Modification of Polyethylene Properties by Implantation with F^+ Ions and Iodination

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SYNOPSIS

Polyethylene samples implanted with 150 keV F^+ ions to the doses $10^{11}-10^{15}$ cm^{-2} were doped with iodine by exposing them to iodine vapors at 90°C for 3 h. The iodine depth profiles, measured by Rutherford back-scattering techniques, evolve dramatically with increasing implanted doses, from "bumpy" profiles at lower fluences to a "depleted" one comprising two concentration maxima with no iodine in between observed at highest dose. The areal density of iodine incorporated into the 500-nm-thick surface layer is proportional to the ion dose for the doses $\leq 1 \times 10^{13}$ cm^{-2} and it achieves a saturation or declines at higher doses. The results support the concept of enhanced iodine diffusion in the radiation-damaged surface layer and its trapping on the radiation defects within. The sheet resistivity of as-implanted PE is practically constant, independent of the implanted dose. Iodine doping of the ion-implanted PE samples results in immediate, strong decrease of the sheet resistivity by 3–4 orders of magnitude which, however, is not stable. The measured temperature dependence of the sheet resistance indicates p-semiconducting character of ion-implanted and iodinated samples at the temperatures below the PE melting point. The iodine redistribution and/or escape with increasing temperature is observed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Steadily increasing interest in the diffusion of various inorganic agents into polymers is due to several unsolved fundamental problems in the field and to the importance of the process for potential applications in membrane production and microelectronics.[1,2] The diffusion of different agents from gaseous, liquid, or solid phases is a relatively simple technique of modification of surface properties of polymers.[3,4] Iodine as a dopant has been found to increase electrical conductivity of polyethylene,[5] poly-2-ethynylpyridine,[6] polyvinylfluoride,[7] and cellulose acetate–butyrate.[8]

The penetration of dopants into polymers may be significantly affected by a prior irradiation with energetic heavy ions leading to dramatic changes in polymer surface structure.[9] Increased permeation of gases through thin polymer foils irradiated by energetic ions is well documented,[10] and an enhanced diffusion of iodine atoms into radiation-damaged polymers has recently been observed.[4,5] Previous experimental data on the diffusion of various agents into polymers modified by ion irradiation are rather scarce and the microscopic mechanism of the penetration and trapping of atoms or molecules on radiation defects remains unclear. Also, little is known about the effect of doping on the modified polymer's physical properties, such as electrical conductivity.

Here, the structure and electrical conductivity of polyethylene implanted with different doses of 150 keV F^+ ions and subsequently doped with iodine are studied with the aim of obtaining new data on the diffusion/trapping process in radiation-damaged polyethylene.

EXPERIMENTAL

The 15-μm-thick polyethylene foils (PE, $\rho = 0.954$ g cm^{-3}, $M_w = 1.8 \times 10^5$) were implanted at room temperature with 150 keV F^+ to doses from 1×10^{12}

to 1×10^{15} cm^{-2}. The ion current density was kept below 50 nA cm^{-2} to avoid possible thermal degradation of the samples. The residual pressure in the implanter target chamber was 10^{-4} Pa. The pristine and the ion-implanted PE samples were exposed to iodine vapors at 90°C for 3 h.

A Keithley Instrument device (487 picoammeter) was used for measurement of the sheet resistance by standard two-point techniques, at room temperature and under pressure of about 1 Pa. To determine the dependence of the sheet resistance on temperature, the PE samples were placed into an LN$_2$ cryostat evacuated to the pressure of 10^{-4} Pa. Before the measurement, the sample was cooled to LN$_2$ temperature and then slowly heated to the temperature of 400 K.

Standard Rutherford back-scattering (RBS) techniques with 1.3 MeV α-particles were used for the determination of concentration depth profiles of elements incorporated in the polymer surface layer. The reproducibility of the RBS measurements were tested by repeated measurements in the same spot on the sample and were found to be within 5%. The precision of the RBS data (arbitrary units corresponding to iodine concentration) depends on the measuring statistics; in the present case it was about ≤ 10%. Standard procedures described earlier[11,12] were used for the evaluation of RBS spectra. Between measurements, the PE samples were stored in air, in darkness, and at room temperature. Melting temperature of the crystalline fraction was examined by differential scanning colorimetry (DSC) on a DSC-DuPont 8900 device using temperature increases of 10 K/min^{-1}.

