

Free Volume-Limited Diffusion in Ion-Modified Polymers

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SYNOPSIS

Iodine diffusion in ion-modified polyethylene (PE) using the Rutherford Backscattering method (RBS) has been studied. PE was irradiated by N⁺, Ar⁺ and As⁺ ions with an energy of 150 keV and doses of 1×10^{13} – 1×10^{15} cm⁻². Iodine diffused in ion-modified PE from vapor at 90°C. Iodine's concentration profile changed its shape dramatically for ion doses over 1×10^{14} cm⁻² when it showed two maxima. A similar profile was exhibited by oxygen, which diffused in PE on implantation. Iodine's concentration dropped in the layer where the most significant polymer carbonization occurred. This range was found ahead of the implanted ions concentration. Iodine diffusion was most intensive for lower ion doses ($\leq 1 \times 10^{14}$ cm⁻²) while for higher doses it was substantially slower due to PE carbonization. The reason was the lower free volume in the PE carbonized layer as compared with the layer where the polymer's degradation was not reflected in such a significant increase in carbon content. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Ion implantation represents one of the ways of polymer modification. In the course of this process, the chemical structure of the polymeric chain in the polymer surface layer changes dramatically in dependence on the energy and dose of implanted ions. Consequently, some polymer properties (e.g. optical, surface, electric) change considerably.

Apart from chain scission, ion implantation in a polymer also results in chain oxidation,¹⁻³ creation of conjugated double bonds,^{2,3} and, at high doses of implanted ions, also to polymer carbonization.^{4,6} The polymer layer damaged by irradiation exhibits other defects as well, resulting from electron interactions, such as, for example, free radicals.^{3,5}

Polymer properties can be largely affected by the diffusion of organic substances from the gaseous, liquid or solid phase in the modified polymer.⁷⁻⁹ It has been shown that iodine as an acceptor dopant increases by several orders the electric conductivity in ion beam-modified PE, which behaves as a semi-

conductor of the p type.⁹ Experimental results have been obtained from iodine diffusion in polymers irradiated by relatively high ion doses. These results are rather partial and controversial in many aspects. They can be summarized as follows: diffusion, or the penetration of a dopant in a polymer damaged by irradiation, does not proceed in a usual way (Fick's law). The dopant's resulting depth profile follows either the profile of vacancies produced by nuclear clashes (iodine in polyimide),⁷ or the profile of electron losses (Pb in PE (see ref. 10), or the combination of both (I in PE (see ref. 11). Diffusion is "more intensive" for lower implanted doses and lighter ions.^{7,10} A rapid decline in iodine⁹ and Pb (see ref. 10) atoms incorporation has been observed in PE irradiated by doses $\geq 5 \times 10^{14}$ cm⁻² of As⁺ and F⁺ ions, both in terms of the incorporated ions' concentration and amount. It has been shown that depth profiles of diffusing atoms follow the theoretically calculated distribution of vacancies, or of electron losses for doses $< 10^{14}$ cm⁻² (see refs. 7, 10, 11).

The present study is focused on iodine diffusion from the gaseous phase into PE modified by ions of different mass (N⁺, Ar⁺, and As⁺), particularly with a view to carbonization as one of the significant structural changes of the polymer.

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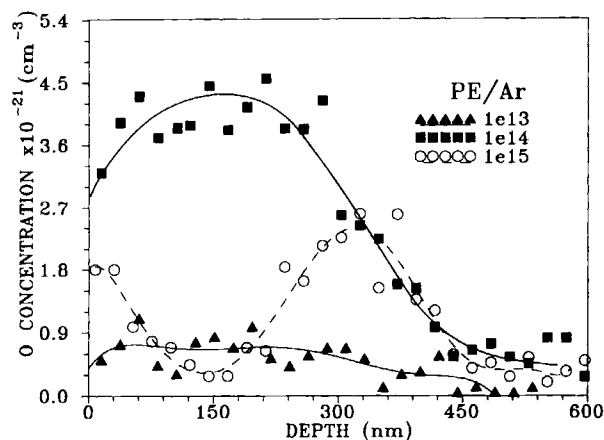


Figure 1 Concentration depth profiles of oxygen incorporated in PE samples irradiated by different doses of 150 keV Ar^+ ions. The solid lines were drawn just for eye guiding.

