

Tuning porosity of silica films by using various surfactants and changing their loading: A study of positron annihilation Doppler broadening based on a slow positron beam

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Abstract. Porous silica films were synthesized via a sol-gel method using a nonionic amphiphilic triblock copolymer (F127) and a cationic surfactant (CTAB) as the structural templates with varying weight ratio. Positron annihilation Doppler broadening spectroscopy based on a slow positron beam was used to study the prepared silica films. For the porous silica films, the S parameter increased gradually with increasing the surfactant loading, which showed that higher porosity was introduced in the silica films with more porogen amount.

1. Introduction

Porous silica films have attracted considerable attention for their potential applications, such as adsorbents, catalysts and catalyst supports, low-k dielectric materials, chemical sensors, host-guest chemistry, antireflective coatings and membrane separations. However, tailoring of the porous structures is indispensable for these practical applications which benefit from highly ordered structures and high porosity. Since the synthesis of silicate mesoporous molecular sieves designated as M41S [1], nonionic amphiphilic block copolymers [2-4] have been subsequently used to direct the formation of a family of mesostructured materials with tunable mesoporous structures and various morphologies. Ionic surfactants [5-7] have also been devoted to design porous structures. Such surfactant-templated porous materials rely on a successful application of sol-gel chemistry and self-assembly between the organic structure-directing agents and the inorganic precursor species. In this method, selection of surfactant is of most importance for determining the porous structure.

In this study, porous silica films were tuned by two kinds of surfactants as pore generators with various loading. The silica films were studied by Doppler broadening spectroscopy of positron annihilation based on a slow positron beam. The porous structure of the silica films was found to be significantly influenced by the additive of surfactant template and preparation conditions.

2. Experimental

2.1. Sample preparation

Tetraethoxysilane (TEOS) was used as the silica source and a nonionic amphiphilic triblock copolymer (EO₁₀₆PO₇₀EO₁₀₆, Pluronic F127) and a cationic surfactant hexadecyltrimethylammonium bromide (CTAB: CH₃(CH₂)₁₅N⁺(CH₃)₃Br⁻) were used as templating agents, respectively. The

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surfactant templates were introduced with various weight ratios, i.e. $W_{\text{template}}/(W_{\text{template}} + W_{\text{TEOS}})$, which were assigned as 0, 5, 10, 15, 20 and 25 wt%, respectively. The silica thin films were prepared on polished silicon wafers by dip-coating using precursor sols of TEOS, surfactant, anhydrous ethanol (EtOH), distilled water and hydrochloric acid (HCl) (the mole ratios: 1 TEOS: x surfactant: 22 EtOH: 8 H₂O: 0.002 HCl; x was determined by the surfactant weight ratio). There was a thin layer of non-porous SiO₂ (~ several nm) on the as-grown silicon substrate. The as-deposited films were elevated at a heating rate of 1 °C/min and subsequently calcined at 450 °C in air for 5 hours in order to remove the organic species. To study the evolution of the pore structure, the same as-deposited silica film templated by CTAB with the weight ratio of 15 wt% was treated successively at 200, 300, 350 and 400 °C in air for 2 hours, respectively.

2.2. Characterization of silica films

Positron annihilation Doppler broadening spectroscopy based on a slow positron beam was used to characterize the synthesized silica films. The Doppler broadening spectra were measured with a high-purity Ge detector as a function of the incident positron energy E by using a monoenergetic positron beam at Wuhan University. A spectrum with about 10^6 counts was collected for each incident positron energy. The low-momentum part was characterized by the S parameter, defined as the fraction of the annihilation line over the energy range of $511 \text{ keV} \pm |\Delta E_\gamma|$ (where $\Delta E_\gamma \sim 0.76 \text{ keV}$) around the central region. The S parameters were used to evaluate the porosity of the mesoporous films, since S parameters in films strongly depend on pore size and/or pore density, which govern positronium formation and annihilation in them.

3. Results and discussion

3.1. Positron annihilation characteristics in silica films

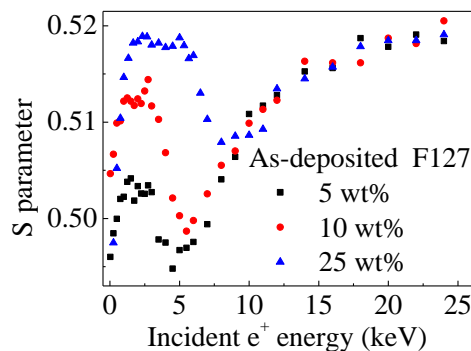


Figure 1. S-E curves of the as-deposited silica films with various loading.

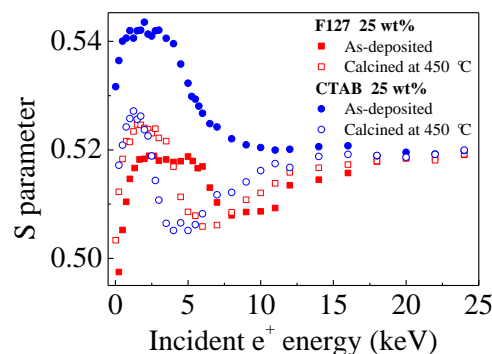


Figure 2. S-E curves of different surfactant-silica films before and after calcination.

