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Positronium annihilation in mesoporous thin films

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Depth-profiled positronium lifetime spectroscopy is used to probe the pore characteristics (size, distribution, and interconnectivity) in porous, low-dielectric silica films. The technique is sensitive to the entire void volume, both interconnected and isolated, even if the film is buried beneath a metal or oxide layer. Our extension of a simple quantum mechanical model of Ps annihilation in a pore adequately accounts for the temperature and pore size dependence of the Ps lifetime for pore sizes in the range from 0.1 nm to 600 nm. It is applicable to any porous media. [S0163-1829(99)51932-2]

Submicron thin films of porous silica and organosilicates are vigorously being developed as low-dielectric, interlayer insulators for use in future high-speed microelectronic devices.[1] Voids are introduced into the film to produce porosity and hence to lower the dielectric constant. Pores must be plentiful to lower the dielectric constant of solid silica from 4 to less than 2, yet they must be small relative to the device element size which is expected to approach 100 nm in the next decade. Important pore characteristics such as average size, size distribution, and degree of interconnectedness are difficult to probe with standard techniques (such as gas absorption) because of the submicron film thickness, the presence of a thick Si substrate and, in some cases, by the lack of pore interconnectivity (i.e., inaccessibility to gas absorption). A less standard technique, positronium annihilation lifetime spectroscopy (PALS), is well known as a bulk probe of subnanometer voids in polymers and insulators and has recently been extended to probe very thin polymer films using keV beams of positrons.[2] The technique looks promising for probing porous films since it is readily applicable to films less than 0.1 μm thick, does not rely on any pore interconnectivity/accessibility, and is expected to be sensitive to pore sizes in the 0.3 nm to 100 nm range.

In this paper we will explore the capability of PALS to probe the pores in two different types of porous silica films that are spin-cast on Si substrates. The first is a 0.5-μm-thick silica-organic composite in which the organic component is removed by thermal decomposition to create pores after the silica component is fully cured and crosslinked. The second is a 0.9-μm-thick film, formed using a sol-gel (aerogel/xerogel) technique. We determined the film porosities using Rutherford backscattering spectroscopy to be 52% and 77%, respectively. Details on the methodology of depth-profiled PALS has been presented elsewhere.[2] Briefly, a focussed beam of several keV positrons forms positronium (Ps, the electron-positron bound state) throughout the film thickness. The binding energy of Ps (6.8 eV in vacuum) is reduced in the solid dielectric and thus Ps tends to localize in the pores. The natural (vacuum) lifetime of Ps (142 ns) is reduced by annihilation with molecular electrons during collisions with the pore surface and thus pore size information can be deduced from measuring this lifetime, τ (or distribution of lifetimes). PALS is routinely used to study bulk polymers where Ps lifetimes of 2–3 ns are indicative of small, sub-nm voids, but there is very little lifetime calibration data for 1–100 nm voids.[3,4] We will show herein how to extend this calibration to the relatively large pore sizes encountered in these films and other porous media.

Three typical lifetime spectra are shown in Fig. 1. There is a prompt peak characterized by positron and Ps lifetimes less than 0.5 ns (typical of annihilation in nonporous, bulk samples) and a long lifetime component indicative of copious (35–40 %) Ps formation in the pores. The fitted value of τ for this long component in both films is 140 ns, suspiciously indistinguishable from the vacuum value and independent of porosity. Either the pores are unphysically large

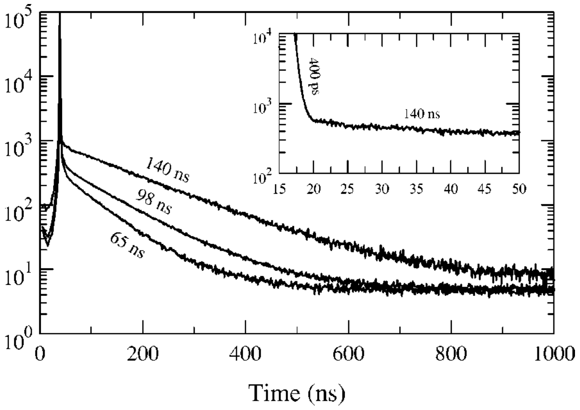

FIG. 1. PALS spectra for the uncapped, 77% porosity, sol-gel film (top); the same film with a sputter-deposited Al cap (middle); and the 52% porosity composite film with a sputtered Al cap (bottom). The inset shows the lack of any intermediate (closed pore) lifetime components in the uncapped spectrum.

