

Median implantation depth and implantation profile of 3–18 keV positrons in amorphous polymers

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Most applications of positron beams require knowledge of the implantation characteristics for an appropriate interpretation of the experimental data. In this work, the median implantation depth as a function of implantation energy, $z_{1/2}(E)$, of 3–18 keV positrons and their implantation profile $P(z, E)$ in a total of 13 thin films of atactic polystyrene, poly(styrene-co-acrylonitrile), and polymethylmethacrylate spin coated onto a silicon substrate were determined from positron lifetime measurements using a pulsed, low-energy positron beam. $z_{1/2}(E)$ and $P(z, E)$ were determined from the measurement of the ortho-positronium yield obtained from the intensity I_3 of the long lifetime. $z_{1/2}(E)$ was parametrized with the commonly used power-law fit $z_{1/2}(E) = (A/\rho)E^n$, with ρ and E in units of g cm^{-3} and keV, respectively, yielding $A = 2.81(\pm 0.2) \mu\text{g cm}^{-2}$ and $n = 1.71(\pm 0.05)$. Excellent agreement between amorphous polymer and literature data on Al and Cu suggests that the median implantation depth of positrons for low- to medium- Z materials in the studied energy range is independent of structure and only a function of mass density. Fitting of the Makhovian implantation profile to the experimental data suggested that the value of the parameter m varies between 1.7 and 2.3, systematically increasing with z at constant implantation energy, but is independent of the implantation energy. Using an equation proposed by Baker *et al.*, the experimental data of 12 of the 13 studied polymer films could be described with a slightly better agreement than the Makhovian equation.

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I. INTRODUCTION

Positron beams provide a unique and nondestructive tool for obtaining depth-resolved information of condensed matter. Two important applications of positron beams are the investigation of inhomogeneously distributed defect concentrations in crystalline materials and the study of properties of thin films, surfaces, and interfaces of layered materials.

In polymers, typically three lifetimes can be resolved from a positron lifetime spectrum, commonly denoted as τ_1, τ_2, τ_3 with the corresponding intensities I_1, I_2, I_3 . They are attributed to the annihilation of para-positronium, free positrons, and ortho-positronium (*o*-Ps), respectively. The lifetime of the *o*-Ps τ_3 , is of particular importance in polymer research, because of its sensitivity to the dimensions of the microscopic free volume cavities present in amorphous polymers.

In polymer applications, positron beams have been used to probe free volume at surfaces and in thin films. Observations have been made of a surface-induced shift in glass transition temperature,^{1–3} increased free volume cavity size close to a surface,^{4–7} and free volume changes induced by weathering⁸ and ion implantation.^{9,10}

One of the main limitations of positron beams for studying surfaces, interfaces, and interphases of polymers and other low-density materials is the intrinsic broadening of the positron implantation profile with implantation energy. A typical experimental situation is that the dimensions of a polymer exhibiting the non-bulk-like properties of interest, such as at the surface or at an interface, is much smaller than the width of the positron implantation profile. Also, the assumed short positron diffusion length in polymers prevents

effective trapping at the surface or interface of interest, which is in contrast to the situation in many metals and semiconductors where positrons diffusion lengths are longer.

The intrinsic shape and size of the positron implantation profile (the implantation depth distribution of monoenergetic positrons) are thus of prime importance in the application of positron beams to polymers. Accurate knowledge of the positron implantation profile could be directly applied to the design of positron beam experiments and to the interpretation of the results. A full description of the positron implantation profile in the direction perpendicular to the surface is given by the median implantation depth as a function of implantation energy, $z_{1/2}(E)$, and the implantation distribution $P(z, E)$, which describes the probability of a positron with the initial energy E thermalizing at depth z in the material.

The first systematic investigation of these relationships was based on measurements, by Mills and Wilson of the transmission of 1–6 keV positrons through thin films of Al and Cu.¹¹ They introduced the power-law equation

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

to describe their median implantation data, with the parameter A in units of g cm^{-2} and E in keV. Equation (1) has become the standard approach for parameterization of data of $z_{1/2}(E)$, with values of A often reported in units of $\mu\text{g cm}^{-2}$. The material and energy dependences of the parameters A and n have been under some debate, with more recent work arguing for material dependent A and n values in Eq. (1),^{12–14} as opposed to some of the experimental earlier work.^{11,15}