RESULTS AND DISCUSSION

Irradiation with energetic heavy ions induces dramatic structural and compositional changes in the polymer surface layer.[9] The irradiation of PE with F$^+$ ions leads to polymer chain scission, creation of unsaturated bonds, oxidative degradation with creation of carbonyl groups, polymer crosslinking at higher ion fluences, and production of conjugated double bonds.[11] Irradiation with higher doses leads also to liberation and escape of volatile degradation products and an enrichment of the surface layer with carbon. All these processes result in enlargement of the effective free volume which, in turn, facilitates penetration of potential dopants into radiation-damaged polymers. At the same time, the radiation defects may serve as centers where the penetrating atoms can be trapped.

The modification of the PE surface layer after the implantation with 150 keV F$^+$ ions and the subsequent doping with iodine is seen in Figure 1, which shows the pertinent RBS energy spectra from the PE samples implanted to different doses. The measurements were accomplished 5 days after the iodine doping. Several interesting features of the spectra should be discussed. In accordance with our previous observations,[11] no traces of implanted fluorine are seen in the RBS spectra above the present detection limit. It is supposed that the light fluorine atoms redistribute in the radiation-damaged layer and partly escape the specimen.[13] The PE samples implanted to higher fluences exhibit a significant oxygen signal, indicating rather strong oxidation of the PE surface layer. The oxygen concentration as a function of the implanted ion dose is shown in Figure 2; the oxygen concentration increases up to the dose of 5×10^{14} cm^{-2} and then slightly declines. Analogous dependence of the oxygen content was observed earlier.[11,14] The oxidation is supposed to occur in the course of the ion irradiation. The oxygen atoms from the ambient residual atmosphere penetrate into the radiation-damaged and excited surface layer where they are trapped on radiation defects and chemically bound, e.g., within carbonyl groups.[11] At higher doses, irreversible structural changes take place in the polymer[9] and part of the incorporated oxygen may be liberated again due to the degradation of the oxygen structures.[15]

The present RBS measurements show easy penetration of iodine atoms even into pristine, unimplanted PE. In this case a nearly homogenous iodine distribution is observed up to the depth of 2 μm, the limit of the present RBS experimental arrangement. For the PE samples implanted to different doses, the iodine penetration is greatly enhanced and an
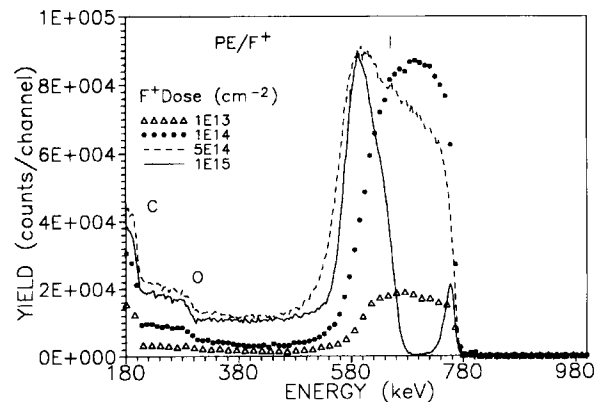

Figure 1 RBS energy spectra from the PE samples implanted with 150 keV F$^+$ ions to different fluences and iodinated by procedure described in text.
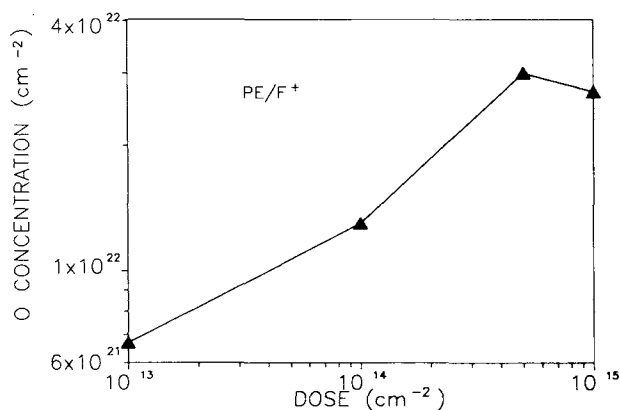
Figure 2 Areal density of incorporated oxygen measured by RBS method in the surface layer 200 nm thick.

