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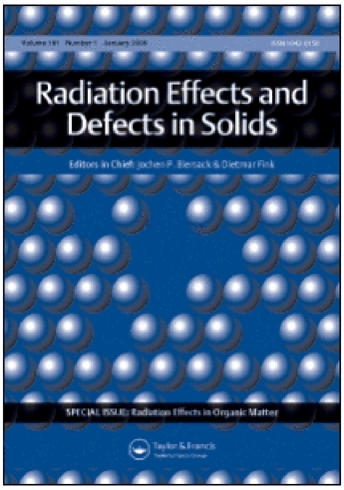

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OPTICAL ABSORPTION STUDIES IN HEAVY ION IRRADIATED POLYMERS

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Heavy ion induced modification in optical absorption studies of the polymers Polypropylene and Polyimide have been carried out to investigate the potential for improvements in their conductivity properties. The polymers were irradiated to four different doses of 140 MeV ^{28}Si and 100 MeV ^{58}Ni ion beams. The optical absorption studies were carried out by UV-Vis spectroscopy. The shift in the absorption edges were correlated to the optical band-gap by Tauc's expression. A decrease in optical band-gap has been observed in the irradiated polymers, but the effect of ^{58}Ni ions were more pronounced in decreasing the band-gap in the polymers.

Keywords: Polypropylene; Polyimide; Optical band-gap; ^{28}Si and ^{58}Ni ion beam irradiation

1. INTRODUCTION

Irradiation of high energy swift heavy ions in polymers leads to a wide variety of property changes in the polymers. They are the consequence of irreversible modifications of the structure and chemical composition

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including processes such as radical composition, main chain scission, intermolecular crosslinking, creation of unsaturated bonds and loss of volatile fragments [1]. The polymer irradiation leads to shift in optical absorption edges, which indicates a lowering of the energy-gap. The decrease in energy band-gap implies an increase in conductivity of the irradiated polymers which might be due to the formation of clusters with rings, or due to the formation of conjugated double bonds or quinonic structures [2].

The optical properties of the ion beam irradiated polymers have been characterised by Elman *et al.* [3] and the modification induced in the optical properties of the polymer has been correlated with the energy deposition by the impinging ion beam by Fink *et al.* [4] and by Davenas *et al.* [5]. Loss of imide structures by pyrolysis with depletion of oxygen and nitrogen containing groups leads to a modification in the electrical properties of Polyimide from initial insulating ($\rho = 10^{16}\,\Omega$cm) to a semiconducting ($\rho < 10^{2}\,\Omega$cm) at 700°C to a metallic ($\rho = 10^{-2}\,\Omega$cm) at 900°C. When Polyimide is heated between 800° to 850°C, the increase in conductivity has been reported due to formation of dense heterocyclic carbon ring networks in the polymer [6]. Electrical conductivity in PI has also been reported on increasing the dose of Argon ions [7]. 2 MeV electron irradiation and 62 MeV proton irradiation on Polypropylene reduced its optical band-gap, but no such change was observed for irradiated Polyimide [8].

In the present work, two polymers namely Polypropylene and Polyimide were irradiated to 140 MeV ^{28}Si and 100 MeV ^{58}Ni in order to carry out a comparative study on the modification in optical absorption properties of the two polymers.

2. EXPERIMENTAL ASPECTS

2.1. Target Preparation and Irradiation

Rectangular pieces of size (10 × 10) mm^2 were cut from commercially available sheets of Polypropylene (composition: $(CH_2)_x$, density: 0.9 gm/cm^3, thickness: 8 μm) and Polyimide (composition: $C_{22}H_{18}O_5N_2$, density: 1.42 gm/cm^3, thickness: 50 μm). The thickness of the sheets were measured by a sensitive Heidenhain device within an accuracy of ± 0.1 μm. The samples were washed thoroughly in soap solution and deionised water. The cleaned samples were dried in a vacuum desiccator. Then four stacks of Polypropylene containing 10 foils each and four stacks of Polyimide containing 2 foils each were prepared for irradiation.

Four stacks of each polymer were irradiated to four different ion fluences *i.e.*, 2×10^{11}, 5×10^{11}, 2×10^{12} and 5×10^{12} ions/sec of 140 MeV ^{28}Si and 100 MeV ^{58}Ni ion beams at an angle of 90° in the Material Science Chamber of 15 UD Pelletron Accelerator at Nuclear Science Center, New Delhi, India.

2.2. Optical Absorption Studies

The UV-Vis spectroscopy of the each foil of all the stacks were taken by Beckman DU-650 spectrophotometer in the ranges varying from 200 nm to 800 nm at the scan rate of 1200 nm/min, taking pristine polymer as reference. The wave-length range of absorption edges were found to be within 300 nm to 500 nm for polypropylene and 455 nm to 570 nm for polyimide.

