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Positronium in low temperature mesoporous films

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We investigate the formation and annihilation of ortho-positronium atoms (o-Ps), the spins parallel electron (e^-)–positron (e^+) bound state, in mesoporous films from 400 to 50 K. At room temperature up to 20% of the implanted e^+ end up as o-Ps which self-annihilates (the bound e^+ and e^- annihilate); this is 50% of the formed o-Ps. One would expect self-annihilation to be suppressed at lower temperatures since, although o-Ps trapped in pores of diameter $\phi > 1$ nm, found in these films, is more likely to self-annihilate, several effects could decrease o-Ps formation and/or o-Ps trapping in a pore. Instead we find that at 50 K the amount of e^+ ending up as self-annihilating o-Ps is up to 19% greater than predicted if *no* suppressing effects played a role. Copious amounts of o-Ps atoms self-annihilate at 50 K (up to 30% of implanted e^+, 75% of formed o-Ps). This amount was found to increase even further down to 10 K making these films ideal substrates in which to confine large amounts of collisionally cooled, self-annihilating o-Ps for the eventual realization of an o-Ps Bose Einstein condensate (BEC).

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Introduction. Beam-based positron annihilation lifetime spectroscopy (PALS)[1–5] and 3γ positron annihilation spectroscopy[6–8] (PAS) are powerful methods to characterize the porosity properties of low-*k* mesoporous films developed to replace SiO_2 as the interlayer dielectric in future electronic devices. Both techniques employ ortho-positronium (o-Ps) as a probe to characterize size, concentration, and/or interconnectivity of nanometer-sized pores. These films are also useful for fundamental o-Ps investigations, e.g., they were employed in a study of the vacuum o-Ps lifetime, resolving a long-standing disagreement between experiment and theory.[9] Here, in a number of mesoporous films, we investigate the low temperature dependence of the fraction of e^+ ending up as confined, self-annihilating o-Ps. A material that exhibits the greatest such amount at low temperatures would be ideal for fundamental studies of large numbers of collisionally cooled o-Ps.[10]

Ps in mesoporous films. We study porous methyl silsesquioxane (MSSQ) films, 0.4- to 0.8-μm thick, prepared with 0, 10, 20, and 29 wt % of a volatile polymer (porogen). The films were spun on Si wafers from a mixture of methyl methacrylate-contained copolymer (porogen) and a MSSQ resin in solution, followed by curing to $\sim$520 K to vitrify the hybrid structure. They were then cured to 670 K to decompose and remove the porogen, introducing open volume additional to that found in films grown without porogen (0 wt %).[11] The films had porosities of 3.5%, 10.4%, 17.3%, and 23.5%, respectively.[5,6]

Implanted e^+ may form Ps inside the film or at the film surface. Ps forms as triplet (spins parallel) o-Ps or singlet (spins antiparallel) *para*-Ps (p-Ps), at a 3:1 ratio. Ps escaping the film (e.g., via free volume extending to the surface) self-annihilates (the bound e^+ and e^- annihilate) in a lifetime depending on the Ps spin state: o-Ps self-annihilates into three γ rays with a lifetime of 142 ns while p-Ps self-annihilates into two γ rays with a lifetime of 125 ps. The o-Ps, which does not escape, may, besides self-annihilating, "pickoff" annihilate where the bound e^+ annihilates via two γ rays with surrounding e^- of opposite spin. The pickoff annihilation rate depends on the surrounding e^- spatial density and can be far greater than the rate of self-annihilation; e.g., o-Ps annihilating in the smallest free volume established for these films exhibits a lifetime of only $\sim$3 ns (see Table I). The e^- spatial density seen by o-Ps depends on the open volume size and geometry as well as the composition of the open volume boundary. These factors in turn influence the o-Ps pickoff annihilation rate. The correlation between the o-Ps lifetime and open volume characteristics is at the heart of models relating the o-Ps lifetime to open volume size that are used to characterize film porosity.

Table I shows the lifetimes and corresponding intensities of o-Ps confined within the films measured at room temperature with beam-based PALS (Ref. 5) at 2-keV e^+ implantation energy. The 29 wt % sample exhibited an additional o-Ps lifetime component due to escaping o-Ps, not shown in Table I. The open volumes were assumed to be spherical pores and their corresponding diameters were deduced from an o-Ps lifetime–pore-size correlation model.[3]

TABLE I. o-Ps lifetime components for the films investigated here. ρ is density, τ lifetime, I intensity, and d the fitted pore diameter.

