Applied Surface Science 255 (2008) 197–200

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Emission of positronium in a nanometric PMMA film

C.A. Palacio [a,b,*], J. De Baerdemaeker [a], D. Van Thourhout [c], C. Dauwe [a]

[a] Department of Subatomic and Radiation Physics, Ghent University, Proeftuinstraat 86, B-9000 Ghent, Belgium
[b] Institute of Physics, University of Antioquia, A.A. 1226 Medellin, Colombia
[c] Ghent University, Department of Information Technology, St. Pietersniewstraat 41, B-9000 Ghent, Belgium

ARTICLE INFO

Article history:
Available online 16 May 2008

PACS:
41.75.Fr
34.80.Uv
82.35.Lr
78.70.Bj
71.60.+z
36.10.Dr

Keywords:
Polymethyl metacrylate (PMMA)
Positronium
Positronium emission
Positron diffusion length

ABSTRACT

Positron beam experiments have been performed for the first time on a self-supporting polymethyl metacrylate (PMMA) film of 310 nm-thick made by spin coating. The positronium (Ps) emission from the PMMA surface is studied as a function of the positron implantation energy by using Doppler profile spectroscopy and Compton-to-peak ratio analysis. When the sample and the Ge-detector are perpendicular to the positron beam, the emission of *para*-positronium (*p*-Ps) is detected as a narrow central peak. By rotating the sample 45° with respect to the beam, the emission of *p*-Ps is detected as a blue-shifted fly-away peak. The bulk Ps fraction, the efficiency for the emission of Ps by picking up an electron from the surface, and the diffusion lengths of positrons (thermal and or epithermal), *p*-Ps and *ortho*-positronium (*o*-Ps) are obtained.

1. Introduction

It is known that many solids emit positronium (Ps) when they are bombarded by low-energy positrons. The study of the positron (e^+) motion is important for understanding the interactions of positrons with matter. An overview about the several mechanisms at the basis of Ps emission in insulators can be found in Ref. [1].

The mechanisms of Ps formation at the materials surface have been described by the following processes: (a) implanted positrons can get trapped into a surface state that can be subsequently thermally activated into Ps emission [2], (b) implanted positrons can reach the surface, capture an electron (e^-) at the surface and thus emerge as a Ps rather than free e^+ [3], and (c) Ps can be formed in the bulk of the material and can diffuse back to the surface where it is emitted [4].

A full description of the e^+ implantation profile in the direction perpendicular to the surface is given by the well-known Makhov distribution [5]. This distribution is in good agreement with the thin-film transmission experiments of Mills and Wilson [6] and extensive Monte Carlo simulations [7,8]. The implantation profile $P(E, z)$ is fully described by

$$P(E,z) = \frac{mz^{m-1}}{z_0^m} \exp\left[-\left(\frac{z}{z_0}\right)^m\right], \quad (1)$$

where $z_0 = z_{1/2}\ (E)(\Gamma((m+1)/m))^{-1}$ (E in keV) and the exponent $m = 2$. The median implantation depth as a function of the implantation energy ($z_{1/2}(E)$) can be parameterised by means of the power-law equation [6]:

$$z_{1/2}(E) = \frac{\alpha}{\rho} E^n \quad (2)$$

where ρ is the density of the material and n and α are empirical parameters. The most common used parameters are $n = 1.6$ and $\alpha = 4.0\ \mu g\ cm^{-2}$ [9]. Recently, Algers et al. [10] have found that in polymers the best fitting parameters for $z_{1/2}(E)$ are $n = 1.71 \pm 0.05$ and $\alpha = 2.81 \pm 0.2\ \mu g\ cm^{-2}$. For comparison, both the most frequently used values and the parameters proposed by Algers et al. were used in our analysis.

Doppler broadening of annihilation radiation (DBAR) is one of the methods that may be used to study the emission of *para*-positronium (*p*-Ps) (see for example [11]). The literature is plenty of reports on experiments where the Doppler broadened line shape parameter $S(E)$ is investigated in function of the energy of the

* Corresponding author at: Department of Subatomic and Radiation Physics, Ghent University, Proeftuinstraat 86, B-9000 Ghent, Belgium. Tel.: +32 9 264 65 73; fax: +32 9 264 66 97.
E-mail address: Carlos.Palacio@UGent.be (C.A. Palacio).

