Identification of pore size in porous SiO_2 thin film by positron annihilation*

ZHANG Zhe(张哲)[1,2] QIN Xiu-Bo(秦秀波)[1,2] WANG Dan-Ni(王丹妮)[1,2] YU Run-Sheng (于润升)[1]
WANG Qiao-Zhan(王巧占)[1] MA Yan-Yun(马雁云)[3] WANG Bao-Yi(王宝义)[1;1)]

1 (Key Laboratory of Nuclear Analysis Techniques, Institute of High Energy Physics, CAS, Beijing 100049, China)
2 (Graduate University of Chinese Academy of Sciences, Beijing 100049, China)
3 (China Institute of Atomic Energy, Beijing 102413, China)

Abstract Positron annihilation lifetime and Doppler broadening of annihilation line techniques have been used to obtain information about the small pore structure and size of porous SiO_2 thin film produced by sputtered Al-Si thin film and etched Al-Si thin film. The film is prepared by an Al/Si 75:25 at.-% (Al75Si25) target with the radiofrequency (RF) power of 66 W at room temperature. A 5 wt.-% phosphoric acid solution is used to etch the Al cylinders. All the Al cylinders dissolved in the solution after 15 h at room temperature, and the sample is subsequently rinsed in pure water. In this way, the porous SiO_2 on the Si substrate is produced. From our results, the values of all lifetime components in the spectra of Al-Si thin film are less than 1 ns, but the value of one of the lifetime components in the spectra of porous SiO_2 thin film is τ = 7.80 ns. With these values of lifetime, RTE (Rectangular Pore Extension) model has been used to analyze the pore size.

Key words Al-Si thin film, porous SiO_2 thin film, positron annihilation

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1 Introduction

Many groups focus their research interests on porous materials because of their unique properties and application potential. Growth of nano wires using the porous materials as the template is an important application field. Among conventional methods, anodic alumina is widely used because of its chemical and mechanical stability and the possibility of producing ideally ordered pore configurations[1, 2]. But the cylindrical pores on an anodic alumina are perpendicular to the substrate and parallel to each other with pore diameters ranging between 10 and 500 nm and pore densities from 10^{12} to 10^{15} pores m^{-2}. The pores with diameters less than 10 nm and pore densities greater than 10^{16} pores m^{-2} are strongly desired in order to improve the characteristics of ultra-high density perpendicular magnetic recording media and the parameter ZT (the thermoelectric figure of merit—a function of the Seebeck coefficient or the thermal electric power and of the electrical and thermal conductivities) in thermoelectric devices[3].

Positron Annihilation Technique (PAT) is an important way to research porous materials, because it is sensitive to small pore in the range 0.2—2 nm[4]. Recently, PAT has been successfully used to research the porous structure of different materials such as polymers[5] and sol-gels[6]. The most important aspect of applying PAT to nanoporous materials begins with the natural formation of positronium (Ps) when positrons are injected into a material. This method is based on the behavior of ortho-positronium (o-Ps), which is the triplet bound state of positron and electron, in materials. There is a relationship between the lifetime τ of o-Ps and the hole radius R. The specific form of this relationship depends on the theoretical model. Recently Gidley et al.[7] proposed rectangular pore extension of Tao-Eldrup model[8, 9] for the Ps

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1) Corresponding author. E-mail: wangboy@ihep.ac.cn

decay rate, $\lambda = 1/\tau$. This model provides the temperature and pore size dependence of the Ps lifetime for pore sizes in the range 0.1—600 nm.

Our goal is to find out the porous structure and pore sizes within the porous SiO_2 thin film produced by sputtered Al-Si thin film and etched Al-Si thin film.

2 Experiment

2.1 Samples

Standard N-type silicon (Si) was selected as the substrate of the thin film in the experiment. The 15 mm×15 mm substrate was cleaned with absolute alcohol in the ultrasonic cleaner for 15 min. The film was prepared by an Al/Si 75:25 at.-% (Al75Si25) target with the radiofrequency (RF) power of 66 W at room temperature. The air pressure for reaction was 0.2 Pa, and the deposition time was controlled to prepare the film with a thickness of about 100 nm.

A 5 wt.-% phosphoric acid solution was used to etch the Al cylinders. All the Al cylinders dissolved in the solution after 15 h at room temperature, and the sample was subsequently rinsed in pure water. In this way, the porous SiO_2 on the Si substrate was produced[10].

2.2 Positron annihilation measurement

The Doppler broadening of the 511 keV annihilation γ-line was measured using a high purity germanium detector of energy resolution 1.2 keV at the 514 keV γ-line of ^{85}Sr. Each spectrum including 500000 counts was collected for about 1000 s. Forty-five spectra have been recorded for each sample.

