Diffusion of positrons in polymers studied by slow positron beam

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Abstract. Using a pulsed slow positron beam, we have measured the positron lifetimes in the systems of thin Ni films on polyethylene and polycarbonate substrates made by the molecular beam epitaxial method. We have estimated the one-dimensional diffusion lengths of positrons in polyethylene and polycarbonate.

1. Introduction

The variable-energy slow-positron beams have enabled studies of atomic vacancy-type defects at surfaces, in sub-surfaces, and in thin films [1]. The positron lifetime method with a slow-positron beam provides important information on species of vacancy defects contained in thin films [2]. The positron mobility is an important quantity for understanding the positron trapping into defects and the positron reemission from surfaces observed using slow positron beams. In the case of polymers, the positron beam allows the determination of local free-volume properties of the polymers as a function of the depth from the surface [3]. Considering the positroniums (Ps) formation, the positron mobility in polymers is especially important [4]. Since various positron spur processes relevant to the Ps formation are strongly influenced by the diffusion of positrons, its mobility plays a crucial role in determining the Ps yields in polymers.

Hirata et al. have reported that the diffusion lengths of Ps in polymers are very small ($D_{Ps} = 2.6 \sim 5.1 \times 10^{-6}$ cm$^2$/s) [5]. Diffusion mobility of free positrons in polyethylene is estimated to be $\mu = 10$cm$^2$/N $\cdot$ s [6], 10.3cm$^2$/N $\cdot$ s [7], 27.7cm$^2$/N $\cdot$ s [4] and 32cm$^2$/N $\cdot$ s [8]. The diffusion constant is given by the Einstein’s relation,

$$D = \mu k_B T / e,$$

where $k_B$ is the Boltzmann constant, $T$ is temperature and $e$ is the elemental charge. The diffusion length is then given by

$$L = \sqrt{6D\tau}.$$  

Having the free positron lifetime of $\tau = 0.52$ nsec for polyethylene and $\mu = 32$cm$^2$/N $\cdot$ s, we obtained the one-dimensional diffusion length $L \equiv \sqrt{D\tau} \approx 210$ nm at room temperature.

In this study, we have determined the one dimensional diffusion lengths of positrons in polyethylene and polycarbonate based on the slow positron lifetime measurements. To avoid complicated effects (like
Ps states at the polymer surface), we deposited the thin Ni films on the polyethylene and polycarbonate. We compare the obtained one-dimensional diffusion lengths with those determined from the above Einstein’s relation.

2. Experiment
Thin Ni films of thickness 25±5 nm and 75±5 nm were deposited on the polyethylene substrates (15mm × 15mm × 1mm, density 0.92 g/cm^3, Japan Custom Co., Ltd.) by the molecular beam epitaxial (MBE) method under a pressure of 8.5 × 10^{-9} Torr at room temperature. Similarly, a thin Ni film of thickness 125±5 nm was deposited on the polycarbonate substrate (15mm×15mm×1mm, density 1.20 g/cm^3, Japan Custom Co., Ltd.). The positron annihilation lifetime measurements were carried out at room temperature using an intense pulsed slow positron beam generated by the electron linac of the National Institute of Advanced Industrial Science and Technology (AIST) LINAC facility.

3. Results and Discussions
First of all, we introduce the general principle to determine the one dimensional diffusion length of positrons. The positron implantation profile is given by

\[ P(z, E) = -(d/dz)\{\exp[-(z/z_0)^m]\}, \tag{3} \]

where \( z_0 \) is given by

\[ z_0 = AE^m/\rho/\Gamma(1 + 1/m), \tag{4} \]

where \( E \) is the incident positron energy in keV, \( \rho \) is the materials density in g/cm^3 (Ni : 8.85, polyethylene : 0.92, polycarbonate : 1.20), \( A, n \) and \( m \) are the constants: \( A = 400, n = 1.6 \) and \( m = 2.0 \) [10]. Figure 1 shows the positron implantation profile in Ni for E=1, 3 and 4 keV calculated by eq. (3). The fraction of positrons stopped in the \( i \)-th layer is given by

\[ \eta_i(E) = \int_{a_i}^{b_i} P(z, E)dz, \tag{5} \]
Table 1. Positron lifetimes and their intensities obtained for the polyethylene substrate.

| τ₁ (ns) | τ₂ (ns) | τ₃ (ns) | I₁ (%) | I₂ (%) | I₃ (%) |
|---------|---------|---------|--------|--------|--------|
| 0.295   | 0.520   | 2.392   | 61.7   | 15.1   | 23.2   |

Table 2. Positron lifetimes and their intensities obtained for the system of the thin Ni film (25±5nm thick) on a polyethylene substrate at E=1 keV, 3 keV and 4 keV.

