

Study of Electrical and Structural Modifications Induced by 100 keV Argon Ions in Poly(ethylene terephthalate)

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ABSTRACT

Poly(ethylene terephthalate) samples were implanted to 100 keV Ar⁺ ions at room temperature at fluence ranging from $1 \times 10^{15} \text{ cm}^{-2}$ to $2 \times 10^{16} \text{ cm}^{-2}$. Surface DC electrical conductivity was found to be enhanced with increase in ion fluence. The energy deposited per unit path length per ion (LET) has been found to be the most important parameter responsible for the observed changes. The formation of a highly cross-linked hydrogenated amorphous carbon structure in the implanted layer of PET was confirmed through Raman spectroscopy. This carbonaceous structure, made of conjugated double or triple bonds, was found responsible for the observed electrical and structural changes in argon implanted PET.

Keywords: Poly(ethylene terephthalate), ion-implantation, electrical conductivity, LET, Raman spectroscopy.

INTRODUCTION

The attractive material properties of polymers combined with relatively low cost of production, the easiness of processing and tailoring of properties through various treatments [1-9], have led to their widespread use in the manufacturing of microwave, electronic and photonic devices. Since last few decades, the technique of ion implantation has attracted considerable attention and has potentially been used to tailor the properties of polymeric materials as per requirements [4-9]. Ion implantation can modify the surface or bulk properties depending on the nature of polymer and ion beam parameters. The ion implantation in polymers results in various effects such as ionization, displacing atoms, sputtering, carbonization, production of free radicals etc. and improve their various properties in a very controlled manner [1,10-13]. It is thus important to study the electrical and structural changes of ion beam modified polymers in a systematic manner for their utility in various applications.

Poly(ethylene terephthalate) (PET) (chemical structure in Figure 1) is a high grade transparent (~90% in complete visible region) thermoplastic polymer resin of the polyester family which is used in making optical lenses, CDs and DVDs, optical fibres, photographic filters [14] etc. In the

present work, PET samples are implanted to 100 keV Ar⁺ ions at fluence up to 2×10^{16} cm⁻². The DC electrical conductivity of pristine and ion implanted PET is determined using two point probe method. Raman spectroscopy of pristine and implanted samples has also been carried out to characterize the implanted PET specimen.

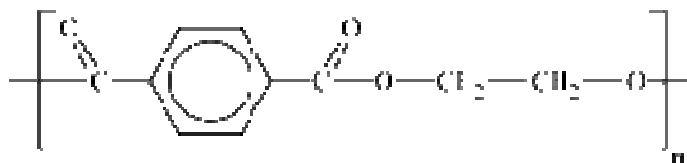


Figure 1: Chemical Structure of PET polymer.

MATERIALS AND METHODS

Experimental Details

The samples of amorphous poly(ethylene terephthalate) [(C₁₀H₈O₄)_n] density 1.39 g/cm³, each of thickness 500 micron were cut from a flat sheet procured from Good fellow, UK. These samples were implanted to 100 keV Ar⁺ ions at room temperature under high vacuum (10⁻⁶ torr) at fluence 1×10^{15} , 5×10^{15} , 1×10^{16} and 2×10^{16} ions/cm² utilizing the Low Energy Ion Beam Facility (LEIBF) available at Inter University Accelerator Centre (IUAC), New Delhi, India. The current density was kept below 1.0 μA/cm² in order to avoid the thermal degradation of the samples. The estimation of depth profile and ion range of Ar⁺ ions in PET target (TRIM simulations for 1000 ions) is shown in Figure 2 [3,5,15].

The average projected range of the implanted ions has been found to be 138 nm as calculated using SRIM code (version 2008.04) [15].

For structural analysis, the Raman spectra of pristine and ion implanted PET samples were recorded using Jobin-Yvon Raman spectrometer with argon ion laser ($\lambda = 488$ nm). For DC conductivity, the I-V measurements were carried out from 0-100 V at room temperature using Keithley 6517 digital electrometer interfaced to computer. The samples were silver coated for making good electrical contacts on the implanted surface keeping a finite distance between the electrodes.