Also, in Mills and Wilson,¹¹ one of the first attempts to experimentally determine the shape of $P(z, E)$ was presented. An exponentially decreasing $P(z, E)$ as a function of z was concluded, which was later refuted by Vehanen *et al.*,¹⁵ who used the S parameter derived from Doppler-broadening measurements, to determine $P(z, E)$ in samples of ZnS and Al₂O₃ layers. The “Makhovian equation”¹⁶

$$P(z, E) = -\frac{d}{dz} \exp\left[-\left(\frac{z}{z_0(E)}\right)^m\right] \quad (2a)$$

or in its differentiated form

$$P(z, E) = \frac{mz^{m-1}}{z_0^m(E)} \exp\left[-\left(\frac{z}{z_0(E)}\right)^m\right], \quad (2b)$$

with

$$z_0(E) = z_{1/2}(E)(\ln 2)^{-1/m}, \quad (2c)$$

was proposed to give a better description of $P(z, E)$ than the previously used exponentially decreasing function. The value of the parameter m in the Makhovian equation was found to be $m=2$ or 2.1. This was in agreement with the earlier predictions from the Monte Carlo simulations.¹⁷

A similar approach to calculate $z_{1/2}(E)$ and $P(z, E)$ was later used for Al, producing similar results, but yielding an implantation profile which could be parametrized more accurately by Eqs. (3a) and (3b) as proposed by Baker and co-workers.^{18–20}

$$P(z, E) = -\frac{d}{dz} \exp\left\{-\left[\left(\frac{z}{z_\alpha(E)}\right)\left(1 + \frac{z}{z_\alpha(E)}\right)^2\right]^{m^*}\right\}, \quad (3a)$$

with

$$z_\alpha(E) = 2.58z_{1/2}(E) \quad (3b)$$

and with $m^* = 1.28$. A number of Monte Carlo simulations of the implantation depths of positrons in metals have been published,^{13,21–25} and they are generally in good agreement with the experimental results.

To the best of the authors' knowledge, there is to date no published systematic work on $z_{1/2}(E)$ and $P(z, E)$ of polymers. The requirement of known $z_{1/2}(E)$ and $P(z, E)$ in the interpretation of previous positron beam data for polymers has left researchers with little other option than to apply parameters extracted for metals and other inorganic materials.^{3–8,26} The most commonly used figures in the evaluation of the positron beam data of polymers have been a power-law equation for the *mean* positron implantation depth.²⁷ However, these figures are not derived from measurements on polymers, but are based on positron transmission measurements on Al and Cu foils using 1–6 keV positrons¹¹ and Doppler broadening of Al₂O₃-ZnS-Al₂O₃ deposited on top of a glass substrate using 0–25 keV positrons.¹⁵

The aim of the present study was to extract $z_{1/2}(E)$ and $P(z, E)$ for 3–18 keV positrons in three different amorphous polymers. A method similar to the previously used binary

sample method²⁰ has been employed, but with the distinction that the *o*-Ps yield from positron lifetime measurements (I_3) has been studied as a function of the implantation energy instead of the S parameter derived from Doppler-broadening measurements. The *o*-Ps implantation profile that has been extracted by these measurements should be representative for all implanted positrons, since the positrons implanted at, e.g., 3 keV at the polymer surface will be in the state of a free positron during most of the distance traveled in the polymer film.

II. MATERIALS AND METHODS

Three widely used amorphous polymers with similar glass transition temperatures but with different ortho-positronium yields were chosen for this study: atactic polystyrene (PS) (Scientific Polymer Products catalog No. 845), atactic poly(methyl-methacrylate) PMMA (Scientific Polymer Products catalog No. 037B), and poly(styrene-co-acrylonitrile) (SAN, 25 wt % AN) (BASF AG type 358N). Silicon wafers, doped with phosphorus at a concentration of approximately 10^{14} cm^{-3} [Topsil, CFZ N (100) 4"] were used as substrates.

PS and PMMA were dissolved in toluene and SAN in CH₂Cl₂ to concentrations between 10 and 100 mg/ml. The polymer film samples were spin coated onto the silicon substrates at 2000 rpm.²⁸ After spin coating, all films were dried at 116 °C for 40 min and then cooled at 0.5 °C/min to 86 °C and then cooled at 2 °C/min to room temperature.

The thickness of the films was measured by atomic force microscopy (AFM) in contact mode. The film thickness was obtained by removing small patches of polymer film and measuring the vertical distance between the silicon surface and the polymer surface at several locations.