0169-4332/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2008.05.235

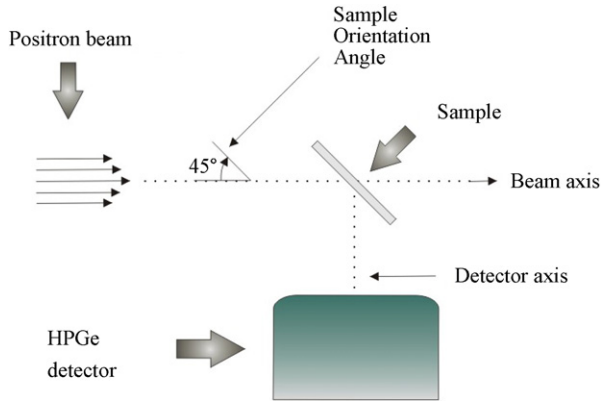

Fig. 1. Experimental setup. The sample is at 45° with respect to the beam and the Ge-detector is perpendicular to the positron beam.

implanted positrons by means of a variable energy positron beam (VEP).

It has been shown that in a longitudinal VEP experiment (i.e. the γ-ray detector located behind the sample on the axis of the beam), the Ps emitted at the surface of the sample has a linear momentum mainly away from the detector, which causes a red shift of the *p*-Ps contribution in the annihilation spectrum [12].

We show in this paper that by using a different geometry, with the sample at 45° with respect to the beam axis and the Ge-detector perpendicular to the positron beam (see Fig. 1), the linear momentum of the Ps emitted at the surface of the sample is given mainly towards the detector which allows the detection of the *p*-Ps emission as a blue-shifted fly-away peak (Fig. 2a), whereas when the sample and the Ge-detector are perpendicular to the positron beam, the *p*-Ps emission is detected as a narrow central peak (Fig. 2b). A blue-shifted peak has an advantage over the red shifted because the low energy tail of the photo peak from low angle Compton scattering can be avoided.

From the analysis of the fly-away *p*-Ps (i.e. the blue-shifted contribution), the bulk *p*-Ps (central narrow contribution), and also the fly-away *o*-Ps observed in the Compton-to-peak ratio analysis, we calculated the thermal and or epithermal e^+ diffusion length, the Ps formed in the bulk and the fraction of e^+ that pick up an e^- from the surface and form Ps.

2. Experimental

The chosen material for this experiment was a standard polymethyl methacrylate (PMMA) resist (used in lithography) with low molecular weight (approximately 450 k) in a spin bowl compatible solvent system (SBC) 5% (purchased from Brewer science). The PMMA density (ρ) was considered to be 1.197 g cm^{-3}. The polymer film was prepared by spin-coating on Si wafer of 2 in. diameter. The coating was performed with the spinning velocity of 2000 rpm and with the spinning time of 30 s. After the spin coating, the sample was immediately heated at 120 °C during 60 s. Then, it was immersed in a distilled water bath for about 24 h. Posteriorly, the PMMA film was easily detached from the silicon wafer by pulling carefully from the borders of the polymer. The floating film was picked up by an aluminium holder with a 3 cm diameter hole in its centre and it was finally dried in a furnace at about 100 °C during 15 min. The film thickness was measured with a surface profilometer (Talystep) and was found to be 310 nm.

The experiments were performed at the variable energy positron beam in Ghent [13]. The DBAR measurements were done with the sample perpendicular and at 45° with respect to the positron beam axis (Fig. 1). They were recorded every 30 min for several implantation energies from 0 to 1.2 keV and were carried out with a Canberra high-purity Ge (HPGe) detector with

