Nuclear Instruments and Methods in Physics Research B 287 (2012) 4–9

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

High electronic excitation induced modifications by 100 MeV O^{7+} and 150 MeV Ni^{11+} ions in Makrofol KG polycarbonate film

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ARTICLE INFO

Article history:
Received 10 January 2012
Received in revised form 29 May 2012
Available online 26 June 2012

Keywords:
Makrofol KG
Heavy ion irradiation
XRD
FTIR
UV–Visible

ABSTRACT

Makrofol-KG polycarbonate (M-KG PC) films are irradiated with 150 MeV Ni^{11+} and 100 MeV O^{7+} ion beams at various fluences ranging from 1×10^{11} to 3×10^{12} ions/cm^2. We have investigated the effect of irradiation parameters such as energy and ions fluence on optical, structural and chemical properties of the studied polymer, respectively. UV–Visible, Fourier Transform Infrared (FTIR) and X-ray diffraction (XRD) spectral studies have been employed in the present investigation. UV–Visible spectra exhibit a shift towards the higher wavelength regime after irradiation. This shift clearly reflects decrease in optical band gap after irradiation. The FTIR spectrum shows a decrease in intensity of the typical bands whereas the formation of new bands indicates the degradation of the polymer after irradiation. The XRD pattern of M-KG PC shows the decreasing intensity of peak positions with increase in ions fluence, which suggests loss of crystallinity of the films due to irradiation. Observed results indicate the formation of disordered system in the irradiated films. Magnitude of effect of irradiation is greater in case of 150 MeV Ni^{11+} rather than 100 MeV O^{7+} ions due to high electronic energy loss of Ni^{11+} ions in M-KG PC. The results can be correlated on the basis of linear energy transfer (LET) of the irradiated ions.

1. Introduction

The increasing use of swift heavy ions (having energy ~MeV/nucleon) for the material modifications due to electronic energy loss, has been gaining interest recently. Ion beam induced modifications have been considered a unique tool in modifying material properties in a desired way. Ion beam induced modifications in materials are classified into two categories: one is surface modification, and the other is uniform modification as a function of depth. The former is related to ion implantation modifications near surface layers, and the latter is ion beam bombardment through a thin film [1,2]. Swift heavy ion (SHI) traverses through material and loses its energy mainly via two independent processes: (a) elastic collisions with the nuclei of the target atoms, and (b) in exciting or ionizing the atoms by inelastic collision. The former is the dominant mechanism at low energies regime (~keV/nucleon) whereas the inelastic collisions dominate at high energies (>1 MeV/nucleon) where the transfer of atoms due to elastic collisions are irrelevant. Such a large electronic excitation (by SHIs) brings out diverse modifications in the target materials [3,4]. In case of implanted ions, they lose their kinetic energy by transferring it to a target, which causes damage in it. Moreover, multiple charge of the implanted ion drastically enhances the electronic stopping in the target material and can lead to a number of related phenomena.

Generally, ions irradiation causes chain scissions [5], creation of unsaturated bonds [6], bond breaking, carbonization [7], cross-linking [8–11], etc. Such effects are accountable for the alterations in structural, optical, electrical, and mechanical properties of the implanted/irradiated polymeric materials [7,12,13]. In the past few years, the effect of ion implantation in polymers has been investigated [14,15]. It is well reported in literature that ion implantation may reduce the crystallinity, induce cross-linking and produces carbonyl groups on the polymers [16–19], which results in polymer degradation. Most studies in the field have shown significant surface carbonization and splitting of chemical bonds on the side of the polymer chain in ion implanted polymers [20–22]. Polymer chain splitting was reported for polymers implanted with ions [23,24]. Recent review on ion implantation of polymers has discussed various important aspects of ion stopping, latent track formation and change of structure and composition of organic materials [25].

An interesting characteristic of the ion insulator interaction is that it produces a columnar type of defect along its path (called as latent ion track) [26]. The final highest density of defects is observed at depths close to the ion range, which is a characteristic of heavy ion irradiation. More details on ion track formation in

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http://dx.doi.org/10.1016/j.nimb.2012.06.010

different materials and their properties are reported in literature [27–29]. Among several models, thermal spike models [30] have been studied extensively to describe the formation of swift heavy ion induced tracks [31]. Szenes has successfully applied the model [32] developed for the analysis of amorphous tracks in insulator to describe the tracks formation in polymers [33,34]. The length and diameter of these tracks predominantly depend on the structure, the ion beam parameters and the nature of the target material itself. In order to study the effects of the electronic stopping power (S_e), the samples here were irradiated with two different ions of increasing S_e.

Although it is well reported in the literature that light as well heavy ion irradiation used for the study of track etch properties of the polymers [35–39], it is still necessary to identify as to what are the physiochemical changes taking in the material. The effectiveness of these transformations produced in the polymer predominantly depends on the structure and the ion beam parameters (energy LET, fluence, ion, mass, charge, etc.) and the nature of the target material itself [4,40]. Research groups across the globe have reported the use of different light as well as heavy ion beams for modifications of polymers [4,41–45].

