Studies on the Thin Films of Poly(di-*n*-hexylsilane) Using Slow Positron Beam Technique

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1. Introduction

Polysilanes are a special class of polymer with Si-Si backbone and organic side chains. The Si-Si σ -conjugation is responsible for some of the interesting properties such as photoconductivity, nonlinear optical property, and so on [1]. Poly(di-*n*-hexylsilane) (PDHS) is one of the polysilanes having Si-Si backbone with hexyl side chains. This polymer undergoes a solid-solid phase transition at ~ 315 K which coincides with a shift in the UV absorption maxima known as thermochromism [2]. This is thought to be brought about by a simultaneous change in the conformation of the backbone as well as disordering of side chains.

Polysilanes showing interesting photoconductivity have a potential application as thin film devices. It is well known that properties of thin films are different from their bulk counterparts. This is because the thin film is a constraint system and considerable experimental and theoretical interest is generated in understanding the thinness-induced constraint on the molecular conformation [3]. In recent years positron annihilation spectroscopy has emerged as a powerful microscopic probe in characterizing free-volume in polymers [4]. However, thin films can not be studied using conventional radioisotopes owing to wide spread in emitted positron energy and consequentially no depth selectivity can be achieved. On the other hand, mono-energetic positron beam can be used for depth profiling studies by suitably changing the beam energy and thin films can be characterized from the surface down to the bulk. In light of the above discussion we have characterized PDHS films with different thickness by measuring the

S-parameter. In addition, temperature dependence of positronium lifetime from surface to bulk have been measured.

2. Experimental

The polymer was synthesized using Wurtz coupling method as described elsewhere [5]. Molecular weight distribution was measured using gel permeation chromatography (GPC), which was seen to be $M_w \sim 4.0 \times 10^5$, $M_w/M_n \sim 5.1$. Differential scanning calorimetric measurement (DSC) showed a solid-solid phase transition at 318 K. Thin films (two samples) were prepared using spin coat method at 2000 r.p.m. with different dilution. Film thickness was measured using a surface profiler, which was seen to be 1.1 μm for the thicker sample. We could not measure the thickness of the thinner film with accuracy using surface profiler due to the softness of the polymer. We have, however, estimated the thickness from our measurement to be 0.35 μm as described in latter section. Doppler broadened annihilation radiation measurements were carried out using the LINAC based slow positron beam from 0.05 to 15 keV for thick and thin samples at The Institute of Scientific and Industrial Research (ISIR), Osaka University. The S-parameter, which is the ratio of the area in central narrow energy window to the total peak area of the annihilation γ rays, was evaluated. The corresponding lifetime was measured using the short-pulsed slow positron beam at Electrotechnical Laboratory (ETL). The lifetime was also measured at 333 K (above the solid-solid transition temperature) for the thicker (1.1 μm) PDHS film at the ETL beam.

Fig. 1. S-parameter versus positron incident energy. Solid lines show fitted curves by VEPFIT Program.

3. Results and discussion

The S-parameter as a function of positron incident energy is plotted in Figure 1 for the thick (1.1 μm) and thin samples. Figure 2 shows the *o*-Ps (ortho positronium; triplet state of positronium that is bound state of positron and electron) pick-off lifetime and intensity for the 1.1 μm thick sample in the ordered (room temperature) and disordered state (333 K). Figure 3 shows the lifetime spectra of thicker and thinner samples in near surface region at room temperature.

There is a direct relationship with positron energy and the mean implantation depth $\bar{z}$ (nm) as $\bar{z} = 40E^{1.6}/\rho$, where E is positron incident energy (keV) and ρ is density of the material (g/cm^3) [6]. Therefore, the positron energy is an indicator of the mean implantation depth. In general, it is seen (Fig. 1) that the S-parameter monotonically increases with increase in energy and reaches a maximum following which a decrease is seen. This is because the S-parameter directly reflects the intensity of Ps as reported by Cao et al. [7]. On the surface, a considerable amount of positron/Ps escape to the vacuum and hence the intensity of Ps is low resulting in lower S-value. As the positron is implanted deeper, the escape probability reduces and the Ps fraction progressively increases reaching a maximum corresponding to the bulk value. This is reflected in the S-parameter. On further increasing the positron energy, positrons annihilate in Si substrate where no Ps formation takes place resulting in wider momentum distribution and hence lower S-value. The increase in Ps intensity (I_3) with increasing energy is clearly reflected in our lifetime measurement data as shown in figure 2(b). Also, the evidence for the long-lived Ps component which escape through the surface and identified as an additional Ps component, namely, τ_4 and I_4 can be seen in figure 2(a) and 2(b), respectively. It may

Fig. 2. *o*-Ps lifetime (a) and *o*-Ps intensity (b) in PDHS film evaluated from lifetime spectra.

Fig. 3. Lifetime spectra for PDHS thin (a) and thick (b) films at positron incident energy of 0.3 keV.

be noted that these components can be seen only close to the surface.

Another, interesting observation is the difference between the thicker and thinner film (figure 1). This difference is not only seen in S-parameter measurement but also in the lifetime measurements which is shown in figure 3. This implies that the microstructures of these polymers are different which is induced by the thickness. It is interesting to note that evidence for the thickness-induced effect on conformation exists in polysilanes [8].

The temperature dependence studies in the 1.1 μm thick sample shows that τ_3 (figure 2(a)) and I_3 (figure 2(b)) are higher in the disordered state compared to the ordered state although the trend in these parameters with energy is identical in either state. This clearly indicates that the side chain disordering and change in molecular conformation has resulted in higher free-volume fraction in the disordered state.

We have analyzed our S-parameter data using VEPFIT program [9] which takes into account the positron implantation profile and positron/Ps diffusion in predicting the layer thickness and diffusion length of positron/Ps. The fitted values are represented as solid lines in figure 1. The obtained PDHS layer thicknesses are 1.2 μm and 350 nm for the thick and thin samples, respectively. The obtained thickness in the thick sample is in good agreement with the surface profile measurement. The positron/Ps diffusion lengths were found to be 19 and 25 nm respectively. These values are simi-

lar to that reported in polymer by other group [7]. The difference in the diffusion length further supports our observation that the microstructures in thin and thick samples are different.

4. Conclusion

We have reported a new result in characterization of PDHS thin films using slow positron beam techniques. Evidence for thickness induced microstructural changes is seen. The disordered state of PDHS film is associated with an increase of free-volume fraction. Positron diffusion length, which is a fundamental parameter in positron and Ps chemistry, have been evaluated for PDHS films. They are seen to be 19 nm and 25 nm for the thicker (1.1 μm) and thinner (350 nm) films, respectively.

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