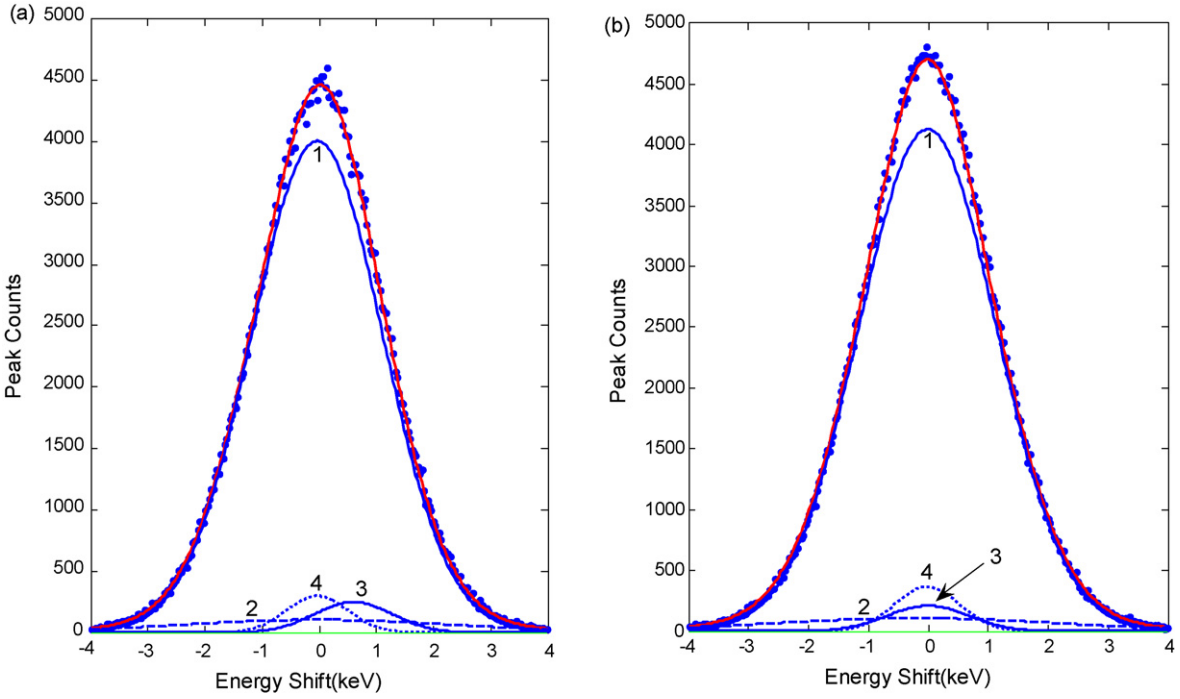

Fig. 2. Annihilation peak obtained for the PMMA sample (a) at 45° with respect to the positron beam and (b) perpendicular to the positron beam with implanted positron energy of 467 eV. The fitting is done with a low momentum (1), high momentum (dashed line) (2), a blue-shifted or centred contribution from the emitted *p*-Ps (3) and annihilation of *p*-Ps in the bulk (dotted line) (4).

a full width at half maximum (FWHM) resolution of 1.16 keV at the 514 keV line of ^{85}Sr. The HPGe detector was coupled to a digital signal processor (DSP) unit, model 2060 from Canberra.

Special care was taken to minimize the effect of the charge of the sample which can influence the measurements when the samples are insulators.

In this experiment, the influence of the charging may be small as it was controlled by limiting the measuring time and also because the presented data are given for the fresh sample, which is the condition of free of charge-up effect.

Time-of-flight (TOF) spectroscopy which uses a specialized setup [4] is the basic method to investigate Ps emission in a direct way. As we do not expect to obtain a detailed description of the energy distribution of the emitted *p*-Ps, the detected photo-peak (by only one Ge-detector) can (in first approximation) be fitted with a superposition of Gaussian distributions whose components arise from the different annihilation channels [14,15].

All the DBAR spectra were therefore independently analyzed with a sum of four Gaussians (see Fig. 2) by using the DBAN program [16]. In this program, the stepwise background is subtracted, and then the 511-keV-line can be fitted with convoluted Gaussians (up to four and by taking into account the detector resolution) so as a result, the observed ($FWHM_{fit}$) values for the Gaussians are obtained.