EXPERIMENTAL

All experiments were carried out on 1.5 mm polyethylene (PE) with a density of $0.945 \text{ g} \cdot \text{cm}^{-3}$. PE samples were irradiated by 150 keV N^+ , Ar^+ and As^+ ions at doses of 1×10^{13} – $1 \times 10^{15} \text{ cm}^{-2}$. The ion beam current density was kept below $50 \text{ nA} \cdot \text{cm}^{-2}$ to avoid thermal degradation of the samples during the ion implantation. Following the ion implantation, PE samples were exposed to iodine vapor for 4 h at a temperature of 90°C . Rutherford Backscattering (RBS) measurements of oxygen and iodine concentration were performed after 20 h with 1.3 MeV alpha-particles, using procedures described earlier.^{3,12} The estimated spatial resolution for the RBS measurements is below 5 nm. Between the measurements, PE samples were stored at room temperature, in darkness, and in the air.

RESULTS AND DISCUSSION

While studying iodine diffusion in ion-modified PE, the oxidation occurring on ion implantation must be taken into account. Oxygen diffuses in the degraded layer from the residual atmosphere in the implanter (pressure of 10^{-4} Pa) and creates chemical bonds with the originating radicals at the place of polymer damage, for example, in the form of carbonyl groups.³ The concentration profile of oxygen following the Ar^+ ion implantation into PE is shown in Figure 1. It reveals that the oxygen profile largely depends on the ion dose. The profile's shape changes significantly on implanting a dose $> 1 \times 10^{14} \text{ cm}^{-2}$,

with two maxima recorded similarly as in article.³ At doses $\leq 1 \times 10^{14} \text{ cm}^{-2}$, the profile exhibits only one maximum. At a dose of $1 \times 10^{15} \text{ cm}^{-2}$, overall oxygen concentration declines. This result can be explained by oxidized structures degradation at high ion doses similarly as in reference.¹⁴

Subsequently, iodine diffused in ion-modified PE. Following As^+ ion implantation into PE, the diffusing iodine's concentration profile appeared to be very similar to the course of energy losses during the implantation.⁹ This result holds for ion doses $\leq 1 \times 10^{14} \text{ cm}^{-2}$. For ion doses $> 1 \times 10^{14} \text{ cm}^{-2}$, iodine's profile changed dramatically after diffusion.⁹ Figure 2 shows the concentration profile of iodine after its diffusion in Ar^+ ion-modified PE. It is evident that the shape of iodine's profile for a dose of $1 \times 10^{15} \text{ cm}^{-2}$ is entirely different from that recorded for lower doses, similarly as in the case of diffusion in As^+ ion-modified PE.⁹ In the depth between 40 and 240 nm, iodine's concentration seems to be lower than the RBS detection limit (about $5 \times 10^{13} \text{ atoms} \cdot \text{cm}^{-2}$). Figure 2 clearly shows that the amount of iodine diffused in the modified layer of PE is significantly lower for a dose of $1 \times 10^{15} \text{ cm}^{-2}$ than for a dose of $1 \times 10^{14} \text{ cm}^{-2}$.

Correlation of Figures 1 and 2 reveals that the concentration profiles of oxygen incorporated on diffusion (chemically bound, diffuses during degradation) and iodine (not chemically bound, incorporated only after implantation) are of the same character. For doses $\leq 1 \times 10^{14} \text{ cm}^{-2}$, the profiles exhibit one maximum that is ahead of the projected range R_p with PE exposed to Ar^+ ions with an energy of 150 keV, $R_p = 242.5 \text{ nm}$. For a dose of $1 \times 10^{15} \text{ cm}^{-2}$, the profiles change their shape significantly, exhibiting two maxima. The most significant of them can

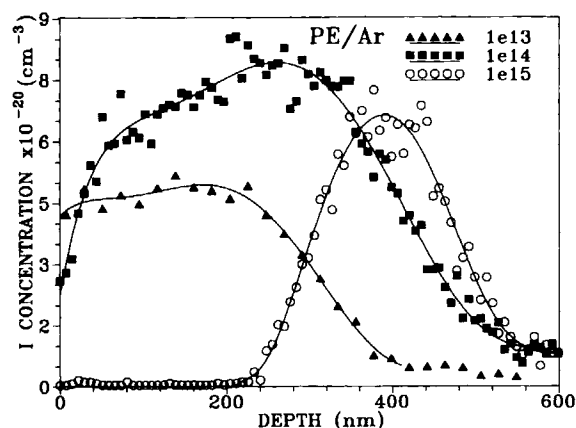


Figure 2 Concentration profiles of incorporated iodine for the same samples as in Figure 1.

