JOURNAL OF APPLIED PHYSICS VOLUME 84, NUMBER 12 15 DECEMBER 1998

# Positron annihilation investigation of porous silicon heat treated to 1000 °C

S. Dannefaer, C. Wiebe, and D. Kerr[a)]
*Department of Physics, University of Winnipeg, Winnipeg, Manitoba R3B 2E9, Canada*

(Received 27 February 1998; accepted for publication 14 September 1998)

Positron lifetime and Doppler broadening spectroscopies were applied to investigate a porous silicon film subjected to heat treatment in an argon atmosphere. Heating between 300 and 500 °C increased the mass of the film by 17% due to oxygen uptake and the concentration of open volume defects associated with the formation of an oxide layer on the silicon nanocrystallites increased by a factor of 3. Between 600 and 1000 °C their concentration decreased gradually to 1/2 the original concentration. Doppler broadening results indicate two distinct electron momentum distributions, one arising from open volume defects and one from pickoff annihilation of positronium at the pore walls caused by electrons with an unexpectedly narrow momentum distribution. © *1998 American Institute of Physics.* [S0021-8979(98)00624-0]

## I. INTRODUCTION

Nanocrystalline semiconductors are presently investigated extensively, in part because of their novel physical properties, but also because nanosized devices are becoming of technological interest. For such small structures one can only expect surface properties to play an important role. Porous silicon is a convenient example of a nanocrystalline form of silicon with a surface area per unit volume in the order of 100 $m^2/cm^3$. It can be formed by anodic etching of crystalline silicon and has the capability of emitting visible light,[1] which is a potentially important technological feature. For extensive reviews of porous silicon, see Refs. 2, 3 and 4.

The photoluminescent properties depend on a host of conditions such as crystallite size, substrate type, electrolyte composition and temperature, drying conditions, aging, irradiation, and heat treatment which, taken together, suggest a significant influence from surfaces. Among these many parameters we have selected in this work one of importance, namely heat treatment, and extend thus our former work[5] by investigating effects arising from heat treatment to high temperatures.

Porous silicon is produced by the anodization of crystalline silicon in a hydrofluoric acid solution, following which infrared spectroscopy[6] indicates an abundance of Si–H bonds on the internal surfaces (i.e., the pore walls); these measurements also show that the hydrogen is completely removed in a brief annealing at ~400 °C in vacuum. Simple aging in air inevitably results in the formation of an oxide layer on the surfaces.

The positron annihilation technique offers the possibility of investigating some important aspects of porous silicon since positrons may be trapped by open volume defects associated with the formation of the oxide layer or they may escape from the crystallites and form positronium in the pores or on the pore walls, thus acting as a surface probe. The lifetime of those positrons which are trapped becomes longer due to the reduced electron density in the vacancy-like defects and depends mainly on the open volume of the defects. Additionally, the momentum distribution of the annihilating positron electron pair, which is reflected in the Doppler broadening of the annihilation gamma-ray line shape, normally becomes narrower as a consequences of the reduced likelihood of annihilation with high momentum core electrons. Those positrons forming positronium produce either parapositronium, which undergoes rapid (125 ps) self-annihilation with very small center of mass momentum, or orthopositronium from which annihilation dominantly occurs by the so-called pickoff process, which is strongly dependent on the surface condition of the pores. In this process the positron does not annihilate with the electron in the positronium but rather with a ''foreign'' electron, hence the term pickoff.

## II. EXPERIMENT

Details of the positron lifetime spectrometer, data acquisition, and analysis procedure were as reported in Ref. 5. Doppler broadening measurements were performed using a Ge detector having an energy resolution of 1.2 keV at 0.511 MeV. The widths of the Doppler broadened line shapes were characterized by the $S$ parameter defined as the ratio of the number of counts in the range $511 \pm 0.7$ keV to the number of counts in the range $511 \pm 4.8$ keV.

The porous silicon layer was formed on $p$-type silicon by anodization in a mixture of 50% hydrofluoric acid and ethanol (4:1) with a current density of 57 $mA/cm^2$ for 22 min. The resulting porous layer had a thickness of 94 $\mu$m.

