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Radiation-induced luminescence of PET and PEN films under MeV ion and pulsed UV laser irradiation

S. Nagata [a,*], H. Katsui [a], K. Takahiro [b], B. Tsuchiya [a], T. Shikama [a]

[a] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[b] Kyoto Institute of Technology, Kyoto 606-8585, Japan

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ABSTRACT

Ion- and photo-induced luminescence of polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) films was investigated during irradiation by MeV H and He ions and an ultraviolet pulsed laser. At the beginning of ion irradiation, the PEN film emitted blue luminescence, whose intensity was an order of magnitude higher than that emitted by the PET film. Successive ion irradiation effectively reduced the luminescence centers, and the rate of decease in luminescence intensity depended on the energy deposited along the trajectory of the ions. Optical absorption measurements in the infrared region revealed an irradiation-sensitive feature of the PEN film. Moreover, a photo-induced band grew remarkably at 470 nm in the PET film under 266 nm pulsed laser irradiation, while the PEN film showed a moderate decrease in luminescence intensity at 440 nm.

1. Introduction

Drastic changes in the structure and electrical properties of polymers due to irradiation are of great interest for their application to fabrication of photo-resistive substrates and nano-structures [1,2]. Ion bombardment of the polymer materials, in particular, causes important chemical transformations, depending on the energy deposition mechanisms [3,4]. Polyethylene terephthalate (PET) films are widely utilized in industrial products such as packaging materials, data storage tapes, and capacitors, owing to their ease of handling and low cost. An aromatic polymer similar to PET is polyethylene naphthalate (PEN), consisting of two benzene rings in a monomeric structure compared to one in the PET. Compared with PET, PEN has a superior Young's modulus, glass transition temperature, and permeability to water. So far, the ion-induced modification and degradation of PET films have been reported, mainly concerning about swift heavy ion irradiation effects on their optical [5–10], and electrical properties [11–13], examined by optical absorption and electrical conductivity measurements after the ion irradiation. Compared to conventional post-irradiation techniques, measuring the ion-beam-induced luminescence (IBIL) of materials enables in situ measurements of the evolution of network degradation and the formation of new structures [14,15]. In the present study, we measured MeV-light-ion- and UV-laser-induced luminescence of PET and PEN films during irradiation to examine the evolution of luminescence characteristics and the relationship between energy deposition and modification of PET and PEN films.

2. Experimental

The examined samples were commercially available PET (Lumilar@, Toray Japan) and PEN (Teonex@, Teijin DuPont Japan) films with a thickness of about 9 μm. Irradiation of 0.5–1.9 MeV H^+ and 2.8 MeV He^{++} ions, which can penetrate the entire thickness of the sample film, was performed at room temperature in a scattering chamber connected with a 1.7 MV tandem accelerator at the Institute for Materials Research, Tohoku University. An area of about 1 mm^2 of the sample was irradiated with a current density less than 5 nA/mm^2 to prevent heating effects during IBIL measurements. The light emitted from the polymer film in the vacuum chamber was collected through a synthesized silica window and a lens focused on a silica fiber connected to an optical spectrometer, which consists of a monochrometer equipped with a back illuminated CCD camera. The evolution of the ion-beam-induced luminescence spectrum was monitored for wavelengths from 300 to 900 nm, with an accumulation for 1 s for each spectrum. The emission intensity was normalized to the number of incident ions evaluated by the target current. The photo-stimulated luminescence (PL) measurement was performed at room temperature using 266 nm (4.7 eV) photons with a pulse width of about 5 ns at a typical energy density of 100 $mJ/cm^2/s$. As the 266 nm photons were obtained from the fourth harmonic wave of a Nd:YAG laser,

* Corresponding author. Address: Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan. Tel.: +81 22 215 2062; fax: +81 22 215 2061.
E-mail address: nagata@imr.tohoku.ac.jp (S. Nagata).

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the primary, second, and third harmonic waves were deflected by a prism to prevent interference. Ultraviolet to visible (UV–VIS) and Fourier-transform infrared (FTIR) absorption spectra were measured after the ion irradiation to examine the chemical changes in the films.

3. Results and discussion

Fig 1(a) and (b) shows 1 MeV H^+-ion-induced luminescence spectra at different fluences for PET and PEN films, respectively. Both films exhibited characteristic luminescence bands mainly in the blue region and the luminescence intensity monotonically decreased with increasing the incident ion fluence. As the luminescence at shorter wavelengths below 400 nm decreased at a higher rate in the PEN film, the observed maximum peak position shifted to longer wavelengths. Under the same irradiation, the PEN film emitted more prominent luminescence with an intensity that is an order of magnitude larger than that from the PET film. Increasing the incident H^+ ion fluence on the PEN film decreased the intrinsic band centered at 440 nm without a significant peak shift. New peaks appeared simultaneously after irradiation to the fluence of 2×10^{14} H/cm^2 in the wavelengths between 550 and 750 nm.