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(>100 nm) or they are so highly interconnected that mobile Ps is able to diffuse out of the film and into the surrounding vacuum system. Ps diffusion out of the film is certainly possible since Ps with a room temperature thermal velocity of 8×10^6 cm/sec makes some 1–2 million collisions per lifetime in pores roughly 5–10 nm in diameter (the suspected pore size) and therefore could diffuse several μm/lifetime. We confirmed the pore connectivity hypothesis by capping the films with a 80 nm layer of sputter-deposited Al, effectively corralling the Ps in the film between the Si substrate and the cap. The beam energy was adjusted to 5 keV to maximize the implantation of positrons through the capping layer and into the film. About 50% of the beam is then lost to the cap and substrate, but the Ps intensity is still 15–20%. The *single* lifetime, τ, fitted in the lower porosity composite film is then 65 ns while $\tau=98$ ns is obtained in the higher porosity sol-gel film. A 100-nm-thick oxide layer (tetraethylorthosilicate, TEOS) was also used to cap the films yielding similar lifetimes. The statistical error in fitting τ ($\leqslant0.5$ ns) is negligible compared to possible systematic errors of around 3 ns. The important result is that a diffusion barrier is required in order to measure the collisionally quenched average lifetime of a thermalized Ps atom that is sampling the entire range of interconnected pore sizes in the film. The higher porosity sample clearly has a larger τ indicative of larger average pores.

It is necessary to calibrate the single value of τ in the capped samples with an average pore size. Ps lifetimes in the range 10–100 ns fall between two extremes that have been quite well calibrated for void size. As noted earlier, sub-nm voids that produce lifetimes of several ns have been extensively studied, and a simple quantum mechanical model of Ps trapped in a spherical well has been empirically fitted to determine a relationship between void radius and τ.[5–7] At the other extreme of very long Ps lifetimes, high porosity (90–98%) powders of fumed silica (Cab-O-Sil$^{\mathrm{TM}}$) produce average Ps lifetimes within a few percent of the vacuum value.[8] In this case where the Ps mean free path between collisions, l, is tens of nm (much larger than the thermal Ps de Broglie wavelength of 6 nm) a quantum mechanical model is unnecessary. The Ps decay rate ($1/\tau$) for Ps of thermal velocity v is then

$$\lambda=\frac{1}{\tau}=\lambda_T+\frac{vP_A}{\ell}, \tag{1}$$

where λ_T is the vacuum decay rate of triplet Ps and P_A is the probability of annihilation per collision with the solid silica. The product vP_A was deduced[8] to be 0.021 ± 0.002 nm/ns for silica powders of two different known grain sizes for which ℓ was systematically varied from 35 nm to 600 nm.

The quantum mechanical model for the collisional annihilation of Ps trapped in small pores was described by Tao[5] and Eldrup,[6] and later reconsidered by Jean and Nakanishi.[7] This model consists of a spherical potential well with infinite walls in which the single particle states of the Ps atom are calculated. The annihilation rate is assumed to be increased to $\lambda_A=(\lambda_S+3\lambda_T)/4$ (which is the spin-averaged Ps decay rate with λ_S being the decay rate of singlet Ps) for that portion of the wave function that is within a small distance δ of the cavity wall, but to remain fixed at λ_T elsewhere. Only the ground state in the well was considered in this model, and hence for large cavities and/or high temperatures, for which significant fractions of the Ps atoms will be in excited states of the potential well, this model is insufficient (the Ps is always assumed to be in its *atomic* ground state). Recently an attempt has been made to include some thermally excited states in the spherical pore model,[3] but computational difficulties with high-order spherical Bessel functions become so intractable that they render this approach of limited use. Our goal is to *fully* extend the quantum mechanical model to the classical, large-pore limit in order to incorporate the measurements taken in the two limiting pore size regimes. To accomplish such a complete calibration of τ vs pore size we have abandoned the assumption of spherical pores in favor of *rectangular* pores wherein we can more easily compute τ for any pore size and aspect ratio, and at any temperature. As will be shown, the exact geometry assumed is of secondary importance as the most relevant quantity for characterizing the average length scale of the complex, interconnected void volume in these films is the mean free path ℓ.[9]