Heat treatments were done in a quartz tube which, prior to a heat treatment, was evacuation to $10^{-2}$ Torr and then filled with flowing high-purity Ar. The sample was then placed in the preheated tube for 1/2 h after which it was rapidly cooled to room temperature in the argon atmosphere. It should be noted that this procedure done *not* remove the air present in the pores nor that adsorbed on the surfaces, so oxidation is still possible despite the Ar ambient. Following cooling, the sample was exposed to air for the duration of the positron experiments, which lasted between 2 and 6 days

a)Electronic mail: don.kerr@uwinnipeg.ca

 © 1998 American Institute of Physics

Downloaded 14 Apr 2006 to 146.201.234.195. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

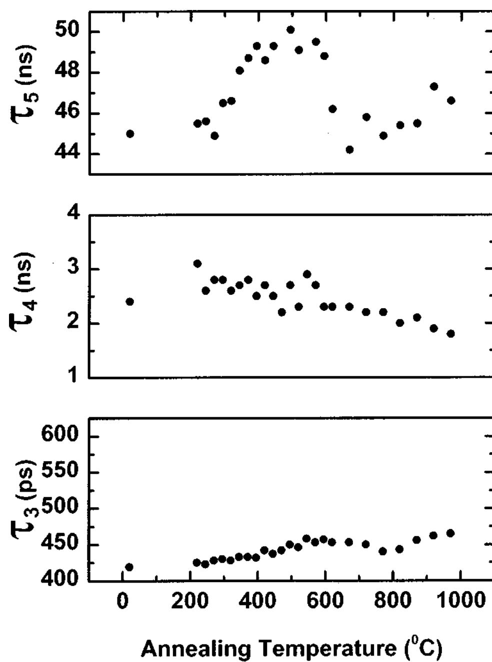


FIG. 1. Lifetime components associated with the film as a function of annealing temperature. Measurements were done at room temperature. The $\tau_1$ and $\tau_2$ lifetime components were fixed at 125 and 217 ps, respectively.

after each heat treatment. All lifetime and Doppler broadening measurements were performed at room temperature.

## III. RESULTS

The thickness of the film is not sufficient to stop all positrons within the film, so a sizable fraction (≅60%) penetrates into the crystalline Si substrate where the positrons annihilate with a lifetime of 217±2 ps. Although the substrate contribution constitutes a numerical disadvantage in the fitting procedure aimed at extracting the porous film contribution, an important advantage is that the mass of the porous film can be monitored *because* of the penetration. Five lifetimes, $\tau_1-\tau_5$, were necessary to adequately describe the lifetime spectra, with associated intensities $I_1-I_5$. According to our earlier interpretation,[5] $\tau_1$ (130±15 ps) arises from annihilation of parapositronium, $\tau_2$ (217±2 ps) from annihilation of positrons in the substrate, $\tau_4$ (2–5 ns) from orthopositronium trapped on pore surfaces, and $\tau_5$ (>40 ns) from orthopositronium located inside the pores.[7] The intermediate component $\tau_3$ has a value (400–450 ps) which is typical of positrons trapped in small open volume defects and was earlier[5] attributed to positrons annihilating in vacancy clusters in the silicon oxide layer covering the silicon nanocrystallites. As will be discussed in the following section, this lifetime could arise from defects elsewhere, such as at the interface between the silicon and the silicon dioxide layer.

Figure 1 shows the positron lifetimes associated with the porous film as a function of temperature of the heat treatment. These lifetimes were obtained with $\tau_1$ and $\tau_2$ fixed at 125 and 217 ps, respectively, the first lifetime arising from parapositronium and the second from the substrate. Note, in particular, the initial increase in $\tau_5$ and subsequent decrease around 600 °C. Above 1000 °C cracking and partial flaking off of the film from the substrate was evident and the substrate visibly bent away from the film, indicating shear stresses between the film and substrate.

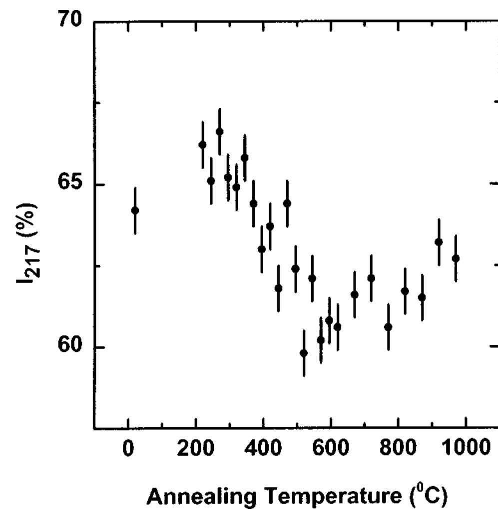


FIG. 2. Intensity of the crystaline Si backing lifetime component (fixed at 217 ps) as a function of annealing temperature.

