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Depth profiles of the Doppler-broadening *S* parameter for polymers obtained with two measuring patterns: The role of accumulated charges

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ABSTRACT

Depth profiles of Doppler broadening *S* parameter for oxygen containing polymer polycarbonate (PC), fluoropolymer poly (tetrafluoroethylene) (PTFE) and chlorine containing polymer polyvinylchloride-unplasticized (UPVC) were obtained with two measuring patterns, i.e. energy increase pattern and energy decrease pattern. The two curves can't coincide with each other for that a trough appeared between 1 and 5 keV in the curve obtained with energy decrease pattern. It was found that charges induced by high energy incident positrons greatly influenced the annihilation of low energy incident positrons, while charges induced by low energy incident positrons showed little influence on the annihilation of high energy incident positrons. With energy increase measuring pattern, charges induced by low energy incident positrons showed little influence on the annihilation of later incident high energy positrons, thus the measurement can give the depth profile of *S* parameter in polymer as it was.

1. Introduction

Doppler broadening energy spectroscopy on a variable-energy positron beam has been widely applied to study damage and defect depth-profiling of polymers [1–4]. By changing the incident energy of positrons, one can obtain information on the depth of damage layer [5,6], and interface layer [7], which are important to macroscopic properties of polymers.

When positron annihilation Doppler broadening energy spectroscopy on slow positron beam is applied, usually the depth profile of sample is obtained using the following measuring pattern, first low energy positrons, and then high energy positrons are injected into sample [8,9] (energy increase pattern). In fact, there is the other measuring pattern, first high energy positrons are used, and then the accelerating voltage is decreased so that low energy positrons could inject into sample (energy decrease pattern). With both measuring patterns, usually, it takes more than 12 h to obtain a depth profile of *S* parameter. It is well known that in normal positron annihilation measurements, prolonged positron irradiation in polymer can cause the drop of *o*-Ps intensity (so called self-irradiation effect) as a result of the build-up of an internal electric field [10–12], since the accumulated charges can't be dissipated in the insulating polymers. While in slow positron beam measurement, where the incident positron energy is much lower compared to fast positron directly emitting from ^{22}Na source, self-irradiation effect is seldom considered. However, even in slow positron beam measurement, long time positron irradiation can cause charges accumulation in polymer, which may influence the characteristics of positron annihilation. In this study, depth profiles of the Doppler-broadening *S* parameter for some polar and nonpolar polymers were obtained with the two measuring patterns. We try to find the measuring pattern which is less influenced by accumulated charges, thus better reflecting the real characteristics of polymer sample.

2. Experimental details

The polymer samples studied here were purchased from Goodfellow (Cambridge, UK), including polycarbonate (PC), poly (tetrafluoroethylene) (PTFE), polypropylene (PP), polyvinylchloride-unplasticized (UPVC). The silicon slice was single crystal. Positron annihilation Doppler broadening measurements were conducted with a magnetically guided variable-energy positron beam (0–20 keV) at IHEP, Beijing. The beam intensity was about 10^5 positrons/s. Positrons are accelerated to specific energy by negative high voltage within the distance of 1 cm from the sample. When no accelerating voltage was applied, positron energy was about 0.18 keV. With energy increase pattern, the accelerating voltage was increased from 0 to 10 (or 20) kV. With energy decrease pattern, the accelerating voltage was decreased from 10 (or 20) to 0 kV. (For convenience, the positron energy below refers only the accelerating energy, not including the initial energy, e. g. the energy of a positron accelerated by 10 kV voltage was denoted

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as 10 keV.) The Doppler broadening energy spectra (DBES) were recorded using a high-purity Ge detector. The obtained DBES spectra were expressed in *S* parameter, which was defined as a ratio of integrated counts in the central parts (510.2–511.8 keV) to the total counts of the 511 keV annihilation peak after proper background subtraction. To obtain depth profiles of *S* parameter for a polymer, two identical films were prepared. One piece of film was measured with energy increase pattern, and the other was measured with energy decrease pattern.

