In Situ Observation of Damage Evolution in Polycarbonate under Ion Irradiation with Positrons

Hidetsugu Tsuchida[1,2,*], Hironori Tsutsumi[2], Masafumi Akiyoshi[2], and Takeo Iwai[3]

[1] *Quantum Science and Engineering Center, Kyoto University, Uji, Kyoto 611–0011, Japan*
[2] *Department of Nuclear Engineering, Kyoto University, Kyoto 615–8530, Japan*
[3] *Faculty of Medicine, Yamagata University, Yamagata 990–9585, Japan*

E-mail: tsuchida@nucleng.kyoto-u.ac.jp

We report β^+–γ coincidence positron annihilation lifetime spectroscopy of *in situ* observation of ion damage in polycarbonate under irradiation by MeV-energy H^+ ions. Ion damage was investigated from changes in the relative intensity of the long-lived *ortho*-positronium pick-off annihilation lifetime component measured under irradiation and non-irradiation conditions. It was found that at fluences of less than 10^{15} ions $\cdot$ cm^{-2} the relative intensity of this component during irradiation was significantly reduced compared to that after irradiation. This reduction disappears at fluences higher than 10^{15} ions $\cdot$ cm^{-2}. Results suggest that at fluences up to 10^{15} ions $\cdot$ cm^{-2}, transient damage structures are formed under irradiation.

1. Introduction

Ion-irradiation modifications of materials are one of the most fundamental methods of ion beam processing. This method is applied for manufacturing porous membranes of polymeric materials as track-etching technology. Polymer modification due to ion irradiation results from dynamical atomic collision processes that occurred along the ion trajectory in a nanometer size region (latent ion tracks). Understanding the damage processes in the tracks is important for controlling the modification structures. For fast ion irradiation of polymers, the damage is induced mainly via ionization or electronic excitation of target atoms. This leads to polymer dissociation, such as radical formation, bond scission and cross-linking of polymer chains. Ion induced damage of polymers has been studied so far by means of various analytical techniques [1–3].

Positron annihilation spectroscopy is a powerful method for investigating radiation damage involving microstructural changes of materials at the atomic level. In our previous work, we have applied positron annihilation spectroscopy for observations of ion damage evolution in metallic materials [4–7]. Vacancy defects produced under irradiation were studied via in situ measurement of positron annihilation Doppler broadening spectra. Results showed that vacancy concentration is enhanced under irradiation, originating from transient vacancy production, compared to that observed after irradiation. Thus, in situ positron annihilation spectroscopy is applicable for detection of radiation defects that are produced during irradiation.

For ion damage of polymers, polymer dissociation results from a variety of time-dependent radiation-chemical reactions. In situ study of damage evolution under irradiation is therefore an important subject for understanding mechanisms of polymer modifications in ion-beam processing. In this work, we present a new method for in situ observation of ion damage evolution in materials by combining a β^+–γ coincidence positron annihilation lifetime spectroscopy apparatus with a high-energy ion accelerator. The use of positron lifetime spectroscopy makes it possible to perform identification of different types of radiation damage. The purpose of this study is to understand initial damage states that are formed in the low fluence range. To investigate irradiation effects on poly-

mers induced via electronic excitation processes, specimens of polycarbonate were irradiated with 2.0 MeV H$^+$ ions. Positron annihilation lifetime spectra were measured alternately under irradiation and non-irradiation conditions. From the analysis of the *ortho*-positronium pick-off annihilation component in the lifetime spectra, we investigated microstructure changes that occurred under irradiation and their depencence on ion fluence.

2. Experimental methods

The experiment was performed using the 1.7 MV tandem accelerator at the Quantum Science and Engineering Center, Kyoto University. Figure 1 shows the experimental setup for in situ observation of ion damage under irradiation with positrons. The apparatus consists of a positron annihilation spectroscopy device and a beam-energy moderator device.

