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Reduction of light elements loss in polymer foils during MeV-proton irradiation by application of an aluminum coating

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ABSTRACT

Backscattering and forward-scattering spectrometry with 2.2 MeV-protons have been applied to detect light elements including H, C, N and O in polymer foils of aromatic polyimide (PI), polyethylene telephthalate (PET) and polyethylene naphthalate (PEN). In the case of PI, no significant loss of H, C, N and O was observed during proton irradiation. In the case of PET and PEN, on the other hand, all the light elements gradually decreased as irradiation fluence increased and the contents of 15%-H, 14%-C, 47%-O in PET and 7%-H, 5%-C 31%-O in PEN were eventually released up to a fluence of 2.1×10^{16} protons/cm^2. An aluminum thin film (thickness ~0.1 μm) was sputter-deposited on the upper surface of 4 μm thick PET and PEN foils to prevent the release of light elements. In Al coated PEN foil, for example, the losses of H, C and O were 2%, 0.5% and 22% of the starting contents, respectively, considerably smaller than those found for uncoated PEN. Thus the Al coating was found to be an effective method to suppress the loss of constituent elements.

1. Introduction

Ion beam analysis (IBA) with MeV energy light ions, e.g., protons and helium ions, is a quick and powerful method to analyze materials surfaces. The analysis is considered to be non-destructive. For metallic and semiconductor materials, in fact, compositional changes as well as structural ones are negligible small. For insulators, by contrast, electronic excitations and ionization induced by MeV ion beams sometimes cause degradation of targets. Especially for polymeric targets, light elements such as hydrogen (H), carbon (C) and oxygen (O) tend to be released from the targets [1–5] resulting in a serious compositional change during the IBA. Very small beam-currents and reduced temperatures may hinder the beam-induced degradation of polymers. Such conditions are, however, not practical for materials analysis because prolonged beam irradiation at low temperatures in conventional vacuum leads to significant hydrocarbon (CH_x) adsorption as contamination on sample surfaces [6–9], giving rise to undesired compositional alterations. In order to lower the compositional changes caused by MeV ion beam irradiation in polymers, a technique for precise determination of atomic composition in IBA is required.

In the present study, polyimide (PI), polyethylene telephthalate (PET) and polyethylene naphthalate (PEN) foils are analyzed by using MeV-proton beams. Irradiation with MeV-protons enables one to detect C, N, O and H atoms simultaneously in the polymer foils of several microns in thickness by backscattering analysis [10–13] and proton–proton scattering [13–16], respectively. First of all, compositional and structural modifications due to analyzing proton beams are examined for these polymer foils. Several workers investigated the compositional and structural changes caused by MeV-proton beam irradiation for PI [17–20] and PET [21–24]. For PEN foils, Laskarakis et al. [25] and Apel et al. [26] reported radiation effects induced by heavy ions. To the best of our knowledge, however, information on the MeV-proton beam irradiation effects in PEN is unavailable. Therefore, firstly, differences in the compositional and structural modifications induced by MeV-proton beam irradiation in PI, PET and PEN are studied. Secondly, we investigate the effects produced by the application of a thin aluminum coating on the compositional changes during proton irradiation, and finally we discuss the possible mechanisms of the effect.

2. Experiment

The samples used were commercially available self-supporting foils of aromatic polyimide (PI) [$(C_{22}H_{10}O_5N_2)_n$, density: 1.43 g/cm^3], polyethylene telephthalate (PET) [$(C_{10}H_8O_4)_n$, density: 1.40 g/cm^3] and polyethylene naphthalate (PEN) [$(C_{14}H_{10}O_4)_n$, density: 1.36 g/cm^3]. The foil thicknesses were 7.9 μm for PI and 1.2–8.5 μm for PET and PEN. An aluminum thin film was applied

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on the upper surface of 4 μm thick PET and PEN foils by sputter deposition. An Aluminum target was sputtered by Ar plasma held at room temperature, at a constant power of 500 W for 180 s. The pressure in the chamber was 1.0×10^{-1} Pa during sputtering. The thickness of Al coating was about 0.1 μm. For convenience, coated samples were named Al/PET and Al/PEN, respectively.

Proton beams (2.2 MeV) were generated by 2.5 MV Van de Graaff accelerator at Hiroshima University. The projected range of 2.2 MeV-protons, predicted by the SRIM calculation [27], is ~70 μm in the foils, much larger than their thickness. For proton beam analysis, the beam size was 1.4 mm in diameter, and the beam current measured with a Faraday cup, which was placed behind the foils, was varied from 5 to 30 nA. Two Si solid-state detectors were used: one was positioned at a scattering angle of 165° with respect to a beam direction to detect backscattered protons from C, N, O and Al atoms, and the other was set at 45° to detect forward scattered and recoiled protons for H analysis. A more detailed set-up was described in Ref. [13]. During irradiation with 2.2 MeV-protons up to proton charge of 51 μC, corresponding to a fluence of 2.1×10^{16} protons/cm^2, backscattering (BS) and forward-scattering (FS) spectra were acquired by a charge of 0.5 or 1 μC. The spectra were taken every 2 μC up to 11 μC, and then they were collected every 10 μC from 20 to 51 μC. As a consequence of such spectrum acquisition, ten BS and FS spectra were obtained during the proton irradiation. Fig. 1 presents typical BS/FS spectra of the 1.5 μm-thick PET foil. In the BS spectra, well-separated peaks, corresponding to backscattering from C and O atoms, appear. In this case, the contents of C and O atoms can be calculated from the integrated yield of the peaks. In the case of BS spectra of 7.9 μm-thick PI, on the other hand, the peaks of C, N and O were overlapped each other. The computer software SIMNRA [28] was, therefore, used to deduce atomic compositions in the PI foils. The use of fitting procedure in the SIMNRA leads to an error of approximately 5%, mainly arising from relatively low yields in BS spectra acquired by 1 μC.

