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Positronium time of flight measurements of an open-pored spin-on low-*k* mesoporous film

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Abstract

Depth-profiled positronium time of flight (Ps-TOF) was measured by implanting slow positron pulses at variable energies into an open-pored spin-on low-*k* mesoporous film with bimodal pore size distribution arising from zeolite micropores and interparticle mesopores. We estimate the energy of the positronium (Ps) that diffuses out of the target into the vacuum to investigate the slowing down of Ps by collisions with the walls of the micropores (0.5 nm in diameter) and mesopores (4 nm in diameter). The obtained Ps-TOF spectra showed that the temperature of the emitted Ps depends on the positron implantation depth, i.e., the number of collisions with the walls. The data indicate that the pore tortuosity is low in the present sample. However, the slowing down rate seems to increase when the Ps temperature is high. This is probably because when the Ps temperature is high, the Ps energy is higher than the Ps confinement energy for micropores (∼3 eV), and the apparent tortuosity increases because there are millions of micropores. The Ps formed in this film has to travel a long distance to escape from the same depth into the vacuum until it slows down below the confinement energy of the zeolite micropores.

1. Introduction

Submicron thin films of porous silica and organosilicates are vigorously being developed as low-dielectric (low-*k*), interlayer insulators for use in high-speed microelectronic devices [1]. The integration of copper with porous ultralow-*k* interlayer dielectrics (ILDs) is required to overcome the resistance–capacitance (RC) time delay of integrated circuits and crosstalk noise problems for future generation computer microprocessors [2–6]. However, Cu is known to have high diffusivity into most of the promising ILD materials, and the presence of Cu in

the pores of low-k materials results in serious device degradation and failure. The ultimate ultra low-k material has not yet been found. The race between spin-on and chemical vapour deposition (CVD) is still ongoing. Spin-on materials have an important advantage over CVD materials because they can introduce a high degree of porosity in the films, reaching k values of 2.0, whereas CVD materials have moderate k values (2.4–2.8). To understand the structural properties of the spin-on porous low-k films, the characterization of a route through an open channel to the surface is necessary. For the purpose of characterizing the shape of an open channel to the surface, it would be interesting to know the diffusion and slowing down behaviour of positronium (Ps) that can be produced in low dielectric constant (low-k) porous materials. In particular, finding out how spatial confinement and its arrangement affect the thermalization of the Ps gas would be interesting. Bose Einstein condensation (BEC) of positronium requires a source of cold Ps. Positronium time of flight (Ps-TOF) spectroscopy is a technique for measuring the energy of triplet positronium in flight and it has been used for studying Ps emission from the surface of various materials [7–17]. Positronium atoms formed in amorphous silica collide millions of times with pore walls before they escape from the sample by finding a route through an open channel to the surface. Ps-TOF spectroscopy may be a unique technique to offer direct information about the Ps atoms that diffuse out of a low-k thin film.

In mesoporous silica the internal free space between the silica nanograins is interconnected to the space outside the film. The positronium atoms therefore easily escape to the free space after a number of collisions with the pore walls. Thermodynamic properties of Ps in a wide variety of powder silica media have been extensively investigated. To date, measurements of the thermalizations in fumed silica of 95% and 87% porosity [12, 13], and in aerogel [13] have been reported. In 1989, Mills *et al* measured positronium thermalization in SiO_2 powder [12] by measuring the Ps time of flight. Subsequently, Nagashima *et al* [13] measured the thermalization of free positronium atoms in silica powders, an aerogel, and a gas with the angular correlation of annihilation radiation (ACAR). They reported the Ps average energy of 0.1 eV with a mean distance of 70 nm ($\varepsilon \sim 2$ K) between silica grains, where ε is the Ps confinement energy. Recently, Yu *et al* performed depth-profiled positronium time of flight measurements on porous low-k films and they found different Ps emission energies from different samples [14]. They explained the difference by pore tortuosity (α). The higher the pore tortuosity, the longer is the Ps travel distance for it to emerge from the same depth to the vacuum. More recently, Ito *et al* applied Ps time of flight spectroscopy to the characterization of different types of nanoclustering porous silica films with a particle diameter of 10–17 nm. They found that the sample porosity does not play an important role in the slowing down rate of Ps atoms. If the total porosities are the same the slowing down rates are also similar, but the Ps emission yield reflects a difference in pore interconnectivity [15].