In the positron annihilation spectroscopy device, we used the β$^+$–γ coincidence positron annihilation lifetime spectroscopy (PALS) method to achieve a specimen-positron source separation arrangement [8]. This makes it possible to simultaneously perform ion irradiation of the specimen during positron lifetime measurements. A radioactive isotope ^{68}Ge was used as the positron source. Positrons emitted from the ^{68}Ge source penetrate through a transmission type avalanche photodiode detector (APD) with a thickness of 150 μm, and then enter the target specimen. The specimen was positioned between two scintillation detectors. A pair of annihilation γ-ray photons, generated in the specimen and emitted in opposite directions, were detected by two different detectors (BaF$_2$ and NaI(Tl)). One of the annihilation γ-rays was detected by the BaF$_2$ detector, and the other was detected by the NaI(Tl) detector. The lifetime of a single positron annihilation event was measured by detecting the time difference between the start signal provided from the APD and the stop signal from the BaF$_2$ detector. The NaI(Tl) detector provides a coincidence gate-signal of a multi-channel analyzer (MCA). This coincidence setup enables us to eliminate components of the positron annihilation that occurred outside of the specimen, and also serves to reduce the lifetime spectra background.
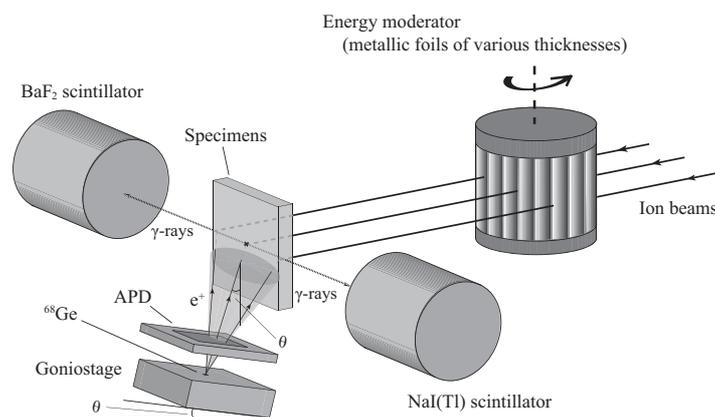

Fig. 1. Schematic diagram of the experimental setup for in situ observation of ion damage under irradiation by β$^+$–γ coincidence positron annihilation lifetime spectroscopy.

Polycarbonate with a thickness of 125 μm, obtained from the Goodfellow Company, UK, was used as a target specimen. The specimen was irradiated by H$^+$ ions with a primary energy of 2.0 MeV. The ion beams were collimated to a spot size of 15 mm × 15 mm, and were directed parallel to the surface normal of the target specimen. Positron lifetime spectra were measured alternately under irradiation and non-irradiation conditions. The average fluence received by specimen after a single
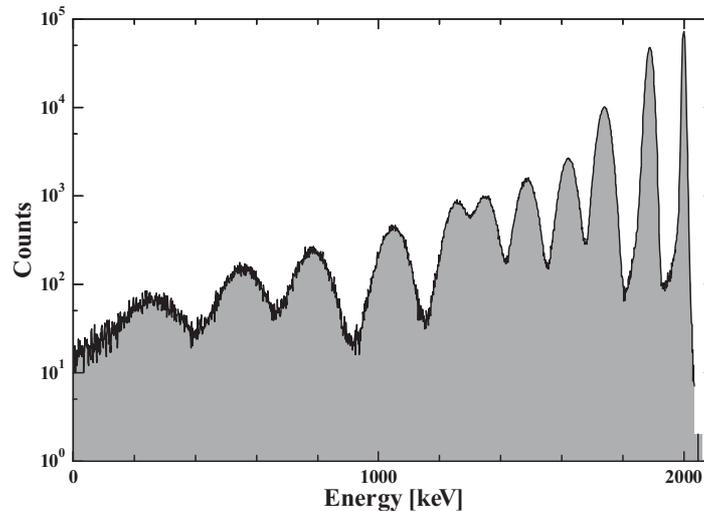
Fig. 2. Energy spectra of projectile beams after passing through the energy moderator. The primary energy of the H$^+$ ion beams from the accelerator (before entering into the moderator) was 2.0 MeV.

irradiation run was on the order of 10^{14} ions $\cdot$ cm^{-2}. The time resolution of the β$^+$–γ coincidence PALS measurement system was less than 300 ps. The coincidence rate was ∼10 cps, depending on the thickness of the measuring specimen. The total number of counts in each spectrum was more than 1.0×10^5. The data-acquisition time was 4 h–5 h for each lifetime spectrum. The lifetime spectra obtained were analyzed using a PALS-fit code [9].