The decrease in the IBIL intensities from the PEN film is plotted as a function of the H^+ and He^+ ion fluence in Fig. 2. The intensity immediately diminished to 1/10 of the initial value at a fluence of about 1013 ions/cm^2, and the reduction in the 440 nm emission

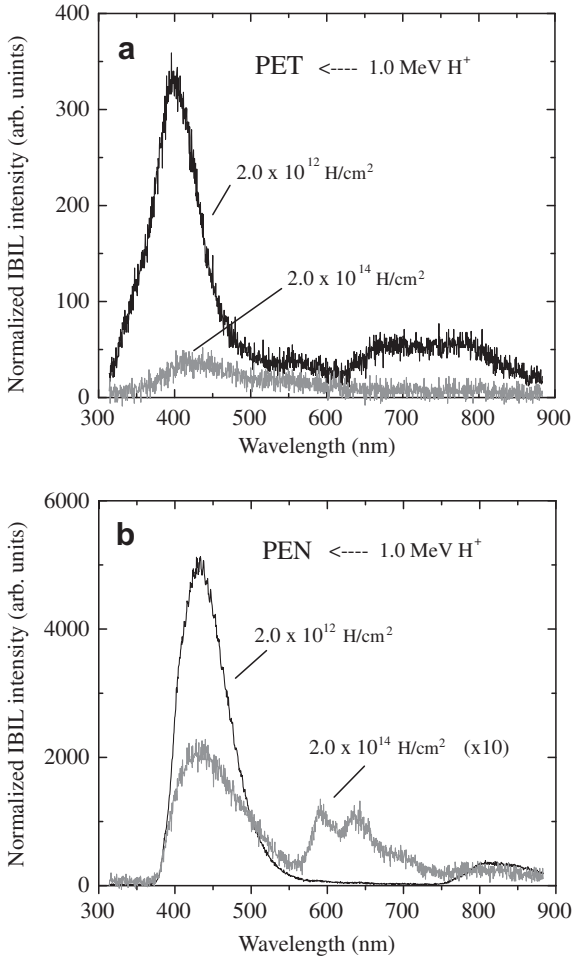

Fig. 1. 1 MeV H^+ ion-induced luminescence spectra irradiated at a fluence of 2×10^{12} and 2×10^{14} H/cm^2 for (a) PET and (b) PEN films.

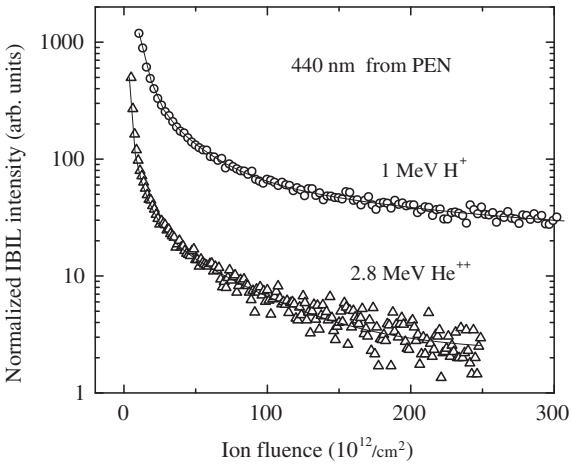

Fig. 2. Evolution of the IBIL intensity at 440 nm from the PEN film irradiated by 1 MeV H^+ and 2. 8 MeV He^{++} ions plotted as a function of the incident ion fluence.

intensity by He ion bombardment occurred more effectively than with H ion bombardment. If we assume that the luminescence centers are damaged by a first-order reaction, the initial decay curve of the IBIL yield at the beginning of the irradiation can be expressed as an exponential decrease with the incident ion fluence [15]. Table 1 shows the damage cross-section evaluated by least-square fitting of the initial part of the decay curve, and also the average stopping cross-section in the film calculated by the stopping and range of ions in matter program (SRIM) [16].

The ratio of the damaged cross-sections σ_H/σ_{He} is comparable for the PET and PEN films. This suggests that the damage processes of the luminescence centers in both films are essentially the same, depending on the energy deposition mechanism. On the other hand, the ratios of the stopping power of H to He are considerably smaller in both films. The energy deposition by H^+ irradiation effectively damaged the luminescence centers, and an excess of the energy was deposited around the He^{++} ion trajectory for altering the luminescent structure. A larger electronic excitation also contributed to the lower luminescence intensity, as shown in Fig. 3, where the fluence dependence of the IBIL intensity was plotted for different H^+ energies. H^+ ions with incident energy above 1.0 can penetrate the 9 μm PEN film, while the mean projected range of the 0.5 MeV H^+ ion is about 7 μm. The initial emission intensity for 0.5 MeV H^+ ion bombardment was about 1/5 of that of higher energies, probably because of the less effective emission for higher energy deposition. Moreover, the identical decay curves of 1.0 and 1.9 MeV irradiation indicate that the ion-induced photon emission efficiency and damaged cross-sections are independent of the electronic energy loss of H^+ ions above 1 MeV.

According to the FTIR measurements of the ion irradiated samples, the CH_2 bending vibration of the trans-configuration of the ethylene glycol residue and typical vibration bands of the para-substituted benzene rings were assigned to the bands at 1471 and 1504 cm^{-1}, respectively [5,6,17]. The former corresponds to

Table 1
Damage cross-sections evaluated by least-square fitting of the decay curves shown in Fig. 2, as well as the calculated average stopping cross-section.

Damage cross-section	σ_H (cm^2) 1 MeV H	σ_{He} (cm^2) 2.8 MeV He	σ_H/σ_{He}	S_H/S_{He} electronic	S_H/S_{He} nuclear
PET	8.7×10^{-14}	2.9×10^{-13}	0.30	0.17	0.12
PEN	1.6×10^{-13}	5.9×10^{-13}	0.27	0.17	0.12