Positron lifetime spectra for all polymer films were recorded in the energy range 3–18 keV, at 34 °C, using a pulsed, low-energy positron system (PLEPS) with a time resolution of approximately 280 ps. Each spectrum contained 2 or 4×10^6 counts, and the peak-to-background ratio was approximately $10^4:1$. The spectra were evaluated with a modified version of PATFIT (Ref. 29) with three lifetimes. All lifetimes, intensities, and background were free fitting parameters in the evaluation procedure.

The yield of the ortho-positronium (*o*-PS), extracted from the lifetime spectra as I_3 , was assumed to be directly proportional to the fraction of the implanted positrons thermalized and annihilated in the polymer film. The lifetime of the *o*-Ps in polymers (1900–2100 ps from pick-off annihilation of the ortho-positronium) is well separated from the two lifetimes of silicon (ca. 220 ps in Si-bulk and 400 ps at the Si-vacuum surface) and can thus be unambiguously attributed to annihilation events in the polymer film.

By measuring I_3 as a function of positron implantation energy, the fraction of the positrons stopped in the film was obtained from the ratio between the energy dependent *o*-Ps yield I_3^E and the *o*-Ps yield for the bulk polymer, I_3^{bulk} . The ratio I_3^{norm} , directly obtained from experimental data, was taken to be equal to the integral of $P(z, E)$ from $z=0$ to $z=d$ (d =polymer film thickness):

$$I_3^{\text{norm}} = \int_{z=0}^{z=d} P(z, E) dz. \quad (4)$$

At the specific energy $E_{1/2}$ in keV, defined as the energy at which $I_3^{\text{norm}} = 0.5$, 50% of the implanted positrons annihilate in the polymer and 50% in the silicon or at the silicon surface. At $E_{1/2}$, the median implantation depth $z_{1/2}$ is thus equal to the polymer film thickness d in nm. By plotting the polymer film thickness d versus $E_{1/2}$, the shape of $z_{1/2}(E)$ was obtained and parametrized with Eq. (1).

Arguably, the measured lifetime spectra could be influenced by positrons backscattered from the silicon surface due to the difference in mass density between polymer (ca. 1 g cm^{-3}) and the silicon substrate (2.33 g cm^{-3}). Also, positrons thermalized in the silicon may diffuse back into the polymer film. However, in this study, the possible corruption of data due to these effects has been neglected, considering the following arguments: (i) Previous measurements have shown that positron backscattering and backdiffusing from elemental surfaces are reduced by surface contamination.³⁰ The surface of the silicon substrates used in this study was expected to be fully oxidized, and the oxide layer of the substrates should thus reduce backscattering and also provide an efficient barrier to positrons diffusing out of the silicon. (ii) In order for backscattered and backdiffusing positrons to influence the extraction of the implantation characteristics based on I_3 measurements, they must form *o*-Ps. As observed in a number of previous investigations, *o*-Ps formation in polymers is drastically reduced at implantation energies of approximately 1 keV and lower.^{4–6,26} This suggests that positrons reemitted from the silicon surface within this energy range, including diffusing positrons at thermal energy, contribute little to the total *o*-Ps yield.

The shape of $P(z, E)$ was investigated by fitting the Makhovian equation (2a) and the equation proposed by Baker and co-workers^{18–20} [Eq. (3a)] to the experimental data. For each measured implantation energy, the equation was integrated over the film thickness, and the value of the integral was compared to the measured value of I_3^{norm} . For the Makhovian equation, the value of the parameter m was fitted to obtain an agreement as good as possible with the experimental data at each energy.

The values of the integrals were found to be very sensitive to the film thickness [$z = d$ in Eq. (4)]. Thus, in the calculation of the integrals, it was necessary to use floating values of z as the upper value for the integrals, i.e., using a value that was consistent with the A and n extracted for the median implantation depth. The deviation between the upper boundary used for calculating the integrals and the film thickness measured by AFM was less than 5% in 10 of 13 films, i.e., within the estimated experimental error of the film thickness measurements.