In the ion irradiation experiments, we used an energy moderator device to produce a uniform damage distribution throughout a specimen thickness. It is necessary to produce a uniform damage distribution because the positrons from the ^{68}Ge source have a broad energy distribution. The energy moderator device consists of rectangular titanium foils of various thicknesses arranged on a rotating drum driven by a pulse motor at a frequency of about 1 Hz, as shown in Fig. 1. A mono-energy beam obtained from the accelerator was converted to an energy-broadened beam by passing through the moderator, and then was incident on a target specimen. Figure 2 shows the energy spectrum of projectile beams after passing through the moderator, as measured by a silicon semiconductor detector. In this measurement, the primary beam was 2.0 MeV H$^+$ ions, and the moderator consisted of titanium foils having eleven different thicknesses of zero (blank), 2.5, 5.5, 8.0, 10.5, 13.0, 15.0, 18.5, 22.0, 25.0, and 28.0 μm. One can see eleven peaks in the energy spectrum, each peak corresponding to the energy-loss of the projectile beam passing through the various foils. We calculated damage distributions for the energy-broadened beam obtained from moderator by the following method. First, we obtained peak energies and intensities (integrated peak intensities) from the energy spectrum shown in Fig. 2. Second, for a projectile with each peak-energy we calculated a damage distribution by using the TRIM code [10]. Finally, by summing up each damage distribution weighted by the corresponding peak intensity, we obtained a damage distribution produced by the energy-broadened beam. Figure 3 shows the obtained damage distributions resulting from nuclear or electronic energy-loss process for the energy-broadening beam. From the results, one can see that more uniform damage distributions are achieved by utilizing the moderator compared to the un-moderated beam.

Positrons from the ^{68}Ge source have a maximum kinetic energy of approximately 1.9 MeV, and hence the penetration depth in matter is in the order of few mm. This means that it is not applicable for analysis of damage depth profiles in the range less than a few hundred μm. In this study, the thickness of specimens used was 125 μm. To overcome this limitation, we utilize the glancing angle

3

incidence method, as shown in Fig. 1. In this method positrons enter the specimen at small angles to the surface. Even if the positron energy is high, the positron implantation depth remains shallow. In the present experiments, the incident angle θ was set to 5 degrees.
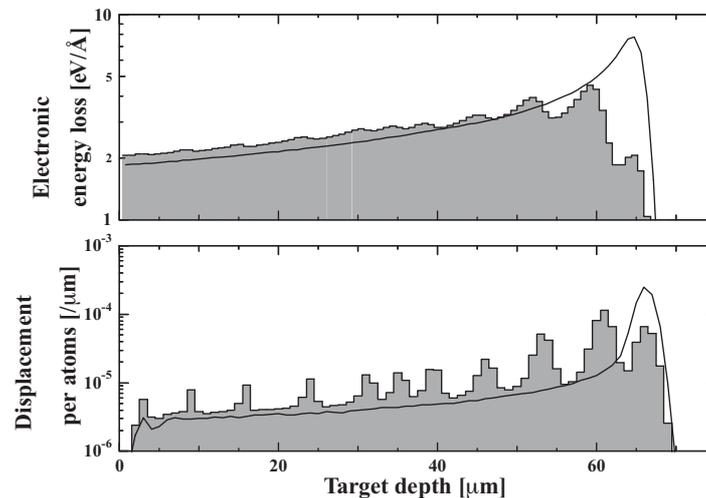

Fig. 3. Calculated damage distributions for the energy-broadened beam: the upper and the lower figures show the damage distributions originating from the electronic energy loss process and the nuclear energy loss process, respectively. Solid curves denote the damage distributions for primary beams of 2.0 MeV H$^+$ ions.

3.   Results and discussion

For each measured positron lifetime spectra a two-component analysis was carried out using the PALSfit program [9]. From the analysis, we obtained the long-lived lifetime component which is attributed to the pick-off annihilation of *ortho*-positronium (*o*-Ps) in the polymer free volume. The lifetime and relative intensity of the *o*-Ps pick-off component is sensitive to induced radiation damage. Figure 4 shows the measured *o*-Ps annihilation lifetime and relative intensity as a function of fluence for irradiation of polycarbonate with MeV-energy H$^+$ ions. Closed and open symbols denote the data observed under irradiation (during irradiation) and non-irradiation (after irradiation), respectively. In this figure, values of fluence for data observed during irradiation were plotted as the central value of the fluence measured before and after irradiation. One can see different behavior in fluence dependence between the lifetime and the intensity. The lifetime value was approximately 2 ns, and remained unchanged irrespective of fluence. In contrast, the intensity of *o*-Ps component decreases with increasing fluence. This intensity decrease is due to increase in new positron annihilation sites produced by ion damage. In addition, the intensity was found to reduce significantly under irradiation at low fluences less than 10^{15} ions·cm^{-2}, compared to that observed after irradiation. This reduction disappears at fluences higher than 10^{15} ions·cm^{-2}. These results suggest that the fluence has an effect on damage structures.

