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Interaction of oxygen (O^{+7}) ion beam on polyaniline thin films

Subhash Chandra[1*], S Annapoorni[2], R G Sonkawade[3], P K Kulriya[3] Fouran Singh[3], D K Avasthi[3], J M S Rana[1] and R C Ramola[1]

[1]Department of Physics, H N B Garhwal University, Badshahi Thaul Campus, Tehri Garhwal-249 199, Uttarakhand, India

[2]Department of Physics and Astrophysics, University of Delhi, Delhi-110 007, India

[3]Inter University Accelerator Center, Aruna Asaf Ali Marg, New Delhi-110 067, India

E-mail : subhash.physics@gmail.com

Abstract : High-energy ion beam irradiation of the polymers is a good technique to modify the properties such as electrical conductivity, structural behaviour and mechanial properties. Polyaniline thin films doped with hydrochloric acid (HCl) were prepared by oxidation of ammonium persulphate. The effect of Swift Heavy Ions irradiation on the electrical and structural properties of polyaniline has been measured in this study. Polyaniline films were irradiated by oxygen ions (energy 80 MeV, charge state O^{+7}) with fluence varying from 1×10^{10} to 3×10^{12} ions/cm^2. The studies on electrical and structural properties of the irradiated polymers were investigated by measuring V-I using four probe set-up and X-ray diffraction (XRD) using Bruker AXS, X-ray powder diffractometer. V-I measurements shows an increase in the conductivity of the film, XRD pattern of the polymer shows that the crystallinity improved after the irradiation with Swift Heavy Ions (SHI), which could be attributed to cross linking mechanism.

Keywords : Polyaniline, XRD, V-I, conductivity, crystallinity

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1. Introduction

The considerable interest in conjugated polymers has led to a large number of applications such as modified electrodes, capacitors, rechargeable batteries and bio sensors among many others [1,2]. The dc conductivity is one of the leading properties of conducting polymers *e.g.* polyanilne and polypyrrole for variety of applications. These conducting polymers are very good for sensors because of the ease of fabrication, possibility of using the same polymer with the different modifications and low cost also. The sensing properties

* Corresponding Author

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are associated with detection of some hazardous gases like chlorine, ammonia and solvent vapors [3–7]. Due to potential applications conducting polymers have become a subject of scientific and industrial interest, so use of ion irradiation of these polymers is of great importance to modify the properties of these materials. By using high-energy heavy ions, dramatic modifications in the polymer material have been observed. Some of the changes have been attributed to the scissoring of polymer chains by incident ions, breaking of covalent bonds, cross-linking, formation of carbon clustures, liberation of volatile species and in some cases even formation of new chemical bonds [8–11]. High energy ions by electronic excitation and ionization create tracks, latent tracks in the polymers and also can cause creation of triple bonds [12,13]. Fink *et al* [14] studied the polyvinyl alcohol (PVA) exposed by 16 MeV electrons and found that for the same transferred energy density heavy ions were more efficient for the damage in polymers than the low energetic ions. Hussain *et al* [15] studied the 160 MeV Ni^{+12} bombarded polypyrrole supercapacitor and found that stability of the supercapacitor increases after irradiation.

2. Experimental method

Self standing films of polyaniline of size 1 cm^2 were irradiated in Material Science Beam Line under high vacuum 5×10^{-6} torr by using the 80 MeV O^{+7} ion with a beam current of 3 PnA available from 15 UD Pelletron at Inter University Accelerator Centre, New Delhi using various fluences ranging from 1×10^{10} to 3×10^{12} ions/cm^2. The thickness in the present work was selected so as to be thin enough to allow the 80 MeV oxygen ions to completely pass through it.

XRD of the polyaniline thin films were carried out by an Bruker AXS, X-ray powder diffractometer with Cu-Kα radiation (1.54 Å) for a wide range of Bragg's angle 2θ ($5<\theta<40$) V-I measurements were done by four probe method.

3. Results and discussions

3.1. X-Ray diffraction :

The XRD pattern of pristine and oxygen beam irradiated polyaniline thin films are shown in Figure 1.

