

Positron Annihilation Study of Silica Films Templated by a Cationic Surfactant

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Porous silica films were synthesized via a sol-gel method using tetraethyl orthosilicate with mixing hexadecyltrimethylammonium bromide (CTAB) as a structural template. Doppler broadening of positron annihilation radiation spectroscopy based on a slow positron beam and ellipsometry were applied to the study of the prepared silica films. The obtained results suggested that a nanoscopic structure change for the porous silica films takes place around 15 wt% of the CTAB loading.

1. Introduction

Porous silica films have attracted considerable attention because of their potential applications to adsorbents, catalysts and catalyst supports, low- k dielectrics, chemical sensors, host-guest chemical processes, antireflective coatings and membrane separations. For such practical applications, it is necessary to produce a highly ordered, concentrated pore structure. Since the synthesis of mesoporous silicates with tunable morphologies, for instance known as M41S [1], nonionic amphiphilic block copolymers [2–4] and ionic surfactants [5, 6] have been subsequently utilized to form porous structures. A successful preparation of such surfactant-templated porous materials using organic, inorganic, and directing agents relies on the sol-gel condition for self-assembling of the precursor. Hence the amount of the surfactant is one of the most important factors for determining the resultant porous structure.

Positron annihilation spectroscopy with a variable-energy positron beam is a powerful, nondestructive tool for characterizing porous thin films [7–11]. In this study, porous silica thin films were synthesized using various amounts of a cationic surfactant as a pore generator. Doppler broadening of positron annihilation radiation spectroscopy (DBAR) based on a slow positron beam and ellipsometry were used to characterize the prepared silica thin films. The effect of the additive surfactant on the nanoscopic pore structure of the thin films was examined.

2. Experiments

2.1 Sample preparation

Silica thin films were synthesized via a sol-gel method [2, 3, 12] using tetraethyl orthosilicate (TEOS; silica source) and hexadecyltrimethylammonium bromide (CTAB ($C_{16}H_{33}N^+(CH_3)_3Br^-$; structure-directing surfactant). Precursor sols were prepared by mixing TEOS, CTAB, anhydrous ethanol (EtOH), distilled water and hydrochloric acid (HCl) with different molar ratios of TEOS : CTAB : EtOH : H_2O : HCl = 1 : x (from 0 to 0.19) : 22 : 8 : 0.002, so that the weight fractions of CTAB relative to TEOS W_{CTAB} were 0, 5 wt%, 15 wt%, 20 wt% and 25 wt%. The prepared sols were dip-coated on polished silicon wafers, having a sacrificial oxide layer with a few nm-thickness on their

surface. The films coated on the silicon substrates were heated at a rate of $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, and were subsequently calcined at $450\text{ }^{\circ}\text{C}$ in air for 5 hours in order to remove the organic species in the films.

2.2 Characterization of silica films

Positron annihilation γ -ray energy spectra with various incident positron energies E_{in} were measured using the energy-tunable positron beam system equipped with a high-purity Ge detector at Wuhan University. Annihilation events for each spectrum were collected with $\sim 10^6$ counts. As a measure of DBAR, the line-shape S parameter for the 511-keV photo-peak was defined as the ratio of the central region ($511\text{ keV} \pm |\Delta E|$, where $|\Delta E| \sim 0.76\text{ keV}$) of the photo-peak to the total area, while the wing W parameter was defined as the ratio of the wing regions ($1.44\text{ keV} \leq |\Delta E| \leq 4.81\text{ keV}$) to the total area. S was used to examine the nanoscopic pore structure of the films, since it is associated with the positronium formation and annihilation in substances.

The thickness and the refractive index n at a wavelength of 632.8 nm for the as-deposited and calcined films were measured at room temperature by means of ellipsometry. The refractive index n of a substance is related to the polarizability via the Lorentz–Lorenz equation [13], and is a function of the bulk composition as well as the density. This means that for a binary system the overall n is estimated by the mean value of the intrinsic n for the respective components based on the mean-field approximation. On the other hand, according to the Lorentz–Lorenz equation, n is inversely proportional to the overall density of a substance, meaning that n can be a measure of its porosity.

