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# Free Volume Profiles at Polymer–Solid Interfaces Probed by Focused Slow Positron Beam

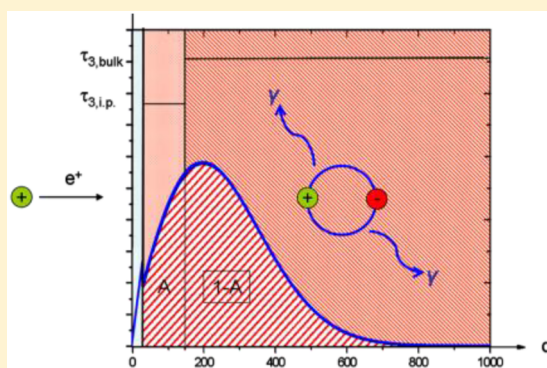
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**ABSTRACT:** The properties of materials involving polymer–solid interfaces are determined not only by the properties of the constituents but also by the interfacial region of the polymer near the solid, the so-called interphase. Here we report on positron annihilation lifetime spectroscopy (PALS) measurements of the free volume near the interface with a focused positron beam. The measurements were performed at an interface between a Teflon AF 1600 film and a 30 nm thick SiN membrane from the backside of a Si substrate which was locally etched away to expose the ultrathin SiN membrane. We were able to focus the positron beam onto the exposed region and to probe the SiN–Teflon AF 1600 interfacial region with low implantation energies, resulting in very narrow implantation profiles and excellent depth resolution. We found a pronounced decrease in orthopositronium lifetime close the interface. On the basis of modeling, we could estimate the interphase width and the average density increase in the interfacial region as  $\sim 12$  nm and 5–7%, respectively.



## INTRODUCTION

It is well-known that the physical properties of a polymer may differ from the bulk values close to a polymer–solid contact, where the interface is the two-dimensional contact area. Energetic and entropic interactions between the polymer and the solid lead to rearrangement of the polymer chains, different segmental motion, confinement effects, a change in the glass transition temperature, and also in free volume and density in the interfacial region.<sup>1–4</sup> This region in the polymer matrix where properties are affected is usually termed the interphase and it is a three-dimensional volume with the interface (see above) on one side. For polymer–nanocomposites several measurements were carried out to determine the change of the physical properties in the interphase region.<sup>5–7</sup> In nanocomposites, due to the large interface to volume ratio of the nanoparticles, a huge volume of the polymer matrix is affected. In contrast, investigations of planar interfaces are rare, and the reported widths of these interphases vary from some nanometers for weakly interacting thermoplastics to above some micrometers for cross-linked polymers.<sup>8,9</sup>

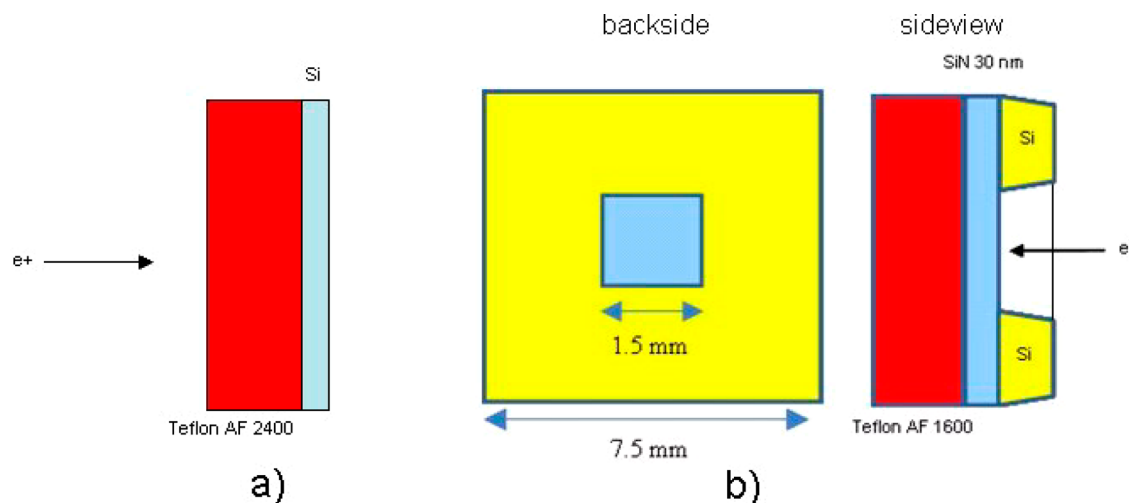
Physical properties like viscosity, diffusion in the polymer matrix, and dynamics of the chains depend on the free volume, the unoccupied space between the polymer chains. Therefore, the free volume is a key property to understand the changes of the properties in the interphase. For the investigation of the free volume in polymers<sup>10,11</sup> and polymer nanocomposites<sup>12–15</sup>