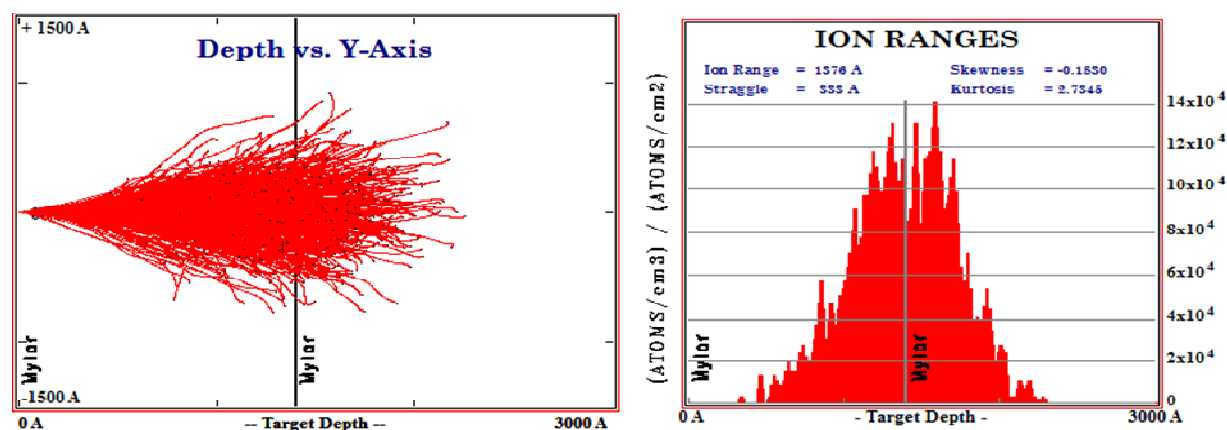


Figure 2: Depth profile and range of Ar⁺ ions in PET target (TRIM simulations for 1000 ions).

RESULTS AND DISCUSSION

The V-I characteristics of Pristine and Ar⁺ implanted PET samples in the voltage range 0-100V are shown in Figure 3.

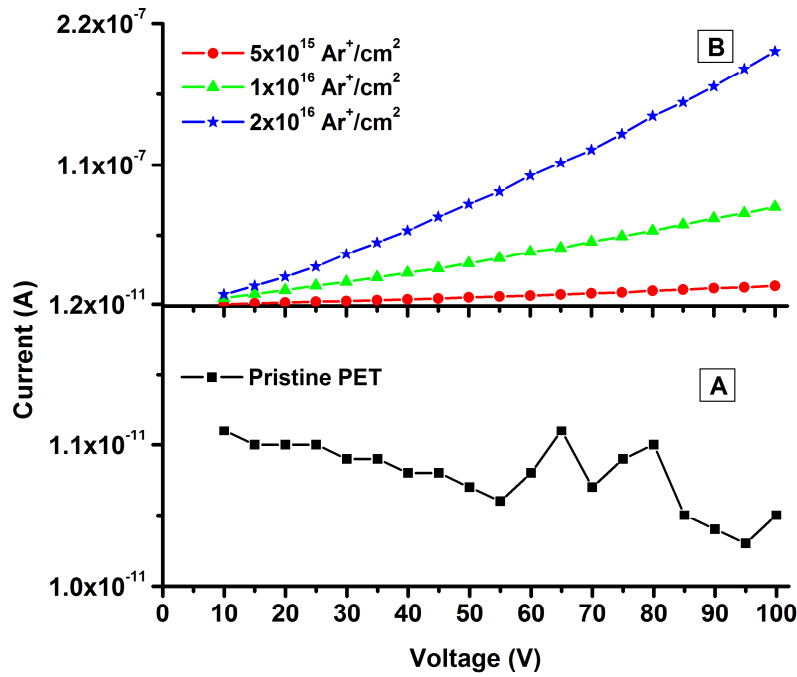


Figure 3: I-V characteristics of pristine and Ar⁺ implanted PET samples.