3. Analysis and results

In the Fig. 2, the two main contributions (labelled with 1 and 2) have the same centroid and they describe the low and high momentum contribution of the annihilation of e^+ in the bulk and / or on the surface. The third Gaussian contribution represents the emitted *p*-Ps. Notice that due to the sample orientation in Fig. 2a it is shifted towards high energy (causing a strong asymmetry in the annihilation peak). The fourth contribution centred and having narrow FWHM is identified as annihilation of *p*-Ps in the bulk.

If Ps is formed in the bulk of the material, we may assume that the initial distribution of Ps is equal to the e^+ implantation profile. We call f_{Ps} the fraction of e^+ that form Ps. The remaining fraction $(1 - f_{Ps})$ of e^+ can diffuse back to the surface and may emerge as *o*-Ps or *p*-Ps by picking up an e^- from the surface. The fraction that captures such an e^- is f_{pu}. The bulk Ps diffuses and is either trapped in free-volume sites or reaches the surface whereupon it is ejected. As stated in Ref. [12], the decay of trapped *p*-Ps is branched into pick-off annihilation and self-annihilation and due to the branching, only a fraction f_b of *p*-Ps is observed as a narrow central contribution in Doppler angular correlation measurements.

Given the implantation profile $P(E, z)$, the probability of reaching the surface is proportional to [17,18]:

$$F_j(E) = \int_0^\infty P(E,z) \exp\left(\frac{-z}{L_j}\right) \mathrm{d}z, \tag{3}$$

where the subscript *j* stands for the positrons (+), *p*-Ps and *o*-Ps. The respective "diffusion lengths" are L_+, $L_{p\text{-Ps}}$ and $L_{o\text{-Ps}}$. The diffusion length is characteristic of the distance that a positron can travel before annihilated or captured in a localized state [18]. The only one experiment found in the literature with the purpose of investigate the e^+ diffusion length in PMMA was done by He et al. [19]. They analyzed PMMA at 30 K and found $L_+ = 6.6$ nm.

The intensities of the fly-away *p*-Ps that is observed in the blue-shifted contribution, the fraction of bulk *p*-Ps that appears as a central narrow contribution in the Doppler profile and also the fly-away *o*-Ps that is observed in the Compton-to-peak ratio analysis, can be described by the following set of equations:

$$I^{e}_{p\text{-Ps}} = \left(\frac{1}{4}\right)[fF_+(E) + f_{Ps} f_e F_{p\text{-Ps}}(E)], \tag{4a}$$

$$I^{e}_{o\text{-Ps}} = \left(\frac{3}{4}\right)[fF_+(E) + f_{Ps} f_e F_{o\text{-Ps}}(E)], \tag{4b}$$

$$I^{b}_{p\text{-Ps}} = \left(\frac{1}{4}\right) f_b f_{Ps}[1 - f_e F_{p\text{-Ps}}(E)], \tag{4c}$$

where $f = f_{pu}(1 - f_{Ps})$, and f_e represents the emission efficiency.

The bulk *p*-Ps is trapped in the free volume and mainly self-annihilates with isotropic low-momentum transfer which makes necessary to add the central narrow contribution to the analysis of the Doppler line-shape.

The experimental fraction of the emitted *o*-Ps at implantation energy *E* is obtained from a Compton-to-peak ratio analysis of the annihilation spectrum [20]:

$$I^{exp}_{o\text{-Ps}} = \alpha\left[1 + \frac{P(0)}{P(\infty)}\frac{R(0) - R(E)}{R(E) - R(\infty)}\right]^{-1} \tag{5}$$

where *P* is the number of counts accumulated in the region centred around the 511 keV annihilation line and $R = C/P$ is the ratio of the number of counts in a chosen fixed area of the Compton region *C* to the peak counts *P*. $P(0)$ and $R(0)$ are the values extrapolated to zero implantation energy and $P(\infty)$ and $R(\infty)$ are the asymptotic values for high implantation energies (i.e. in the bulk of the material). Eq. (5) is applied only if $P(\infty)$ and $R(\infty)$ correspond to a situation where no *o*-Ps is detected by three-quantum annihilation.

The fly-away *o*-Ps may annihilate at several cm in front of the specimen [21], and thus the solid angle for the detection of the corresponding three-quantum annihilation is increased by a factor ≈2.26 with respect to all two-quantum annihilation. Such an effect is taken into account by adjusting the value of the proportionality constant α in the way that $I^{e}_{o\text{-Ps}}(0)/I^{e}_{p\text{-Ps}}(0) = 3$.