Figure 3 Concentration depth profiles of iodine incorporated in radiation-damaged PE surface layer as a function of implanted fluence.

additional, pronounced component appears on the iodine depth profile (see Fig. 1). The additional component is superposed on the weak, constant component, characteristic of pristine PE, and it extends from the specimen surface to a depth close to the calculated projected range of 150 keV F^+ ions in PE (R_P = 440 nm). The shape of the additional component changes dramatically with the implanted dose as seen in Figure 3, which shows the relevant parts of the iodine depth profiles. For doses of $\leq 1 \times 10^{14}$ cm^{-2}, the additional component has a "bumpy" shape, closely resembling the theoretical depth dependence of the electronic energy losses of 150 keV F^+ ions. For higher fluences, the iodine concentration in the near-surface region declines and finally an iodine depth profile with two concentration maxima and no iodine in between is observed for the ion dose of 1×10^{15} cm^{-2}. The absence of iodine (above RBS detection limit) in the central profile region from 60–200 nm is probably related to deep structural changes in the polymeric matrix.[16] This assumption is in qualitative agreement with known theoretical depth dependence of the stopping power of 150 keV F^+ in PE.

The dependence of the iodine areal density in the additional profile component on the implanted dose is shown in Figure 4. The iodine areal density is proportional to the F^+ dose for the doses $\leq 1 \times 10^{13}$ cm^{-2}, i.e., in the regime of nonoverlapping latent tracks. For higher doses a saturation is observed due to latent track overlapping, which is followed by a slight decrease in iodine content for the highest implanted dose. These findings, along with the shape and evolution of the iodine depth profile discussed above, indicate enhanced iodine penetration into the radiation-damaged region (maybe along ion latent tracks) and the trapping of iodine atoms on radiation defects produced by ion irradiation. The present re-
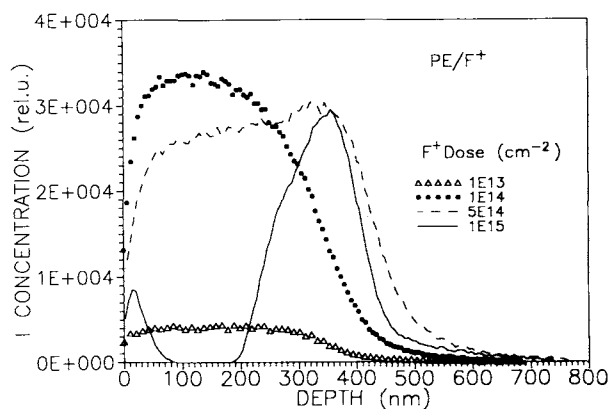
sults are in agreement with those obtained recently on PE implanted with As^+ ions.[5,17]

Additional information on the properties of incorporated iodine was obtained by measuring of sheet resistance (R_s) of the ion-implanted and iodine-doped PE. The dose dependence of the sheet resistance is shown in Figure 5. For as-implanted PE specimens, no significant change in the R_s was observed (curve A). This result should be compared with analogous data obtained for PE implanted with 150 keV As^+ ions.[5] In the latter case, an abrupt decrease of the sheet resistance by more than two orders of magnitude was observed for the specimens implanted to the dose of 1×10^{15} cm^{-2}. The difference, which can be explained by the much higher energy density deposited by heavier As^+ ions, indicates that the significant resistance decrease may be connected with polymer carbonization. Iodine doping of the ion-implanted PE samples results in a significant decrease in the R_s, as seen from curve B of Figure 5, which was measured immediately after
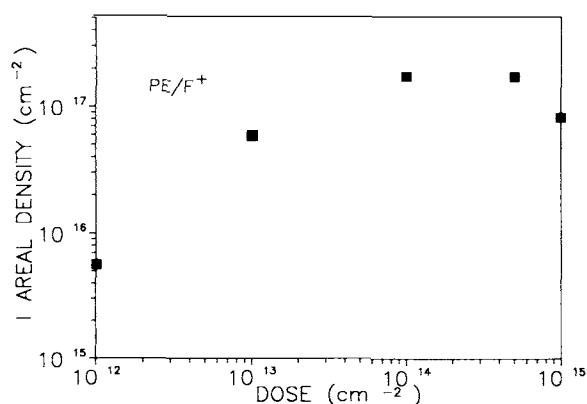

Figure 4 Dependence of the iodine areal density in 500-nm-thick surface layer on the implanted fluence.
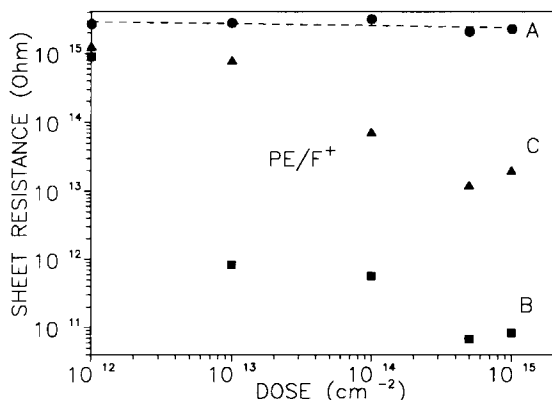
Figure 5 Sheet resistance of the ion-implanted and iodinated PE as a function of the implanted fluence. (A) As implanted PE; (B) implanted and iodinated PE measured immediately after iodination; (C) implanted and iodinated PE measured 72 h after iodination.