We discuss type of damage structures formed under the present experimental conditions. It is known that two major types of damage structures are produced in ion irradiation of polymers: chain scission and cross-linking [11]. Mechanisms of these damage structures depend on the following parameters: irradiation conditions (ion species, ion energy, fluence) and energy deposition processes (nuclear and electronic stopping powers, or linear energy transfer (LET)). The most important of these parameters are the LET value and fluence. The LET affects the track structure. Tracks are
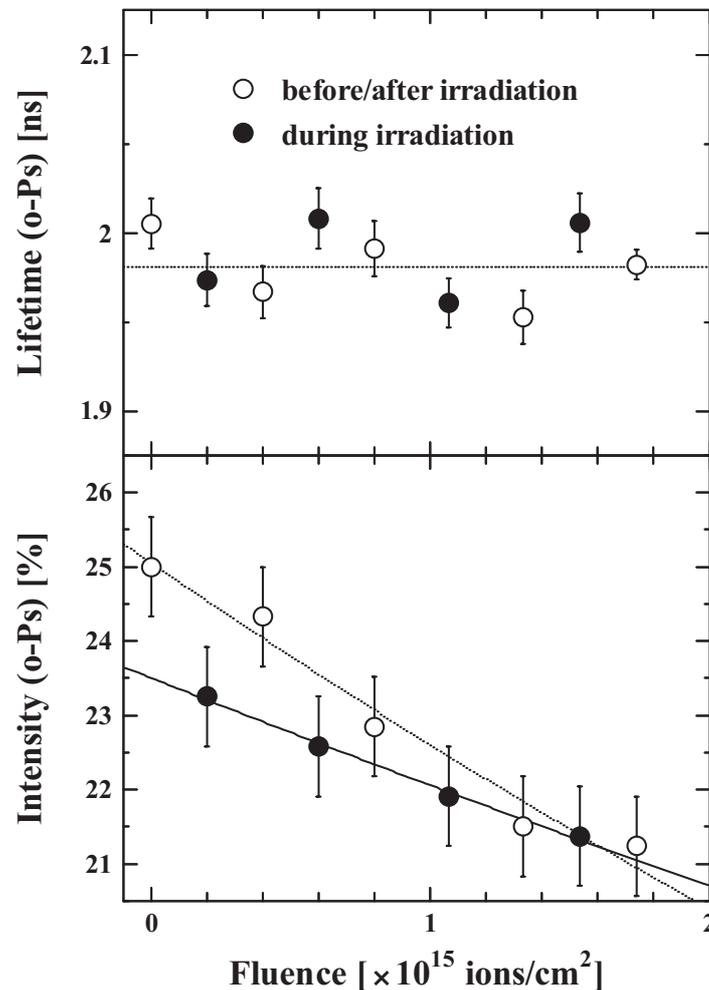
Fig. 4. Variation of the lifetime and the intensity of o-Ps component as a function of the fluence. Solid and dashed lines denote guide of the eyes.

composed of a random succession of spurs which are small localized regions of energy deposition by the primary particle and by secondary electrons. A typical value of the energy deposited in one spur is less than 100 eV. The track structure varies depending on the density of spurs. For low LET, spurs are produced sparsely in a track. Such isolated spur affects only simple molecular chains, leading to chain scission of polymers. For high LET, spurs overlap each other and reactive free radicals are formed in high concentration over many neighboring molecular chains. This causes cross-linking to occur between those scission chains. The description above is applicable to the fluence effect on damage mechanisms i.e. the fluence effect is related to track density. At low fluence, damage with a simple structure such as chain scission is dominantly formed because of the low damage density (non-overlapping of tracks). With increasing fluence, tracks overlap and interactions between damage formed in the tracks occur, leading to a complex damage structure such as cross-linking of polymer chains. Thus, damage structures change from chain scission to cross-linking with increasing fluence.