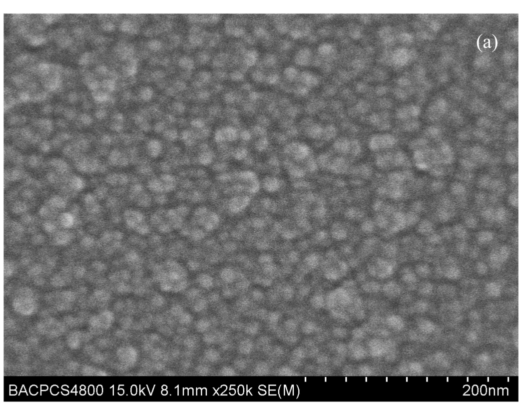
The annihilation γ-line was characterized with usual shape S parameter. The S- parameter is defined as a ratio of the counts in the annihilation line central region (0< $|\Delta E|$ <0.7 keV) and the total counts $N_{\rm total}$ in the line.

The lifetime spectrometer consisted of three parts—a reflection type chopper, a prebuncher and a buncher. The frequencies of the chopper and the prebuncher were both 37.5 MHz, and that of the buncher was 150 MHz. The positron energy before the chopper was 79 eV, therefore DC 90 V was used as the chopping- voltage, and a negative pulse whose amplitude is 20 V as the chopping-signal. After chopping the beam of positron, the beam has been changed into a pulse one with its time range about 3 ns. Because the pulse width after chopper was too wide for the buncher, a prebuncher was used to compress the pulse width further. As this method, the range time of the positron beam could be changed into about 1 ns. The signal of prebuncher and the gamma rays into which positrons annihilated were used to stop the timing block and start the timing block respectively. The time resolution of this lifetime spectrometer system is about 295 ps with a peak-to-background ratio of about 600:1. The channel width of multi-channel analyzer was Δ = 0.0256 ns/channel. Each lifetime spectrum contained 10^6 counts. The experimental spectra were compared and analyzed by the software LIFETIME 9.

3 Results and discussion

3.1 Results from scanning electron microscope (SEM)

The top-surface and cross-sectional Scanning Electron Microscopy (SEM) images of Al-Si thin film are shown in Fig. 1(a) and (b) respectively.



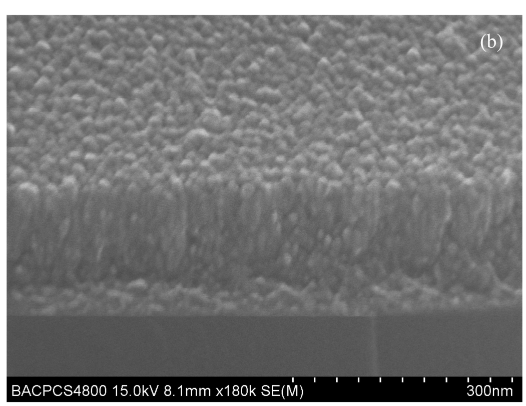


Fig. 1. (a) Top-surface SEM image obtained from the Al-Si film prepared by an Al/Si 75:25 at.-% (Al75Si25) target at room temperature; (b) Cross-sectional SEM image of the Al-Si film.

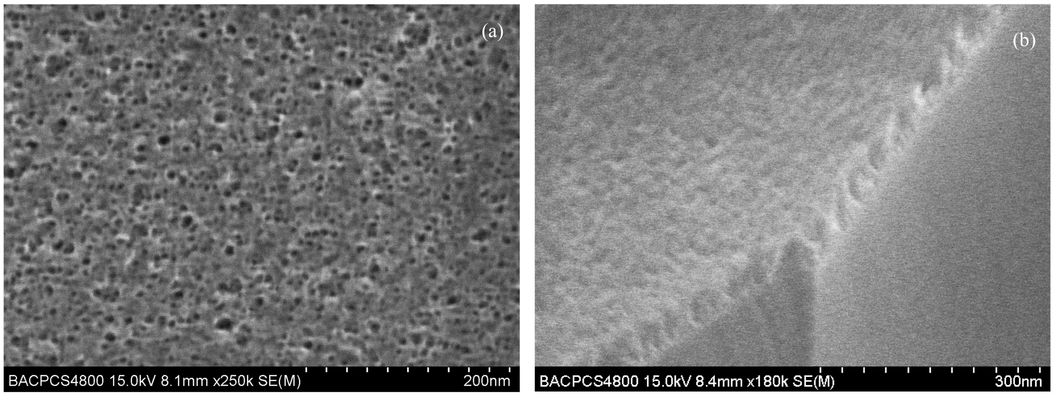


Fig. 2. (a) Top-surface SEM image of the nanoporous thin film; (b) Cross-sectional SEM image of the nanoporous thin film.

