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Positron implantation and transmission experiments on free-standing nanometric polymer films

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Abstract. Positron transmission experiments were performed on free-standing poly(methyl-methacrylate) (PMMA) and polystyrene (PS) films of nanometric thicknesses made by spin coating. The power_law equation $z_{1/2}(E)$)=$(\alpha/\rho)E^n$ was determined from the measurements of the S-parameter as a function of the positron implantation energy. These transmission experiments indicate that n = 1.90(±0.08) and α = 1.33(±0.10) μg cm^{-2} which deviates from the values found by Algers *et al.* (n = 1.71(±0.05) and α = 2.8(±0.2) μg cm^{-2}) and the commonly used parameters (n = 1.6 and α = 4.0 μg cm^{-2}).

Introduction

The median penetration depth as a function of the implantation energy, $z_{1/2}(E)$, related to the well-known Makhov distribution $P(E,z)$ [1] can be parameterized by means of the power-law $z_{1/2}(E)=(\alpha/\rho)E^n$ [2]. Where ρ is the density of the material and n = 1.6 and α = 4.0 μg cm^{-2} are the most frequently used empirical parameters [3]. In the case of polymers, by analyzing the ortho-positronium yield from positron lifetime experiments Algers *et al*. have found the values n = 1.71(±0.05) and α = 2.81(±0.2) μg cm^{-2}. In this work, we performed positron transmission experiments on free-standing PMMA and PS films of nanometric thicknesses. From the measurements of the S-parameter as a function of the positron implantation energy we are able obtain the parameters n and α that characterize $z_{1/2}$(E). The results suggest that the parameters proposed by Algers *et al*. [4] are not valid, at least in the case of self-supporting polymer films.

Experimental

The materials used for this study are a poly(methyl-methacrylate) (PMMA) resist with low MW (approximately 450k) in a Spin Bowl Compatible solvent system 5% (Brewer science) and polystyrene (PS) (Acros Organics ref No. 17889; average MW 240,000 (SEC)) dissolved in toluene to concentrations of 10, 30, 50 and 70 mg/mL. For allowing the comparison with the data of Algers *et al*., the densities (ρ) were considered to be the 1.197 and 1.040 g cm^{-3} for PMMA and PS respectively [4].
The films were prepared by spin-coating on Si wafers varying the spinning velocities (500 to 4000 rpm during 30 sec.) and the concentrations in the case of PS. The preparation of each of the films is described elsewhere [5]. The thickness of the films was measured with a surface profilometer (Talystep). The DBAR experiments were performed at the positron beam in Ghent [6] with an

HPGe detector having a FWHM resolution of 1.17 keV at the 514 keV line of ^{85}Sr. Special care was taken to minimize the effect of the charge as we present the analysis of the data corresponding to the first run (fresh sample) and also the measuring time for each data point was relatively short (10 min) in comparison to the charging time constant which for PMMA and PS respectively is 4.8 and 3.1 hours.

Analysis and results

The S-parameter directly obtained from the experimental data represents both implanted and transmitted positrons. At the specific energy $E_{1/2}$ in keV, defined as $S = S_{1/2}$, 50% of the implanted positrons annihilate in the polymer and 50% are transmitted. At $E_{1/2}$, the median penetration depth ($z_{1/2}$) is thus equal to the film thickness d in nm. By plotting d versus $E_{1/2}$, we are able to obtain the parameters n and α that characterize $z_{1/2}(E)$. By internally shielding the chamber walls with Teflon, the constant level observed for the S-parameter at high energies ($E > \sim$10keV in Fig. 1.) changes to the value obtained for a Teflon sample, which suggests that the main contribution of the transmitted positrons comes from the annihilations on the chamber walls.