3. Results and discussion

3.1 Positron annihilation characteristics for the CTAB-silica composite films

Figure 1 shows the variation of the S parameter for the as-deposited film samples, prepared with various CTAB weight ratios W_{CTAB} , as a function of incident positron energy E_{in} . The solid lines in the figure represent fitting results to the data by the VEPFIT program [14]. S for all the curves

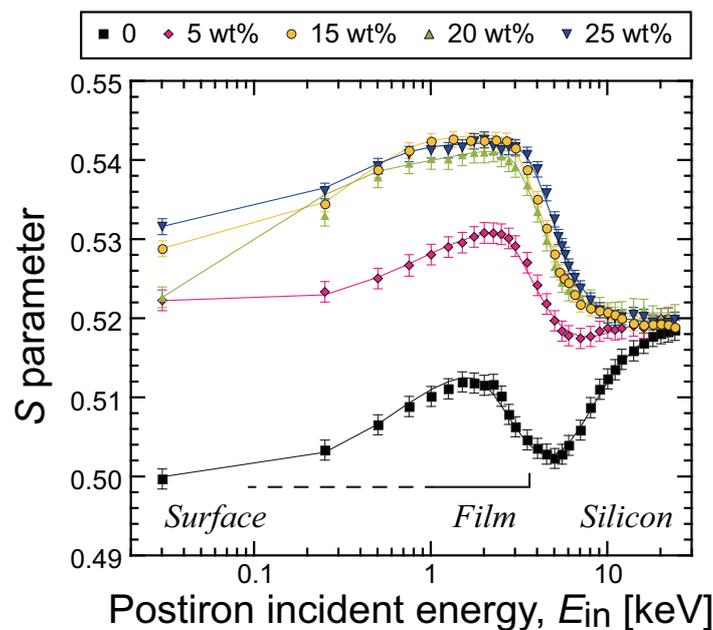


Fig. 1. S - E curve for the as-deposited film samples with various CTAB weight ratios W_{CTAB} . The solid lined through the data represent fitting results by the VEPFIT program.

increases with increasing E_{in} up to ~ 1.0 keV, and then maintains a constant value from 1 keV to ~ 3.5 keV, indicating positron annihilation near the film surface at $E_{in} < 1.0$ keV, and in the CTAB-silica composite films at $1.0 \text{ keV} < E_{in} \lesssim 3.5 \text{ keV}$, respectively. Note that the S - E curve at E_{in} from ~ 3.5 keV to 7.0 keV for the film sample prepared at $W_{CTAB} = 0$ shows a remarkable dip, probably attributable to positron annihilation at the interface between the film and the silicon substrate. With further increasing E_{in} from 7.0 keV, S for all the samples approaches the same value of around 0.52, indicating that most positrons are implanted into the silicon substrate and they annihilate therein. As a result, the S - E curves for the present samples are divided into four regions in terms of E_{in} , namely, $E_{in} \lesssim 1.0$ keV, $1.0 \text{ keV} \lesssim E_{in} \lesssim 3.5$ keV, $3.5 \text{ keV} \lesssim E_{in} < 7.0$ keV, and $E_{in} > 7.0$ keV. By considering the positron implantation profile in condensed matter [15], the four regions are ascribed to positron annihilation (1) in the near-surface, (2) in the CTAB-silica composite film, (3) in the interface between the film and the silicon substrate, and (4) in the silicon substrate. S for the CTAB-silica composite films on the silicon substrates is closely associated with the physiochemical characteristics of the films. As in Fig. 1, S for the second region, solely attributed to the as-deposited films, increases gradually with increasing W_{CTAB} from 0 to 15 wt%. The enhanced S with increasing W_{CTAB} may be due to the chemical composition [16, 17] of the films. Further increasing W_{CTAB} , no change in S is observed. The E_{in} range for the plateau region expands for the films prepared at the higher W_{CTAB} , indicative of the increased film thickness. In addition, the dip in the S - E curve, observed at $E_{in} \sim 5.0$ keV for the film sample without CTAB, becomes weak at $W_{CTAB} = 5$ wt%, and it disappears at $W_{CTAB} \geq 15$ wt%, implying a change in the annihilation process of positrons near the film/substrate interface.

