Anomalous Diffusion of Iodine Ions into Polypropylene Implanted with F^+ and I^+ Ions

VLADIMÍR HNATOWICZ,[1,*] J. KVÍTEK,[1] VÁCLAV ŠVORČÍK,[2] VLADIMÍR RYBKA,[2] and VLADIMÍR POPOK[2]

[1]Institute of Nuclear Physics, Academy of Sciences of Czech Republic 250 68 Řež, Czech Republic; [2]Institute of Chemical Technology, Department of Solid State Engineering, 166 28 Prague, Czech Republic

SYNOPSIS

The diffusion of K and I atoms from 5 *M* water solution of KI into polypropylene implanted with 150 keV F^+ and I^+ was studied at boiling temperature. Standard Rutherford back scattering (RSB) technique was used for the determination of concentration depth profiles of diffused atoms. It was found that the I and K atoms penetrate the polymer surface layer affected by ion implantation and they are captured by trapping centers produced by electronic energy losses of implanted ions. The uptake of K atoms is several times higher than that of I atoms, and the relative K concentration exceeds the KI stoichiometric value. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Diffusion of different agents in polymers is of great importance for potential applications in membrane production and in microelectronics. Only a little information is hitherto available on the microscopical mechanism of the diffusion in polymers. It is known that the diffusion in polymers can be affected by some preliminary treatment, e.g., by ion implantation leading to drastical structural changes of the polymer surface layer.[1-3] Fink et al. have observed nonregular depth profiles of atoms implanted into photoresists[4] and several polymers.[5] The nonregularities have been explained by diffusion of implanted atoms through a radiation-damaged layer where they are trapped by free radicals and other defects produced via electronic interactions. The anomalous profiles copy the expected profile of electronic energy losses. Recently, the diffusion of iodine from gaseous phase into polyimide films implanted with different ions has been studied by Davenas et al.[6] In some cases, they have found anomalous iodine depth profiles closely resembling the calculated profiles of nuclear energy losses of implanted ions. The observed decrease of incorporated iodine for higher implanted doses and heavier ions was explained by a compaction of polymer surface layer.

Experimental data on the diffusion in radiation-damaged polymers are rather scarce, and the microscopical mechanism of the diffusion and trapping of atoms on different defects is still unclear. In this study, the diffusion of iodine from a water solution of KI into polypropylene implanted with 150 keV F^+ and I^+ ions was studied by standard Rutherford backscattering spectrometry (RBS) with the aim to elucidate the diffusion mechanism in this specific system.

EXPERIMENTAL

The samples of 10 μm thick polypropylene (PP) foils of ($\rho = 0.901\ g \cdot cm^{-3}$) were implanted at room temperature with 150 keV F^+ and I^+ ions to the dose of $1 \times 10^{14}\ cm^{-2}$. The ion current was kept below 50 $nA \cdot cm^{-2}$ to avoid possible thermal degradation of the samples. The pristine and the ion implanted PP samples were treated for 30 min in 5 *M* ($mol \cdot l^{-1}$) water solution of KI at the boiling temperature.

Standard RBS technique was used for the determination of concentration depth profiles of elements incorporated in the polymer surface layer. The 1.3 MeV ^4He ions scattered under 160° scattering angle

* To whom correspondence should be addressed.

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were registered with a Si(Au) surface barrier detector coupled to a standard electronics and a multichannel analyzer. The system energy resolution was FWHM = 15 keV (25 nm depth resolution on the sample surface). The RBS spectra were evaluated using standard PC programs. The stopping powers used for the transformation of the particle energy into the depth were calculated using a universal Ziegler–Biersack–Littmark procedure RSTOP adopted from TRIM code.[11,12]

RESULTS AND DISCUSSION

Typical RBS spectra of the PP samples implanted with F^+ and I^+ ions and treated in 5 *M* KI water solution are shown in Figures 1 and 2. Besides the bulk carbon signal at about 340 keV, one can see a strong oxygen signal at 480 keV, indicating polymer surface oxidation during the ion implantation. Analogous oxidation phenomena have been reported earlier.[13,14] The observed concentration depth profiles of K (below 875 keV) and I (below 1150 keV) are similar in shape, but the total number of incorporated I atoms and the K/I atomic ratio depend strongly on implanted ion mass (see also below).