Our extension of the Tao-Eldrup model for the Ps decay rate in a rectangular pore having sides a, b, and c in the x, y, and z directions is given by

$$\lambda(T)=\lambda_A-\frac{\lambda_S-\lambda_T}{4}F(a,\delta,T)F(b,\delta,T)F(c,\delta,T), \tag{2}$$

where

$$F(x,\delta,T)=1-\frac{2\delta}{x}+\frac{\displaystyle\sum_{i=1}^{\infty}\frac{1}{i\pi}\sin\left(\frac{2i\pi\delta}{x}\right)e^{-\beta i^2/x^2kT}}{\displaystyle\sum_{i=1}^{\infty}e^{-\beta i^2/x^2kT}}, \tag{3}$$

$$\beta=h^2/16m=0.188\ \mathrm{eV\,nm}^2. \tag{4}$$

Here, T is the absolute temperature of the Ps and m is the electron mass (the Ps mass is $2m$). This equation is obtained by integrating the normalized wave function of each state over the volume contained within a small distance δ of the cavity walls and by assuming that each Ps atom continuously samples a Boltzman population distribution of the particle energy levels. This assumption (based on the very small energy differences between states) leads to a single, temperature-dependant, average value of τ. In the computation we include terms in the series until the relative size of the exponential factor compared with the exponential in the $i=1$ term is below 10^{-6}. We note that Eq. (2) above includes pores of all aspect ratios, from cubic, through tubular, to planar. In the limit $x\rightarrow\infty$ for tubular and planar cavities, the appropriate $F(x)$ functions are simply replaced by unity.

In Fig. 2, we plot the calculated lifetime for cubic pores of side length a at several temperatures. For these curves, we have set $\delta=0.18$ nm by demanding that for small pores the ground state *rectangular* model agree with the Tao-Eldrup *spherical* model, since this latter model was empirically calibrated with known sub-nm pore sizes in zeolites and molecular solids. This calibration resulted in the selection $\delta=0.165$ nm for spherical pores[10] and thus δ appears to be somewhat geometry dependent. In fact, with $\delta=0.18$ nm our ground state rectangular model is indistinguishable from

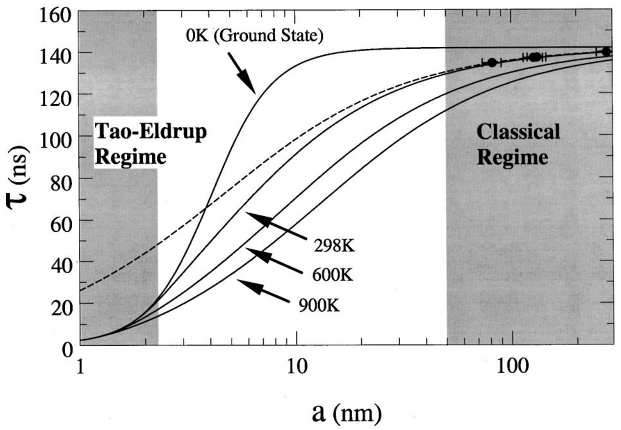

FIG. 2. Theoretical τ vs a (cubic pore side length) for several temperatures (solid lines) and the classical τ vs a (dashed line) fit to silica powder data (shown) and extrapolated to small pore size. For cubic pores the Ps mean free path is $l=(2/3)a$.

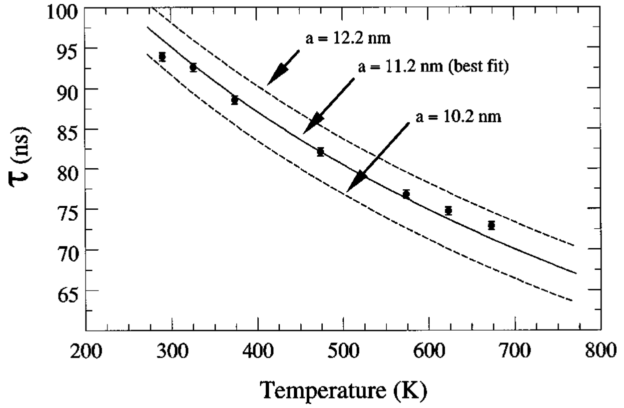

FIG. 3. The predicted temperature dependence for three different cubic pore sizes, a. The data shown are average values acquired during five heating cycles (to assure reproducibility and reversibility) of the TEOS-capped sol-gel film.

the Tao-Eldrup model for *all* pore sizes. As can be seen in Fig. 2, at room temperature the ground state $T=0$ curve (equivalent to the Tao-Eldrup model) is adequate only for $a<2.5$ nm.

