Evaluation of the diffusion barrier continuity on porous low-*k* films using positronium time of flight spectroscopy

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A depth-profiled positronium time of flight experiment was performed to investigate a diffusion barrier on a spin-on low dielectric constant (low-*k*) porous silica film. We studied a capping layer of 50 nm SiO_2, which was optimized for 3-keV positron (e^+) penetration through the capping and stopping in the porous layer. Maximum positronium intensity was found with a positron implantation energy of 3 keV that reflects the sample structure and is consistent with an open pore fraction $\eta < 2 \times 10^{-4}$ of the capping layer.

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I. INTRODUCTION

Bose-Einstein condensation (BEC) effects of many positronium atoms (Ps; the electron bound state with its antiparticle, the positron) would be interesting to observe in a material in which there are a great many interconnected pores, such that Ps can diffuse over long distances (on the order of microns[1]). If we can confine the Ps in a very thin porous film by preventing escaping into vacuum, a dense Ps gas can be more easily produced. For the purpose of the production of a dense Ps gas, a diffusion barrier must be continuous and very thin, and the tradeoff between continuity and thickness of the barrier affects the Ps gas density in the porous layer underneath. It is therefore important to establish a method to characterize such film properties. Positronium annihilation lifetime spectroscopy (PALS) has been applied to determine whether a diffusion barrier on an open-pored low-*k* film is continuous.[2–4] From such measurements one can infer whether or not Cu atoms (or ions) can penetrate into the dielectric and degrade the electrical properties. A Ta barrier only 5 nm thick is not completely effective in preventing Ps diffusion out of a low-*k* film.[5] On the other hand, a capping layer of 80 nm silica effectively blocks the diffusion of Ps out of a low-*k* film.[2] Recently, depth-profiled positronium lifetime spectroscopy is used to probe the pore characteristics in porous, low-*k* silica films.[1] An alternative or complementary method measuring permeability of such a diffusion barrier would be useful.

In the past several years, on the other hand, positronium time of flight spectroscopy (Ps-TOF) has become an established technique for probing Ps emission from surface or Ps diffusion in matter.[6,7] Ps-TOF spectroscopy might be a complementary method to obtain further understanding by separating decays in the porous matrix from decays attributed to Ps escape into vacuum.[8] In this work, we used the Ps-TOF spectrometer developed at Slow Positron Facility, High Energy Accelerator Organization (KEK-SPF) to investigate the interrelated effects of the implantation positron energy on the Ps-TOF spectrum in a capped low-k film. At KEK-SPF, the positron beam is completely depolarized. If the positrons from which the positronium is formed are not perfectly spin polarized, there could be spin exchanging triplet positronium-triplet positronium collisions of dense Ps in the porous medium that would increase the average annihilation rate.[9] Our goal is to understand the structural effects of the sample that will enable us to optimize the barrier thickness as required for eventual measurements of spin exchange cross section and possibly the Bose-Einstein condensation of Ps atoms.

II. EXPERIMENT

The pore interconnectivity of the diffusion barrier was examined by Ps-TOF spectroscopy at room temperature. The present experiment was performed at Slow Positron Facility, High Energy Accelerator Research Organization.[10] The facility consists of a 50 MeV linac, an assembly of slow positron generator, a slow positron transport line and an experimental station for positron time of flight (Ps-TOF) spectroscopy. The experimental setup is shown in Fig. 1. The principle of the Ps-TOF method has been previously discussed,[11] and is only briefly introduced here. In the TOF measurement, the sample is bombarded with a slow positron beam. The time interval between the linac signal and the detection of the gamma ray from the emitted o-Ps self annihilation is measured to obtain the energy distribution of the emitted Ps. In the present experiment, the lead collimator was adjusted to effectively reduce the annihilation gamma rays from the sample region to detect only the decay events from self-annihilation of Ps in the view of the plastic scintillator through a 4.5-mm lead slit. And at the same time, however, the counter also detects a part of the decay events after passing through the lead shield from the sample region (the decay events from the sample are not totally shielded by the lead blocks). If the diffusion barrier is not impervious, Ps can diffuse out of the film and it can be easily detected by the Ps-TOF spectrometer.