The purpose of the present experiment is to investigate the mechanism for the thermalization of positronium in a spin-on low-k film having bimodal pore size distribution as a function of positron impact energy to find out how spatial confinement affects the thermalization of the positronium atoms. The present film has a large porosity of 73.2%, containing periodic zeolite micropores (0.5 nm in diameter) and interparticle worm-like mesopores (4.0 nm in diameter). We have implanted positrons into an open-pored spin-on low-k porous silica film and measured the escaping positronium velocities by time of flight (TOF). In this work, we used an intense pulsed slow positron beam and Ps-TOF spectrometer developed at the Slow Positron Facility, High Energy Accelerator Organization (KEK-SPF). The following sections will describe the apparatus, present the data, and discuss the results. All the measurements were performed at room temperature.

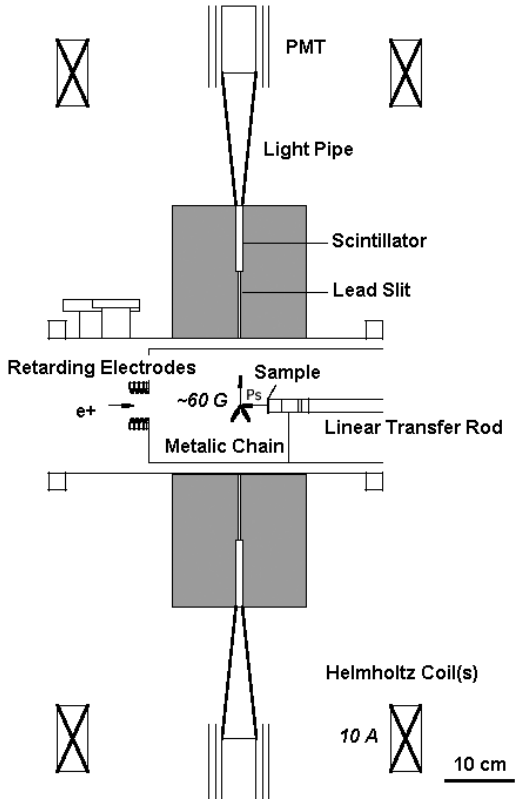


Figure 1. Experimental setup used in the present positronium time of flight measurement.

2. Experimental details

Our apparatus consists of a pulsed source of slow positrons, an open-pored spin-on low-k film at room temperature, a time of flight spectrometer for measuring Ps velocities, and associated electronics. The experiment was performed at the Slow Positron Facility, High Energy Accelerator Research Organization [18]. 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. Positrons are obtained from a bremsstrahlung pair production target. Figure 1 shows the experimental setup. A pair of Helmholtz coils applies a magnetic field B of $\sim$60 G at the sample position, which corresponds to 10 A of current in the coils. It produces a longitudinal laminar magnetic flows for the guidance of the slow positrons. The sample is moved by means of a linear transfer rod. The rod is contacted to the retarding electrodes via a metallic chain. 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. The pressure in the vacuum chamber during the measurements was 10^{-8}–10^{-9} Torr. A Pb shield having a 4.5 mm wide gap defines a spatial region for measuring the Ps-TOF. 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. We performed the Ps-TOF measurement experiment at the downstream end of the beam

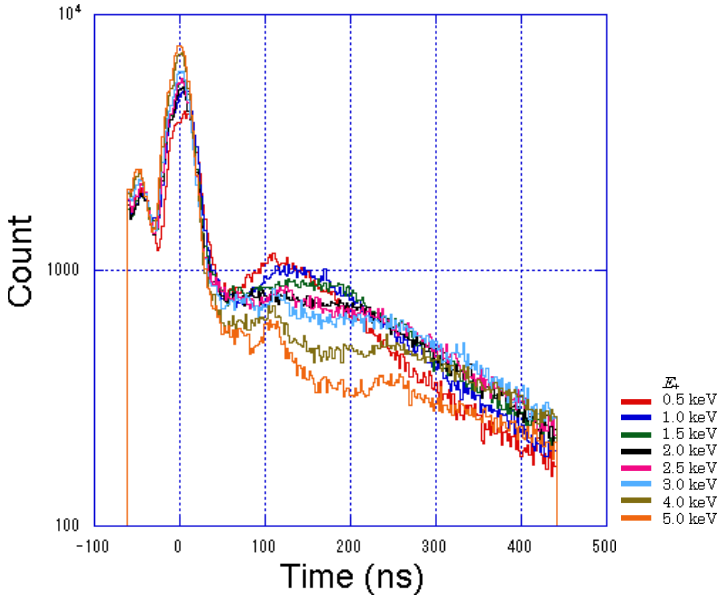
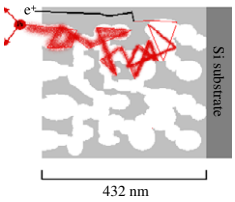