| E (keV) | τ₁ (ns) | τ₂ (ns) | τ₃ (ns) | I₁ (%) | I₂ (%) | I₃ (%) |
|---------|---------|---------|---------|--------|--------|--------|
| 1       | 0.347   | —       | 3.985   | 96.0   | —      | 4.0    |
| 3       | 0.317   | 0.520   | 2.324   | 71.5   | 11.4   | 17.1   |
| 4       | 0.311   | 0.520   | 2.286   | 66.0   | 13.5   | 20.5   |

where \( a_i \) and \( b_i \) are the boundaries of the \( i \)-th layer. The forward and backward reemission yields, \( YF_i \), \( YB_i \), can be derived immediately from the Green’s function

\[
YF_i = \left[\frac{1}{\sinh(T_i/L_i)}\right] \int_{a_i}^{b_i} \sinh(z/L_i)P(z, E)dz,
\]

\[
YB_i = \left[\frac{1}{\sinh(T_i/L_i)}\right] \int_{a_i}^{b_i} \sinh(T_i - z/L_i)P(z, E)dz,
\]

where \( L_i \) is the one-dimensional diffusion length of positrons in the \( i \)-th layer, \( T_i \) is the thickness of the \( i \)-th layer. The fraction of positrons (\( F_i \)) that annihilate in the \( i \)-th layer is given by

\[
F_i = \eta_i - YF_i - YB_i + YF_{i-1} + YB_{i+1}.
\]

Having the annihilation fraction determined from the measurements and the stopping fraction calculated by eq. (5) in the \( i \)-th layer, one can determine the one-dimensional diffusion length, \( L_i \), in the \( i \)-th layer using eqs. (6) through (8).

Table 1 summarizes the positron lifetimes and their intensities obtained for the polyethylene substrate [9]. The first component correspond to the mixture of annihilations of para-positronium and free positrons. The second component and third component are attributed to the annihilation of free positrons and the pick-off annihilation of ortho-positronium, respectively.

Table 2 lists the positron lifetimes and their intensities obtained for the system of the thin Ni film (25±5nm thick) on a polyethylene substrate at \( E=1 \), 3 and 4 keV. In the case of 1keV, the observed lifetime spectrum is well fitted with two lifetime components. Most positrons annihilate within the Ni-film as shown in from Fig. 1. The lifetimes \( \tau_1 \) and \( \tau_2 \) represent small vacancy clusters in the Ni layer and the pick-off annihilation of ortho-positronium at the Ni surface, respectively. For \( E=3 \) keV and 4keV, the observed lifetime spectra are well fitted with three lifetime components. The lifetime \( \tau_1 \) corresponds to the mixture of small vacancy clusters in the Ni film and free-positron annihilation in polyethylene. The values of \( \tau_2 \) and \( \tau_3 \) correspond to the annihilation of free positrons in polyethylene and the pick-off annihilation of ortho-positronium in polyethylene. The ratio of \( I_3/I_2 \) are 1.51 and 1.52 for \( E=3 \) keV and 4 keV, respectively. These results are consistent with those listed in table 1 [9]. Thus, from the comparison between tables 1 and 2, the annihilation fraction in the polyethylene substrate is estimated as \( I_2/15.1 (=I_2 \) in table 1).
Table 3. Annihilation and stopping fractions in the Ni layer and the polyethylene substrate estimated for the system of the thin Ni film (25±5nm thick) on the polyethylene substrate at $E=3$ keV and 4 keV.

| $E$ (keV) | Ni | Polyethylene |
|-----------|----|--------------|
|           | $F$ (%) | $\eta$ (%) | $F$ (%) | $\eta$ (%) |
| 3         | 24.7 | 36.5 | 75.3 | 63.5 |
| 4         | 10.7 | 16.6 | 89.3 | 83.4 |

Table 3 summarizes the annihilation and stopping fractions ($F$ and $\eta$ in eq. (8)) in the Ni layer and the polyethylene substrate estimated for the system of the thin Ni film (25±5nm thick) on the polyethylene substrate at $E=3$ keV and 4 keV. We integrated the positron stopping profile within polyethylene, taking into account of only the diffusion length Ni (near surface 6nm) [1]. Following the manner explained at the beginning of this section, we obtained the one-dimensional diffusion length as $L \sim 10 \pm 2$ nm in polyethylene.

We have measured the positron lifetimes for the system of a Ni film (75±5nm thick) on a polyethylene substrate at $E=1, 2, 4, 6$ and 8 keV. Subsequently, we obtained the one-dimensional diffusion length in the polyethylene to be $L \sim 10 \pm 2$ nm, which is comparable to that obtained for the case of the 25±5 nm thick Ni on a polyethylene. We have further measured the positron lifetimes for the system of a thin Ni film (125±5 nm thick) on a polycarbonate substrate at $E=1, 2, 6$ and 8 keV. The one-dimensional diffusion length in polycarbonate was obtained to be $L \sim 32 \pm 2$ nm.

The one-dimensional diffusion lengths obtained here (10~30 nm) for the polyethylene and polycarbonate are much shorter as compared to the value ~200 nm derived from the mobilities of positrons and Einstein’s relation as mentioned in the introduction. The positron in polymers pushes on polymer molecules to make space for itself. This effect reduces the positron kinetic energy. Large space in polymer of sphere, however, is costly in terms of polymer free energy, so the polymer molecules push back. The balance between the positron kinetic energy and the polymer compressibility, which is relatively low in comparison with other solid materials, results in the stable structure. In the case of the positron diffusion in this state, it might not be adequate to use the Einstein’s relation.

4. Conclusion
We have determined the one-dimensioned diffusion lengths in the polyethylene and polycarbonate based on the positron beam technique. The obtained diffusion lengths are one order of magnitude shorter than those reported previously using the Einstein’s relation.

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