Figure 2 shows the intensity $I_{217}$ arising from $\tau_2$ when fixed at 217 ps ($I_{217}$ is the percentage of positrons penetrating into the substrate). The intensities of the $\tau_3$, $\tau_4$, and $\tau_5$ components associated with the film are shown in Fig. 3 as normalized to the fraction of positrons annihilating in the film. The balance to 100% of $\Sigma_{i=3}^{5} I_i$ constitutes the intensity $I_1$ of the $\tau_1$ component arising from parapositronium (in calculating these intensities care was taken to account for the unobserved 3-$\gamma$ annihilation of the $\tau_5$ component, discussed in Ref. 5). The ratio $(I_4+I_5)/I_1$ is 3.4±0.3 based on measurements up to 1000 °C. Associating $I_4$ and $I_5$ with orthopositronium and $I_1$ with parapositronium, a ratio of 3 is predicted from the formation kinetics of positronium.

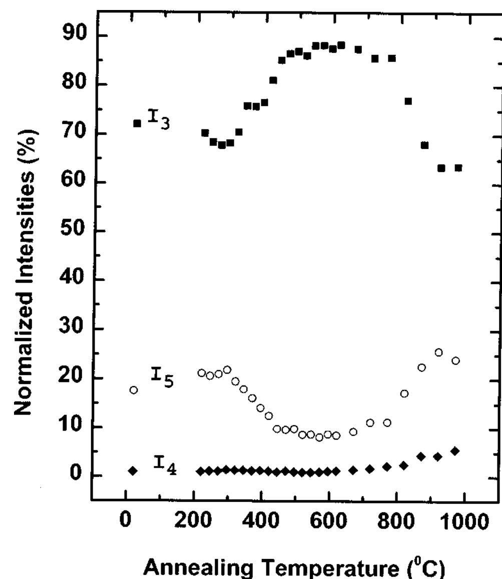


FIG. 3. Intensities of the film-associated lifetime components normalized to the film contribution $(100-I_{217})$. The balance to 100% constitutes the intensity of the $I_1$ component arising from parapositronium.

Downloaded 14 Apr 2006 to 146.201.234.195. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

TABLE I. Lifetime and $S$ parameter data for a porous silicon sample in air or in vacuum ($10^{-2}$ Torr). Data pertain to the porous layer only. 45% of the positrons are annihilated in the layer independent of the ambient. $\tau_1$ and $\tau_2$ were fixed at 125 and 217 ps, respectively, in the analyses.

| Ambient | $\tau_3$ (ns) | $\tau_4$ (ns) | $\tau_5$ (ns) | $I_3$ (%) | $I_4$ (%) | $I_5$ (%) | $S$ |
|---|---|---|---|---|---|---|---|
| Air | 0.407 ±0.005 | 2.7 ±0.2 | 41.8 ±0.4 | 54 ±1 | 0.8 ±0.1 | 31.1 ±0.2 | 0.580 ±0.003 |
| Vacuum | 0.418 ±0.006 | 3.3 ±0.3 | 64.9 ±0.4 | 55 ±1 | 0.7 ±0.1 | 32.5 ±0.2 | 0.541 ±0.003 |

In order to evaluate the effects of air in the pores, measurements in air and in vacuum were made on a separate, but similar, porous silicon sample with the results shown in Table I. Here it is seen that air in the pore increases the value of $S$ significantly and decreases $\tau_5$ relative to vacuum while the total positronium contribution $(I_1+I_4+I_5)$ stays constant. This shows (i) that $S$ arising from air is larger than $S$ arising from positronium annihilating at the pore surfaces and (ii) that air and pore surfaces compete in the annihilation of positronium without influencing the total yield of positronium.

Doppler results are shown in Fig. 4. These are for the film alone, i.e., the backing *and* air contributions have been corrected for.

As mentioned in the introduction, as-grown porous silicon shows effects arising from aging and such could also occur after each of the heat treatments. Hence, lifetime and Doppler spectra were measured following several of the heat treatments as a function of time up to 6 days, but in no case was any time dependency discernible. If aging indeed takes place, it is then either too fast to be detectable during a single measurement (3 h) or too slow to be observed within 6 days.