We performed a Ps-TOF measurement experiment at the downstream end of the beam line. The pulse heights and

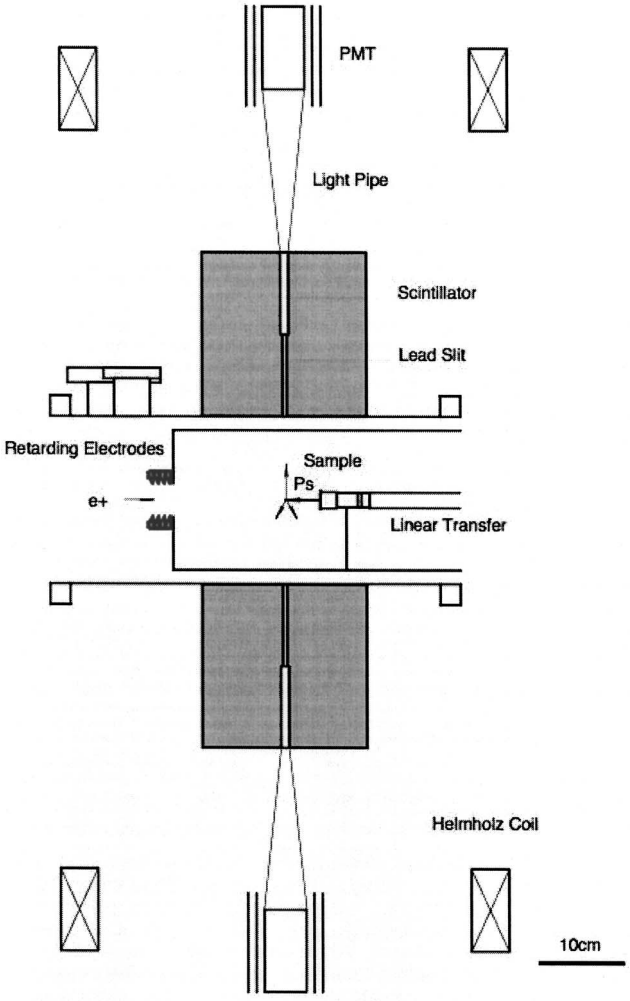


FIG. 1. Experimental setup of Ps-TOF spectroscopy.

annihilation gamma rays and the time when annihilation events occur are recorded by a digital oscilloscope (LeCroy Wavepro 960). A pulse fed from the linac triggered the start. The scintillator was 600 mm in diameter and 10 mm in thickness and was coupled on opposite sides to a photomultiplier tube (HAMAMATSU H 1949) through a Lucite light guide. The vacuum level in the sample chamber was kept to be $10^{-8}-10^{-9}$ torr throughout the present experiment period. The sample bias can be varied in the range of 0–9 keV by changing the electric potential at the sample by using a retarding element (RET). The energy of the slow positron beam is 5 keV. The beam size was 1 cm in diameter. The beam intensity and the pulse width were 2×10^5 positrons/pulse and 22 ns, respectively.

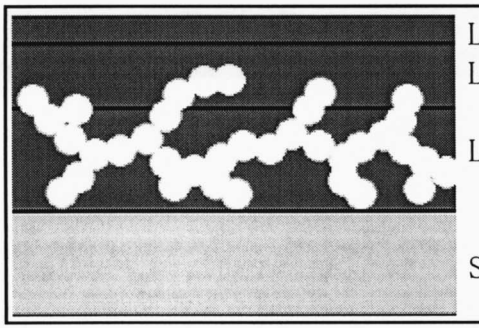
The porous silica film sample was prepared under collaboration with Yan's laboratory, Bourns College of Engineering, University of California, Riverside. The present films were prepared by a spin-on process on Si wafers to form a porous film and a capping nonporous layer. The thickness of the porous layer was optimized for 3-keV positron (e^+) penetration through the capping and stopping in the porous layer.[13] The thickness and the porosity of each layer were measured by a spectroscopic wavelength ellipsometer (Jobin Yvon UVISEL Spectroscopic Phase Modulated Ellipsometer), and the pore diameter was measured by a nitrogen gas absorption/desorption method. The obtained values are shown in Table I. The layer on top (layer 1) is pure amorphous silica without any zeolite. The other two layers (layers 2 and 3) are composed of both zeolite nano crystals and amorphous silica. The thickness of the nonporous layer is ~50 nm. The porous layer with a thickness of ~220 nm has a gradual porosity distribution in layer 2, ranging from 50.6% to 4.6% towards the nonporous layer, having the average porosity of 40.3%.