The proton beam spot was enlarged to 6 mm in diameter to prepare the proton-irradiated foils for structural characterization. In this case, the beam current was kept almost constant at 150 ± 10 nA. Before and immediately after irradiations with 2.2 MeV-proton beams up to a fluence of 2.1×10^{16} protons/cm^2, the structures of the foils were characterized by Fourier-transform infrared (FT-IR) spectroscopy in wavenumber range between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} using the Shimadzu FTIR-8200PC spectrometer.

3. Results and discussion

3.1. PI

Fig. 2(a) shows yields of H, C, N and O peaks in FS/BS spectra as a function of proton charge. In Fig. 2, the yields are normalized by the peak intensities in the spectrum taken at proton charge of 0–1 μC. The proton beam current was kept at 15 nA. As mentioned above, the thickness of the PI foil (7.9 μm) is too thick to decompose peaks of C, N and O in BS spectra, the peak intensities are calculated using SIMNRA [28], giving rise to an error of approximately 5%. Apparently, there is no significant change in the normalized yields, implying that atomic composition does not change in PI

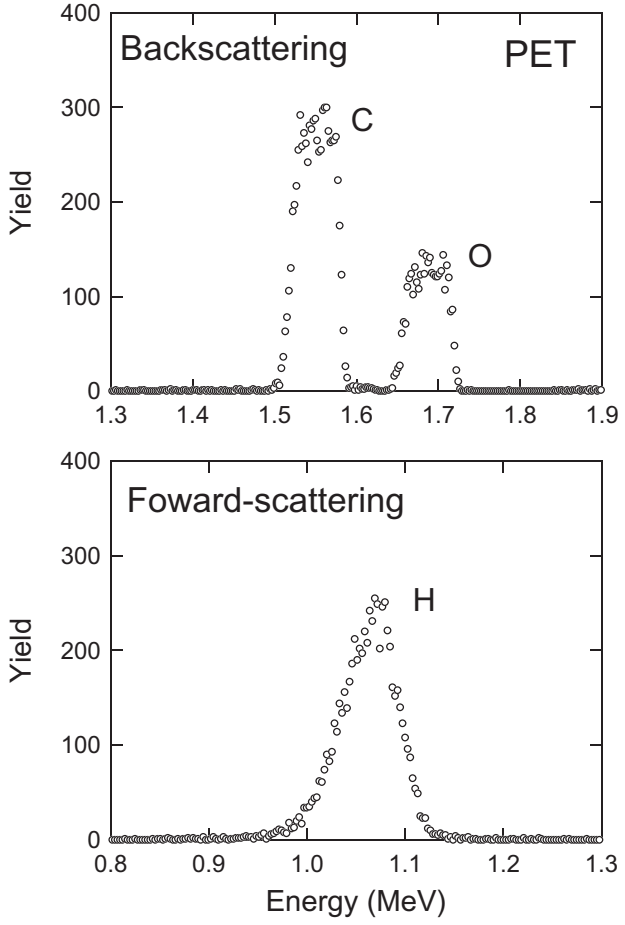

Fig. 1. Typical backscattering and forward-scattering spectra of a 1.5 μm-thick PET foil. The spectra were simultaneously acquired by proton charge of 0.5 μC.

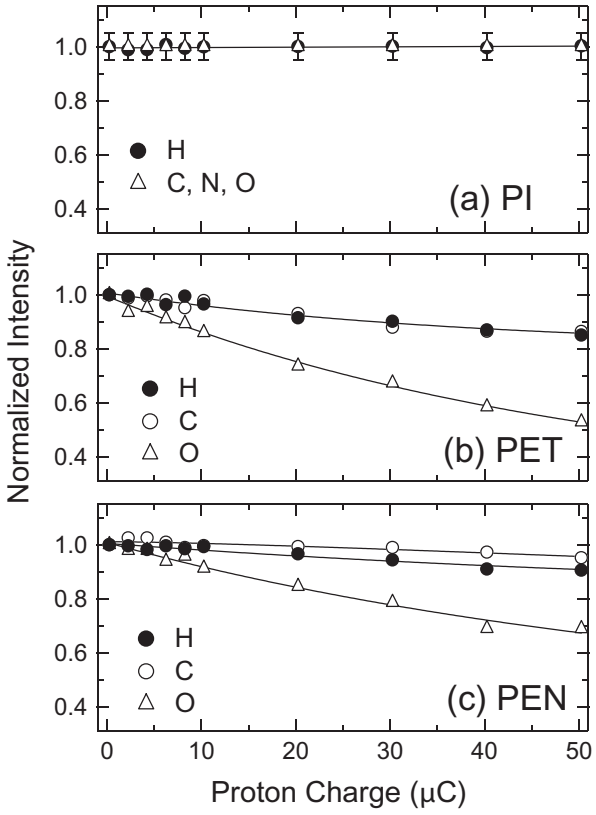

Fig. 2. Normalized yields of H, C, O and N signals in BS/FS spectra of (a) 7.9 μm-thick PI, (b) 1.5 μm-thick PET and (c) 1.2 μm-thick PEN as a function of proton charge. Proton beam current was 15 nA. The solid curves are drawn as a guide to the eyes.