III. RESULTS

Positron lifetime spectra of 13 polymer films ($d = 220\text{--}2200 \text{ nm}$) were recorded as a function of energy (3–18 keV). The lifetimes and intensities as a function of energy for a 1390-nm-thick polystyrene film are displayed in

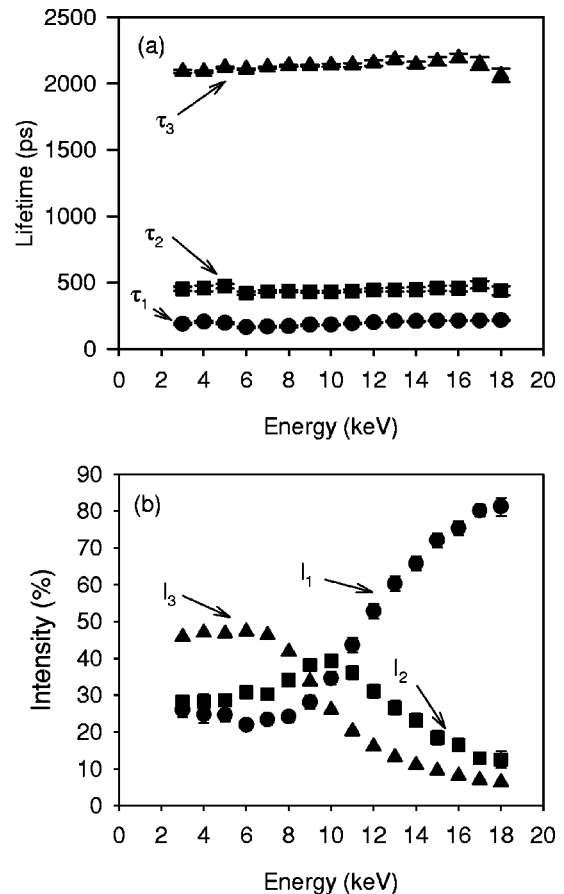


FIG. 1. Lifetimes (a) and intensities (b) as a function of positron implantation energy for a 1390-nm polystyrene film spin coated onto silicon. The spectra were evaluated without any constraints on lifetimes or intensities.

Figs. 1(a) (lifetimes) and 1(b) (corresponding intensities). The results are typical for all 13 films studied. The most salient features are the nearly constant values of the lifetimes as a function of energy and the large variations of the corresponding intensities as a function of energy.

The constant value of the lifetimes as a function of energy results from the overlap between the two short lifetimes of the polymer (ca. 200 and 400 ps) and the lifetime found in bulk silicon (ca. 200 ps) and the surface lifetime of silicon (ca. 400 ps). The long lifetime at 2100 ps is, however, unique for the polymer and could be determined from the spectra for $I_3 > 3\%$.

The intensities in the energy range 3–7 keV are independent of energy and result from an implantation profile that is distributed only in the polymer. At higher energies ($>8 \text{ keV}$), the value of the intensities approaches the bulk silicon ($I_1 = 100\%$). The small, but clear, maximum of I_2 at 10 keV results from a maximum fraction of positrons annihilated in the silicon surface with a lifetime of ca. 400 ps.

The full set of data used to determine $z_{1/2}(E)$ and $P(z, E)$ is displayed in Table I and Fig. 2. Figure 2 displays the intensities of the long lifetime (approximately 2100, 1900, and 2000 ps for PS, PMMA, and SAN, respectively) normalized by the bulk value of I_3 of each material (45%, 33%, and

TABLE I. Median implantation depths $z_{1/2}$ as a function of positron implantation energy E for polystyrene (PS), poly(methylmethacrylate) (PMMA), and poly(styrene-co-acrylonitrile) (SAN). $z_{1/2}$ is the thickness of each polymer film as measured by atomic force microscopy, and $E_{1/2}$ is the energy at which the median implantation depth is equal to the film thickness, obtained as the energy at which $I_3=0.5$ of its polymer bulk value in Fig. 2. The symbols correspond to those used in Fig. 2.

Material	$E_{1/2}$ (keV)	$z_{1/2}$ (nm)
○ PS	5.05	440
○ PS	7.10	800
● PS	10.50	1390
□ PMMA	4.60	300
■ PMMA	5.70	510
■ PMMA	8.45	925
■ PMMA	11.60	1500
■ PMMA	13.30	2000
△ SAN	3.45	220
△ SAN	5.40	450
△ SAN	6.90	690
△ SAN	10.20	1350
▲ SAN	13.00	2200

25%, respectively, obtained from the spectra at the low-energy range) and are plotted as a function of the implantation energy in keV.