Nitrogen adsorption-desorption measurements were conducted on powder samples by a Micromeritics ASAP 2010 analyzer. The observed pore size distribution was bimodal, which comprises the intrinsic zeolite microporosity of 5.5 angstrom in diameter and interparticle mesoporosity of 4 nm in diameter. The *o*-Ps lifetime of 50–60 ns, as obtained by assuming the rigid spherical potential model[12] is long enough to see the effect in a pore with a size of 4 nm in diameter. The sample with a size of 23 nm $\times$ 23 nm was attached to the aluminum sample holder and installed in the Ps-TOF spectrometer. The positrons were implanted to the porous layer through the nonporous layer.

III. RESULTS AND DISCUSSION

Figure 2 shows a positron implantation energy dependence of the Ps-TOF spectrum for various positron impact energies, ranging from 0.5 keV to 3.0 keV. In the present experiment, the difference between the positron transport energy (5 keV) and the voltage at the sample was employed as the positron energy at the sample. All the data were normal-

TABLE I. Sample properties as obtained from the ellipsometer and nitrogen gas absorption-desorption measurements.



	Thickness (Å)	Porosity (%)	Pore size (Å)
Layer 1	523	4.6	40±10, 5.0
Layer 2	830	40.3	40±10, 5.0
Layer 3	1448	50.6	40±10, 5.0

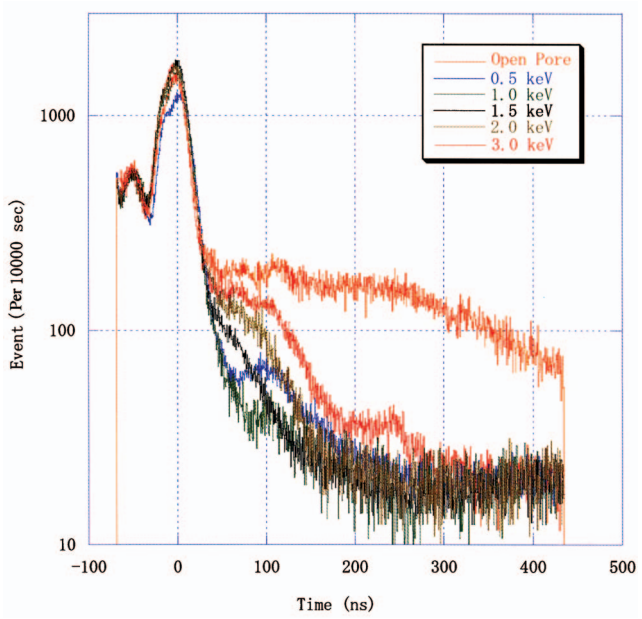


FIG. 2. (Color) Obtained Ps-TOF spectrum with different positron implantation energies, ranging from 0.5 keV to 3.0 keV. The distance between the sample and the detector slit is 45 mm. The Ps yield from an open pored low-k film with a positron implantation energy of 3.0 keV is also shown. The zero of time was fixed at the prompt peak. The width of the peak is due to the linac pulse width. The counts for $t<0$ are associated with gamma rays and neutrons from the bremsstrahlung pair production target.

ized to the measurement time (10 000 sec). The prompt peak in Fig. 2 is a convolution of fast Ps decay events, which does not provide information about the nanoporous structure in the sample and neglected in the following discussion. The zero of time was fixed at the prompt peak. The width of the peak is due to the linac pulse width. The counts for $t<0$ are associated with gamma rays and neutrons from the bremsstrahlung pair production target. The Ps yield from an open pored low-k film with a positron implantation energy of 3.0 keV is also shown. The open pored low-k film was produced with the same procedure.

We now construct a picture of the positronium in our porous structure in order to interpret our data and arrive at an estimate for the fractional open area of its capping layer. Let the porous material have a thickness w and the thickness of the capping layer be y. Our picture of the various layers is as follows.