We also plot in Fig. 2 the classical lifetime curve [$1/\lambda$ from Eq. (1)] along with the actual data from fumed silica powder.[8] Interestingly, our quantum mechanical model perfectly merges with the classical model at precisely the pore sizes for which these independent measurements were acquired. In fact, we can extract a value of vP_A from the quantum mechanical model in the classical limit of large a ($a \gg \delta$). Expanding the sine function to third order and using the statistical mechanical result that $\ell=4V/A$ for a cavity of volume V and surface area A, we can cast Eq. (2) into a form similar to Eq. (1) and identify the quantity vP_A in terms of δ,

$$vP_A \approx \frac{\pi^2 kT}{3\beta}(\lambda_S-\lambda_T)\delta^3. \tag{5}$$

[In obtaining this formula, we have also used the fact that $\beta/a^2kT \ll 1$, which allows us to replace the series in Eq. (2) with corresponding integrals.] We find $vP_a \simeq 0.020$ nm/ns, which is in complete agreement with the value determined experimentally from the silica powders. This lends support to the soundness of the quantum mechanical model. This agreement is also quite remarkable when considering that $\delta=0.18$ nm was determined by demanding that the model accurately describe sub-nm voids (many orders of magnitude smaller than those found in the powders) in entirely different materials (zeolites). Evidently the detailed interaction of Ps with the pore surface is small enough to treat Ps as a free particle with minimal material specificity of the annihilation rate. Thus, this model should be applicable to any porous media for which the Ps-surface interaction is not strong.

To further test this model we have measured the temperature dependence of τ in the TEOS-capped sol-gel film and compared this in Fig. 3 with our calculations where the only fitted parameter is the pore length a. The inability to include a sufficient number of excited states, and hence accurately reproduce measured temperature dependences, is a major limitation of the earlier work using spherical cavities.[3] As can be seen in the figure, the trend in the data is in reasonable agreement with theory at $a=11.2\pm0.5$ nm and lends support to our model of thermalized Ps trapped in the silica pores. Since the interconnected pores are clearly not cubes, a more general way to characterize a length scale is to extract an average Ps mean free path of $\ell=\frac{2}{3}a=7.5\pm0.3$ nm, which should be nominally independent of geometry. In fact, if we repeat the calculations assuming infinitely long square *channels*, we fit a side length of $a=7.9$ nm which, for this geometry, is also ℓ. Thus we take $\ell=7.7\pm0.4$ nm to be the Ps mean free path in the 77% porosity sol-gel film. In a similar fashion we find $\ell=3.4\pm0.3$ nm in the 52% porosity composite film.

In addition to characterizing the average pore size by ℓ, PALS can also be used to probe the interconnectivity of pores by comparing the capped and uncapped samples. The uncapped samples facilitate a direct search for any *closed* porosity that is not accessible to gas absorption methods. As shown in the inset to Fig. 1 the spectrum beyond the prompt peak is fitted well by a single, long lifetime. This is consistent with the interpretation that the pores in these samples are highly interconnected. Thus Ps effectively samples all the void volume as it diffuses throughout the entire film thickness and one average lifetime corresponding to an average pore size is observed. Isolated pores that can trap Ps would appear in the spectrum as other lifetime components. In particular, there is no evidence of closed microporosity (pore size $a<2$ nm) at the 1% level. By contrast (and to demonstrate sensitivity), the TEOS capping layer clearly contained some microporosity as evidenced by a 2 ns lifetime component that grows in intensity as the positron beam energy is reduced and more positrons stop in the capping layer. Moreover, there is no evidence at the few percent level of closed mesoporosity ($2<a<20$ nm) because the resulting lifetimes in the 10–100 ns range would measurably reduce the weighted average lifetime below the observed value of 140 ns in the uncapped samples. Sensitivity to closed pores with $a>20$ nm drops off as τ in such large pores approaches the same (vacuum) 140 ns value observed with the uncapped sample. However, one can then search for such a long lifetime in the spectra acquired with capping layers. We can rule out such closed macroporosity at the 5% level for the composite film, but cannot do so for the sol-gel film. At the

5–10 % level this higher porosity sample may contain some large pores and their possible presence is the major source of systematic error in determining τ. Their presence may also render such a film unsuitable in microelectronic applications.

In summary, PALS with positron beams appears to be a useful probe of average pore size in the highly interconnected porous networks of the present silica films. The degree of interconnectivity can be explored by comparing spectra with and without capping layers. Similarly, closed pores that trap Ps and are inaccessible to gas absorption techniques can be characterized. Nominally none was found in the present samples, but some composite organosilicate films such as mesoporous poly(methylsilsesquioxane) are expected to have isolated pores[11] that should produce a continuum of lifetimes commensurate with the distribution of pore sizes. The important calibration of τ with pore size/Ps mean free path appears to be converging on consistent results as the simple quantum mechanical model is fully extended to larger pore size and to elevated temperatures. Finally, we note that pore parameters can be determined with PALS for films underneath diffusion barriers and/or metal overlayers and in porous media with isolated (not interconnected) pores that are much less accessible to traditional techniques.

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