The energy $E_{1/2}$ of each film, defined as the energy at which $z_{1/2}$ =polymer film thickness, is obtained from Fig. 2 as the location on the energy axis of $I_{3\text{norm}}=0.5$. The intensity of the long lifetime was determined with an error of typically 1% at $I_{3\text{norm}}=0.5$ (error estimated by PATFIT). The thickness of the polymer films was determined by AFM (Table I) with an estimated error of $\pm 5\%$. The values of the bulk densities of the polymers were taken from literature data on density

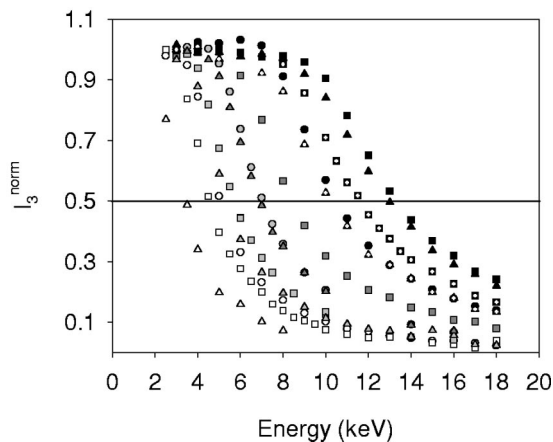


FIG. 2. Normalized intensities I_3^{norm} as a function of energy for all 13 polymer films. I_3^{norm} is the measured value of I_3 at energy E for each film, normalized by the corresponding bulk value of I_3 [45%, 33%, and 25% for polystyrene, poly(methyl-methacrylate), and poly(styrene-co-acrylonitrile)]. The line $I_3^{\text{norm}}=0.5$ yields at which energy 50% of the positrons have stopped in each polymer film.

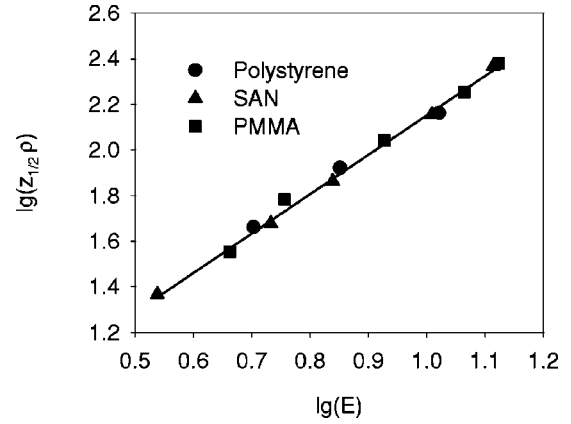


FIG. 3. Median implantation depth times mass density, in units of $\mu\text{g cm}^{-2}$, vs implantation energy in keV (logarithmic scale). The line plot is the result from a linear regression from the data: $\lg(z_{1/2}\rho) = 1.71 \times \lg E + 0.4488$, $R^2 = 0.9951$; $n = 1.71$, $A = 2.81 \mu\text{g cm}^{-2}$.

measurements of identical materials (PS=1.040 and SAN = 1.057, PMMA=1.197, in g/cm^3).^{31,32}

The commonly used power-law equation (1) was used to parametrize $z_{1/2}(E)$ from Table I. A and n are fitting parameters, and ρ is the mass density. The parameters A and n were fitted to a log-log plot of the $z_{1/2}(E)$ data (Fig. 3) and were found to be $2.81(\pm 0.2) \mu\text{g cm}^{-2}$ and $1.71(\pm 0.05)$, respectively. The median implantation depth for positrons in amorphous polymers was thus found to be described by

$$z_{1/2} = \frac{2.81}{\rho} E^{1.71}, \quad (5)$$

with $z_{1/2}\rho$ having units of $\mu\text{g cm}^{-2}$ and E in keV. The errors in the given values of A and n were estimated from the linear fit of Fig. 3 and originate mainly in the measurements of film thickness.

The ability of Eqs. (2a) and (3a) to describe the shape of the implantation profile was investigated by studying the deviation between the measured value of I_3^{norm} and the value predicted by the respective equation for each implantation energy. The error of each equation was calculated as the deviation between the value predicted by the equation ($I_3^{\text{norm,eq}}$) and the measured value of I_3^{norm} , divided by the measured value of I_3^{norm} , i.e., $\text{error} = (I_3^{\text{norm,eq}} - I_3^{\text{norm}}) / I_3^{\text{norm}}$. By using this procedure, the error of each equation naturally becomes very large as I_3^{norm} approaches zero, but it has the advantage that it reflects the limitations of the equations in predicting the fractions of positrons annihilating close to a polymer surface. The results of one of the polymer films (PMMA, 510 nm) are plotted in Fig. 4.