The experimental data for the intensities of the fly-away *p*-Ps, the fly-away *o*-Ps and the bulk *p*-Ps for the PMMA film are shown in Fig. 3. The solid lines represent the fit of Eqs. (4a)–(4c) to determine

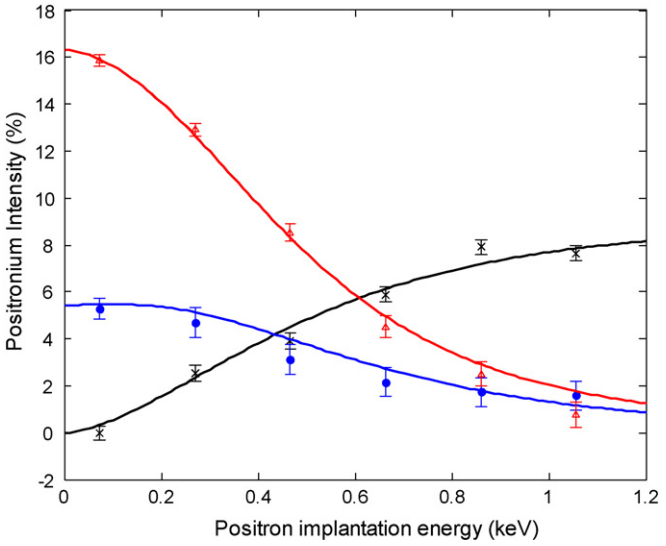

Fig. 3. Ps emission from a PMMA film of 310 nm-thick (spin-coated at 2000 rpm). The figure shows the intensity of the *p*-Ps formed in the bulk (×), the intensity of the *p*-Ps emitted from the surface (●) and the intensity of the emitted *o*-Ps (△). The solid lines represent the fit of Eqs. (4a)–(4c) to determine the e^+ diffusion lengths (thermal and or epithermal) L_+, $L_{p\text{-Ps}}$ and $L_{o\text{-Ps}}$. using the most common values for the Makhovian equation.

the e^+ diffusion length L_+ (thermal and or epithermal). It can be seen that the intensity of the bulk *p*-Ps increases as function of the positron implantation energy mainly at the expenses of the intensity of the emitted *p*-Ps.

For comparison, the fitting was done by using the most frequently used values of the power-law equation on the Makhov distribution ($n = 1.6$ and $\alpha = 4.0\ \mu g\ cm^{-2}$) and by using the parameters proposed by Algers et al. ($n = 1.71$ and $\alpha = 2.81\ \mu g\ cm^{-2}$).

In the first case (which is the one of the Fig. 3), the fitted (thermal and or epithermal) e^+ diffusion lengths are $L_+ = (5.18 \pm 0.20)$ nm, $L_{p\text{-Ps}} = (12.68 \pm 0.09)$ nm and $L_{o\text{-Ps}} = (8.67 \pm 0.08)$ nm.

The total bulk Ps formation fraction is $f_{Ps} = (40.07 \pm 0.03)$, and the fraction of surface positrons that pick up an e^- and are emitted as Ps is $f_{pu} = (0.47 \pm 0.08)$.

In the second case, by using the values proposed by Algers et al., the fitted parameters are $L_+ = (3.456 \pm 0.001)$ nm, $L_{p\text{-Ps}} = (8.38 \pm 0.09)$ nm and $L_{o\text{-Ps}} = (5.82 \pm 0.03)$ nm. The total bulk Ps formation fraction is $f_{Ps} = (39.87 \pm 0.03)$, and the fraction of surface e^+ that pick up an e^- and are emitted as Ps is $f_{pu} = (0.47 \pm 0.08)$.

When comparing both results, the diffusion lengths obtained by the values proposed for Algers et al. in polymers, are lower. The total bulk Ps formation are about the same and the fraction of surface e^+ that pick up an e^- and are emitted as Ps are the same. These results suggest that for the diffusion length, special care with the chosen model has to be taken into account when analyzing the experimental data.