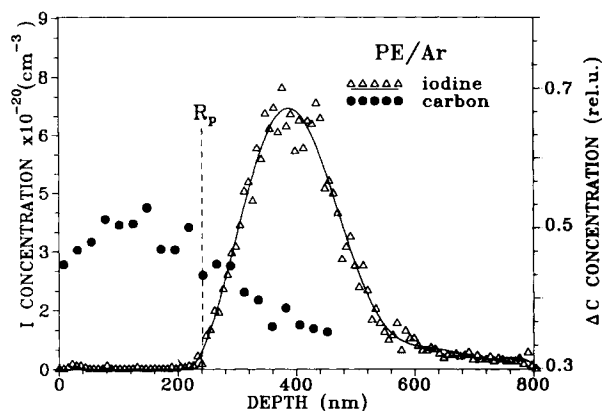


Figure 3 Depth profiles of incorporated iodine and the carbon atomic fraction for PE samples implanted with 150 keV N^+ ions at a dose of $1 \times 10^{15} \text{ cm}^{-2}$.

be found in the range behind R_p , for instance, in a greater depth.

As indicated above, polymer carbonization occurs at ion doses exceeding $1 \times 10^{14} \text{ cm}^{-2}$. In our experimental conditions, RBS did not confirm carbonization at doses $\leq 1 \times 10^{14} \text{ cm}^{-2}$. The profile of a relative increase in carbon content after Ar^+ ions implantation at a dose of $1 \times 10^{15} \text{ cm}^{-2}$ together with the profile of diffused iodine is shown in Figure 3. It is evident that a significant increase in carbon content occurs in depths down to about 400 nm. The carbon profile exhibits a maximum before R_p ($R_p = 242.5 \text{ nm}$). This feature of material defects running ahead of the implanted ions concentration is known from inorganic materials.¹⁵ Figure 3 also reveals that an increase in iodine concentration occurs only after a carbon content decline in the layer. The maximum concentration of iodine was measured in a depth where a relative increase in carbon content was practically not recorded. Correlation of Figures 1 and 3 for a dose of $1 \times 10^{15} \text{ cm}^{-2}$ shows the largest decline in oxygen content (degradation of oxidized structures) in a depth where the most significant carbonization occurs, for instance, before R_p .

Figure 3 presents the concentration profile of diffused iodine and the relative increase in carbon content for Ar^+ ion-modified PE. Identical relations were measured after the implantation of N^+ (Fig. 4) and As^+ (Fig. 5) ions at a dose of $1 \times 10^{15} \text{ cm}^{-2}$, for instance, ions that are significantly lighter and heavier, respectively, than Ar^+ . The results shown in Figures 3, 4, and 5 can be summarized as follows: a significant maximum of I concentration was measured behind the projected range; near of PE surface is an evident small increase of I concentration over

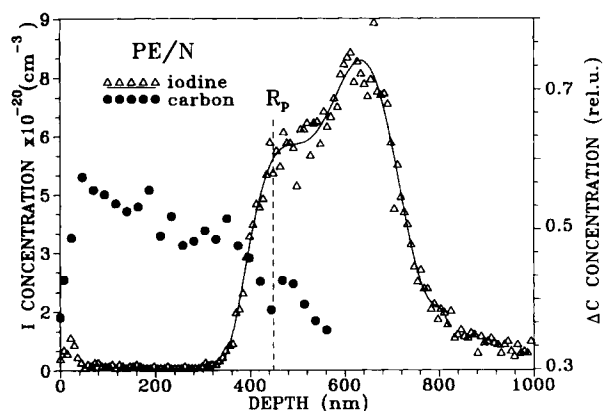


Figure 4 Same as Figure 3 for PE implanted with 150 keV Ar^+ ions.

the detection of RBS; a significant increase in carbon content was recorded in a depth where iodine was not detected; maximum concentration of carbon was found before R_p ; maximum concentration of iodine was measured in a depth where PE carbonization was not detected. This leads us to the conclusion that after the N^+ , Ar^+ , and As^+ ions implantation in PE and subsequent iodine diffusion, the measured results are of the same character.