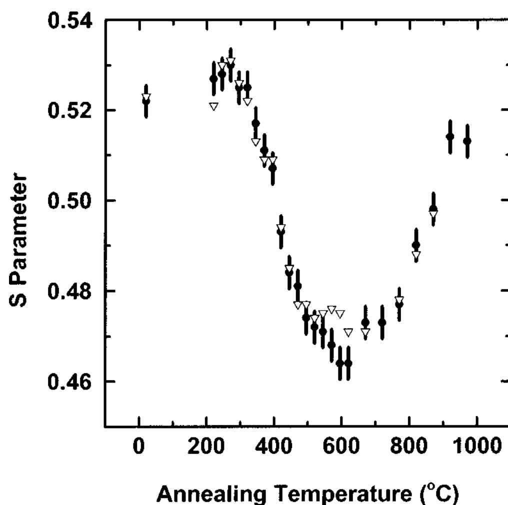


FIG. 4. $S$ parameter for the film as a function of annealing temperature. The circles show the results of measurements originally done in air but then corrected for the air contribution and the silicon backing. The triangles are values calculated as described in the text. Measurements were done at room temperature.

## IV. DISCUSSION

We discuss first the implications of the change in the fraction of positrons penetrating the film as shown in Fig. 2. This fraction is given by

$$I_{217}=\exp(-t\alpha), \tag{1}$$

where $t$ is the thickness of the film and $\alpha$ is given (empirically) by[8]

$$\alpha=17.6\rho/E^{1.47} \quad (\mathrm{cm}^{-1}), \tag{2}$$

where $\rho$ is the density of the film in g/cm$^3$, and $E$ the maximum kinetic energy of the positrons in MeV. Therefore, if the mass (per unit area) of the film changes due either to desorption of gases or gas uptake, $I_{217}$ would change, thus providing the basis for an assessment of mass changes of the porous film.

Heat treatment of the film produces changes as indicated by the behavior of $I_{217}$ in Fig. 2, and Table II lists the calculated relative changes in mass of the film at selected temperatures. The decrease in mass between 20 and 200 °C we suggest arises from removal of adsorbed gases. The increase in mass between 300 and 550 °C can be understood in terms of oxygen uptake when oxygen replaces effusing H atoms, a process which is in accordance with several infrared spectroscopy measurements which show that the disappearance of Si–H bonds is accompanied by the appearance of Si–O bonds.[9–11]

The increase in mass between 300 and 550 °C amounts to (17±2)% which corresponds to an oxygen uptake of $17\times m_{\mathrm{Si}}/(m_{\mathrm{O}}-m_{\mathrm{H}})=(32\pm4)\%$ of the silicon atoms in the film. If only $SiO_2$ were formed that would mean that 16% of the available silicon atoms became part of $SiO_2$ (and in the case of a suboxide an even larger percentage of Si would be required). Since H bonds are replaced by oxygen bonds this implies that the H uptake during the formation of the porous silicon is (at least) 32% of the silicon atoms.

Above we have argued that the mass increase is due to oxygen uptake, which may seem surprising since the heat treatments were done in argon. However, others[9,11] who used similar heat-treatment procedures observed infrared absorption from Si–O bonds, so the oxygen most likely comes from air adsorbed on the pore walls, being replenished at each annealing step.

We now turn to a discussion of the lifetimes $\tau_3$ and $\tau_5$ associated with the porous layer. The less energetic posi-

Downloaded 14 Apr 2006 to 146.201.234.195. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

TABLE II. Relative change in layer mass as a function of heat-treatment temperature.

| Temp. (°C) | 20 | 200 | 250 | 300 | 400 | 450 | 500 | 550 |
|---|---|---|---|---|---|---|---|---|
| $\Delta m/m_0(\%)$ | 0 | −5.8 | −5.8 | −5.8 | 2.0 | 7.7 | 11.3 | 11.3 |

trons, which do not penetrate through to the silicon backing, are reduced to thermal or near-thermal energies in the nanocrystallites comprising the porous layer. Since the positron diffusion length in defect-free silicon is large (~200 nm) compared to the size of the crystallites (~10 nm), most of the positrons, unless trapped at defects, will diffuse to the surface region without annihilating. There, they may be trapped at open volume defects associated with the formation of the oxide layer, or they may form positronium, which either remains attached to the surface or is deposited into the pores. Positronium in the pores will then undergo pickoff annihilation with gas atoms in the pores or the pore walls.

