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Study of mesoporous silica films by positron annihilation based on a slow positron beam: Effects of preparation conditions on pore size and open porosity

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Abstract

Positron annihilation spectroscopy (PAS) based on an intense pulsed slow positron beam was applied to the study of mesoporous silica films, synthesized using tetraethyl orthosilicate (TEOS) as the network precursor and a triblock copolymer ($EO_{106}PO_{70}EO_{106}$) as the structure-directing agent. With positron annihilation lifetime spectroscopy (PALS), pore sizes were obtained from *ortho*-positronium (*o*-Ps) lifetimes of the films capped with a 20 nm thick SiO_2 layer. Influences of preparation conditions such as heating, TEOS vapor infiltration and precursor solution ageing on the pore size were studied. Moreover, the effect of ageing of the precursor solution on film pore interconnectivity/open porosity was investigated through lifetime–energy correlation measurements by observing intrinsic annihilation of *o*-Ps diffused out from the uncapped film surface.

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Keywords: Positronium; Slow positron beam; Micropore; Mesopore; Copolymer; Silica film

1. Introduction

Mesoporous materials have attracted much attention because they can be used not only in separation, catalysis, encapsulation, chemical sensing, but also as low-dielectric constant (low-*k*) films and optical coatings. These applications in most cases require well defined pores with narrow size distribution in addition to high stability and processability [1–6]. Various techniques such as gas adsorption porosimetry, small angle X-ray scattering (SAXS), small angle neutron scattering (SANS), transmission electron microscopy (TEM), ellipsometric porosimetry (EP) and positron annihilation spectroscopy (PAS) have been used to characterize the porous materials [6]. Of these, PAS possesses significant and unique advantages. First, one can measure the pore size down to a few angstrom and pore size distribution with positron annihilation lifetime spectroscopy (PALS). Secondly, the use of variable energy positron beams enables depth-profiling of thin films, since positrons can be injected into desired depths of a few nanometer to 1μm by adjusting the positron energy. Because of these advantages, PAS is often used to study mesoporous films and low-*k* dielectrics [7–14].

PAS relies on that the positron, the anti-particle of an electron, has unique annihilation properties in condensed matter. In porous materials, positronium (Ps), the bound state of a positron and an electron, forms either as a singlet state (*para*-Ps, *p*-Ps) or a triplet state (*ortho*-Ps, *o*-Ps). The ratio of the formation probability of *p*-Ps to *o*-Ps is 1:3. The intrinsic lifetime of *p*-Ps via 2γ-annihilation is 0.125 ns,

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while that of *o*-Ps via 3γ-annihilation in a vacuum is 142 ns. However, when localized in a nanopore, *o*-Ps undergoes 2γ pick-up annihilation and its lifetime is shortened to a few – a few tens nanoseconds depending on the pore size. This makes it possible to estimate the pore size from the measured *o*-Ps lifetime [7,11,12,15–21]. In the presence of interconnected, open pores, *o*-Ps may escape through the pores into a vacuum and then undergoes 3γ-annihilation, which provides information on pore interconnectivity/open porosity.

Mesoporous silica films can be synthesized by removal of polymer templates (surfactants) from mesostructural silica composite films prepared by the sol–gel processes [5,22]. The pore size, its distribution and open porosity are influenced by the molecular weight [22,23] and hydrophilicity of the surfactants [23,24], precursor sol and post-treatments of the deposited films [22,25]. Understanding the relationship between the pore structures and preparation conditions is very important for synthesizing mesoporous silica films with desired pores. In the present work, PAS was applied to study the pore size and pore interconnectivity/open porosity of the mesoporous silica films synthesized under various conditions, using tetraethyl orthosilicate (TEOS) as the network precursor and a triblock copolymer $EO_{106}PO_{70}EO_{106}$ (BASF surfactant, Pluronic F127) as the structure-directing agent. The effects of such preparation conditions as calcination, TEOS vapor infiltration and precursor ageing on the mesopore characteristics are discussed.