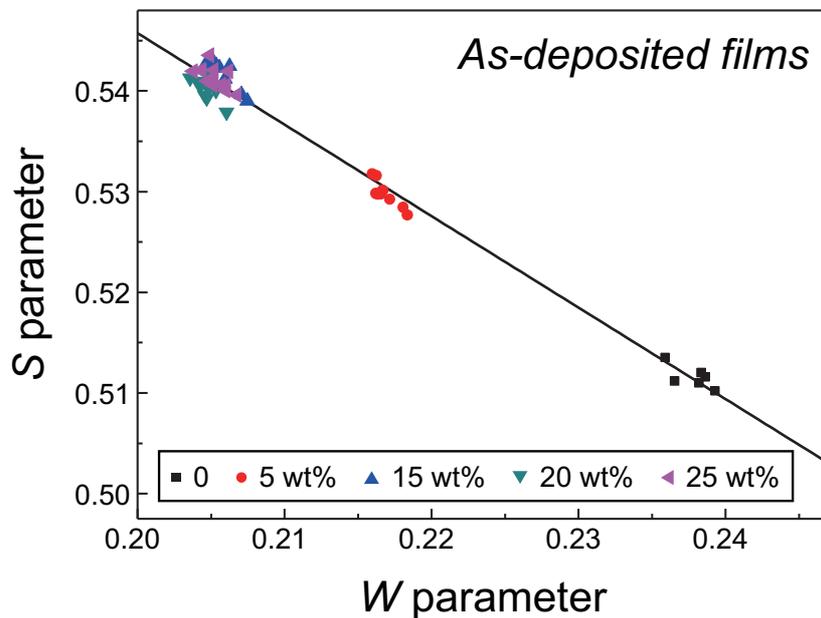


Fig. 2. S - W plot for the as-deposited films prepared with various W_{CTAB} .

Figure 2 depicts the relationship between S and W obtained for the CTAB-silica composite films, corresponding to the respective highest value of S . It is known that a linear relationship between the S and W parameters is observable not only when the annihilation site of positronium gradually changes with constant formation probability of positronium for a given system [16, 17], but also when positrons annihilate at the same kind of pores with different concentrations [18, 19]. As seen in Fig. 2, for the S - W plot of all data in CTAB-silica composite film region, all the points fall on

the same straight line with a slope of -1.087 ± 0.017 . This may be caused by the gradual change in the annihilation sites of positrons with varying W_{CTAB} along with the fractional change of the silica moiety and the CTAB micelles in the as-deposited films.