As noted earlier, we attribute the $\tau_3$ component with a value of 400–450 ps to positrons trapped at small open volume defects. This lifetime could, in principle, be due to orthopositronium, but the absence of a corresponding contribution from parapositronium argues against this possibility. Further, a similar lifetime was found in amorphous silicon[12] in amorphous silicon dioxide,[13] and was in both cases attributed to vacancy clusters. We have also found a similar lifetime in crystalline $\alpha$ quartz. In our earlier work,[5] the $\tau_3$ component was assigned to vacancy clusters in the oxide layer but, in view of the complexity of the oxidized porous silicon system, there are other possibilities. Slow positron beam studies of $SiO_2/Si$ systems,[14–18] have indicated the presence of positron traps at the interface between the two materials. The precise nature of the traps has not been firmly established; candidates have included open volume defects, dangling Si bonds ($P_b$ centers), and, in the case of thin oxide layers, divacancies in Si domains at interfaces.[18]

Figure 3 shows that the intensity $I_5$ of the $\tau_5$ component (due to orthopositronium in the pores) changes oppositely to $I_3$ throughout the entire temperature range of heat treatments. This lends support to the general notion implied above, i.e., that positron traps, whose concentration varies as heat treatment and oxygen uptake proceed, determine the amount of positrons available for positronium formation in the pores. To quantify this, we write

$$I_3 = \kappa_3/(\kappa_3 + T_r), \tag{3}$$

where $\kappa_3$ is the positron trapping rate and $T_r$ is the transmission rate through the silicon, the interface, and the oxide layer into the pores in the absence of trapping.

The oxide layer in our porous silicon sample is likely very thin (~1 nm) prior to the heat treatment due to the hydrogen passivation of the surface. Although we cannot measure the oxide layer thickness resulting from the heat treatments, it is still likely to be quite thin because of the very low oxygen concentration. By way of comparison, high-temperature oxidation of porous silicon in an atmosphere containing only a small percentage of oxygen results in an oxide layer only a few monolayers thick.[19] Slow positron beam measurements show the positron diffusion length in oxide layers (which are amorphous) grown on Si wafers to be only ~10 nm (Ref. 14) while, in contrast, measurements in fused quartz yield a value of ~30 nm.[20] The smaller value in the amorphous layer is likely a result of a higher defect concentration: a positron lifetime study of a very thick (60 $\mu$m) amorhpous $SiO_2$ film showed a high concentration of vacancy clusters and voids.[13] Based on these comments, we assume that the oxide layer thickness is less than the diffusion length in defect-free oxide and that $T_r$ is essentially independent of heat-treatment temperature. Denoting by $\kappa_3^0$ the value of $\kappa_3$ before heat treatment and by $\kappa_3(T)$ that for any heating temperature, the ratio $R = \kappa_3(T)/\kappa_3^0$ can be calculated when assuming $T_r$ constant. Figure 5 shows that during oxygen uptake the defect concentration increases by a factor of 3, but these defects are not materially different from those initially present because of the near-constant value of $\tau_3$. Above 600 °C, where oxygen uptake has stopped, the decrease in $R$ suggests thermally induced relaxation not involving defect migration ($\tau_3$ is nearly constant), which at 800 °C has returned the film to its original defect concentration. Above this temperature $R$ decreases rather slowly and the value of $\tau_3$ increases (Fig. 1), suggesting defect migration with the formation of larger open volume defects.

The increase in the value of $\tau_5$ with increasing annealing temperature (cf. Fig. 1) indicates a decrease in pickoff annihilation of orthopositronium. Pickoff annihilation arises from two sources, the pore surface as well as the air contained in the pores. To establish the contribution of air to the pickoff process, we use the data in Table I. The pickoff rate associated with the pore surface alone is $1/\tau_5(\text{vacuum}) = 0.0154$ ns$^{-1}$, while the rate for the combination of the pore surface and air is $1/\tau_5(\text{air}) = 0.0239$ ns$^{-1}$. Thus, the pickoff rate associated with air alone is 0.0085 ns$^{-1}$. Generally then, the