2. Experimental

2.1. Preparation of mesoporous thin silica films

The mesoporous silica films were deposited by dip-coating [26] on a polished silicon (1 0 0) wafer. The coating solution was prepared by the addition of an ethanol solution of a PEO–PPO–PEO triblock copolymer (BASF Pluronic F127, $EO_{106}PO_{70}EO_{106}$, with a molecular weight of 12600 g/mol) to silica sol–gel made by an acid-catalyzed process [25]. First, the silica sol was prepared by stirring the mixture of calculated amounts of TEOS (4.16 g), EtOH (3.5 ml), H_2O and HCl (molar ratio = 1:3:8:0.003) at about 70 °C for 90 min. After aging at about 60 °C for 25 min, the triblock copolymer solution (1.512 g $EO_{106}PO_{70}EO_{106}$: 32.5 ml EtOH) was added with stirring. The final molar ratio of TEOS:$EO_{106}PO_{70}EO_{106}$:EtOH:H_2O:HCl was 1:0.006:30:8:0.003. The film thickness was controlled to a few hundreds nm by adjusting the dip-coating rate.

After the precursor solution aged at RT for 25 days, films A and B were deposited and dried overnight in air before calcination. Films C and D were deposited after 45 days and dried in air for a few days. After drying, the deposited films were placed in a tube furnace under Ar flow. After they were maintained in Ar for more than 30 min, the furnace temperature was raised, and then the films were calcined at 450 °C for 3 h under Ar gas flow before being cooled slowly. After calcination, the mass of the films decreased by ~52% due to the removal of the solvent and polymer template.

The effect of pretreatment on the pore properties was studied with films subjected to different thermal treatments and a film subjected to TEOS vapor infiltration. Film A was heated with an increasing rate of 15 °C/min and calcined at 450 °C for 3 h. Films B and C were treated under Ar gas flow around 90 °C for 3 h and heated with an increasing rate of 1.5 °C/min before calcination at 450 °C for 3 h. Film D was subjected to TEOS vapor infiltration around 90 °C for 3 h before calcination. To prevent Ps diffusion out of the surface, some films were capped with a 20 nm thick SiO_2 layer using electron beam deposition. Thicknesses of the calcined films were 300–440 nm and their refractive indices were around 1.27 as measured by an ellipsometer. The refractive indices were lower than the value of 1.46 for nonporous SiO_2, indicating introduction of porosity in the films after calcination. The total porosity of the calcined films was estimated to be about 40%. The film preparation conditions are listed in Table 1.

2.2. PALS and lifetime–energy correlation measurement

An experimental setup based on a variable energy intense pulsed slow positron beam at the National Institute of Advanced Industrial of Science and Technology was used to record positron annihilation lifetime spectra and lifetime–energy correlation data [27]. The positron annihilation signals were detected by a truncated BaF_2 scintillator coupled to a photo-multiplier tube (PMT, Hamamatsu R2083Q). The output of the PMT was divided; one signal was connected to a constant fraction discriminator (CFD) and the other to a spectroscopy amplifier. The energy window was set to accept both 2-γ and 3-γ annihilation events. The positron annihilation lifetime spectrum was recorded by measuring the time difference between the CFD signal and the timing signal of the pulsing system using a time-to-amplitude converter (TAC) and analog-to-digital-converter (ADC). Another ADC was used to record the γ-ray energy data from the spectroscopy amplifier. To record lifetime–energy correlation spectra, coincident lifetime and energy signals were stored in a two-dimensional multi-channel analyzer (2D-MCA).

Before the PAS experiments, all films were baked at 300 °C for 30 min in order to remove absorbed water.

Table 1
Film preparation conditions

Film	Aging time (day)	Treatment	Heating rate (°C/min)
A	25		15
B	25	~90 °C 3 h	1.5
C	45	~90 °C 3 h	1.5
D	45	With VI, ~90 °C 3 h	1.5

VI means TEOS vapor infiltration. All films were finally calcined at 450 °C for 3 h in order to remove the template.