However, a wide spectrum of systematic investigation is yet to be carried out so as to find out the conclusive and definite role of irradiation agents in modification process. In the present investigation, M-KG PC films have been considered as the point of interest. For the irradiation purpose, facilities at Material Science Beam Line of 15 UD Pelletron at the Inter University Accelerator Center, New Delhi, India, were made available. The films were irradiated with 150 MeV Ni^{11+} and 100 MeV O^{7+} ion beams of various fluences. The unirradiated and irradiated films were subjected to UV–Visible, XRD and FTIR spectral studies. An attempt has been made to explain the modifications on the basis of different LET of the ions.

2. Experimental details

The samples (about 40 μm thick) were made of polycarbonate films (Makrofol KG, Bayer, Germany). The 1×1 cm^2 films were irradiated in a Material Science Beam Line from the 15 UD Pelletron at the Inter University Accelerator Center (IUAC), New Delhi, India, using various fluences of 150 MeV Ni^{11+} and 100 MeV O^{7+} ions, respectively. A high vacuum (UHV) of $\sim 5 \times 10^{-6}$ Torr was maintained in the target chamber during the bombardment. Irradiations were performed at room temperature with low ion current of 0.5 pnA so as to avoid the thermal degradation of the samples. The beam was scanned in X–Y plane so as to expose the optimum area. The electronic (S_e), nuclear (S_n) energy loss, and maximum penetrable ranges of the ions were calculated using SRIM 2008 programme, shown in Table 1. It is clear from table that the energy transferred from the ion beams to the target was mainly due to electronic process and the nuclear energy loss is low to be ignored. Although, Ni^{11+} ion irradiation resulted in ion implantation because the thickness of sample is more than the range of ion while O^{7+} ion beam irradiation completely penetrated the M-KG PC films. Our main aim was to investigate the effect of heavy ion irradiation on M-KG polymer. The nature of the changes induced by the ion beams have been carried out using U-3300 UV–Visible spectrophotometer in the range 250–700 nm in order to investigate the variation in optical energy gap (E_g). The structural studies were carried out by a Bruker AXS, X-ray diffractometer with Cu-Kα radiation (1.54 Å) for a range of Bragg's angle 2θ ($10 < \theta < 50$) at the scanning rate of 1°/min with a step size of 0.02°. FTIR spectra were measured by Nexus 670 FT-IR system, in the range of 4000–400 cm^{-1}.

3. Results and discussion

3.1. UV–Visible spectroscopy

We investigated the basic optical properties of M-KG PC, such as absorbance spectra and band gap before and after irradiation in the wavelength range of 250–700 nm. The spectra of Ni^{11+} and O^{7+} ion irradiated M-KG PC films are shown in Figs. 1 and 2 respectively. The absorbance spectrum of M-KG PC reveals the shift in spectra towards higher wavelength regime. This clearly reflects the decrease in band gap after irradiation [42].

Not only this, we observed broadening of the absorption edges after irradiation, i.e. broadening of peak at FWHM. This may be due to superimposition of vibrational and rotational levels on top of the electronic levels due to irradiation. The reason of broadening of absorption edge is the formation of extended system of conjugated bonds i.e., the formation of defects after irradiation [46–48]. At higher fluences, the latent damage tracks get overlapped which leads to polymer degradation to higher level [25]. Obviously, this decline in band gap leads to the increase in conductivity of the irradiated M-KG PC [49]. In the studied range of wavelength, the maximum absorption is caused by the π–π^* electronic transitions [4,45,50,51] and the cause at the back is smaller energy requirement for excitation by π electrons. These transitions need an unsaturated group in the molecules (i.e., compound containing double or triple bonds and in aromatics) to provided the π electrons. The broadening of the peaks can also be attributed to the production of ion beam induced defects which may further result in the formation of new energy levels leading to the peak broadening. From the absorption spectra, the band gap of PC films was calculated by the extrapolation of the plot of $(\alpha h\nu)^2$ versus $(h\nu)$ on the $h\nu$ axes. The Tauc's expression [37] is given by

$$\alpha(h\nu) = B(h\nu - E_g)^2/h\nu \tag{1}$$

where α is the absorption coefficient, $h\nu$ is the photon energy, and E_g is the value of the optical energy gap.

The values of extrapolated intercept for different ions fluences are listed in Table 2. From this table, it can be seen that the band gap for M-KG PC samples decreases as a result of ions irradiation. The variation of optical band gap with ion beams irradiation can be explained on the basis of LET. Nathawat et al. [18] have reported that optical band gap of polycarbonate decreases after ion implantation. The authors stated that this decline in band gap is attributed to the π–$\pi*$ transition of the carbon-enriched graphite-like cluster as a function of increasing fluence.

The number of carbon hexagon (N) rings in the cluster, can be calculated by Robertson relation [52]

$$E = \frac{2\pi\beta}{\sqrt{N}}\ \text{eV}, \tag{2}$$

where 2β gives the band structure energy of a pair of adjacent π sites. The value of β is taken to be ~2.9 eV for six numbered carbon ring. From the Robertson relation, cluster size can be calculated [53] and then following relation can be used to calculate the number of carbon atoms per cluster [51]

Table 1
SRIM calculated S_e, S_n values and range of ions for Makrofol KG.

Energy (MeV)	Ion	Electronic energy loss (S_e) (keV/μm)	Nuclear energy loss (S_n) (keV/μm)	Range (μm)
100	Oxygen	4.476×10^2	2.58×10^{-1}	137.48
150	Nickel	5.022×10^3	5.982	36.43