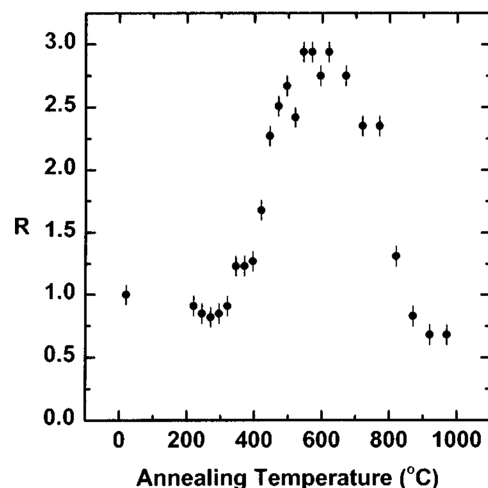


FIG. 5. Ratio $R$ of the trapping rate at temperature $T$ relative to that before heat treatment.

Downloaded 14 Apr 2006 to 146.201.234.195. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

surface pickoff rate is related to the measured $\tau_5$ through

$$\lambda_{\mathrm{p.o.}}^{\mathrm{surface}} = 1/\tau_5 - 0.0085 - 1/142 \ \ (\mathrm{ns}^{-1}), \quad (4)$$

where 142 ns is the vacuum lifetime for 3-$\gamma$ annihilation of orthopositronium. For the initial value of 45.0±0.5 ns of $\tau_5$, $\lambda_{\mathrm{p.o.}}^{\mathrm{surface}}$ is 0.0067±0.0002 $\mathrm{ns}^{-1}$, while for the (average) peak value of 49±1 ns, $\lambda_{\mathrm{p.o.}}^{\mathrm{surface}}$ is 0.0049±0.0004 $\mathrm{ns}^{-1}$. This corresponds to a (19–35)% decrease in $\lambda_{\mathrm{p.o.}}^{\mathrm{surface}}$ between 20 and 500 °C but the physical origin for this is unclear because many different sources can be envisaged. A main contribution might be that gas adsorption in air passivates potential pickoff annihilation sites so decreasing $\lambda_{\mathrm{p.o.}}^{\mathrm{surface}}$, a mechanism which also explains why $\lambda_{\mathrm{p.o.}}^{\mathrm{surface}}$ *increases* upon vacuum annealing[5] since, in this case, little passivation would be possible. The small pickoff rates show that orthopositronium in the pores interacts rather weakly with the pore walls.

The decrease in $\tau_5$ close to 600 °C might have a unique origin because none of the other positron parameters showed changes around this temperature (including $S$, see Fig. 4). This temperature is significant in that crystalline $SiO_2$ undergoes the reversible $\alpha \leftrightarrow \beta$ phase transition at a temperature of 573 °C and it is also at this temperature that Arita[21] found a noticeable change in the oxidation activation energy, which was attributed to a change from grain-boundary oxidation to oxidation of crystallites. We suggest, therefore, that the decrease in $\tau_5$ is caused by a structural change of the silicon oxide surface, which in turn exposes more pickoff annihilation sites for orthopositronium situated in the pores.

The interpretation of the $S$ parameter rests on the lifetime data since $S$ is a composite of several contributions as indicated by the lifetime analyses. The value of $S$ can be written

$$S = I_1 S_1 + I_3 S_3 + I_4 S_4 + I_5 S_5, \quad (5)$$

which pertains to the film in vacuum. The $I_i$'s are the fractions of positrons annihilating with electron momentum distributions giving rise to the respective $S$ parameters, and are the intensities of $\tau_1$, $\tau_3$, $\tau_4$, and $\tau_5$ lifetime components. $S_1$, which is associated with the self-annihilation of thermalized parapositronium, is approximated by the $S$ value associated with the intrinsic resolution of the system because of the negligible center-of-mass momentum of parapositronium. This value was obtained from a measurement of the $^{137}$Cs 614 keV line and scaling to the 511 keV annihilation line yielding $S_1 = 0.890 \pm 0.001$. In the analysis of $S$, the $S_4 I_4$ term can be disregarded due to the small value of $I_4$.