Figure 1 showed the S-E curves of the as-deposited silica films using F127 as the structure-directing agent. For a typical S-E curve, for instance, in as-deposited film with 25 wt% F127, the S parameter increased sharply with increasing positron energy from 0 keV to around 2 keV, from which to ca. 5 keV it almost kept at a constant value resulted from positron annihilation in the as-deposited film. With increasing positron energy from about 5 to 10 keV, the S parameter showed a dip, which was attributed to positron annihilation in the nonporous SiO₂ thin layer on the silicon substrate. Finally, with implanting positron deeper the S parameter gradually increased and reached a plateau. Considering the positron implantation profile in condensed matters [8, 9], three regions were revealed by the S-E curves for the as-prepared films on silicon wafers: The first region was the surfactant-silica film; the second one was the nonporous SiO₂ thin layer on silicon substrate, and the third region was the silicon itself. Keep in mind that S parameters in the films on Si substrates were closely associated with physiochemical characteristics of the films. The S parameters of the as-deposited films were

found to increase gradually with loading more additive from 5 to 25 wt%. For the as-deposited films with the same weight ratio, much higher S parameter was found in the CTAB-silica film than that in the F127-silica film (Figure 2), due to the different characteristics of positron annihilation in the two kinds of surfactant-silica nanocomposites. Several factors could be taken into consideration to interpret the different S parameters in silica films: film chemical composition [10, 11], Ps formation probability and porosity of the film. In this work, different chemical compositions in CTAB-silica and F127-silica were responsible for the large difference in S parameters of the as-deposited films.

After being calcined at 450 °C for 5 hours, the S parameter of CTAB-templated film decreased significantly, meanwhile, a distinct increase was observed for F127-templated film due to the removal of the additives. Similar S values in both calcined films were due to Ps annihilation in porous structures [12, 13] resulted from removal of the surfactants with the same loading. Because of thinning of the porous silica film due to condensation of inorganic species, and formation of mesopores during calcination, the dip of S-E curves shifted to the lower energy region, for instance, from ac. 9 to 6 keV for the F127-templated silica film.

3.2. Evolution of porous structure depending on treatment temperature

Figure 3 showed the S-E curves of the same silica film treated successively at different temperatures. The S parameter of as-deposited silica film increased gradually and approached a plateau ac. 0.54 in the energy range of 1 to 4 keV. After being heated at 200 °C for 2 hours, the S parameter distinctly increased to ac. 0.55, which was attributed to the removal of water and ethanol in surfactant-silica film during the drying process. Little change in the width of the plateau could be found after the treatment at 200 °C, indicating that the template was hard to decompose at about 200 °C. However, the S parameter decreased remarkably to around 0.53 by successive heating at higher temperatures due to the removal of CTAB template, meanwhile, significant reduction in the width of the plateau was observed upon successive treatment at higher temperature up to 300 °C due to the condensation of inorganic species and the formation of porous framework. No changes were found for the S parameters in the porous silica film treated from 300 °C to 400 °C, revealing good thermal stability of the porous silica film.

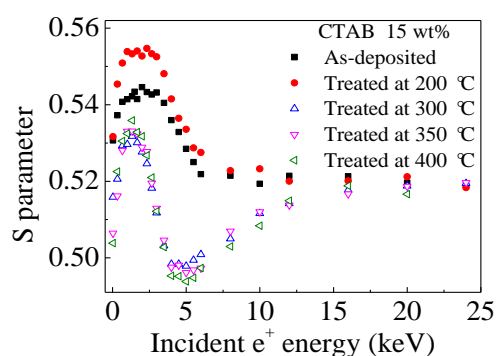


Figure 3. S-E curves of the same silica film treated successively at different temperatures.

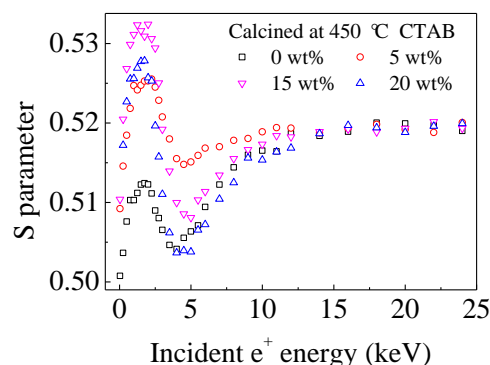


Figure 4. S-E curves of porous silica films with increasing loading of CTAB.

3.3. Evolution of pores depending on porogen loading

Figure 4 showed S-E curves of the silica films, which were prepared by adding CTAB with various weight ratios and calcined at 450 °C for 5 hours. The S parameter of silica film was low (around 0.51) when no surfactant was loaded. A sharp increase of S parameter was found in the calcined silica film using 5 wt% CTAB as the template, revealing that pores were introduced by the addition of surfactant. For the porous silica films, the S parameter was found to increase gradually with increasing porogen loading from 5 wt% up to 15 wt%, which showed that higher porosity was introduced in the silica

films prepared with more porogen amount. Similar results of pore evolution depending on the porogen content were reported in a previous paper, in which a triblock polymer Pluronic F38 (BASF surfactant) was used as a pore generator [14]. In this study, the S parameter decreased distinctly with further increasing the porogen loading up to ca. 20 wt% perhaps because of formation of ordered mesostructures [6] and their contraction [15] upon calcination.

4. Conclusion

In conclusion, porous silica films were prepared via a sol-gel synthesis by two kinds of surfactants as the templating agents: a nonionic copolymer F127 and a cationic surfactant CTAB. Positron annihilation Doppler broadening spectroscopy based on a slow positron beam was used to study the synthesized silica films. Results indicated that the mesostructures of the silica films were successfully tuned by varying the additive and loading. The S parameter of porous silica films increased gradually with increasing the porogen loading, which showed that higher porosity was introduced with more loading. Furthermore, the temperature dependence of evolution of the mesostructures was also studied. After being treated at 200 °C for 2 hours, the S parameter of the CTAB-silica nanocomposite films increased distinctly, however, it decreased remarkably due to the removal of the surfactant template when successively treated at higher temperatures.

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