The total number of I atoms detected in pristine PP sample, treated in the same way, of $(0.3 \pm 0.1) \times 10^{15}$ cm^{-2} is close to the present detection limit. The ion implantation enhances dramatically the diffusion of K and I atoms from the KI solution into polymer. The respective total contents of incorporated I atoms in the PP sample implanted with F^+ and I^+ ions are $(5.2 \pm 0.2) \times 10^{15}$ cm^{-2} and $(0.9 \pm 0.1) \times 10^{15}$ cm^{-2}. Two effects are probably responsible for much lower I uptake in the PP sample implanted with heavier I^+ ions, the lower thickness of the polymer surface layer affected by ion implantation and diffusion blocking due to a compaction of ion-implanted film. The latter effect has recently been observed under similar conditions.[6]

The concentration depth profiles of I atoms incorporated in the polymer surface layer calculated from the spectra of Figures 1 and 2 are shown in Figure 3. One can see that the depth profiles differ from those expected in accord with Fick law for diffusion in semiinfinite solid exposed to solution with constant KI concentration. In Figure 3, the profiles are compared with the profiles of electronic energy losses of implanted F^+ and I^+ ions calculated using TRIM code.[11,12] Theoretical projected ranges for 150 keV F^+ and I^+ ions are also marked for comparison. The TRIM calculations were performed assuming the irradiated polymer preserves the composition

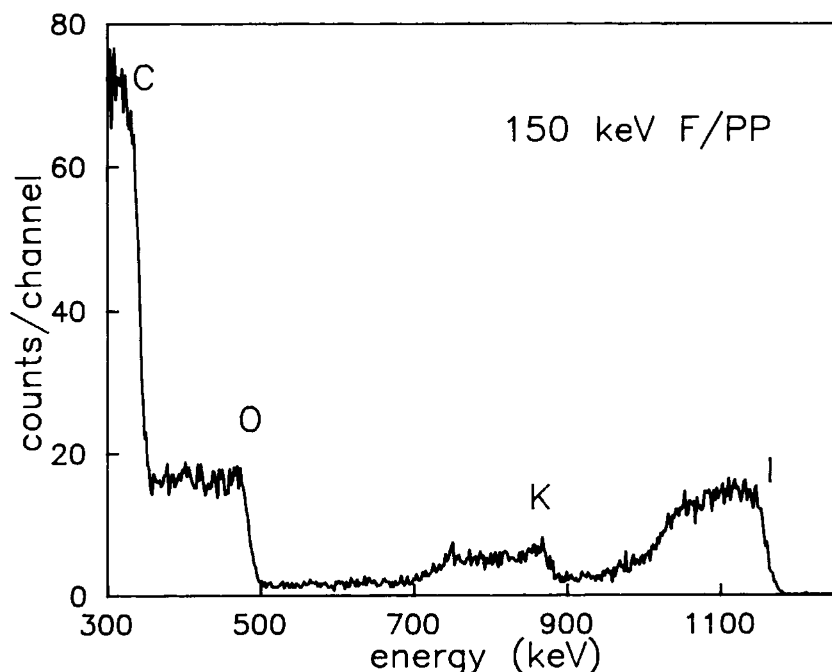

Figure 1 The RBS energy spectrum of polypropylene sample implanted with 150 keV F^+ ions to the dose of 1×10^{14} cm^{-2} and treated for 30 min in 5 *M* water solution of KI at boiling point.

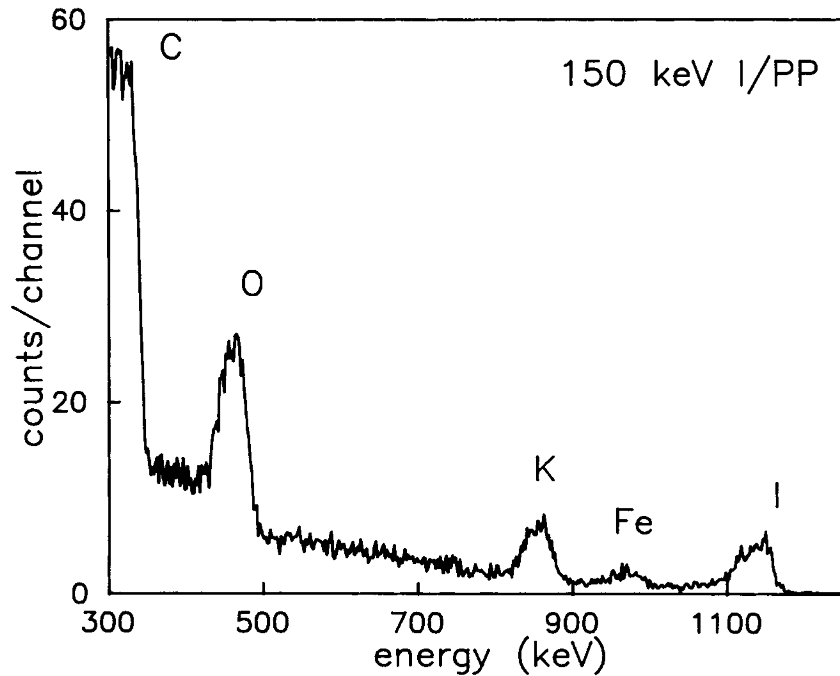

Figure 2 The same as in Figure 1 but for polypropylene sample implanted with 150 I^+ ions to the dose of 1×10^{14} cm^{-2}. Surface contamination with Fe arose during sample treating.