Porogen	0 wt %	10 wt%	20 wt %	29 wt %
ρ (g/cm^3)	1.26	1.13	1.01	0.89
τ_{I} (ns)	3.4	2.7	3.1	3.6
I_{I} (%)	26.2	6.3	6.0	2.4
d_{I} (nm)	1.2	1.2	1.2	1.2
τ_{II} (ns)	6.1	7.2	15.4	13.4
I_{II} (%)	16.1	7.2	3.8	3.2
d_{II} (nm)	1.5	1.6	2.0	1.9
τ_{III} (ns)	N/A	17.2	31.1	37.6
I_{III} (%)	N/A	26.1	30.1	29.9
d_{III} (nm)	N/A	2.1	2.8	3.2

Experimental. We investigate o-Ps self-annihilation via beam-based 3γ PAS, which measures the $3\gamma/2\gamma$ ratio (the ratio of o-Ps 3γ self-annihilation to all other 2γ annihilation processes) as a function of e^+ implantation energy from 50 to 400 K. The $3\gamma/2\gamma$ ratio is proportional to the amount of implanted e^+ ending up as self-annihilating o-Ps. Self-annihilation can also be measured with PALS (Refs. 2 and 3) since PALS and 3γ PAS are related: The mean lifetime for a material is $\tau_{mean}=\Sigma_i I_i\tau_i$, where τ_i is the ith lifetime component and I_i its intensity. The o-Ps mean lifetime, $\tau_{mean}^{o\text{-}Ps}=\Sigma_i I_i^{o\text{-}Ps}\tau_i^{o\text{-}Ps}$, considers *all* the o-Ps components. In materials that form significant amounts of Ps, such as the ones studied here, the $3\gamma/2\gamma$ ratio is proportional to τ_{mean} and $\tau_{mean}^{o\text{-}Ps}$.[12]

We prefer 3γ PAS over PALS for several reasons: (1) PALS measurements at each e^+ implantation energy take several hours and up to six lifetime components ranging from 125 ps to 140 ns need to be separated reliably. With 3γ PAS the entire experiment over *all* implantation energies is carried out in a *single* 2.5 h cooling run. (2) The long PALS measurement times mean substantial residual gas contamination at low temperatures. (3) PALS suffers from systematics due to different detection efficiencies for 3γ and 2γ decay. The samples were mounted on a closed cycle He cryostat and cooled to <50 K. The cold finger was surrounded by a 5.7-cm diam Al radiation shield mounted on the 80-K stage of the cryostat. The samples were heated to 400 K for ~ 10 h to remove absorbed water and at $\sim 5\times 10^{-9}$ Torr base pressure cooled to 50 K within ~ 2.5 h. Less than a few monolayers of water form during a single cooling cycle. Cooling and heating runs were reproducible and showed no evidence for e^+ irradiation effects[13,14] or chemical changes at the pore surface.[15] A magnetically guided, variable energy e^+ beam[16] of ~ 5 mm diam and 1×10^5 e^+/s rate profiled the film as a function of implantation depth. The mean implantation depth (z) is related to the implantation energy (in keV) by $z=(40/\rho)\,E^{1.6}$ where z is in nanometers and ρ, the sample density in g/cm^3. At each selected energy, a γ spectrum with 5×10^5 counts was acquired with a HpGe detector at right angles to the incoming beam. The $3\gamma/2\gamma$ ratio was calculated as[17] $3\gamma/2\gamma=(T-P)/P-C$ where T is the total spectrum counts, P the number of integrated counts in the photopeak region (511 ± 9 keV), and C the ratio for no Ps, as found in Si. A unity $3\gamma/2\gamma$ ratio corresponds to $\sim 30\%$ of the implanted e^+ forming o-Ps, which self-annihilates.

Results and discussion. Figure 1 shows the $3\gamma/2\gamma$ ratio vs temperature for the 20 wt % sample at selected z. Since we are interested in o-Ps confined within the films we need to find z beyond which o-Ps no longer escapes into vacuum. This can be determined in two ways: (a) Room temperature PALS observed no Ps escape at 2-keV implantation energy ($z=118$ nm for the 20 wt % sample) for samples up to 20 wt %.[5] This may be an overestimate since no implantation energy <2 keV was considered. (b) By plotting the $3\gamma/2\gamma$ ratio vs z we can determine z beyond which o-Ps no longer escapes.[6] Figure 2 shows such a plot for the 20-wt % sample obtained by interpolating the data in Fig. 1 at selected temperatures. The $3\gamma/2\gamma$ ratio maximum at 400 and 200 K is explained in terms of more Ps forming with increasing implantation energy (Spur model).[7,17,18] The decrease for $z>7$ nm is due to more o-Ps pickoff annihilating because it is confined in pores not interconnected to the surface and/or because it has to undergo more collisions to reach the surface via interconnected pores. Ps no longer is emitted at z where the $3\gamma/2\gamma$ ratio remains constant.