The pristine polyaniline shows the semi crystalline nature, after irradiation with SHI intensity of the peaks increases, which show the polymer crystallinity increases. This may be due to cross linking of the polymer chains or by the formation of single or multiple helices, which produces more crystalline regions in the polymer films [2]. The degree of crystallinity for the polymers calculated by following formula [16] :

$$C = \frac{A}{A'} \times 100\%$$

where *A* is the total area of the peaks (area of crystalline and amorphous peaks) and *A′* is the total area under the diffractogram. The % crystallinity calculated by above relation

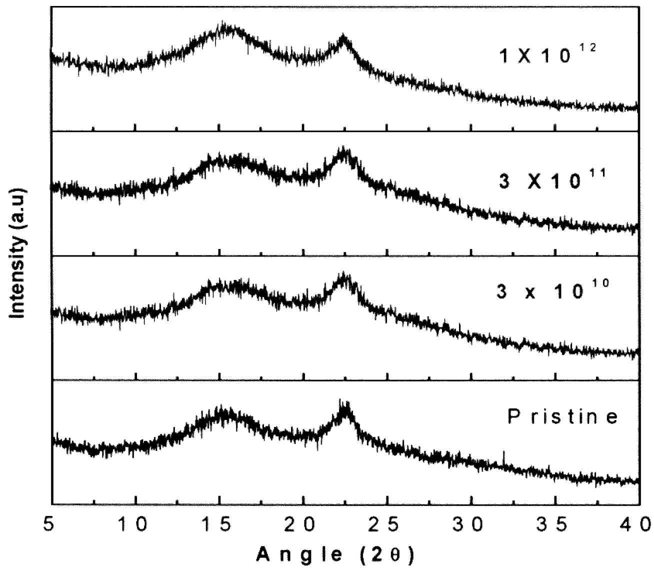

Figure 1. X-Ray diffraction pattern of polyaniline irradiated by oxygen beam.

is shown in Table 1. Hussain *et al* [17] also studied the polypyrrole irradiated with Ni^{+12} ions and found that the crystallinity of PPY increases after irradiation.

Table 1. The crystallinity of pristine and polyaniline irradiated by oxygen beam.

Oxygen beam fluence (Ions/cm^2)	% Crystallinity of polyaniline
Pristine	26.48 ± 0.61
3×10^{10}	29.32 ± 0.63
3×10^{11}	32.68 ± 0.68
1×10^{12}	34.56 ± 0.68

3.2. V-I Measurement :

The electrical conductivity of polyaniline thin films before and after irradiation were measured at room temperature by four-probe method. The measurements are shown in Figure 2.

The conductivity of polyaniline thin films was found to increase after irradiation with SHI; this increase in electrical conductivity may be due to the formation of polaron created at defect sites, which moves towards the polymer backbone. The increase in conductivity of the polymer films after SHI irradiation could also be ascribed to the inter-chain cross-linking due to huge electronic energy loss [12].

4. Conclusions

From this study we conclude that Swift Heavy Ions irradation is a good technique to modify the properties of the polymers. The degree of crystallinity of the polymer films was

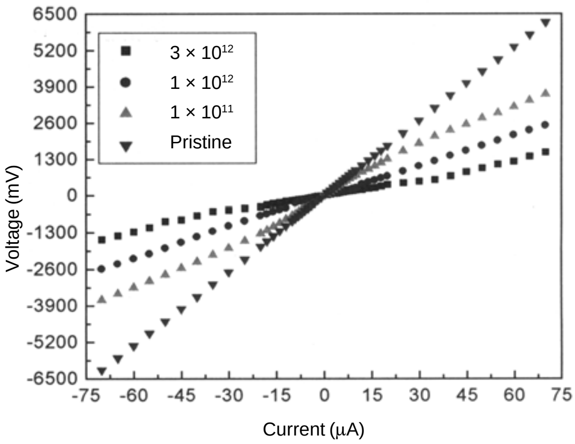

Figure 2. Current-voltage plots of polyaniline thin films.

found to increase with increasinng fluence, which may be due to the cross linking and formation of single and multiple helices. It is clear from the V-I measurement that the dc conductivity of the irradiated films increases with increasing the fluence, which may be due to the creation of polaron and defect sites in the polymers.

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