(1) When the positrons are implanted into the middle of the capping layer using an implantation energy of 1 keV, they find themselves in an amorphous silica layer that forms positronium efficiently. However, the lifetime of the positronium will be under 1 ns and the Ps diffusion length will be very short. A small amount of Ps will diffuse to the surface and will be emitted into the vacuum with an energy of about 3 eV characteristic of the Ps negative affinity for amorphous silica. This Ps will be emitted essentially instantaneously compared to the relevant times of flight which are about 100 ns, thus leading to the small delayed peak at the position of the vertical bar in Fig. 2.

(2) Positrons are implanted into the middle of the porous layer by giving them about 3 keV of implantation energy. The porous layer is about $w=200$ nm in thickness and comprises a network of interconnected pores with characteristic dimensions of about 4 nm.

(a) We assume the a-silica cap layer is almost impervious so that the Ps leakage rate out of the porous layer is small compared to its decay rate in the porous layer.

(b) The Ps diffusion coefficient D is such that w^2/D is much less than the time of flight of ~ 100 ns so that the Ps density is nearly constant throughout the porous layer. We can easily see that this is so because the diffusion coefficient is roughly the pore size times the mean thermal velocity or $D \approx 4\ \text{nm} \times 10^7\ \text{cm/s} = 4\ \text{cm}^2\ \text{s}^{-1}$. Thus $w^2/D \approx (200\ \text{nm})^2/4\ \text{cm}^2\ \text{s}^{-1} = 10^{-10}\ \text{s} \ll 100$ ns.

(c) It is thus clear that the rate of Ps leaking out of the porous region is the rate of an ideal gas hitting the capping layer times the fractional open area η of the capping layer. Thus the leak rate per positronium atom is $\Gamma = 1/4 \nu \eta / w \approx 10^{11}\ \text{s}^{-1} \times \eta$. It follows that the long time part of the time of flight curve (in the steady state limit) will have a characteristic lifetime that is the same as the lifetime of the Ps in the porous layer. This turns out to be about 55 ns, which is just the same as found in previous measurements on porous materials of similar characteristics, i.e., having 4 nm pores.

(d) Our assumption that the porous layer is nearly impervious is consistent with the delayed 55 ns component seen in Fig. 2 for the 3 keV curve. It must therefore be that $\Gamma < (50\ \text{ns})^{-1} = 2 \times 10^7\ \text{s}^{-1}$. We therefore have an upper limit on the open area fraction:

$$\eta = \Gamma / 10^{11}\ \text{s}^{-1} < 2 \times 10^7\ \text{s}^{-1} / 10^{11}\ \text{s}^{-1} = 2 \times 10^{-4}. \quad (1)$$

(3) At very low energy, in this case 0.5 keV, the positron stop near the surface of the a-silica capping layer and one should observe the full 3 eV Ps emission energy as reported by Sferlazzo, Berko and Canter[14] and a small Ps time of flight peak due to the rather efficient Ps emission from the surface.

(4) At high energies, in this case 4 keV, the positrons are starting to reach the substrate from which no positronium is emitted. Thus the amount of positronium in the time of flight peak is reduced.

In conclusion, at 0.5 keV surface Ps escapes and gives us the small bump at about 100 ns time of flight as observed in Fig 2. At 1 keV the positrons are stopped in the a-silica from which little Ps escapes due to its short diffusion length and short lifetime. At 3 keV, Ps forms copiously in the porous layer, thermalizes and escapes through cracks or other gaps in the capping layer. Finally at 4 keV the delayed Ps time of flight bump is attenuated because positrons are being lost to the solid substrate. We note that the cracks in the capping layer do not themselves lead to significant Ps emission at 1 keV because the crack density is very low compared to the inverse of the positronium diffusion length which is rather short (~ 100 nm) in the cap layer.

In conclusion, a capped low-k film has been characterized by using a Ps-TOF spectrometer. The measurements are consistent with the Ps produced in a porous layer being confined to the porous layer because of the low porosity of the

capping layer. The methodology for producing a high density positronium gas in a thin low-k material has been established.

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