Figure 2. Ps-TOF time spectra with different positron implantation energies. The peaks at $t = 0$ are due to gamma rays which originate from prompt positron annihilation and scatter into the slits. The counts for $t < 0$ are associated with gamma rays and neutrons from the bremsstrahlung pair production target.

Table 1. Sample properties of the open-pored sample as obtained with the ellipsometer and nitrogen gas absorption/desorption measurements.



Sample thickness (nm)	431.7
Zeolite content (%)	38.3
Porosity in zeolite (%)	11.49
Porosity outside zeolite (%)	61.7
Total porosity (%)	73.19
Pore size (nm)	4, 0.5
Density thickness (g cm^{-2})	2.55×10^{-5}

line. The pulse heights and annihilation gamma rays and the time when annihilation events occur are recorded by a digital oscilloscope (LeCroy Wavepro 960). The digital oscilloscope is started by a pulse fed from the linac. The sample can be biased up to 9 keV for the purpose of decelerating the positrons into the low-k film target. 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 repetition rate of the pulses was 50 Hz. After the interaction of a positron with amorphous silica, the positron and spur electrons diffuse during slowing down to near thermal energy; then Ps formation might occur. From 10 to 20% of implanted positrons are emitted from the wall of the pore as positronium with an energy of ∼3 eV characteristic of the Ps negative affinity for amorphous silica. The positronium slows down further by colliding with the walls of the pores of the sample.

The positron target was an open-pored spin-on low-k film, consisting of zeolite nanocrystals. The porous silica film sample was prepared under collaboration with Yan's laboratory, Bourns College of Engineering, University of California, Riverside. A pure silica

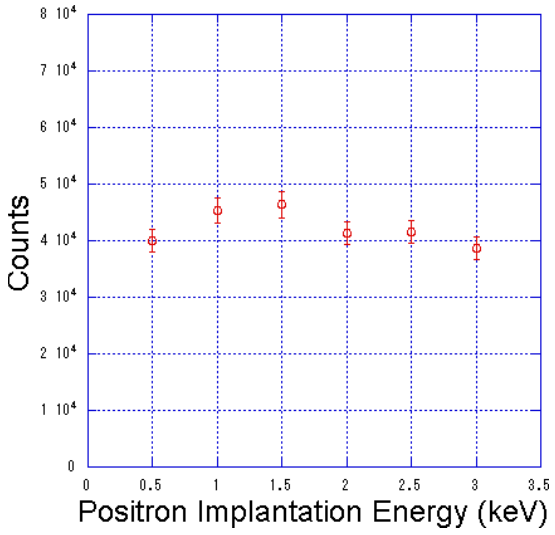


Figure 3. Ps yield integrated over the time region 100–500 ns.