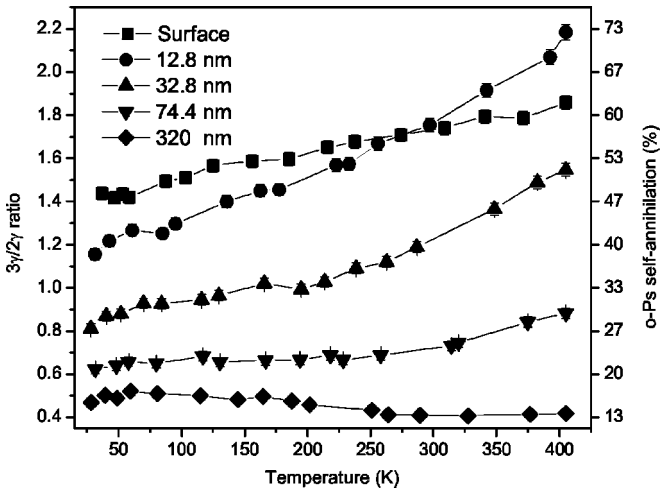

FIG. 1. $3\gamma/2\gamma$ ratio vs temperature of the 20 wt % sample. The lines are guides to the eye.

Figure 3 shows the temperature dependence for o-Ps confined within the samples obtained by fitting with VEPFIT (Ref. 19) the $3\gamma/2\gamma$ ratio for z beyond which o-Ps cannot escape. The temperature dependence of the data in Fig. 3 is influenced by several factors. For $\phi>1$-nm pores, as found in all investigated samples (see Table I), Ps samples excited states.[2,3] With decreasing temperature, Ps samples fewer excited states (less pickoff for o-Ps) in the confining quantum wells, increasing the o-Ps lifetime and thus the ratio of self-annihilating o-Ps to the number of implanted e^+. However the increase in this ratio may be suppressed significantly by a decrease in the amount of Ps in these pores due to reduced e^+/Ps trapping rates,[20] reduced e^+/Ps diffusion lengths, pin-

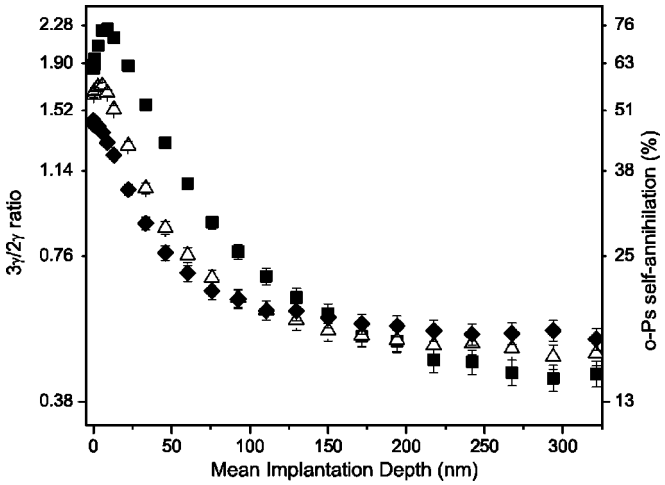

FIG. 2. Interpolated $3\gamma/2\gamma$ ratio (logarithim scale) vs z at selected temperatures for the 20-wt % sample. Squares: 400 K; up triangles: 200 K; diamonds: 50 K.

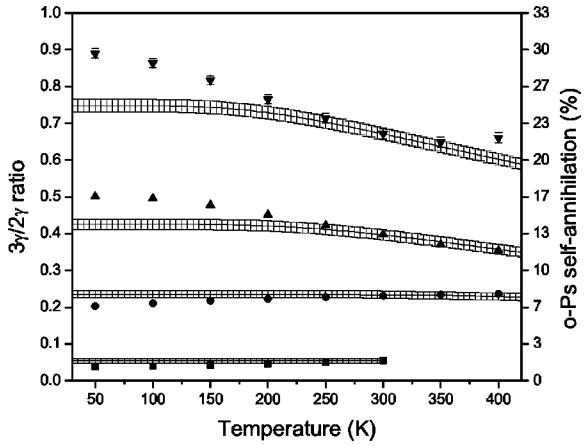

FIG. 3. $3\gamma/2\gamma$ annihilation ratio as a function of temperature for the 0% (squares) ($z>70$ nm), 10% (circles) ($z>100$ nm), 20% (up triangles) ($z>225$ nm), and 29 wt % (down triangles) ($z>300$ nm) samples. The error bars are the size of the dots. Lines: Calculated $3\gamma/2\gamma$ ratio assuming that only $\tau_i^{o\text{-}Ps}$ changes. Line width: Uncertainty in relation between τ_{mean} and $3\gamma/2\gamma$ ratio.