3.2 Effect of the calcination on the thickness and the S parameter

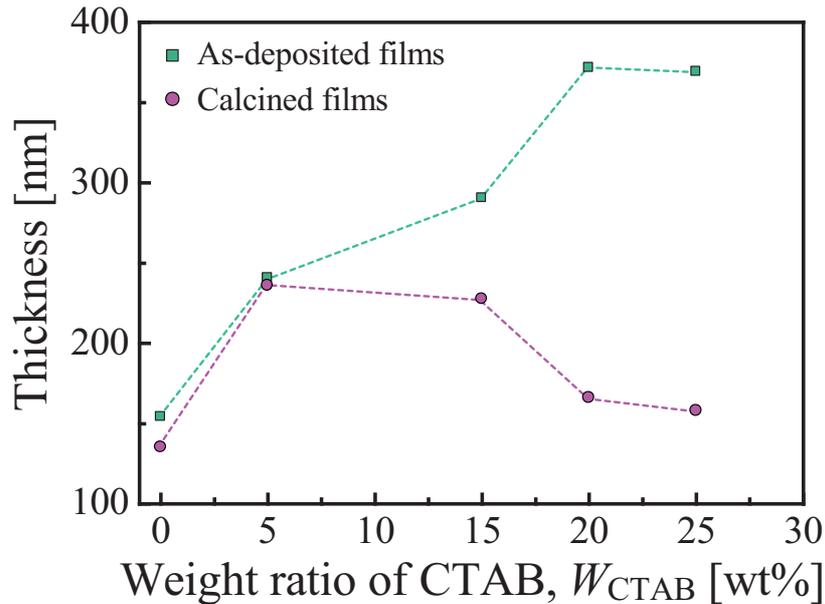


Fig. 3. Variation of the thickness for the as-deposited and calcined films as a function of W_{CTAB} .

Figure 3 displays the variation of the thickness for the as-deposited and calcined films as a function of CTAB weight ratio W_{CTAB} , obtained by means of ellipsometry. For the films with lower W_{CTAB} (≤ 5 wt%), no clear difference in the thickness is observed between the as-deposited and calcined films. In contrast, for the films with W_{CTAB} above 15 wt% remarkable reductions are found after the calcination, where the difference in the thickness before and after the calcination becomes larger with higher W_{CTAB} . This is possibly due to the removal of larger amounts of the additive as well as due to condensation of the inorganic species upon calcination, resulting in significant collapse of the films.

Figure 4 shows S - E curves for the calcined silica film samples prepared with various W_{CTAB} . Similarly to the case of the as-deposited film samples, the S - E curves for the calcined films are divided into four regions with respect to E_{in} , namely, $0 < E_{\text{in}} < 1.0$ keV, 1.0 keV $< E_{\text{in}} \lesssim 2.5$ keV, 2.5 keV $\lesssim E_{\text{in}} < 7.0$ keV, and $E_{\text{in}} > 7.0$ keV, attributable to the near-surface, the silica film, the film/substrate interface and the silicon substrate, respectively. In contrast to the result of Fig. 2, the dips due to the positron annihilations around the interface for the calcined film samples at $W_{\text{CTAB}} > 15$ wt% are clearer than for the respective as-deposited film samples. This signifies that the positron annihilation at the near-interface region is influenced by the decomposition of CTAB, resulting in the lowered S at the interface region. Note that the S value shows the highest value with $W_{\text{CTAB}} = 15$ wt%.

3.3 Comparison of the S parameter with the refractive index

Figure 5 displays the variation of the refractive index n for the as-deposited and the calcined films as a function of W_{CTAB} . For the as-deposited films n increases slightly from 1.44 to 1.47 with increasing

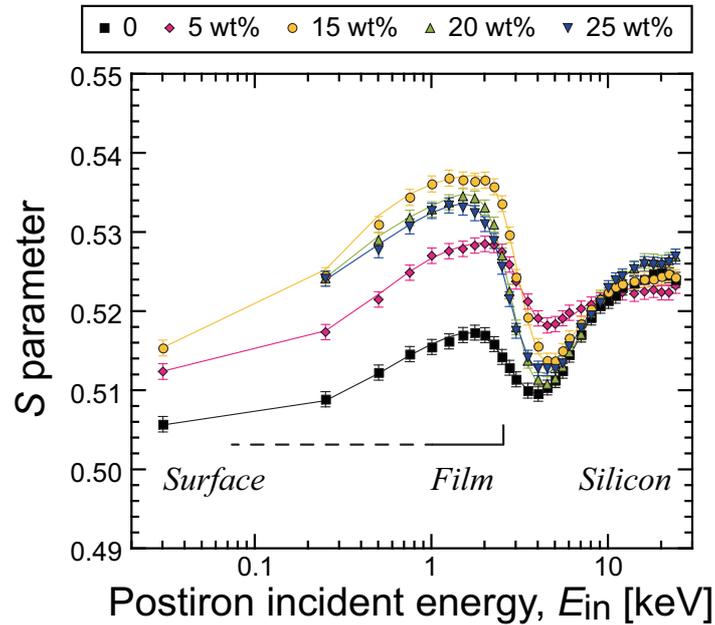


Fig. 4. S - E curve for the calcined film samples prepared with various CTAB weight ratios. The solid lined through the data represent fitting result by the VEPFIT program.