From this figure it is clear that the current is continuously increasing with increase in implantation dose in the entire applied DC voltage range. The charge conduction process can be identified by determining the value of m in light of the equation $I \propto V^m$. We find $m = 1.1$ for the fluence $5 \times 10^{15} \text{ cm}^{-2}$ which changes to $m=1.2$ and $m=1.3$ at the fluences $1 \times 10^{16} \text{ cm}^{-2}$ and $2 \times 10^{16} \text{ cm}^{-2}$ respectively. This shows that the nearly ohmic conduction for the fluence $1 \times 10^{15} \text{ cm}^{-2}$ shifts towards SCLC behaviour [4] at $2 \times 10^{16} \text{ cm}^{-2}$. The electrical conductivity (σ_{DC}) of the implanted surface has been determined using the following relation [16].

$$\sigma_{DC} = \frac{\cosh^{-1}(d/2r_o)}{\pi R}$$

where, d = separation between electrodes, r_o = radius of the circular electrode and R = resistance measured on the conductive surface.

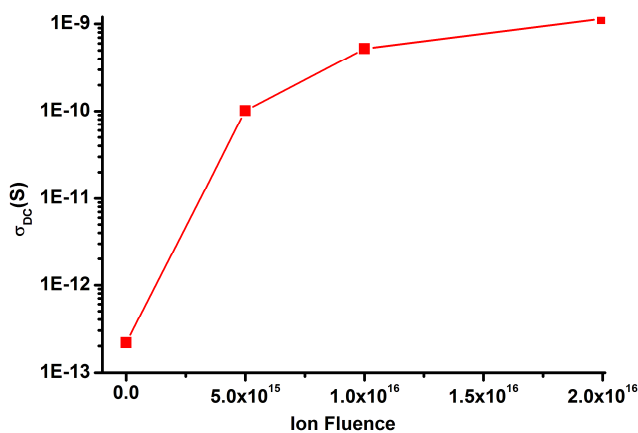


Figure 4: DC conductivity of pristine and Ar⁺ implanted PET.

Figure 4 shows the variation of DC conductivity with ion fluence for argon implanted poly(ethylene terephthalate) and the values of σ_{DC} are listed in Table 1.

TABLE 1. DC Conductivity of Pristine and Ar⁺ Ion Implanted PET

Sr. No.	Ion Dose (ion/cm ²)	σ_{DC} (S)
1	virgin	2.18E-13
2	5x10 ¹⁵	1.01E-10
3	1x10 ¹⁶	5.23E-10
4	2x10 ¹⁶	1.14E-09

From Figure 4 and Table 1, it is clear that DC electrical conductivity is an increasing function of the implantation dose. Such an increase in the conductivity may be explained on the basis of the fact that ion implantation in polymers leads to the formation of free radicals & dangling bonds and release of low molecular weight volatile species like hydrogen resulting in the creation of cross-linked carbonaceous clusters on the implanted surface of polymer and provide the continuous path for the charge transfer within the insulating polymer chains [5,13]. The formation of such a cross-linked structure, responsible for the enhanced conductivity after implantation can be explained in terms of the linear energy transfer (LET) by the implanted ions [3], in the following manner.

An energetic ion while passing through the polymeric medium loses its energy mainly via two processes i.e. electronic energy loss and nuclear energy loss. In electronic energy loss, the energy from the incident ion is transferred to the electrons of the medium resulting in the excitation and ionization processes while the nuclear energy loss generally results the displacement of target atoms from their original positions. Although, both of these energy loss processes may cause chain scissioning and cross-linking in polymers but the electronic energy loss mainly favours the cross-linking and nuclear energy loss favours the chain-scissioning [3-5,13]. From the SRIM simulation program run for 1000 Ar⁺ ions of energy 100 keV in PET target, it has been found that about 62% of the total incident energy is transferred through electronic processes (ionization/excitation) and about 38% via nuclear processes (creating vacancies and phonons). Therefore, the electronic component of LET dominates over its nuclear counterpart upto a penetration depth of about 140 nm resulting in cross linking and hence in increased electrical conductivity due to carbonization of implanted surface.