the well-known technique of positron annihilation lifetime spectroscopy (PALS) can be used. PALS probes the electron density distribution by measuring the orthopositronium (*o*-Ps) lifetime, the time difference between a well-defined start time before the positron is injected into the material, and a stop time when an annihilation  $\gamma$ -ray is detected. With the help of a simple quantum mechanical model the measured *o*-Ps lifetime can be converted to a hole size as described below.

Once a positron is emitted into a polymer, it has three different decay possibilities. It can either decay as a free positron or it can recombine with the electrons from the polymer and can form parapositronium (*p*-Ps) with an electron with an antiparallel spin (singlet state) or orthopositronium (*o*-Ps) with an electron with a parallel spin (triplet state). The *p*-Ps can easily decay and has a short lifetime of 125 ps, in contrast to the *o*-Ps, which decays via a so-called pick-off annihilation with an electron from the walls of the free volume holes. The pick-off annihilation of the *o*-Ps depends on the local electron density distribution, and thus the *o*-Ps lifetime can be used to determine the average free volume hole size radius by applying a standard quantum mechanical model originally developed by Tao.<sup>10,16,18</sup> In this model the *o*-Ps is assumed to be confined in

Received: January 27, 2015

Revised: January 28, 2015



**Figure 1.** (a) Sample geometry used by Harms et al.<sup>18</sup> (b) and for the present measurements where the beam impinges from the backside.

a spherical potential well with an electron layer at its wall where it can decay by pick-off annihilation. The calculation of the overlap integral of the positronium probability density function and the electron layer leads to a direct relationship between the *o*-Ps lifetime  $\tau_3$  and the average free volume hole radius  $r$  which is shown in the equation

$$\frac{1}{\tau_3} = \lambda_0 \left( 1 - \frac{R_h}{R_h + \delta R} + \frac{1}{2\pi} \sin \frac{2\pi R_h}{R_h + \delta R} \right) \quad (1)$$

This equation includes the reciprocal *o*-Ps decay rate  $\tau_3$ , the spin averaged decay rate in the electron layer at the edge of the potential well  $\lambda_0$ , the thickness of the electron layer  $\delta R = 0.166$  nm, which has been determined by using materials with a well-known pore size,<sup>17</sup> and the average free volume hole radius  $R_h$ . Further information can be obtained from the intensities, which are the relative probabilities of the three decay possibilities discussed in the previous paragraph. The positronium intensities (*o*-Ps and *p*-Ps) depend on the formation probability of positronium in the respective polymeric material, which are not known a priori and are often also related to the hole concentration.<sup>11</sup> Additionally, the measured *o*-Ps intensity is proportional to the amount of polymer “seen” by the positrons, which is in particular importance for the layered materials investigated here.

PALS measurements for bulk polymers and nanocomposites are well established, whereas investigations of the change in free volume close to a polymer–solid interface are very rare due to the necessity of an energy tunable positron beam. Energy variation of the beam allows variation of the implantation depth and provides a well-defined depth resolution in planar samples. The higher the implantation energy, the deeper the positrons are implanted, however at the expense of a reduced depth resolution. For details of the calculation of the implantation profile we refer to the Appendix.