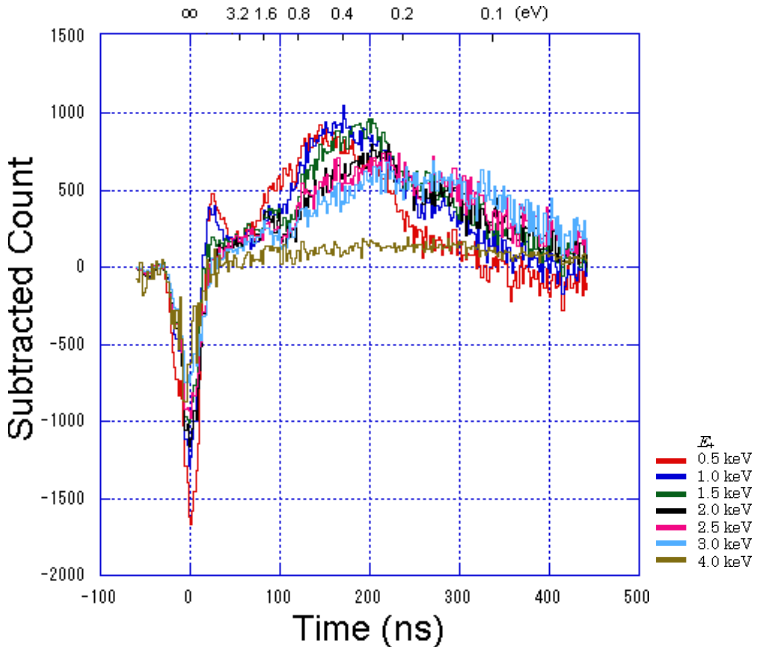


Figure 4. Positronium time of flight spectra subtracted by the background spectrum.

zeolite low-*k* thin film was prepared by spin-on processes as reported previously [19, 20]. 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 (Micromeritics ASAP 2010 analyser). The sample configuration is listed in table 1. The film is composed

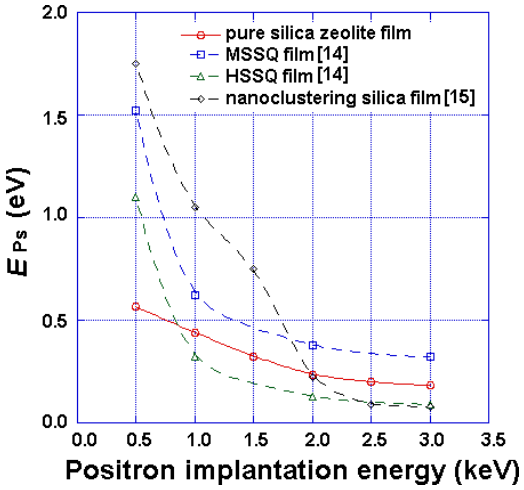


Figure 5. Average Ps energy plotted as a function of positron implantation energy. The Ps-TOF results for methyl-silsesquioxane (MSSQ) (□) and hydrogen-silsesquioxane (HSSQ) (△) spin-on-glass films [14], and nanoclustering silica porous films (◇) [15] are also plotted.

of both zeolite nanocrystals and amorphous silica. The observed pore size distribution was bimodal, comprising the intrinsic zeolite microporosity of 5.0 Å in diameter and interparticle mesoporosity of 4 nm in diameter. The sample, with a size of 20 × 20 mm^2, was attached to the aluminium sample holder and installed in the Ps-TOF spectrometer.

3. Results and discussion

Figure 2 shows the Ps-TOF spectra for different positron implantation energies as obtained with the open-pored spin-on low-k film at room temperature (300 K) and located a distance $z_0 = 45$ mm from the mid-point of the slit, where z_0 is the distance between the sample and the region of sight seen by the gamma detectors. The data taking time was fixed as 12 500 s (625 000 pulses) for all the positron implantation energies. The prompt peak in figure 2 is a convolution of fast Ps decay events that we attribute to scattered gamma rays from the prompt annihilation of the positron pulse in the target. It does not provide information about the Ps diffusion in the sample and is 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 major feature of the obtained Ps-TOF spectra is delayed components that are broadened, and their delay time becomes large as the positron implantation energy increases. The behaviour of these delayed components is interesting for our present study and will be discussed later. With a positron implantation energy E_+ of 5.0 keV, where most of the injected positron stops at the silicon substrate, there are small peaks at about 110 and 240 ns. These peaks are beam-associated constant backgrounds and are independent of positron implantation energies. The spectrum for $E_+ = 5.0$ keV is subtracted from other spectra as a background in the following discussion.