The results of iodine diffusion in N^+ , Ar^+ , and As^+ ion-modified polyethylene mainly at high ion doses are shown in Figure 6. After ion implantation into PE, the profile of its damage copies the profile of energy losses¹⁶—curve 1. Degradation occurs in the area of damage, particularly chain scission and its dehydrogenation (C—H bonds scission). This leads to the decline in polymer density in the area of damage as compared with nonmodified PE ($\rho_0 > \rho_1$). This means that the free volume increases in the area of damage due to ions implantation. Consequently, iodine from vapor as an infinite source

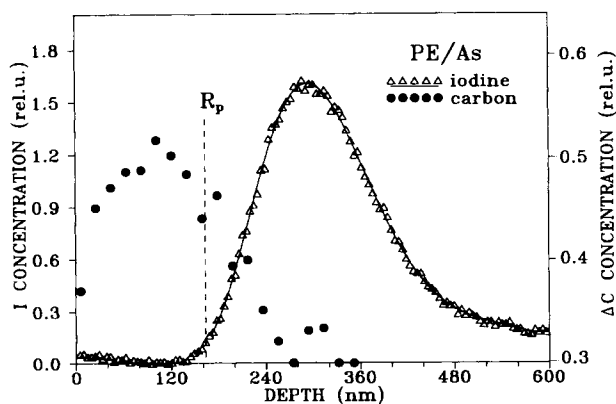


Figure 5 Same as Figure 3 for PE implanted with 150 keV As^+ ions.

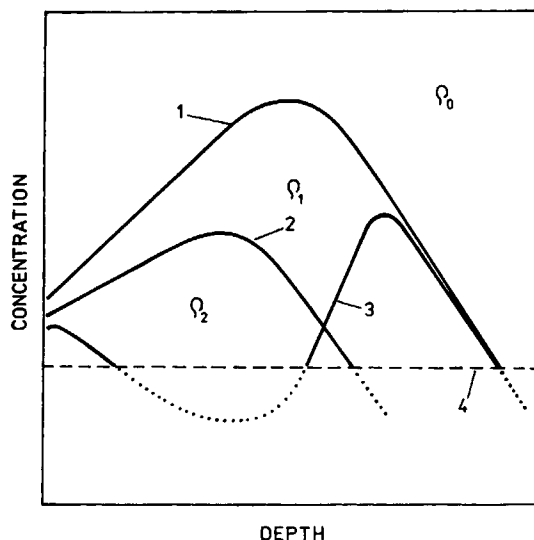


Figure 6 Diagram of polymer damage (1), carbon atomic fraction (2), and iodine concentration profile (3) after high-dose ion implantation in PE. RBS detection limit is indicated by the dashed line (4). ρ_0 is the density of non-degraded, ρ_1 of degraded, and ρ_2 of carbonized PE.

diffuses in the damaged area. RBS has not confirmed iodine diffusion in pristine PE. On implanting ion doses $> 1 \times 10^{14} \text{ cm}^{-2}$, PE carbonization, for instance, a relative increase in carbon content, occurs. This means that new C—C bonds are created in the material and its density increases in that area, or that the free volume decreases as compared with nonmodified PE. Consequently, a lower amount of iodine diffuses in the carbonized layer (lower than the RBS detection limit). That is the reason we are speaking about free volume-limited diffusion in ion-modified polymers. The diffusant penetrates through the carbonized layer into a greater depth due to diffusion from an infinite source at a higher temperature. Iodine rediffusion from ion-modified PE, as mentioned,⁹ seems to be slowed down by the carbonized layer, because at a constant temperature, rediffusion proceeds from a finite source.

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