Least-squares fitting of $S$ using experimental values of the intensities from the lifetime measurements gave $S_3 = 0.454 \pm 0.005$ and $S_5 = 0.64 \pm 0.02$ and the triangular points in Fig. 4 are based on these values. The value of $S_3$ is significantly lower than for silicon ($S_{\mathrm{Si}} = 0.5070 \pm 0.0008$) and, since an open volume defect in silicon would normally result in an increased $S$ parameter, this value is not likely associated with the silicon nanocrystallite but rather with the oxide layer or its interface with silicon. Slow positron beam measurements[14] result in an interface $S$ value of about $0.93 \times S_{\mathrm{Si}}$ (=0.472 based on our silicon value) and an oxide layer value of $0.98 \times S_{\mathrm{Si}}$ (=0.497). Both values are substantially higher than that for single-crystaline $SiO_2$: In a crystalline sample containing vacancies causing ≃50% trapping,[22] $S$ was found to be 0.4524±0.0018 from which the bulk $SiO_2$ value may be estimated to be about 0.430 (assuming that vacancies contribute by a 5% higher $S$ value than for the bulk). Thus, Doppler measurements are consistent with a $\tau_3$ component associated either with the interface or with vacancy-like defects in oxide layer (since $S_3$ is larger than the bulk $SiO_2$ value).

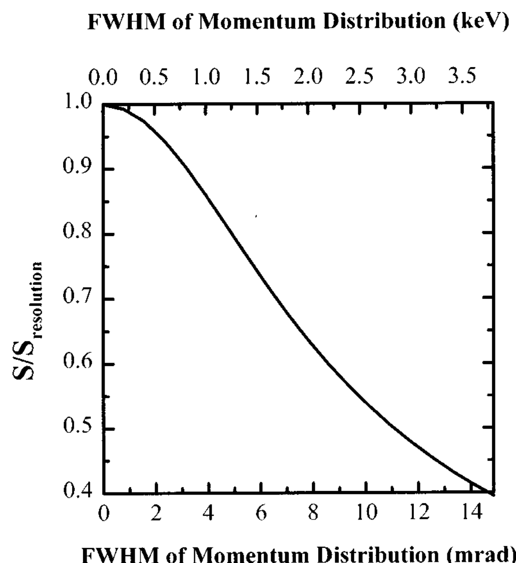


FIG. 6. Calculated change in $S$ relative to that of $S_{\mathrm{resolution}}$ as a function of the full width at half maximum (FWHM) of a *Gaussian* distribution of electron momenta.

The value of $S_5$ is surprisingly large (0.64±0.02) and suggests that pickoff annihilation of orthopositronium involves electrons with exceptionally small momenta. To obtain a measure of their momenta we performed calculations of $S$ for various *Gaussian* distributions of electron momenta convoluted with a Gaussian approximation to the resolution function of our detector. Figure 6 shows the results from these calculations. On the vertical axis is plotted the ratio $S/S_{\mathrm{resolution}}$ which, for a full width at half maximum (FWHM) of zero for the electron momentum distribution, has the value of 1. As the FWHM increases, the ratio decreases according to the curve shown from which one can obtain FWHM values of the electron momentum distribution in reasonable agreement with angular correlation measurements which have at least five times better resolution. As examples, for Si, $S/S_{\mathrm{resolution}}$ is (for out detector system) 0.507/0.89, thus predicting a FWHM of 9.5 mrad, whereas angular correlation yields ~10 mrad. For $SiO_2$ ($\alpha$ quartz, $S = 0.430$) we find a FWHM of 11.7 mrad, whereas angular correlation gives 12 mrad. It should be noted, however, that in the case of diamond this procedure yields a FWHM of 14 mrad, whereas 19 mrad is found by angular correlation (for the [100] direction). In this extreme case the Gaussian approximation to the electron momentum distribution is clearly inadequate, as shown by the angular correlation data of Liu, Berko, and Mills.[23]

Downloaded 14 Apr 2006 to 146.201.234.195. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

According to Fig. 6, the pickoff annihilation of orthopositronium, which gave an $S$ value of 0.64, corresponds to an electron momentum distribution with a FWHM value of 7 mrad, significantly less than that for bulk $SiO_2$ (12 mrad). This suggests that the pickoff annihilation is associated with electrons at the surface rather than in the bulk.

Though no photoluminescence measurements were done in this work, a few comments are in order as to the possible connection with positron data. In nonoxidized porous silicon photoluminescence is dominated by red luminescence which, upon oxidation, shifts toward the blue.[2] The positron data indicate that defects are created when H effuses and is replaced by oxygen. These defects are likely candidates for nonradiative recombination centers, thus reducing photoluminescence (both red and blue). But annealing above 500 °C gradually reduces the defect concentration so that the blue photoluminescence due to oxygen becomes observable. The above suggests that open volume defects may play an important role in reducing photoluminescence.