In a previous work, Harms et al. investigated a Teflon AF2400/silicon interface as a model for a polymer–solid interface and estimated the width of the interphase with the pulsed-low-energetic-positron system (PLEPS) in Munich.<sup>18</sup> They found a general decrease in the *o*-Ps lifetime in the interphase and estimated the width of the interphase as some tens of nanometers in spin-coated polymer films. For evaporated Teflon AF films with very low molecular weight, a

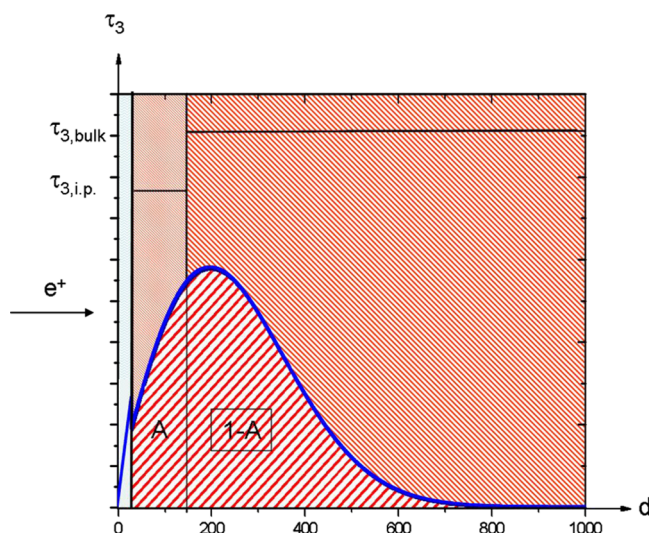
sharp interface was found within experimental error margins in accord with expectations. In their investigation they analyzed their samples with the positron beam impinging from the polymer side to get information on the free volume in the interphase close to the polymer–solid interface. The polymer film thicknesses varied between 65 and 220 nm. For these thicknesses, relatively high positron energies were required to reach the interfacial region, and due to the resulting broad implantation profiles, only a rough estimate of the interphase width could be achieved. Jean et al. investigated polymer films on substrates with a positron beam in a similar manner. They determined the glass transition temperatures in polystyrene films on a silicon substrate for several film thicknesses. In this investigation a decrease in the surface glass transition temperature within an interphase region of about 40 nm was found.<sup>19</sup> These authors also determined from Doppler broadening including a VEPFIT analysis the width of the interphase region in polystyrene–Si systems. The details will be discussed in connection with our measurements in the discussion part of the present paper.

In our present investigation we measured the free volume hole size distribution from the backside through a 30 nm thick SiN membrane. The advantage of this setup is that only low positron energies are needed to penetrate into the interphase and so the spatial resolution of the free volume hole size distribution is much higher. However, unlike in previous investigations<sup>20</sup> a focused beam, available at AIST in Tsukuba, Japan,<sup>21</sup> was necessary to guide all of the beam through the 1.5 mm × 1.5 mm hole in the substrate (see Figure 1b).

The calculation of implantation profiles in our layered system is given in detail in the Appendix including formulas and the necessary numerical values. For the investigation at hand, Teflon AF 1600 was used because Teflon AF 1600 has a very long *o*-Ps lifetime component of between 5 and 6 ns, and so the large change of this lifetime component in the interphase can be easily detected.<sup>22</sup> In the SiN substrate, no *o*-Ps is formed,<sup>21</sup> so we can exclude an influence on the measured *o*-Ps lifetime from the substrate. A schematic of the sample setup and the implantation profile can be seen in Figure 2.

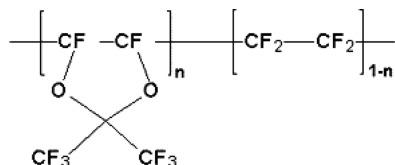
## EXPERIMENTAL SECTION

Teflon AF 1600 is an amorphous copolymer consisting of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole tetrafluoroethylene with a



**Figure 2.** Schematic of the implantation profile and the different layers (SiN, interphase, bulk polymer layer). The x-axis is the distance from the surface, and the y-axis is o-Ps lifetime. A = area under implantation profile in the interphase region; 1 - A = area under implantation profile in the bulk region.

mole fraction of 0.35. The polymer was obtained by Dupont in solid form and was dissolved in the solvent FC-40 obtained from the 3M Company for spin-coating.