In Fig. 4, the o-Ps intensity decreases with increasing fluence, its value becomes constant at fluences higher than 10^{15} ions $\cdot$ cm^{-2}. This fluence dependence may be attributed to the difference in damage structures. Similar results have been reported in the study of ion damage of polymeric materials different from the specimens used in this study [12]. For poly(methyl methacrylate), PMMA, ir-

radiated with 1.5 MeV H^+ ions (low LET radiations), it was found that chain scission is formed at fluences of less than 10^{13} ions·cm^{-2} and cross-linking occurs at higher fluence above 10^{15} ions·cm^{-2}.

In this study, H^+ beams with energy distributions as shown in Fig. 2 were used. These belong to low-LET radiations because the electronic stopping power (or the LET value) for the projectiles in polycarbonate is less than 100 eV/nm from the SRIM calculation [10]. Therefore, it is likely that the damage structure produced is a simple chain scission. As shown in Fig. 4, the o-Ps intensity observed under irradiation is lower than that after irradiation at fluences of less than 10^{15} ions·cm^{-2}. This implies that some of the ion damage produced under irradiation recovers after irradiation. A possible damage recovery process includes molecular breakage due to the formation of reactive intermediates such as free radicals, ions and excited states. These intermediates are formed under irradiation, but are unstable and hence recombine after irradiation [13]. It is therefore phenomenologically concluded that transient damage structures consisting of molecular chain scission induced by reactive intermediates are formed under irradiation at fluences up to 10^{15} ions·cm^{-2}. Further study is needed to identify in detail the types of defects formed under irradiation. We plan to obtain information about the lifetime values of damage component in the lifetime spectra, by further improvement of the time resolution.

4. Conclusion

We studied the ion damage evolution in polycarbonate by in situ observation of positron annihilation lifetime spectra. The β^+–γ coincidence positron annihilation lifetime spectroscopy method was applied for investigating microstructural changes of materials under ion irradiation. We investigated effects of electronic collision process on polymers for polycarbonate irradiated by MeV-energy H^+ ions. The relative intensity was found to reduce significantly under irradiation at low fluence less than 10^{15} ions·cm^{-2}, compared to that observed under non-irradiation. This result implies that damage concentration during irradiation is high compared with that surviving after irradiation. It was also found that the reduction disappears at fluences higher than 10^{15} ions·cm^{-2}. This suggests that transient damage structures consisting of molecular chain scission induced by reactive intermediates are formed at fluences up to 10^{15} ions·cm^{-2} under the present experimental conditions.

Acknowledgment

References

[1] T. Venkatesan: Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms **7–8** (1985) 461.

[2] L. S. Wielunski, R. A. Clissold, E. Yap, D. G. McCulloch, D. R. McKenzie, and M. V. Swain: Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms **127–128** (1997) 698.

[3] J. Zhang, J. Kang, P. Hu, and Q. Meng: Appl. Surf. Sci. **253** (2007) 5436.

[4] H. Tsuchida, T. Iwai, M. Awano, M. Kishida, I. Katayama, S. C. Jeong, H. Ogawa, N. Sakamoto, M. Komatsu, and A. Itoh: J. Phys.-Condens. Matter **19** (2007) 136205.

[5] H. Tsuchida, T. Iwai, S. Kasai, H. Tanaka, N. Oshima, R. Suzuki, T. Yoshiie, and A. Itoh: J. Phys.-Conf. Ser. **262** (2011) 012060.

[6] T. Iwai and H. Tsuchida: Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms **285** (2012) 18.

[7] H. Tsuchida, T. Iwai, M. Awano, N. Oshima, R. Suzuki, K. Yasuda, C. Batchuluun, and A. Itoh: J. Nucl. Mater. **442** (2013) S856.

[8] P. Chalermkarnnon, M. Yuga, S. Nakata, S. Kishimoto, H. Araki, and Y. Shirai: RADIOISOTOPES **50** (2001) 576.
[9] PALS-fit computer program, http://palsfit.dk/.
[10] J. Zieglar, J. F. Biersack, and U. Littmark: The Transport of Ions in Matter (TRIM) Monte-Carlo Calculation Including in Computer Program SRIM Version (2008), http://www.SRIM.org.
[11] E. H. Lee, G. R. Rao, and L. K. Mansur: Radiat. Phys. Chem. **55** (1999) 293.
[12] T. M. Hall, A. Wagner, and L. F. Thompson: J. Vac. Sci. Technol. **16** (1979) 1889.
[13] E. H. Lee: Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms **151** (1999) 29.