The fitted value of the shape parameter m in the Makhovian equation was found to be dependent on I_3^{norm} and is plotted as a function of I_3^{norm} in Fig. 5. A value of $m = 2.2$ or 2.3 was found to give a good description for most films in the region $I_3^{\text{norm}} > 0.5$, while $m = 1.7$ or 1.8 was found to give a better description at $I_3^{\text{norm}} < 0.5$. The lower values of m at lower intensities were thus considered to give a better de-

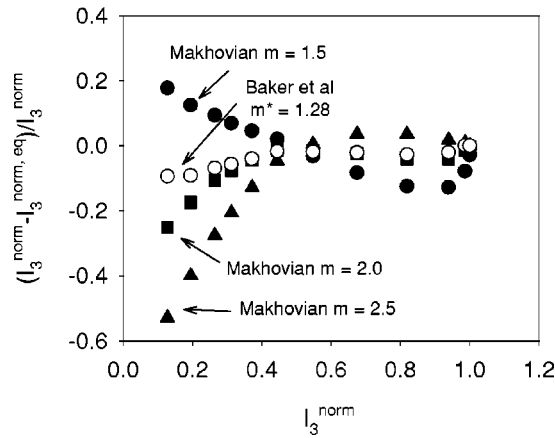


FIG. 4. Error of Makhovian equation and the equation proposed by Baker and co-workers [Eq. 3(a)] (Refs. 18–20), calculated as the relative error in estimating the fraction of positrons stopping in the polymer film, $I_3^{norm, eq}$, in comparison to the experimental data.

scription of the positrons with $z < z_{1/2}$ (i.e., the profile at low z), while $m = 2.3$ gave the best fit of the whole implantation profile (implying $m > 2.3$ for positrons stopping at $z > z_{1/2}$).

The relationship between m and I_3^{norm} was thus found to be independent of E ; i.e., the optimal value of m was, within experimental error, always the same at a certain value of I_3^{norm} for any film at any energy. The parameter m of the Makhovian equation was thus concluded to be a function of z for an implantation profile at constant energy rather than a function of energy.

The fit of the equation proposed by Baker and co-workers^{18–20} [Eq. (3a)] yielded good agreement with the experimental data using one constant fitting parameter ($m^* = 1.28$). More than 75% of the data points were predicted with an error smaller than 10% of the measured absolute value of I_3 , which was a better fit than using any value of m

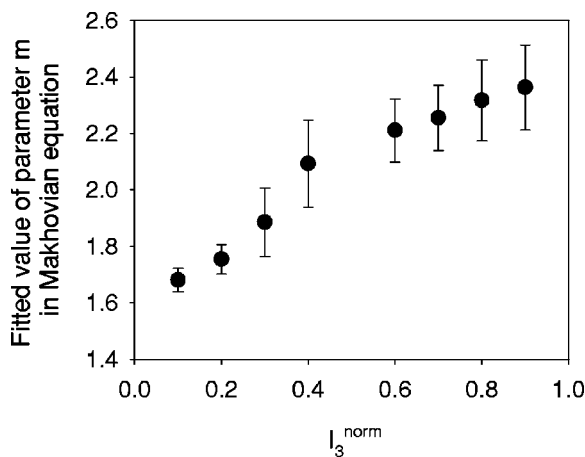


FIG. 5. Parameter m of the Makhovian equation fitted to the experimental data, plotted as a function of the fraction of positrons stopped in the polymer film, I_3^{norm} . Each value of m is the average of the fitted value of m for all 13 films at a constant value of I_3^{norm} . The relationship between m and I_3^{norm} was found to be independent of positron energy, suggesting that the parameter m is mainly a function of z at constant implantation energy.