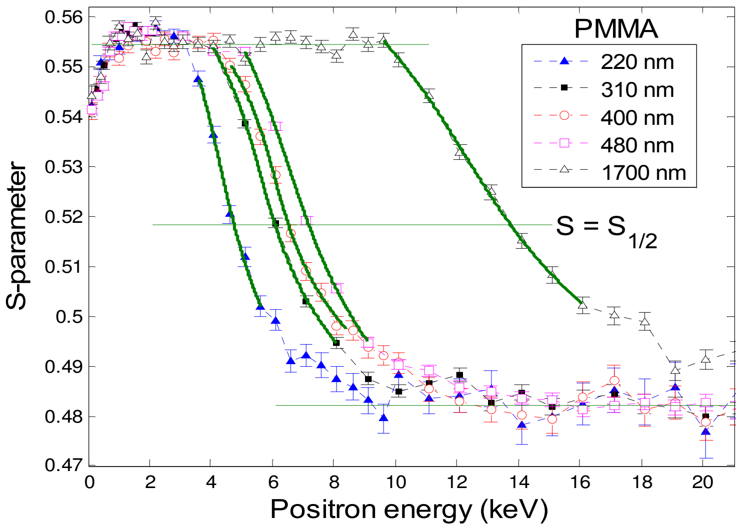

Figure 1. S-parameters as a function of the implantation energy for the poly(methyl-methacrylate) (PMMA) films.

The obtained S-parameter for the PMMA films is shown in Fig. 1, the same was done for PS films. The smooth lines in the region where the data intercept with $S = S_{1/2}$ correspond to a polynomial fitting. The extracted $E_{1/2}$ are visualized in Fig. 2 and the validity of the power-law is clear. The parameters for the power-law resulting from the linear fit in Fig. 2 are $n = 1.90 \pm 0.08$ and $\alpha = 1.33 \pm 0.10$ µg cm^{-2}.

These results differ from the ones proposed by Algers *et al.* ($n = 1.71(\pm 0.05)$ and $\alpha = 2.8(\pm 0.2)$ µg cm^{-2}). In their experiment the spin-coated films were not detached from the silicon substrate and thus interaction at the interface and with the substrate could contribute to more annihilation of positrons in the polymer than in the case of the self-supporting films.

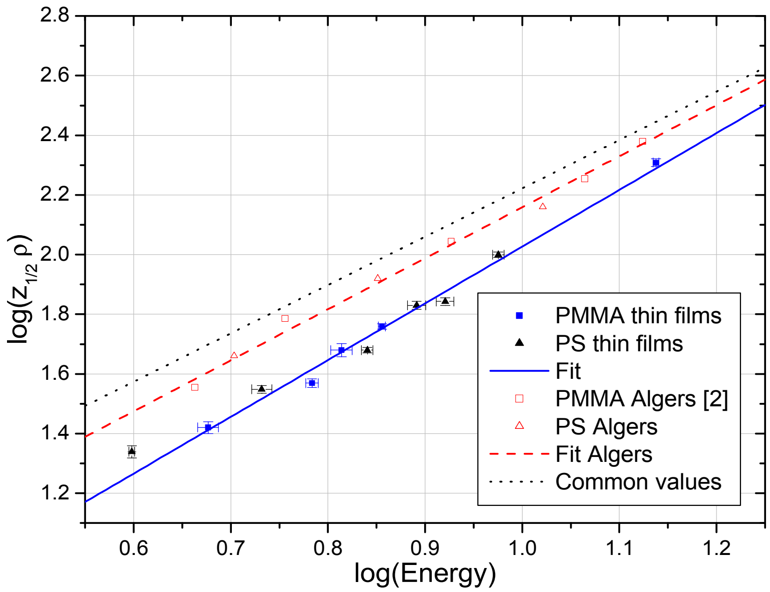

Figure 2. Graphical presentation of the power-law $z_{1/2}(E)=(\alpha/\rho)E^n$ according to the data of the transmission experiment compared to the results of Algers et al.

Summary

Positron transmission experiments have been performed on free-standing polystyrene and poly(methyl-methacrylate) films of nanometric thicknesses. From the measurements of the S-parameter as a function of the positron implantation energy and with the films thickness we found n= 1.90 ± 0.08 and α = 1.33 ± 0.10 μg cm^{-2} so that the median penetration depth $z_{1/2}(E)=(\alpha/\rho)E^n$ can be characterized. This finding suggests that special care has to be taken into account when analyzing the experimental data as standard values might lead to wrong results. Our results seem to indicate that, at least in the case of self supporting films, the parameters proposed by Algers *et al.* are not valid.

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