**Figure 3.** Chemical structure of Teflon AF 1600.

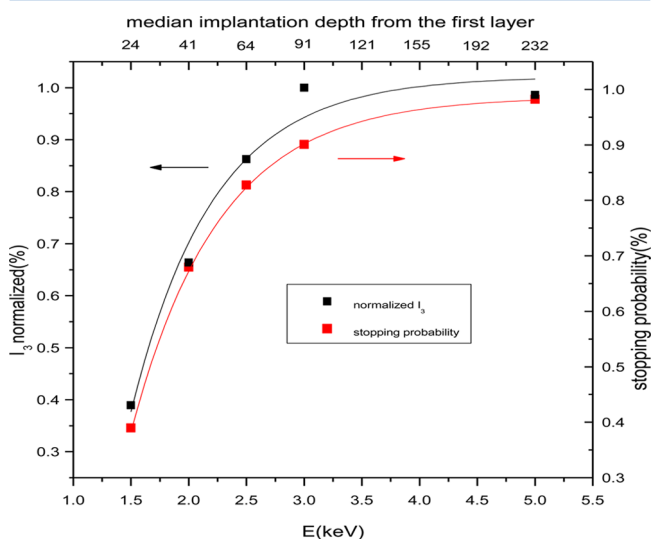
The silicon nitride membrane window used as a substrate was obtained from Silson Ltd. The substrate consists of a 1.5 mm  $\times$  1.5 mm silicon nitride membrane with a thickness of 30 nm in a 7.5 mm  $\times$  7.5 mm silicon supporting frame. Before spin-coating, the silicon nitride membrane window was rinsed in acetone and flushed with isopropanol. Then an ionic RCA-Clean was applied (5:1:1  $H_2O:NH_3:H_2O_2$  at 75  $^\circ C$  for 15 min). The spin-coating with the Teflon AF 1600/FC-40 solution was done with a maximum speed of 1000 rpm for 90 s. After spin-coating, the sample was annealed for 24 h at a temperature of 180  $^\circ C$  well above the glass transition temperature  $T_g$  ( $T_g = 160$   $^\circ C$ ) in high vacuum ( $<10^{-5}$  mbar) to remove residual solvent. The film thickness after annealing was approximately 850 nm and was determined with a profilometer (DektakXT). The PALS measurements were done from the backside of the substrate through the 30 nm SiN membrane into the polymer, so the interphase could be analyzed with low positron implantation energies resulting in narrow implantation profiles. The positron annihilation lifetime spectroscopy measurements were carried out at the LINAC based Positron Probe MicroAnalyzer (PPMA) with beam energies between 1.5 and 5.0 keV. For positron energies lower than 1 keV the positrons are almost fully implanted in the SiN membrane. Details of the calculation of the implantation profiles and the respective contributions in bulk of polymer and interphase region can be found in the Appendix.

The AIST PPMA is a positron lifetime measurement system using a pulsed, brightness-enhanced slow positron beam.<sup>23</sup> A positron beam produced by an electron linear accelerator<sup>24,25</sup> is brightness enhanced by focusing the beam with a magnetic lens at a transmission type remoderator.<sup>26</sup> The remoderated positrons are again accelerated and focused on to the sample by an objective lens. The beam is pulsed with

a combination of two kinds of bunchers so that positron lifetime can be measured with a time resolution of less than  $\sim 300$  ps. A detailed description of the complex apparatus is given in ref 27. The beam spot size of the positron beam was below 600  $\mu m$  for all the measurements in this study and was determined by scanning over a  $SiO_2$ /stainless steel interface and calculating the balance point for each spectrum.<sup>21</sup> A lifetime spectrum with  $3 \times 10^6$  counts was taken for every run with a count rate of 350–400 cps. The data were evaluated using the software program LT 9.2<sup>28</sup> by fitting with a sum of three exponential decays, whereas the lifetime for *p*-Ps was fixed to 125 ps. The background for each energy was determined by measuring a lifetime spectrum for Kapton with a known lifetime of 385 ps. This background was subtracted from the lifetime spectra of the SiN/Teflon AF 1600 sample to reduce false coincidences.