4. Conclusions

The emission of Positronium from the PMMA film surface as a function of the positron implantation energy has been studied by means of Doppler broadening, blue-shift spectroscopy and Compton-to-peak ratio analysis.

In our analysis we have approximated the detected photo-peak by a Gaussian decomposition as we do not expect to obtain a detailed description of the energy distribution of the emitted *p*-Ps. The narrow component attributed to the *p*-Ps emission is centred when the sample and the detector are perpendicular to the positron beam axis. However, it is shifted towards high energy when the sample is at 45° with respect to the beam axis. This fact has been explained as the linear momentum of the Ps emitted at the surface of the sample is given mainly towards the detector causing a blue shift of the *p*-Ps.

From a detailed analysis of the experimental results, the thermal and or epithermal positron diffusion length, the fraction f_{Ps} of positronium formed in the bulk and also the fraction of positrons that pick up an electron from the surface and form positronium can be obtained.

Special care has to be taken into account in selecting a correct model when analyzing the diffusion length of the experimental data as standard values might lead to wrong results.

Acknowledgments

This work is supported by IUAP/PAI V/01—Network program of the Belgian Federal Government, and by the Fonds voor Wetenschappelijk Onderzoek FWO-project G.0170.06.

References

[1] C. Dauwe, T. Van Hoecke, D. Segers, Condensed matter studies by nuclear methods, in: K. Tomala, E. Görlich (Eds.), Proceedings of the XXX Zakopane School of Physics, Institute of Physics, Jagielloian University and H. Niewodniczanski Institute of Nuclear Physics, Kraków, (1995), p. 275.
[2] P. Sferlazzo, S. Berko, K.F. Canter, Phys. Rev. B 32 (9) (1985) 6067.
[3] R.M. Nieminem, J. Oliva, Phys. Rev. B 22 (5) (1980) 2226.
[4] P. Sferlazzo, S. Berko, K.F. Canter, Phys. Rev. B 35 (10) (1987) 5315.
[5] A.F. Makhov, Sov. Phys. Solid State 2 (1961) 1934.
[6] A.P. Mills, R.J. Wilson, Phys. Rev. E 26 (1982) 490.
[7] S. Valkealahti, R.M. Nieminem, Appl. Phys. A 32 (1983) 95.
[8] S. Valkealahti, R.M. Nieminem, Appl. Phys. A 35 (1984) 51.
[9] A. Vehanen, K. Saarinen, P. Hautojärvi, H. Huomo, Phys. Rev. B 35 (10) (1987) 4606.
[10] J. Algers, P. Sperr, W. Egger, G. Kögel, F.H.J. Maurer, Phys. Rev. B 67 (2003) 125404.
[11] M. Eldrup, A. Vehanen, P.J. Schultz, K.G. Lynn, Phys. Rev. B 32 (11) (1985) 7048.
[12] S. Van Petegem, C. Dauwe, T. Van Hoecke, J. De Baerdemaeker, D. Segers, Phys. Rev. B 70 (2004) 115410.
[13] J. De Baerdemaeker, J. Colaux, G. Terwagne, C. Dauwe, Radiat. Phys. Chem. 68 (2003) 605.
[14] O.E. Mogensen, Positron Annihilation in Chemistry, Springer–Verlag, Berlin, Heidelberg, 1995.
[15] G. Dlubek, M.A. Alam, Polymer 43 (2002) 4025.
[16] DBAN program is written in MATLAB by Nikolay Djourelov and it is available on request (nikdjour@inrne.bas.bg).
[17] W. Swiatkowski, Nucleonika 48 (3) (2003) 141.
[18] A. Dupasquier, A. Zecca, Riv. Nuovo Cimento. 8 (12) (1985) 1.
[19] C. He, V.P. Shantarovich, T. Suzuki, S.V. Stepanov, R. Suzuki, M. Matsuo, J. Chem. Phys. 122 (2005) 214907.
[20] A.P. Mills Jr., Phys. Rev. Lett. 41 (1978) 1828–1831.
[21] H.H. Jorch, K.G. Lynn, T. Mc Mullen, Phys. Rev. B 30 (1) (1984) 93.