## V. CONCLUSIONS

Positron annihilation investigations of heat-treated porous silicon have shown that uptake of oxygen during hydrogen effusion can be quantified by this technique. In this case, the uptake amounted to one-third of the silicon atoms present in the film. The formation of the oxide layer was accompanied by a threefold increase in the concentration of open volume defects. Heat treatments above 600 °C gradually decreased their concentration, by means of relaxation, which was then followed at temperatures above 800 °C by defect migration creating larger open volume defects.

One of the two Doppler $S$ parameters deduced from this work ($S = 0.454$) supports the association of the 400–450 ps lifetime with annihilation in open volume defects in the silicon oxide layer or at the interface while the other $S$ value (0.64) suggests that surface electrons of 40% lower momenta than in bulk $SiO_2$ are involved in the pickoff annihilation of positronium in the pores.


## ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada. The authors are indebted to Dr. T. Bretagnon, Université Montpellier II, Montpellier, France, for supplying the samples.



[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[2] A. G. Cullis, L. T. Canham, and P. D. J. Calcott, J. Appl. Phys. **82**, 909 (1997).
[3] B. Hamilton, Semicond. Sci. Technol. **10**, 1187 (1995).
[4] Y. Kanemitsu, Phys. Rep. **263**, 1 (1995).
[5] S. Dannefaer, D. Kerr, D. Craigen, T. Bretagnon, T. Taliercio, and A. Fourcaran, J. Appl. Phys. **79**, 9110 (1996).
[6] S. Gardelis and B. Hamilton, J. Appl. Phys. **76**, 5327 (1994).
[7] As described in Ref. 5, the $\tau_5$ component was first measured using a coarse time calibration (103 ps/channel), while the shorter lifetimes were obtained from spectra measured with a finer time calibration (25 ps/channel).
[8] W. Brandt and R. Paulin, Phys. Rev. B **15**, 2511 (1977).
[9] F. Möller, M. Ben Chorin, and F. Koch, Thin Solid Films **255**, 16 (1995).
[10] L. A. Balagurov, V. F. Pavlov, E. A. Petrova, and G. P. Boronina, Semiconductors **31**, 815 (1997).
[11] M. Shimasaki, Y. Show, M. Iwase, T. Izumi, T. Ichinohe, S. Nozaki, and H. Morisaki, Appl. Surf. Sci. **92**, 617 (1996).
[12] S. Dannefaer, B. G. Hogg, and D. Kerr, J. Appl. Phys. **54**, 155 (1983).
[13] S. Dannefaer, T. Bretagnon, and D. Kerr, J. Appl. Phys. **74**, 884 (1993).
[14] For a review, see P. Asoka-Kumar, K. G. Lynn, and D. O. Welch, J. Appl. Phys. **76**, 4935 (1994).
[15] B. Nielsen, K. G. Lynn, Y. C. Chen, and D. O. Welch, Appl. Phys. Lett. **51**, 1022 (1987).
[16] H. L. Au, P. Asoka-Kumar, B. Nielsen, and K. G. Lynn, J. Appl. Phys. **73**, 2972 (1993).
[17] J. P. Peng, K. G. Lynn, P. Asoka-Kumar, and D. P. Becker, Phys. Rev. Lett. **76**, 2157 (1996).
[18] H. Kauppinen, C. Corbel, L. Liszkay, T. Laine, J. Oila, K. Saarinen, P. Hautojärvi, M.-F. Barthe, and G. Blondiaux, J. Phys. Condens. Matter **9**, 10595 (1997).
[19] P. M. Fauchet, J. von Behren, K. D. Hirschman, L. Tsybeskov, and S. P. Duttagupta, Phys. Status Solidi A **165**, 3 (1998).
[20] A. Uedono, S. Tanigawa, K. Suzuki, and K. Watanabe, Appl. Phys. Lett. **53**, 473 (1988).
[21] Y. Arita, J. Cryst. Growth **45**, 383 (1978).
[22] S. Dannefaer, T. Friessnegg, D. Kerr, A. Uedono, X. Li, and S. Tanigawa, Phys. Rev. B **54**, 15051 (1996).
[23] W. Liu, S. Berko, and A. P. Mills, Jr., Mater. Sci. Forum **105-110**, 743 (1992).


Downloaded 14 Apr 2006 to 146.201.234.195. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp