Modifications induced in the polycarbonate Makrofol KG polymer by Li (50 MeV) ion irradiation

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Abstract. Swift heavy ions interact predominantly through inelastic scattering while traversing any polymer medium and produce excited/ionized atoms. Here samples of the polycarbonate Makrofol of approximate thickness 20 μm, spin coated on GaAs substrate were irradiated with 50 MeV Li ion (+3 charge state). Build-in modifications due to irradiation were studied using FTIR and XRD characterizations. Considerable changes have been observed in the polymer while varying the fluence from 1E11 ion/cm^2 to 1E13 ion/cm^2 Li ions. AFM images of the surface modifications caused by ion irradiation on the polymer are also presented.

1. Introduction

Whenever an energetic ion passes through a medium it causes noticeable changes in it. Depending upon the material (insulator, conducting or semiconducting), ion energy and type, different types of modifications are expected. Energy loss during ion passage from the medium can be described via two independent processes, viz., ion–atomic nucleus interaction that dominates at low energies ($\sim$0.1 MeV/amu) and ion–electron interaction prevalent at high energy for heavy ions. Thermal spike [1] and Coulomb explosion [2] models have been proposed to describe the conversion mechanism for the energy of the excited electrons into the kinetic energy of the target atoms. The former model assumes the excited electrons to be confined in a cylinder around the ion path. The Coulomb explosion model described the creation

of a cylinder of highly ionized matter along the ion track that is unstable due to Coulomb repulsion.

Energy distribution in the matter leads to various modifications in the target. Till now, lot of work has been done to see the modifications in single medium such as polymers [3–6] and semiconductors separately [7–10]. Latest trends include the study of the effects at the interface of two media such as metal–polymers, polymers–semiconductors. When a polymer is exposed to high energy ion beam it leads to radical formation, main chain scission, intermolecular cross linkage, creation of triple bonds and unsaturated bonds, volatile fragments etc. In the present investigation, the effect of Li beam has been studied on the polymer (polycarbonate, Makrofol KG) coated onto a semiconductor substrate (GaAs in the present work).

2. Experimental

We have used n-type GaAs(1 0 0) as a semiconducting substrate coated with a thin layer of polymer. Makrofol KG is a polycarbonate; chemically it is bis-phenol-A-polycarbonate and is available in two forms – crystalline and amorphous; it was procured from General Electrics West Germany and has a chemical composition and 3D network as
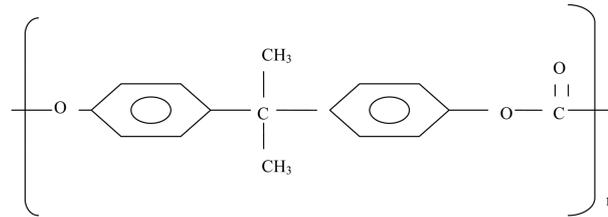
Thin Makrofol KG sheets were dissolved in dichloromethane (volatile solvent) and spin-coated on semiconducting substrates at rpm ranging from 3000 to 4000 so as to obtain a coating of about 20 μm thickness. Later on, all samples were normally irradiated at room temperature and under vacuum with different ion fluences 1E11 ions/cm^2, 1E12 ions/cm^2 and 1E13 ions/cm^2 of Li ion (50 MeV) beam at 15 UD Pelletron, IUAC, New Delhi.

The range of 50 MeV Li ions in the polymer has been calculated using SRIM 2006 and is found to be 451 μm. Here the range of the ion is greater than the thickness of the polymer, due to which ions just pass through the polymer and enter the semiconductor leading to some diffusion at the interface of the polymer and semiconductor. The SRIM 2006 calculated electronic energy loss $(dE/dx)_e$ for the Li ion beam in Makrofol is of the order of 8.538E-01 MeV/(mg/cm^2) and nuclear energy loss $(dE/dx)_n$ is 8.879E-02. Later FTIR, XRD and AFM studies are carried out to observe the ion beam effect on the polymer-coated substrate.
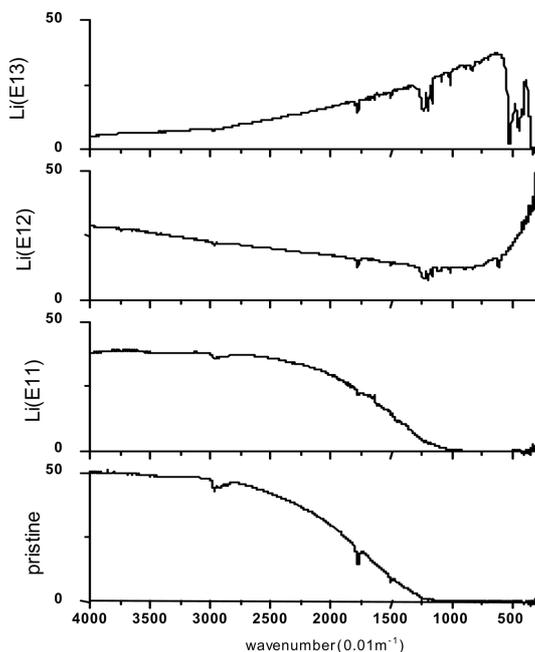
Figure 1. FTIR analyses for Li ion-irradiated and pristine samples.

3. Results

3.1 *FTIR analysis*

The nature of the chemical bond of the polymers can be studied through the characterization of the vibrational modes determined by infrared spectroscopy [11–14]. The FTIR spectra of pristine and irradiated samples depicted in figure 1 show various absorption bands appearing and disappearing after irradiation and the effect of enhanced fluence can also be observed. As we move from lower fluence to higher one, transmission intensity decreases at higher frequencies but at lower frequency it increases along with the appearance of some new peaks. As the fluence increases, transmission intensity also increases and at lower wave numbers transmission is found decreasing. It can be noticed in figure 1 that the absorption at low frequency is decreasing, i.e., there is a great change in the bonding properties of the polymer. There is an appearance of a peak corresponding to normal bending of ≡CH, stretched C–O and out-of-plane bend aromatic ring. Along with that, intensity of these peaks also increases with fluence. There is complete disappearance of the peak corresponding to stretch antisymmetric CH_2 bonding. Further, peaks corresponding to normal bending of ≡CH, stretched C–O and out-of-plane bend aromatic ring are becoming more intense.
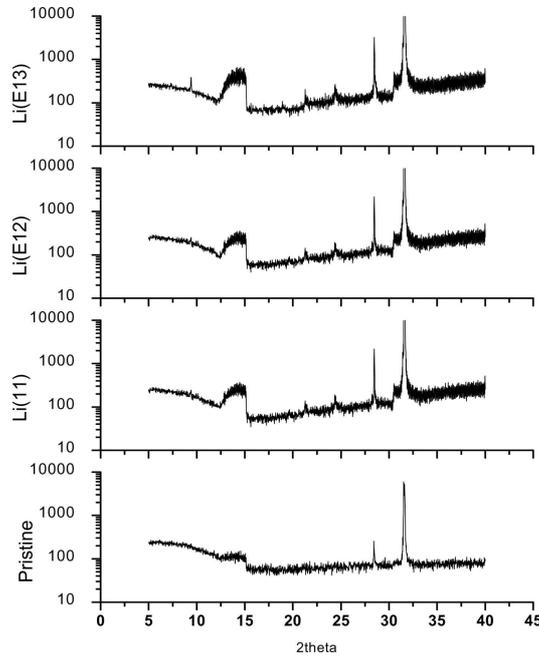
Figure 2. XRD analyses for Li ion-irradaited and pristine samples.

3.2 *XRD analysis*

XRD of the samples is shown in figure 2. As can be seen, the peak corresponding to the appearance of partial crystallinity in polymer [5,6] is lying between 15 and 20° (2θ) and the other peaks correspond to the substrates. Here for GaAs, however, we can see the appearance of new peaks when 2θ varies from 20 to 30° and the intensity of the peak also changes with fluence. Also there is a broad peak at 2θ less than 15°. There is, of course, some change in the intensity of peaks with fluence but there is a regular trend indicating that the intensity is decreasing first and then increasing. This shows that the crystallinity of the samples is changing slowly.

4. Surface modifications

Generally, irradiation affects not only the chemical and morphological properties but also the surface. Irradiated samples were scanned using AFM in tapping mode and the comparison with pristine samples shows drastic surface modifications. A typical AFM image of the pristine sample in height mode is shown in figure 3. For irradiated samples AFM image shows the presence of craters (figure 4) with specific rims around them. The interaction of ions with the material leads to the formation of damage zones, and these damaged zones are chemically more reactive compared to the surrounding region. Research on ion-bombarded polymer shows that gases like H_2, CH_4, O, CO_2 etc. are released in the target. Along the path, the incident
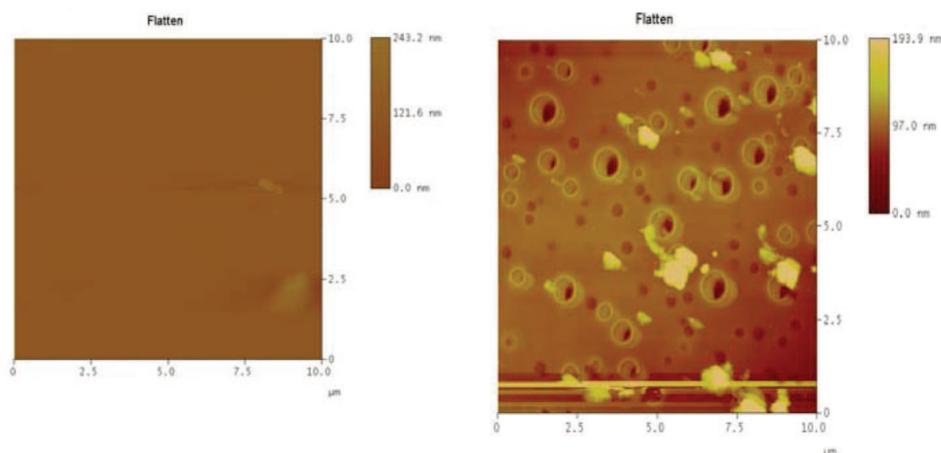
Figure 3. AFM image for pristine samples.　**Figure 4.** AFM image for Li ion-irradiated samples.

ions apart from creating a large amount of defects as a result of chain scission in polymer, release gases like H_2, CH_4, O, CO_2 etc. [15–18]. As suggested by He and Bassim [19], the basic process in the model proposed by this group involves the diffusion and trapping of gases, forming bubbles on the surface, breaking of blisters with gas release, and eventual formation of craters on the surface.

5. Conclusion

On the basis of the above discussion, FTIR results reveal that the polymer coating on semiconductor suffers serious degradation through bond scissions and cross linkages. There is effective change in intensity of transmission peaks as fluence changes. XRD measurements reveal the effect of substrate on the crystallinity of the sample. Apart from that, the surface shows drastic surface modifications. Generally, irradiated polymers never show that much clear patterns without etching but here this may be because of the GaAs substrate below the polymeric layer.

Acknowledgments

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