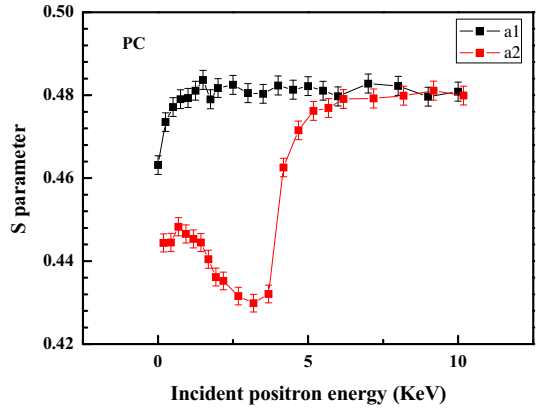
3. Results and discussion

Fig. 1 shows the depth profiles of Doppler broadening *S* parameter for oxygen containing polymer PC, fluoropolymer PTFE and chlorine containing polymer UPVC obtained with the two measuring patterns. With energy increase pattern, PC, PTFE and UPVC give different depth profiles of *S* parameter. For PC, *S* parameter increases with increasing incident positron energy until 4 keV, and then reaches leveling-off at higher energies. For PTFE, *S* parameter decreases from polymer surface to bulk. And for UPVC, *S* parameter is independent of incident positron energy and remains nearly constant. As discussed in our previous paper [13], the increase of *S* parameter for PC is owing to depth-dependent positronium formation, the decrease of *S* parameter for PTFE is due to the influence of highly electronegative atoms on positron annihilation characteristics, and nearly constant *S* parameter for UPVC is the result of equivalent effect of depth-dependent positronium formation and highly electronegative atoms. However, depth profile obtained with energy decrease pattern is very different from the one obtained with energy increase pattern. For all the three samples, though *S* parameter after 5 keV can accord with the data obtained with energy increase pattern, a trough forms in the energy range from 1 to 5 keV.

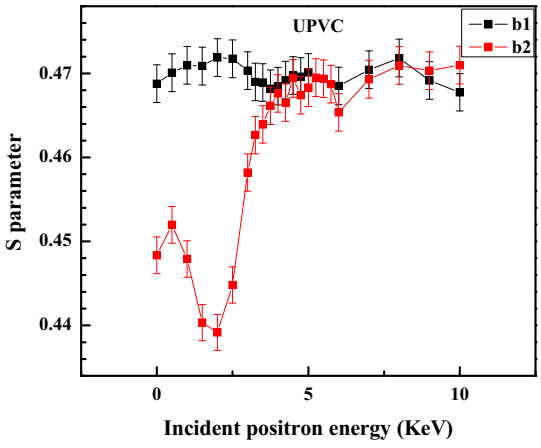
To examine whether the trough is due to some problems of our slow positron beam, depth profiles of *S* parameter for silicon slice are measured with the two measuring patterns, as in Fig. 2. It is clear that the curve measured with energy increase pattern and the one obtained with energy decrease pattern can accord with each other within the error range in the whole energy range. There is no doubt that the beam is on the normal operation condition.

Silicon slice is conductive, while PC, PTFE and UPVC films are insulating. Besides, from positron lifetime experiments using standard ^{22}Na fast positron sources it is known that self-irradiation effects in polymers may induce electrical charging of the samples [14]. It is inferred then that the notable difference observed in polymers may relate to accumulated charges during Doppler broadening energy spectroscopy measurement.

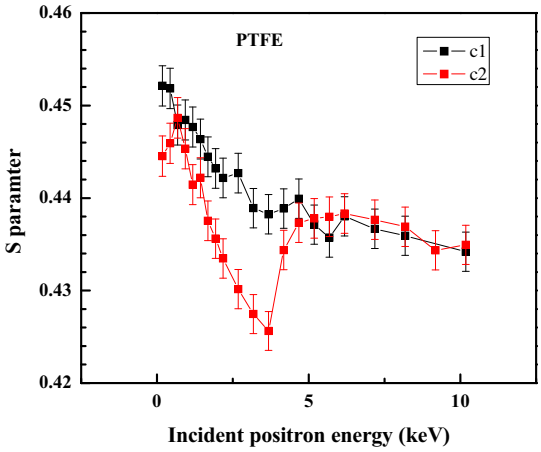
With both measuring patterns, charges will accumulate. It is necessary to pick out the one which is less influenced by accumulated charges. As the two measuring patterns give different depth profiles of *S* parameter, the better one may be found by study the interaction of the two measuring patterns. Four identical PTFE films are prepared. First, a piece of film is measured with energy increase pattern, and another one is measured with energy decrease pattern. Then the rest two films are continuously measured with both measuring patterns (energy increase pattern and energy decrease pattern) but in different sequence. The results are shown in Figs. 1(c) and Fig. 3. In Fig. 1(c), curve c1 and c2 represents the depth profile of *S* parameter independently obtained with energy increase pattern and energy decrease pattern, respectively. Fig. 3(a) shows the result of a PTFE film first measured with energy increase pattern (curve e1) and then measured with energy decrease pattern (curve e2), Fig. 3(b) shows the result of another PTFE film first measured with energy decrease pattern (curve f1) and then measured with energy increase pattern (curve f2). It is



(a)



(b)



(c)

Fig. 1. Depth profiles of *S* parameter for PC, UPVC, and PTFE polymers; black curves were measured with energy increase pattern, red curves were measured with energy decrease pattern. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reasonable that curve e1 and c1, f1 and c2 are nearly the same, since these two curves are measured on the same condition. It is quite interesting that curve e2 and curve c2 are quite similar, with the only difference being a little shallower trough in curve e2. In contrast, curve f2 shows notable difference from curve c1. It is inferred that charges accumulated during the measurement with energy decrease pattern show much greater influence on depth profile of *S* parameter.