Figure 6 Temperature dependence of the sheet resistance on the PE sample implanted to the fluence of 1×10^{14} cm^{-2} measured immediately after iodination.

iodination. The resistance decrease of 3–4 orders of magnitude is observed on the PE samples implanted to the doses $\geq 1 \times 10^{13}$ cm^{-2}. The next measurement of the same specimens, performed after 72 h (curve C of Fig. 5), shows an increase in the resistance which could be due to spontaneous iodine inward diffusion or to its escape from the specimen (see also below).

In order to obtain more information on electrical properties of incorporated iodine atoms, the temperature dependence of the sheet resistance was measured after iodination. The result for the PE specimen implanted to the dose of 1×10^{14} cm^{-2} (highest iodine content) is shown in Figure 6. Below 240 K, the resistance is above the sensitivity of Keithley device of 5×10^{15} Ω. Two different regions are seen on the measured dependence. Up to the temperature of 330 K the R_s is a decreasing function of temperature, which is typical for semiconductors.[18] Next, the R_s increases from 330 to 375 K, followed by a strong resistance decrease by more than 3 orders of magnitude in the interval from 375–430 K. This latter increase and rapid decrease may be due to PE melting and a transition from crystalline to amorphous phase. Starting temperature of PE melting is 380 K; melting temperature T_m = 405 K; and final temperature of PE melting is 414 K. Only a small part of the incorporated iodine was shown to play a role in PE conductivity.[5] Nearly nothing is known about the physical and chemical states of incorporated iodine atoms or about the microscopic mechanism by which iodine may affect conductivity. Iodine is known as an electron acceptor, and iodination of ion-implanted PE may result in p-semiconducting properties observed at lower temperatures.
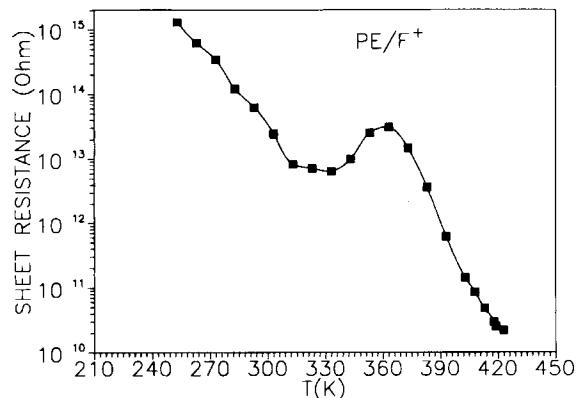
The temperature dependence of the sheet resistivity could also be affected by a redistribution of the iodine. With the aim of answering this question, we used the RBS method to measure the iodine areal densities in the depth interval 0–500 nm on the PE samples treated at the temperatures of 295, 330, 375, and 400 K. The results, summarized in Table I, show a decrease of the iodine content with increasing temperature. The decrease may be due to inward iodine diffusion or to an escape of part of the iodine atoms through the sample surface. The RBS measurement gives no conclusive information on which of the two processes is more important.

CONCLUSION

The structure and the electrical properties of the PE samples implanted with 150 keV F$^+$ ions to different doses and doped with iodine were investigated. In accordance with previous studies on similar systems,[5,17] the iodine content was found to be an in-

Table I Iodine Areal Density in 500-nm-thick Surface Layer of PE Sample Implanted to the Fluence of 1×10^{14} cm^{-2} and Iodinated as a Function of Temperature

Temperature (K)	Iodine Density ($\times 10^{17}$ cm^{-2})
295	1.72
330	1.43
375	1.37
400	1.12

Samples were heated under temperature conditions allowed in cryostat.

creasing function of the implanted ion dose; a dramatic evolution of the iodine depth profile with the implanted dose was also confirmed. The iodination of ion-implanted PE samples results in an immediate, strong decrease of the R_s which, however, is not stable. The measured temperature dependence of the sheet resistance indicates the p-semiconducting character of ion-implanted and iodinated samples at temperatures below the PE melting point. Other experiments are needed in order to identify the physical and chemical states of incorporated iodine atoms and to elucidate the microscopic mechanism of electrical conductivity in modified PE.

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