation in meso-structural silica films was studied. Useful information on mesoporous silica films were obtained from the positron annihilation characteristics in them.

2. Experimental

Meso-structural silica films were synthesized using triblock copolymer $EO_{106}PO_{70}EO_{106}$ (BASF surfactant, Pluronic F127) as the structure-directing agent and tetraethyl orthosilicate (TEOS) as a network precursor. The mesoporous silica films were deposited by dip-coating the precursor solution on a polished (100) silicon wafer. The coating solution is prepared by the addition of an ethanol solution of PEO–PPO–PEO triblock copolymer (BASF Pluronic F127, $EO_{106}PO_{70}EO_{106}$ with molecular weight of 12,600) to silica sol–gel made by an acid-catalyzed process [19]. Details of preparation of the precursor solution were presented elsewhere [20]. The final molar ratio of TEOS:$EO_{106}PO_{70}EO_{106}$:EtOH:H_2O:HCl was $1:6 \times 10^{-3}$:30:8:0.003.

A series of films were deposited after the precursor solution was stirred for 1 h. Then, the deposited films were dried rapidly at 90, 200 and 250 °C for 3 h, respectively. Finally, they were calcined in a tube furnace at 450 °C under air condition in order to remove the copolymer templates. Another two films were deposited after the precursor solution was stirred for a few minutes. Then, one of them was placed in a closed vessel with some TEOS inside and treated at ~90 °C for 3 h. Another one was also dried at ~90 °C for 3 h without TEOS vapor infiltration (VI). The dried films were calcined at 450 °C for 3 h.

Fourier transform infrared (FTIR) spectra for the as-deposited film and a calcined one were recorded in the range of 450–4000 cm^{-1} using a FTIR spectrometer (Perkin-Elmer Instruments). Field emission-scanning electron microscopy (FE-SEM, Hitachi S4800) was applied to record the cross section image of a calcined film at an accelerating voltage of 2 kV.

Positron annihilation lifetime spectroscopy (PALS) based on a variable-energy intense pulsed slow positron beam at Advanced Industrial Science and Technology (AIST) was used to investigate various films. The time resolution (full width at half maximum, FWHM) was about 250 ps. The positron energy was fixed at 2 keV. The positron annihilation pulse height obtained from a scintillation detector was recorded simultaneously by a two-dimensional PALS (2D-PALS), so as to provide three-gamma annihilation fraction as a function of positron age [21–23]. Positron annihilation lifetime spectrum in Kapton film was used as a reference for the purpose of subtracting the background. Positron annihilation lifetime spectra were resolved into five discrete components, by PATFIT [24] and a continuous distribution by the CONTIN program [25–27], respectively. The micropore size was calculated from τ_3 and τ_4 for the capped films according to the Tao–Eldrup model [15–17], while the mesopore size was calculated from τ_5 according to the rectangular Tao–Eldrup model [3,4].

3. Results and discussion

3.1. As-deposited and calcined films

As shown in Fig. 1, the positron lifetime spectrum for as-deposited film showed an *o*-Ps component with a few nanoseconds, which corresponds to *o*-Ps annihila-

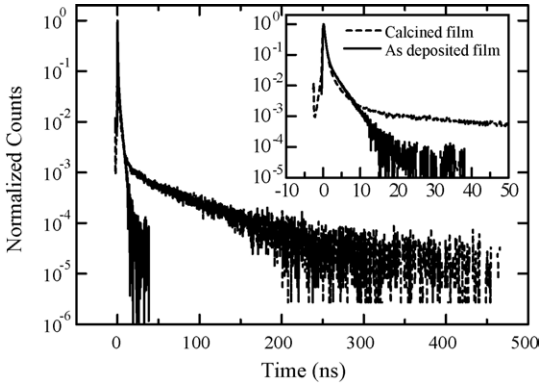

Fig. 1. Positron lifetime spectra for a synthesized film and a calcined one.