## RESULTS AND DISCUSSION

The measured o-Ps intensity ( $I_3$ ) and o-Ps lifetime ( $\tau_3$ ) as a function of the positron implantation energy are plotted in Figures 4 and 5, respectively. Both the o-Ps intensity ( $I_3$ ) and o-

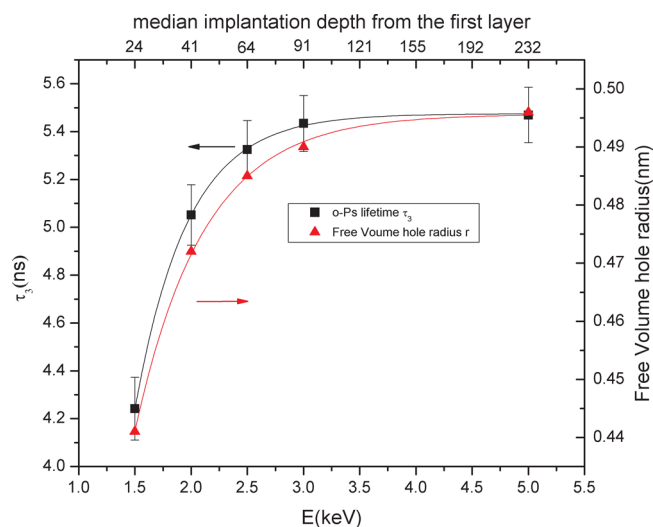


**Figure 4.** Normalized o-Ps intensity  $I_3$  and theoretical stopping probability in the polymer layer vs positron implantation energy.

Ps lifetime ( $\tau_3$ ) increase with increasing positron implantation energy. With increasing positron implantation energy more positrons annihilate in the polymer; thus, the o-Ps intensity  $I_3$  increases.  $\tau_3$  approaches the bulk value at the high energies. For low implantation energy, the o-Ps lifetime is lower than in the bulk, indicating that the existence of an interphase with smaller free volume.

Before analyzing the free volume changes and the width of the interphase by a simple model for the o-Ps lifetimes, it is necessary to check the o-Ps intensity to avoid artifacts from spurious contributions from the annihilation process. Therefore, we compare the measured o-Ps intensity from the measured spectra with an expected intensity, calculated from the implantation profile of the positrons. As detailed in the Introduction, the o-Ps intensity is to a first approximation proportional to the o-Ps formation probability, which is the product of number of positrons implanted into the polymer times the formation probability there. The implantation probabilities of the positrons in the polymer layer, taking into account the implantation into the SiN membrane, were calculated and compared to the measured o-Ps intensities for the five measured implantation energies. The measured o-Ps





**Figure 5.** Measured *o*-Ps lifetimes (left-hand scale) vs implantation energy (lower scale) for the measured implantation energies; line between data points is to guide the eyes. For the sake of clarity, corresponding free volume (right-hand scale) and respective median implantation depth (upper scale) are also depicted.

intensity was hereby normalized to the “bulk” values of the thin film at 3 keV and can be seen in Figure 4.

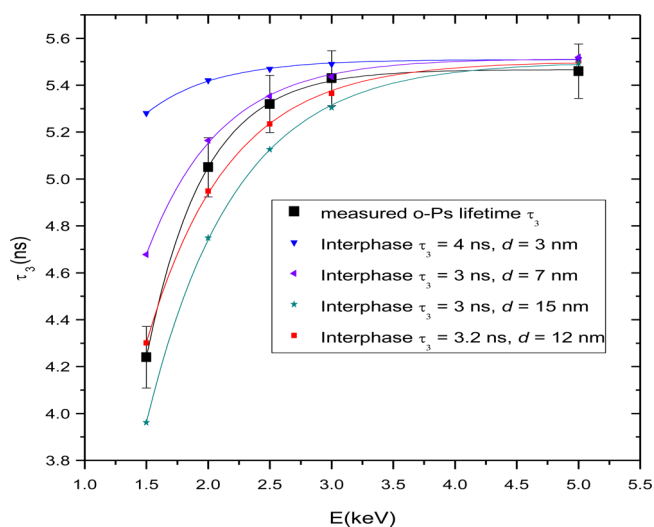
By adjusting the relative scales of the measured *o*-Ps intensity and calculated stopping probability, the two curves are seen to be very similar. Thus, the positronium formation probability and/or the hole concentration is constant, as also seen in previous investigations.<sup>10,19</sup> The constant hole concentration will be used below to estimate the change in density in the interphase region. The constant positronium formation probability allows us to interpret the course of the corresponding *o*-Ps lifetime in the interfacial region.