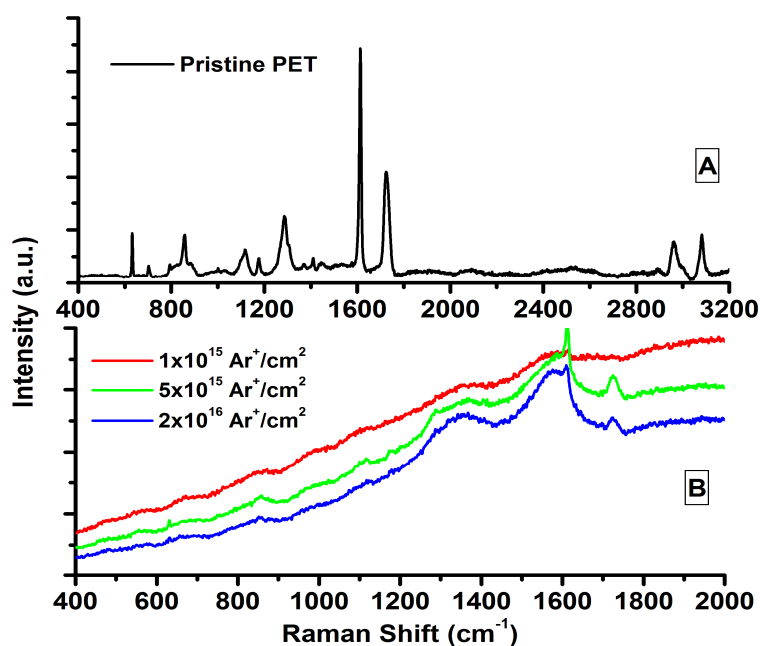


Figure 5: Raman spectra of pristine and implanted PET samples.

Table 2: Assignment of the Raman modes of Poly(ethylene terephthalate) polymer

Wavenumber (cm ⁻¹)	Type of Vibration
2962, 3083	C-H stretching
1725	C=O stretching
1613	Ring mode 8a
1442, 1470	CH ₂ deformation
1288	C(O)-O stretching
1118	C(O)-O stretching and ethylene glycol CC stretching
857	Ring CC and C(O)-O stretching
632	Ring mode 6b

The creation of cross-linked carbon network on the implanted surface of PET was confirmed through Raman spectroscopy. The Raman spectra of pristine and argon ion implanted PET have been shown in Figure 5(A) and 5(B). Figure 5(A) depicts the Raman spectrum of pristine PET sample. The positions of various Raman peaks along with their corresponding vibrations [17-21] are presented in Table 2.

After implantation to 1×10^{15} Ar⁺/cm², the original peaks in PET start disappearing (Figure 5(B)) and two new bands at ~ 1590 cm⁻¹ and ~ 1360 cm⁻¹ start appearing which correspond to the characteristic G-band and disordered D-band of hydrogenated amorphous carbon [3,5]. As the implantation dose increases to 5×10^{15} cm⁻² and 2×10^{16} cm⁻², a clear cut increase in the intensities of G and D bands can be observed which reveals the increased carbonisation and hence the increased conductivity of PET with increasing implantation dose. Further, the decreasing slope of photoluminescence background observed in the Raman spectra of ion implanted samples shows the decrease in hydrogen content [22] resulting in increased carbonization.

CONCLUSION

The charge conduction mechanism in 100 keV Ar⁺ implanted PET has been found to be shifted from nearly ohmic to nearly SCLC with the increasing ion fluence. The surface conductivity increases up to 4 orders of magnitudes at the implantation dose of 2×10^{16} ions/cm². The electronic energy loss by the implanted ions seems to play the major role in the formation of a highly cross-linked carbon network. The increased conductivity of Ar⁺ implanted PET may be due to the formation of a three dimensional carbonaceous network consisting of disordered bonds emerging in the implanted layer of PET. The large increase in the conductivity at the surface of PET may suggest the possibility of applications of polymers with conducting surfaces.

Acknowledgements

The authors are thankful to Dr. D. Kanjilal, IUAC, New Delhi, for valuable discussions. Thanks are due to Dr. P. Kumar, IUAC for helping during irradiation. Raman spectroscopic measurements were performed at UGC-DAE Consortium for Scientific Research, Indore, India. Authors are grateful to Prof. Vasant Sathe and Mr. Manoj Kumar for their kind cooperation during the Raman experiments. Two of the authors (PKG & VK) are thankful to CSIR, New Delhi for financial assistance in form of SRF.

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