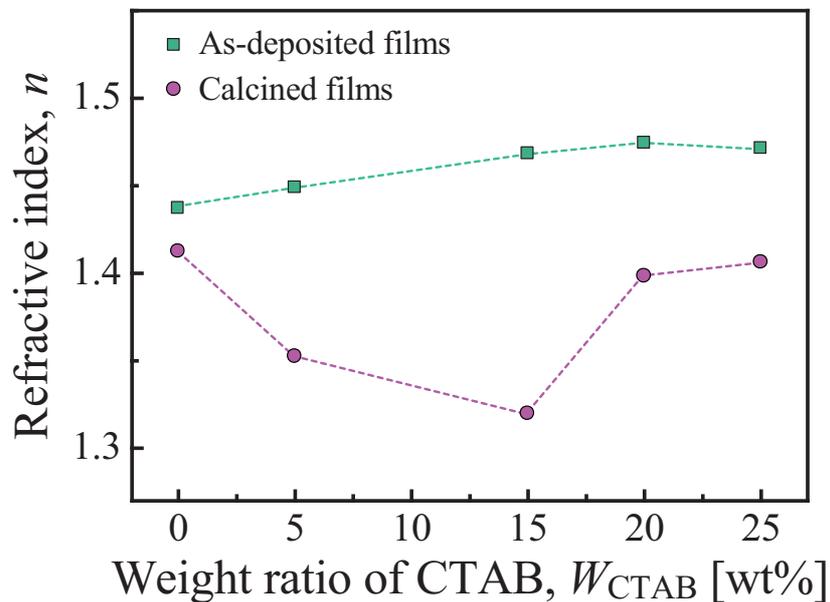


Fig. 5. Variation of the refractive index n for the as-deposited and calcined films as a function of W_{CTAB} .

W_{CTAB} from 0 to 25 wt%. The value of 1.44 for n at $W_{\text{CTAB}} = 0$ is close to that for the bulk silica ($n = 1.45$), indicating that the film deposited at $W_{\text{CTAB}} = 0$ is regarded as nonporous. The slight increase of n with the increased W_{CTAB} signifies the enhanced polarizability of the films deposited with higher W_{CTAB} . As for the calcined films, with increasing W_{CTAB} from 0 to 15 wt% n linearly decreases from 1.41 to 1.32. The reduction of n signifies enhanced film porosity, due to the decomposition of the

CTAB component by calcination, consistent with the evidence of the mesopore formation for similar systems previously reported [12]. Further increasing W_{CTAB} to 25 wt%, n increases to 1.41, a similar value to the film prepared at $W_{\text{CTAB}} = 0$, meaning that the film porosity with $W_{\text{CTAB}} = 20$ wt% and 25 wt% is comparable to the film with $W_{\text{CTAB}} = 0$. This is probably due to the considerable collapse of the films after the one-step calcination, as seen in Fig. 3, even the larger amounts of CTAB are decomposed.