For low implantation energies of the positrons, the *o*-Ps lifetime is decreased, indicating an interphase close to the substrate with a change in density. At ~3 keV (corresponding to a depth of ~90 nm from SiN layer), the *o*-Ps lifetime has reached the bulk value (~5.53 ns) of the polymer film as determined by Rudel et al.<sup>22</sup> As it is known from another investigation<sup>29</sup> that the shape of the free volume holes does not change from the bulk to the interphase region, the *o*-Ps lifetime of ~5.53 ns can be converted with the model originally developed by Tao into an average free volume hole radius of  $r_{\text{bulk}} \approx 0.498$  nm.

The measured *o*-Ps lifetimes of Figure 5 are averaged values due to the broad implantation profile, which average over both the interphase region and the “bulk” of the polymer film. To separate the contributions, a simple step model was applied (see Figure 2). The measured (averaged) *o*-Ps lifetime is a weighted average over the lifetime in the interphase region  $\tau_{o\text{-Ps,interphase}}$  and the “bulk” of the thin film  $\tau_{o\text{-Ps,bulk}}$ . Weighing factors are the areas under the implantation profile in the respective regions (see Figure 2, where  $A$  = area of implantation profile in the interphase region and  $1 - A$  = area of implantation in the bulk polymer).

$$\tau_{o\text{-Ps,total}} = A \cdot \tau_{o\text{-Ps,interphase}} + (1 - A) \cdot \tau_{o\text{-Ps,bulk}} \quad (2)$$

The measured (averaged) *o*-Ps lifetimes and the calculated *o*-Ps lifetimes in the interphase region for different interphase widths and different *o*-Ps lifetimes in the interphase are depicted in Figure 6.



**Figure 6.** Calculation of the average *o*-Ps lifetime for different interphase widths and *o*-Ps-lifetimes in the interphase according to eq 2.

The deviation between calculated and the measured lifetimes is the lowest when we use an interphase with a width of 12 nm and an *o*-Ps lifetime of 3.2 ns in the interphase. This *o*-Ps lifetime in the interphase can be converted with the help of the model by Tao to an average hole size radius of 0.3765 nm. The *o*-Ps lifetime in the bulk is 5.53 ns, which correlates with an average hole size radius of 0.498 nm as already mentioned above. Therefore, the average hole size radius is reduced by ~25% in the interphase corresponding to a reduction in free volume to ~42% of its initial value. Thus, it is clear that the average free volume hole size clearly decreases; i.e., the density increases in the interphase region. With this information the present investigation goes beyond our previous work<sup>18</sup> where only a rather vague estimate on interphase width of several tens of nanometers could be made, and no quantification of the decrease in free volume was possible. This value for the interphase width (~12 nm) is significantly higher than that determined from molecular dynamics (MD) simulations.<sup>29</sup> Part of this deviation might be explained by the diffusional broadening of the positron implantation profile, although the typical diffusion distance is generally assumed to be around 2 nm.<sup>10,11</sup>

Density is mass per volume, and the volume is sum of the volume occupied by the atoms, the interstitial volume, and the “free volume”. As discussed above, it is reasonable to assume a constant positronium formation probability and hole concentration in the polymer layer. In order to estimate the density increase in the interphase region, we use the observation that crystallization of polymers usually increases the density by ~10%, which is only related to the disappearance of the free volume. Thus, a reduction of free volume in the interphase region can be converted to an increase in density by approximately 5–7% in the interphase region within a simple model and some rough assumptions. We know from simulations that density fluctuation close to the interface occur with an overall average slightly increase in density in the first nanometers from the substrate for temperatures above the glass transition temperature.<sup>29</sup> Although a direct interpretation of the density increase is not possible, one might speculate that the substrate interface induces by a chemical or steric interaction a different arrangement of the chains.