The difference in chemical composition and nanometer-scale phase separation of the eutectic Al-Si system are clearly shown in Fig. 1(a) and (b). Fig. 1(a) indicates that one component forms cylinders with a nanometer-scale diameter, and the other component forms a matrix surrounding the cylinders. The cylinders shown in Fig. 1(b) are perpendicular to the substrate and parallel to each other. Fig. 1 indicates that the average diameter of cylinders is less than 10 nm.

The top-surface and cross-sectional scanning electron microscopy (SEM) images of nanoporous thin film are shown in Fig. 2(a) and (b) respectively.

Cylindrical pores, which are perpendicular to the substrate and parallel to each other, can be seen in Fig. 2(b) and the depth of the cylindrical pores is approximately 60 nm. The average diameter, estimated from the SEM images, is less than 4 nm. These values are consistent with those obtained for the Al cylinders shown in Fig. 1.

3.2 Doppler broadening of gamma line

The line shapes are characterized by the S-parameters. The relationship between S-parameters and varied implanting energy and the difference of that between different samples are shown in Fig. 3.

The three curves have the same trend and they are very near to each other from 15 keV to 25 keV, and the solid cube is for the sample — Standard Si, therefore the status of spectrometer was stable and the spectra were reliable. To both the Al-Si thin film and the porous SiO_2 thin film, the S-E curves with more than 15 keV positron implanting energy could only express the information from the substrates.

Comparing the solid point curve and the hollow triangle curve, we can see clearly that the peak of the hollow triangle curve is on the left to the peak of the solid point curve, and the former corresponds to lower implanting energy. It means that the SiO_2 thin film is thinner than the Al-Si thin film. The conclusion corresponds to the images of SEM shown in Fig. 1(b) and Fig. 2(b).

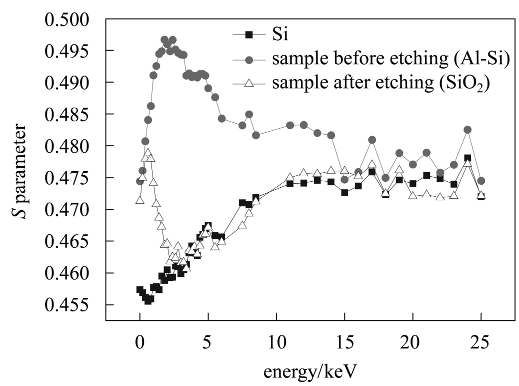


Fig. 3. S-E curves of different samples (the solid cube is for the sample — Standard Si; the solid point is for the Al-Si thin film; and the hollow triangle is for the etched Al-Si thin film — Porous SiO_2 thin film).

The S parameter of Al-Si thin film is obviously larger than that of the Si substrate because of the existence of the aluminum whose S parameter is much greater than that of the silicon, also the defects in aluminum and amorphous silicon of the Al-Si thin film produced by RF sputtering system have some contribution to it. After etching, there is no aluminum left and the silicon is oxidized, so the S parameter decreased obviously. But countless pores appeared in thin film after being etched, seen from Fig. 2(a), so positronium exists in the porous SiO_2. Hence the S-E curve is still higher than that of standard Si[11, 12].

The trend of the curve—Al-Si thin film falls from 2.2 keV to 15 keV. The trend is different from that of the other two S-E curves. The S-parameters of Al-Si thin film are great, and what positron annihilation can express is the average depth-dependent information, therefore the S-parameters are still much greater than those of Si substrate after 2.2 keV, although the positrons with implanting energy more than 2.2 keV have been implanted into the Si substrate.

The trend of S-E curve-Al-Si thin film rises from 0 keV to 2.2 keV at first, then falls from 2.2 keV to 15 keV and flattens after 15 keV; The trend of S-E curve — porous SiO_2 thin film rises from 0 keV to 0.6 keV at first, then falls from 0.6 keV to 2.2 keV, and then rises to 15 keV and flattens after 15 keV. So 2.2 keV, is an important implanting energy for us to analyze the characteristic of the thin film.

3.3 Positron lifetime measurements

The comparison of lifetime spectra between Al-Si thin film and porous SiO_2 thin film is shown in Fig. 4. The implanting energy of positrons is 2.2 keV.