In figure 3, the numbers of the produced positronium integrated over the time region 100–500 ns are plotted versus the positron implantation energy. The amount of Ps emission at $E_+ = 3.0$ keV (the median implantation depth $\lambda \sim 400$ nm) does not differ from that at $E_+ = 0.5$ keV ($\lambda \sim 10$ nm). This result is in good agreement with our picture of the geometrical configuration of the present sample. In our sample, pores at all depths should be

interconnected to the surface and open to vacuum. Also, this depth-independent Ps emission yield indicates that the sample has low pore tortuosity (α) [15] as the ratio of the length between two arbitrary points in a long pore along the wall to the corresponding distance is a straight line. $\alpha = 1$ indicates a completely straight line. If the porous layer comprises a network of interconnected pores with characteristic dimensions of ∼4 nm, the Ps decay rate $\Gamma_{4\text{ nm}}$ in that the Ps density is nearly constant throughout the porous layer is small compared to Ps leakage rate out of the porous layer, i.e., $\Gamma_{4\text{ nm}} = \tau_{4\text{ nm}^{-1}} \sim 2 \times 10^7\text{ s}^{-1} \ll w^{-2}/D^{-1} \sim (400\text{ nm})^{-2}/(4\text{ nm} \times 10^7\text{ cm s}^{-1})^{-1} = 2.5 \times 10^9\text{ s}^{-1}$, where w is a thickness of the porous layer and D is the diffusion constant that is roughly the pore size times the mean thermal velocity. The Ps leakage rate out of a zeolite nanocrystal is much larger than that out of the porous layer, and is negligible.

The positronium time of flight spectra subtracted by the background spectrum are shown in figure 4 plotted on an energy scale given by $E_{\text{Ps}} = m_{\text{e}}z_0^2/t^2$. Figure 5 shows the average Ps energy calculated from these Ps-TOF spectra. The Ps-TOF results for methyl-silsesquioxane (MSSQ) and hydrogen-silsesquioxane (HSSQ) spin-on-glass films [14], and nanoclustering silica porous films [15] are also plotted in this figure. The initial emission energy of Ps from the silica matrix into the micropore is a few eV [7]. After emission of Ps into the zeolite micropores, some positronium atoms diffuse out from the micropores before annihilating, and are collected into mesopores. Because of the different Ps confinement energies they do not reenter into the micropores after the Ps thermalizes. Ps continuously loses energy by colliding with the pore wall until it is emitted from the film surface into vacuum. Comparing with the results for other samples, we find the cooling rate of the present sample is relatively small. This result indicates that this sample has low pore tortuosity (α), as expected from the behaviour of Ps emission. On the other hand, the Ps temperature at $E_+ = 0.5$ keV is almost the same as that from HSSQ sample and lower than that from other samples. This result indicates that α is higher at high Ps temperature and it decreases as the Ps thermalizes. It seems that there are two stages to cool down Ps in our sample—low and higher temperature regimes.

We construct a picture of the positronium in our porous structure in order to interpret our data and arrive at an estimate of the pore structure of the pure silica zeolite low-k thin film. This two-stage cooling behaviour is probably due to the bimodal structure of the sample. In the present sample, there are also a great many interconnected micropores with a size of 0.5 nm in diameter having a Ps confinement energy $\varepsilon_{\text{micro}} = \pi^2\hbar^2N^2/2m_{\text{Ps}}r_p^2 \sim 3$ eV (for $N = 1$), where $\varepsilon_{\text{micro}}$ is the confinement energy of zeolite micropores. When the Ps temperature is high ($E_{\text{Ps}} \gtrsim \varepsilon_{\text{micro}}$), the apparent tortuosity (α) becomes large, because at high temperature hardly any particles get stuck in the larger pores. There are millions of small pores. The Ps energy is higher than the Ps confinement energy for micropores. As positronium thermalizes ($E_{\text{Ps}} < \varepsilon_{\text{micro}}$), Ps atoms accumulate in the larger pores, and they do not reenter into the micropores. As a result, the Ps in this film does not have to travel a long distance per diffusion length. The apparent tortuosity decreases.

4. Conclusions

In conclusion, we performed Ps-TOF studies by implanting slow positron pulses at various energies into the target at room temperature. An open-pored pure silica zeolite low-k thin film was used to form Ps. The Ps-TOF data indicate that the pore tortuosity (α) is low in the present sample. However, α seems to increase when the Ps temperature is high. This is probably because when the Ps temperature is high, the positronium formed in this film has to travel a long distance to escape from the same depth into the vacuum because of the existence of numerous zeolite micropores in the sample.

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