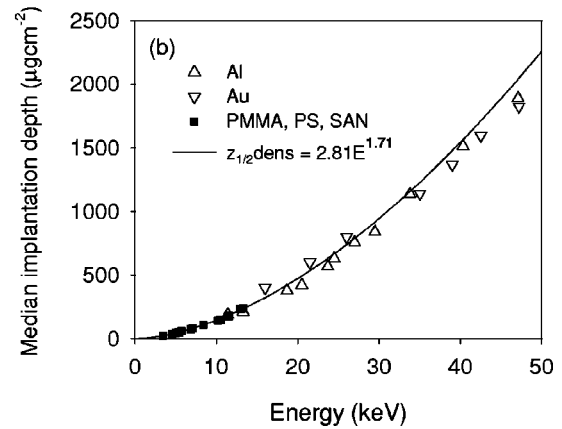
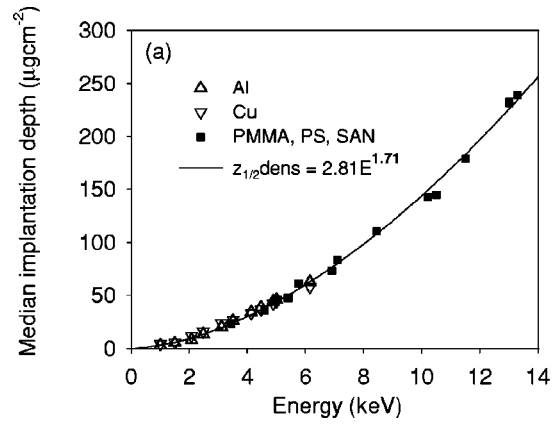


FIG. 6. Median implantation depths $z_{1/2}$ times mass density in units of $\mu\text{g cm}^{-2}$ for (a) Al, Cu (Ref. 11), and polymer in the 0–14 keV range and for (b) Al (Ref. 18), Au (Ref. 12), and polymer in the 0–50 keV range. The same polymer data are plotted in (a) and (b). The line plot is the commonly used power law equation (1) with constants A and n derived from the experimental data of polymer in this study.

in the Makhovian equation, provided both the Makhovian equation and the equation proposed by Baker and co-workers^{18–20} were used with a constant fitting parameter for all films and all at all used energies.

IV. DISCUSSION

If the median positron implantation depth is expressed in $\mu\text{g cm}^{-2}$, excellent agreement is obtained between the present polymer data and the data of some previously studied metals. This is clear from the power-law fit based on the polymer data of this investigation, which when extrapolated, also gives a good description of the data of Al and Cu by Mills and Wilson¹¹ in the 0–6 keV region [Fig. 6(a)], as well as data of Al by Baker *et al.*¹⁸ in the 10–50 keV region [Fig. 6(b)] and, to a somewhat lesser degree, also of the data of Baker *et al.*¹² of Au in the 10–50 keV range [Fig. 6(b)]. Thus the simple power-law equation (1) seems to hold very well for low- to medium- Z materials, including polymers. That the mass density is a sufficient scaling property for the positron implantation depth in Al, Cu, and amorphous polymers also indicates that the thermalization of positrons is to a large

TABLE II. Experimentally determined values of A and n in the power-law fit of the median implantation depth $z_{1/2}(E) = (A/\rho)E^n$.

Material	$A(\mu\text{g}/\text{cm}^2)$	n
PS, PMMA, SAN ^a	2.81(\pm 0.2)	1.71(\pm 0.05)
Aluminum ^b	3.32	1.60
Copper ^c		1.43
Aluminum ^d	2.62	1.71
Gold ^e	8.31	1.42
ZnS and Al ₂ O ₃ ^f	3.8	1.62
<i>a</i> -Si ^g	2.58	1.7

^aThis investigation.

^bReference 11.

^cReference 11.

^dReference 12.

^eReference 12.

^fReference 15.

^gReference 35, calculated from original value of $A=2.75\pm 0.25$ given for the power-law fit of the mean implantation depth.

degree independent of the microscopic structure in the energy range studied for low- to medium- Z materials.

In light of the good agreement between the single power-law equation for $z_{1/2}(E)$ found for polymer and the data of Al, Cu, and Au in Figs. 6(a) and 6(b), it is interesting to note the comparatively large differences in the corresponding values of A and n which have been extracted from the data in Figs. 6(a) and 6(b) (Table II). The differences in the reported values in Table II can, to some extent, be attributed to the interdependence of A and n and the limited energy ranges of the experiments.

Within experimental errors, the parameters A and n were found to be energy independent within the studied energy range, since there was no evident systematic error between the experimental data and the power-law fit as seen in Fig. 3. This is in agreement with early experiments;^{11,15} however, the opposite is stated in some more recent experiments^{14,18} and Monte Carlo simulations.^{13,33} The investigations suggesting energy-dependent A and n were based on relatively large energy ranges of 10–50 keV (Ref. 18) and ca. 0–30 keV (Ref. 14), which appears to be required for the energy dependency to be appreciable.