As mentioned in the Introduction, there are already similar investigations in the literature. Jean and co-workers<sup>31,32</sup> evaluated Doppler measurements of PS/Si and PS/metal layers with a modeling program and found best fits for an interphase layer thickness of approximately 20 nm, which is in reasonable accordance with our results. However, the density of there fit was less than half of the bulk density of the polymer, which is surprising not only on its own but also in contrast to the present results.

Generalizing this density increase on a 10 nm scale to nanocomposites, we would expect a deviation from simple mixing rule for polymer properties, which are related to free volume changes. However, a direct experimental proof for the present system was not performed yet.

In conclusion, using PALS measurements with a focused beam, we found an obvious reduction of the *o*-Ps lifetime (free volume size) and as a consequence were able to determine density changes at a Teflon AF 1600/SiN interface. An average decrease in *o*-Ps lifetime by ~42.1% was observed within an interfacial layer of about 12 nm extension. Within a rough estimation this corresponds to an increase in density of about 5–7% in the so-called interphase.

## ■ APPENDIX. DETAILS OF THE CALCULATION OF THE IMPLANTATION PROFILE

The implantation probability  $\eta_i$  for the implanted positrons in a multilayer structure can be calculated for the *i*th layer with the following formulas:<sup>21</sup>

$$\eta_i = \int_{x_i}^{x_{i+1}} P_i(z, E) dz \quad (\text{A1})$$

$$P_i(z, E) = -\frac{d}{dz} \exp \left[ -\left( \frac{z - \delta z_i}{z_0(E)} \right)^m \right] \quad (\text{A2})$$

or in the differentiated form

$$P_i(z, E) = \frac{mz^{m-1}}{z_0^m(E)} \exp \left[ -\left( \frac{z - \delta z_i}{z_0(E)} \right)^m \right] \quad (\text{A3})$$

$$z_0(E) \Gamma \left( 1 + \frac{1}{m} \right) = \frac{A}{\rho_i} E^n \quad (\text{A4})$$

$P_i(z, E)$  describes the probability of a positron with the energy *E* to penetrate into the material at a depth *z* (nm).  $x_i$  is the depth from the surface to the interface between (*i* − 1)th and the *i*th layer (in our case the thickness of the SiN membrane 30 nm),  $\rho_i$  is the density of the *i*th layer ( $\rho_{\text{SiN}} = 3.0 \text{ g/cm}^3$ ,  $\rho_{\text{Teflon 1600}} = 1.78 \text{ g/cm}^3$ ) material, and  $\Gamma$  is the gamma function. Both density values are from the respective manufacturers.

$\delta z_i$  is a correction value for the depth and is given by

$$\delta z_i = \begin{cases} x_i - z_0(E) \left[ -\ln \left( 1 - \sum_{k=1}^{i-1} \eta_k \right) \right]^{1/m} & \text{for } i \geq 2 \\ 0 & \text{for } i = 1 \end{cases} \quad (\text{A5})$$

The parameters *A*, *m*, and *n* for the calculations are numerical values and are given for various materials in the literature;<sup>20,32</sup> the densities of the materials are given from the producing company.

**Target sample:** SiN (30 nm)/Teflon AF1600 (850 nm). First layer: 3.0 g/cm<sup>3</sup>, 30 nm thick; second layer: 1.78 g/cm<sup>3</sup>, infinity thick.

For the calculation of the implantation profile the following parameters were used:

**Stopping profile parameter:** First layer (SiN): *A* = 3.8 μg/cm<sup>2</sup>, *n* = 1.6, *m* = 2.0; second layer (Teflon AF 1600): *A* = 2.81 μg/cm<sup>2</sup>, *n* = 1.71, *m* = 2.0.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Financial support by DFG through Ra 796/5-2 within the SPP 1369 (Polymer solid contacts: Interfaces and Interphases) is gratefully acknowledged. The authors thank M. Sc. T. Koschine for the Matlab software for calculation of the implantation profiles and the determination of the interphase width.

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