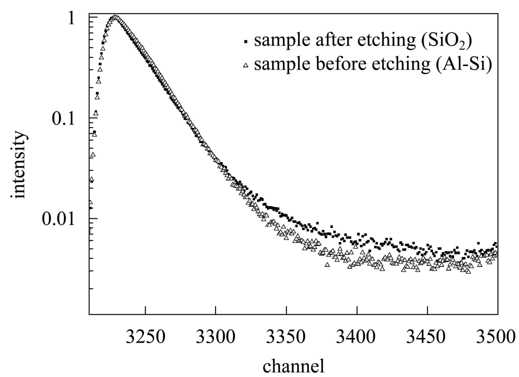


Fig. 4. Lifetime spectra (the hollow triangle is for the Al-Si thin film and the solid cube is for the etched Al-Si thin film — porous SiO_2 thin film).

There is one more longevity component in the positron lifetime spectrum of porous SiO_2 thin film. We can see clearly from Fig. 1, that the Al-Si thin film is very compact, and the main components of Al-Si thin film are metallic elements — Al and semiconductor — Si, therefore much free positron annihilation occurs in the Al-Si thin film. Hence the positron lifetime is very short in it. We can also see clearly from Fig. 2 that there are many pores in the SiO_2 thin film, where o-Ps is localized before annihilation, hence longevity component appears.

The values of lifetime were calculated by software LIFETIME 9. The evaluation was done on the basis of the Gidley et al. model[13]. This model for the ground state of Ps (0 K) with an appropriate chosen value of electron layer thickness δ[13] is indistinguishable from the often used Tao-Eldrup model[8, 9]. Gidley et al. proposed that the positronium free path between collisions, l, was used for characterization of pore sizes. In this sense, a cubic pore with a hard wall of side a is equivalent to a spherical one with hard wall diameter $2R = a$. From our results, all lifetime components in spectrum of the Al-Si thin film are less than 1 ns, but one of the lifetime components in spectrum of the porous SiO_2 thin film is $\tau = 7.80$ ns, which is caused by o-Ps annihilation. According to Formula (1)[7] and Fig. 5[7], $\tau = 7.80$ ns corresponds to the pore size 1.8 nm with compact three-dimensional (3D) cubic pores model.

$$\lambda(T) = \lambda_{\mathrm{A}} - \frac{\lambda_{\mathrm{S}} - \lambda_{\mathrm{T}}}{4} F(a,\delta,T)F(b,\delta,T)F(c,\delta,T) \quad (1)$$

where

$$F(x,\delta,T) = 1 - \frac{2\delta}{x} + \frac{\sum\limits_{i=1}^{\infty} \frac{1}{\mathrm{i}\pi} \sin\left(\frac{2\mathrm{i}\pi\delta}{x}\right) \mathrm{e}^{-\beta i^2/x^2 kT}}{\sum\limits_{i=1}^{\infty} \mathrm{e}^{-\beta i^2/x^2 kT}}, \quad (2)$$

$$\beta = h^2/16m = 0.188 \text{ eV} \cdot \text{nm}^2 . \quad (3)$$

Here, a, b, and c are three sides of the rectangular pore in the direction x, y, and z. T is the absolute temperature of the Ps and m is the electron mass (the Ps mass is $2m$). δ is a free parameter, which is analogous to ΔR in the TE model.

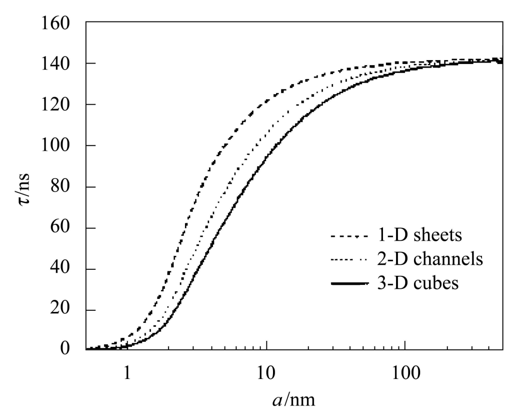


Fig. 5. Ps lifetime calculated with the RTE (Rectangular Pore Extension) model vs pore size for three pore dimensionalities.

It might seem that the size calculated by positron annihilation lifetime spectrum is little less than what SEM indicated. But because the film is very thin, some positrons with implanting energy 2.2 keV have diffused into the Si substrate. As the lifetime of positron in Si substrate ($\tau = 0.243$ ns[14]) is much shorter than that in SiO_2 thin film, the value of positron lifetime in such thin film is little smaller than that in the pure porous SiO_2 cubic samples. In addition, different from SEM, PAT expresses the internal and average information of pores in the thin film, hence there is no contradiction.

4 Conclusion

It is observed that small size pores exist in the porous SiO_2 thin film produced by sputtered Al-Si thin film and etched Al-Si thin film. O-Ps annihilation in these small pores causes longevity component in spectrum of the porous SiO_2 thin film. The average value of pores size has been calculated by positron annihilation spectra, the results of which correspond to the images of SEM.

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