In the fitting of the shape parameter m of the Makhovian equation to the experimental data, it is clear that the integral used for the fitting crucially depends on the values of A and n . For instance, in the case of implanting positrons at 3 keV into PMMA (density = 1.197 g/cm³) and estimating the fraction of positrons thermalized within 100 nm from the surface ($z_{1/2} = 154$ nm), a change in the value of A by 5% (e.g., from 2.81 to 2.66 $\mu\text{g}/\text{cm}^2$) causes a change in the value of the integral by almost 20%, while changing the value of m by 10% (e.g., from 2.0 to 2.2) changes the value of the integral by only ca. 10%. As has been pointed out elsewhere,^{19,20} the requirement of accurate knowledge on the median implantation depths is one of the drawbacks of fitting the shape of $P(z, E)$ to data of the integral of $P(z, E)$. The problem is, however, difficult to circumvent using conventional methods

and instruments. Since the method of floating boundaries of the integral of $P(z, E)$ yielded systematic and consistent results for all 13 polymer films, the observed dependence of the shape parameter m on the implantation depth z for a constant implantation energy was nevertheless considered as typical for the shape of $P(z, E)$ in amorphous polymers. The difference between the integrals of, e.g., the Makhovian equation ($m = 2.2$) and the equation suggested by Baker and co-workers^{18–20} ($m^* = 1.28$) is also within the error introduced by A and n , but can for the same reason be considered to be at the least indicative of the shape of $P(z, E)$ due to consistent results.

The influence of backscattered positrons on the determination of the parameters A and n in the present investigation may be estimated from literature data on the backscattering of positrons as a function of atomic number and energy. The backscattering probability from C and Si was found to be approximately 7% and 12%–16%, respectively, in the energy range of $E_{1/2}$ in this study.^{30,34} In a worst-case scenario, the probability of backscattering from the silicon surface is unaltered by the presence of the polymer film, and all backscattered positrons thermalize in the polymer film with the bulk *o*-Ps formation probability. In the region $I_3^{\text{norm}} = 0.5$, i.e., when 50% of the positrons are nominally implanted into the silicon, the absolute increase of I_3^E based on these assumptions should thus be no more than 3.6% for PS, 2.7% for PMMA, and 2.0% for SAN. The shift in $E_{1/2}$ of each film due to this increase depends on the slope of I_3^{norm} at the intersection with the line $I_3^{\text{norm}} = 0.5$. The magnitude of the shift is related to the polymer film thickness, but should be on the order of 0.5 keV for most films. The maximum influence on the implantation depth parameters due to backscattering from the silicon surface can thus be estimated to a decrease in A by 30% and an increase in n by 7%. However, the backscattered fraction may be expected to be smaller from a polymer-silicon surface than a vacuum-silicon surface, due to a smaller change in mass density at the interface.

The influence of backscattering and backdiffusion on the present method of extracting the implantation parameters could, in future experiments, conveniently be elucidated by performing similar measurements on a sample, where the substrate of silicon has been exchanged for a polymer with a very low *o*-Ps yield, e.g., polyamide. Effects of backscattering and diffusion would hence be reduced to a minimum. However, the fact that the present results are in very good agreement with previous investigations gives an indication that effects of backscattering and backdiffusing have not been dominant.

V. CONCLUSIONS

Thin films of three different polymers having different thickness, positron lifetimes, and intensities were prepared from solution by spin coating, and positron lifetime spectra were measured as a function of energy in the range 3–18 keV. The relative yield of ortho-positronium was used to parametrize the positronium implantation characteristics. The median implantation depth as a function of energy could be described with the commonly used power-law fit with A

$=2.81 (\pm 0.2) \mu\text{g cm}^{-2}$ and $n=1.71(\pm 0.05)$, in good agreement with experimental data on positron implantation in Al, Cu, Au, ZnS, Al₂O₃, and *a*-Si found in the literature.^{11,12,15,18,35}

Fitting of the Makhovian equation to $P(z,E)$ suggested that the parameter m was independent of the positron implantation energy, but dependent on z at constant implantation energy. The fitted value of m in the Makhovian equation varied systematically between ca. 1.7 and 2.3 as a function of the fraction of positrons annihilated in the polymer. The equation proposed by Baker and co-workers^{18–20} yielded a slightly better fit to the experimental data than the Makhovian equation.

The agreement between the implantation characteristics between polymer and previously studied metals and semiconductors suggests that the thermalization of positrons in matter is independent of microscopic structure in the studied energy range.

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