ning of the e^+ to the pore surface,[15] reduced Ps formation and/or reflection of the e^+ wave function at the pore wall.[21]

To investigate the extent to which these effects suppress self-annihilation we calculate the temperature dependence of self-annihilation associated solely with excited states of Ps in the confining quantum wells and compare the calculated values with the experimental results. The calculations were performed in the following manner: for the samples investigated here the $3\gamma/2\gamma$ ratio is proportional to τ_{mean} and $\tau_{mean}^{o\text{-}Ps}$. At room temperature, $\tau_{mean}=\Sigma_i I_i\tau_i$ is obtained directly from the PALS results (Table I). Variation of the o-Ps lifetimes with temperature is calculated according to Ref. 3; intensities are kept at the room temperature value. The non-o-Ps lifetimes and intensities remain unchanged. The calculated variation in τ_{mean} was converted back to the $3\gamma/2\gamma$ ratio and is plotted as a line in Fig. 3. The width of the line equals the error in the τ_{mean} to $3\gamma/2\gamma$ ratio calibration. For the 0-wt % sample the data agree within the error bars with the calculations that predict no increase in the $3\gamma/2\gamma$ ratio. Thus there is no change in the amount of Ps formed in the film material unless it is masked by free volume changes. This is unlikely, since the thermal expansion coefficient (at 300 K) for similar materials (HSSQ) is 17 ppm per K,[22] amounting to negligible changes in the $3\gamma/2\gamma$ ratio.

In the case of the 10-wt % sample the data fall below the calculated value at temperatures below 100 K. This can be accounted for by a decreasing e^+/Ps diffusion length (measured for the 0-wt % sample) so that the amount of Ps inside the porogen introduced pores decreases.

Unlike for the 0- and 10-wt % samples, the measured $3\gamma/2\gamma$ ratio for the 20- and 29-wt % samples increases with decreasing temperature (see also $z=320$ nm in Fig. 1). In fact, at <200 K the measured values exceed by $\sim$19% the calculations that assume that *no* suppressing effects play a role. This is not due to an increase in Ps formation (cf. 0 wt % sample), changes in the chemistry of the pore walls[15] (results were reproducible), pickoff annihilation of o-Ps at the film–substrate (Si) interface (found to be below the detection sensitivity[12]) or due to Ps/e^+ preferring to trap in $d>2$ nm pores (see Table I) at lower temperatures. The latter statement holds since the data for the 10-wt % sample, which also has $d>2$ nm pores, cannot be modeled in terms of Ps/e^+ preferring to trap in $d>2$ nm pores. To understand why the suppressing effects appear to be negligible and why the data exceed the calculations will require further theoretical investigations.

These samples are ideal candidates for fundamental investigations of large amounts of confined, collisionally cooled, self-annihilating o-Ps: At 50 K, self-annihilation in the 20- and 29-wt % samples is $\sim$45% greater than at 400 K. For the 29-wt % sample at 50 K (400 K), $\sim$75% (50%) of the formed o-Ps self-annihilates and $\sim$30% (20%) of the implanted e^+ end up as self-annihilating o-Ps. In a recent extension of these experiments, self-annihilation was found to increase even further down to 10 K in capped low-*k* samples. Compare this with a proposed scheme for the generation of an o-Ps Bose Einstein condensate:[10] There it is estimated that only 25% of implanted e^+ form Ps inside a cavity in a Si substrate. Of the formed Ps, 75%, i.e., 19% of implanted e^+, form o-Ps and of that not all will self-annihilate. The materials studied here form almost twice as much self-annihilating o-Ps at 50 K and even more at <50 K. It would be very interesting to see what happens for samples of >29 wt % porosity. There the above-mentioned effects would be more pronounced.

Conclusion. Beam-based 3γ PAS was employed to measure o-Ps self-annihilation in mesoporous films from 50 to 400 K. Self-annihilation in the film was found to decrease slightly with decreasing temperature for lower porosity samples while it increases by as much as 45% for the larger porosity sample. This is beyond what could be expected even if there were no effects which suppress self-annihilation and requires further theoretical investigations. The large amount of o-Ps self-annihilation (as much as 30%) at 50 K, and even more at lower temperatures, make these samples interesting candidates for substrates in which to form a BEC of collisionally cooled o-Ps.

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