and the density of the pristine material. One can see that in both cases the iodine atoms penetrate the surface layer affected by implanted ions, and the resulting iodine depth profiles imitate well the theoretical profile of electronic losses. It may, therefore, be concluded that in this experiment an enhanced

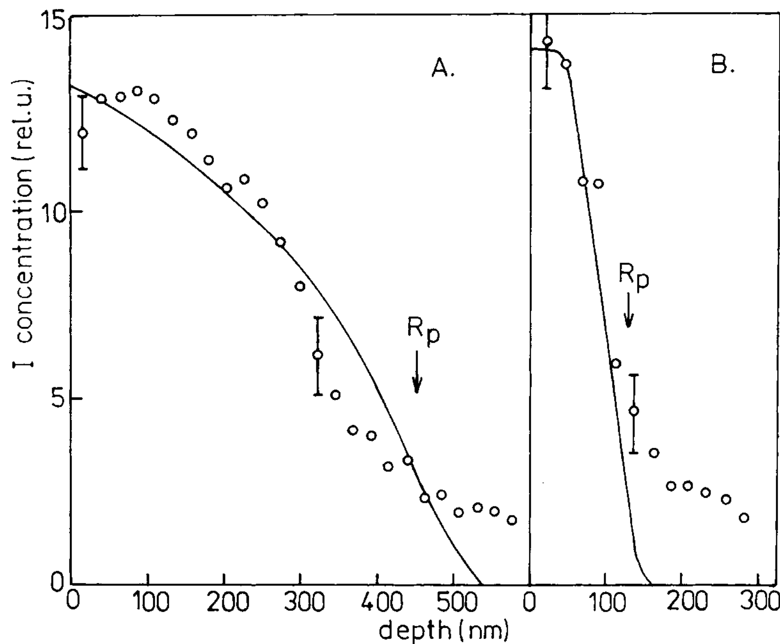

Figure 3 The concentration depth profiles of I atoms calculated from RBS spectra of Figure 1(A) and of Figure 2(B). The measured profiles (circles) are compared with the depth profiles of electronic energy losses calculated using TRIM code (full line).

iodine diffusion is observed accompanied with trapping of iodine atoms on deffects created via electronic energy losses of implanted ions. The measured surface concentration of iodine atoms of 2.5×10^{20} cm^{-2} in the PP sample implanted with F^+ ions is three times higher than that for the PP sample implanted with I^+ ions. This concentration ratio is, however, opposite to the ratio of electronic energy loss densities of 320 and 900 eV/nm · ion calculated using TRIM code for respective 150 keV F^+ and I^+ implantations. The obvious discrepancy should be explained by the above-mentioned diffusion blocking due to the polymer compaction, which is expected to be more pronounced in the case of the implantation of heavier I^+ ions.

The present results are similar with those of "self-dopping" reported experiments.[4,5] Quite different diffusion-trapping behavior of iodine atoms in ion-implanted polyimide as observed in Ref. 6 may be connected with higher reactivity of elemental gaseous iodine and different polymer structure.

The depth profiles of incorporated K atoms are analogous to the iodine profiles discussed above. The total number of incorporated K atoms, however, depends on the mass of implanted ions and it exceeds the stoichiometric KI value several times. The respective ratios of K and I atomic areal densities, K/I = 1.9 ± 0.1 and 5.0 ± 0.3, are observed for PP samples implanted with F^+ and I^+ ions. Different uptake of I and K atoms clearly indicates different interaction mechanism of K and I atoms with trapping centers created by ion implantation. The reason for large difference between K/I ratios in samples implanted with the F^+ and I^+ ions remains unclear. Present experimental results, however, are insufficient for unambigous explanation of the phenomenon.

CONCLUSION

The diffusion of I and K atoms from water solution of KI into polypropylene samples implanted with F^+ and I^+ ions were studied by RBS method. The depth profiles of iodine atoms were found to follow closely expected profiles of electronic energy losses of implanted ions. The reason for observed different uptake of I and K atoms remains unexplained.

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