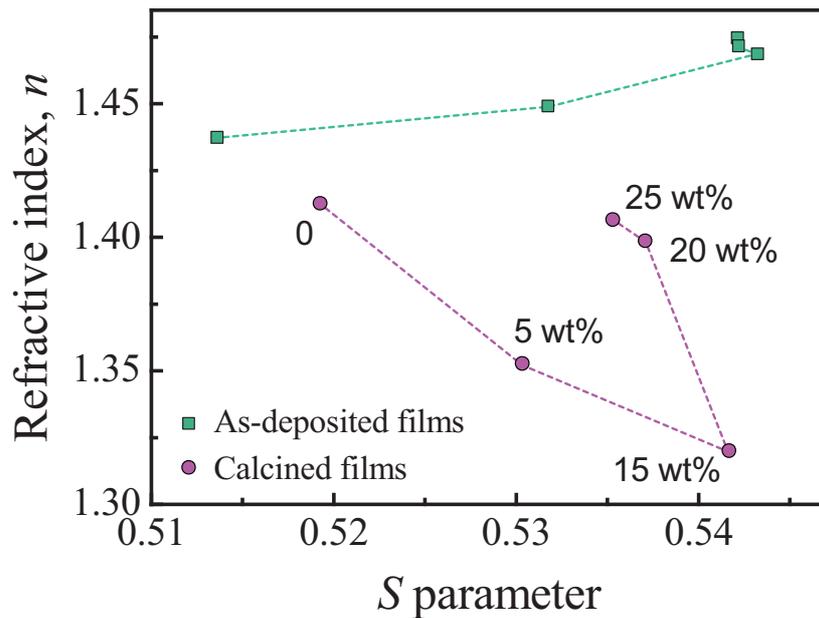


Fig. 6. Plot of the refractive index n versus the S parameter for the as-deposited and the calcined films with various W_{CTAB} . The numbers denote W_{CTAB} .

A plot of n versus S for the as-deposited and calcined films with different W_{CTAB} is shown in Fig. 6. S for the respective films was estimated from the fitting to the S - E curves. For the as-deposited films n increases linearly as S increases along with W_{CTAB} from 0 to 15 wt%. As W_{CTAB} is further increased, n increases slightly, whereas S decreases. S is known to be influenced by the film composition as well as the pore structure [17]. The overall trend between n and S for the as-deposited films suggests that increased amounts of CTAB in the films enhances both n and S simultaneously, while the source of the slight deviation at the higher W_{CTAB} of 20 wt% and 25 wt% is not clear at this time. On the other hand, for the calcined films with increasing W_{CTAB} from 0 to 15 wt% n decreases along with the increase of S , whereas with further increasing W_{CTAB} from 15 to 25 wt% n recovers similar values to that at $W_{\text{CTAB}} = 0$ with a slight reduction of S . From this result we can reasonably expect as follows. At $W_{\text{CTAB}} < 15$ wt% the film porosity is enhanced more by the decomposition of the larger amounts of CTAB. This possibly leads to the self-annihilation of *ortho*-positronium in the formed mesopore and/or positron annihilation with carbonaceous species, instead of oxygen groups, on the pore wall, accordingly, S is significantly increased [16, 17]. At $W_{\text{CTAB}} > 15$ wt% the reduction of the film porosity should lead to decreasing of S , however, the plots for films prepared with $W_{\text{CTAB}} = 20$ wt% and 25 wt% significantly deviate from the correlation by the data with $W_{\text{CTAB}} < 15$ wt%. This may be due to the positron annihilation with carbonaceous components effectively introduced into the intermolecular, subnanoscopic spaces, specifically on their surfaces, upon calcination, giving rise to a relatively high value of S with lower porosity. Indeed, by means of Fourier transform infrared

spectroscopy measurements we confirmed that small amounts of C-H groups still remain in the films even after the calcination.

4. Conclusion

Silica films have been prepared via the sol-gel process using TEOS and the cationic surfactant CTAB as the network skeleton precursor and the templating agent, respectively. Doppler broadening of positron annihilation radiation spectroscopy based on a slow positron beam and ellipsometry were used to investigate the synthesized silica films. The results indicated the following: (1) the nanoscopic pore structures of the silica films are altered by varying the CTAB weight ratio, (2) the positron annihilation sites of the as-deposited films are influenced by the CTAB weight ratio, leading to a change in the film composition, and (3) the nanoscopic pore structure change for the calcined films occurs around 15 wt% of the CTAB weight ratio.

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