The range of 140 MeV ^{28}Si in polypropylene is 92.4 μm and in polyimide is 73.6 μm, while that of 100 MeV ^{58}Ni in polypropylene is 32.4 μm and in polyimide is 26.8 μm, as obtained from the computer code RANGE [9]. Accordingly, we could notice the changes in the spectra of corresponding foils up to a certain penetration depth depending upon the range of the ion through the target material.

The shift of absorption edge of the UV-Vis spectra towards the visible region, was correlated with optical band-gap E_g by Taucs expression [10]:

$$\omega^2\sqrt{\varepsilon(\lambda)} = (\hbar\omega - E_g)^2 \tag{1}$$

where, $\varepsilon(\lambda)$ is the optical absorbance and λ is the wavelength. The intersection of the extrapolated spectrum with the abscissa of the plot: $\sqrt{\varepsilon}/\lambda$ *vs.* $1/\lambda$ yields the gap wavelength λ_g from which energy gap is derived as

$$E_g = hc/\lambda_g. \tag{2}$$

2.3. Experimental Errors

The error involved in the determination of ion-energy was within 0.5%. The error in the measurement of the thickness of the foils is of the order of ± 0.1 μm. For determining the wave-length gap, the best linear fit of the points on the curve $\sqrt{\varepsilon}/\lambda$ *vs.* $1/\lambda$ was always taken. So, the maximum probable error in determining the energy band-gap can be estimated to be ± 0.1 eV.

3. RESULTS AND DISCUSSIONS

3.1. Polypropylene

The optical band-gap of the pristine Polypropylene was found to be 5.2 eV. But on heavy ion irradiation, it undergoes pre-dominant cross-linking resulting in formation of free radicals. This causes a significant reduction in energy band gap, thus implying an increase in conductivity. The energy-gap was found to decrease with increase in ion-fluence as shown in Figure 1. At the highest fluence of 5.0×10^{12} ions/sec of 140 MeV ^{28}Si in Polypropylene, the optical band-gap reduced to nearly 50% *i.e.*, 5.2 to 2.4 eV. For lower ion

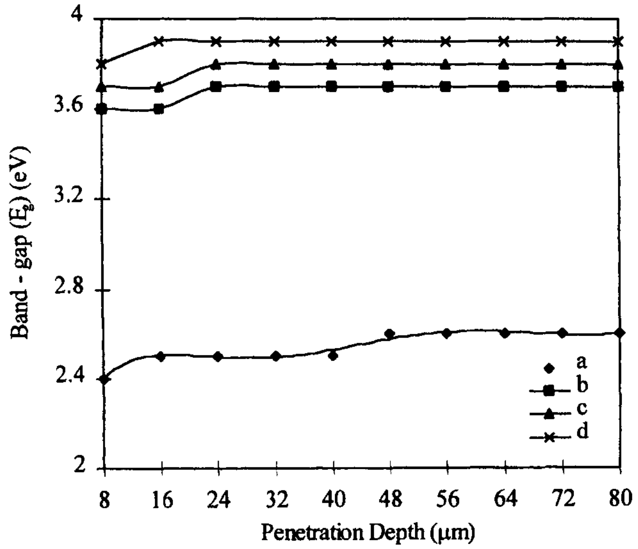

FIGURE 1 Variation in Band-gap (E_g in eV) with penetration depth of Polypropylene by four different doses [$a = 5 \times 10^{12}$ ions·cm^{-2}, $b = 2 \times 10^{12}$ ions·cm^{-2}, $c = 5 \times 10^{11}$ ions·cm^{-2}, $d = 2 \times 10^{11}$ ions·cm^{-2}] of ^{28}Si.

fluences $\approx 10^{11}$ ions/sec and 2.0×10^{12} ions/sec, the value of E_g lies between 3.6 to 3.9 eV as shown in Figure 1.

Similarly, in case of 100 MeV ^{58}Ni, the ion fluences of the order of 10^{12} and 5.0×10^{11} ions/sec reduced the energy band-gap more than 50% *i.e.*, 5.2 to 2.0 eV, which is obtained exactly at the penetration depth of 8 μm. Beyond that penetration depth of the polymer, the value of E_g becomes 3.9 eV and remains the same through out the range of the ion in the target, while in case of lowest dose of 2.0×10^{11} ions/sec, E_g retains the only value of 3.9 eV from penetration depth 8 μm to 40 μm as shown in Figure 2.

Due to higher mass, the effect of 100 MeV ^{58}Ni was found to be more pronounced than that of 140 MeV ^{28}Si, in enhancing the conductivity of polypropylene, even though the energy is less for ^{58}Ni. This reduction in band-gap is penetration-depth dependent as the energy-loss of the ion increases in the course of its passage through the stack of several foils as evident from the Figures 1 and 2. This effect is also more upto a penetration depth of 16 μm, beyond which the value of E_g remains almost unchanged through out the range of the energetic ion.

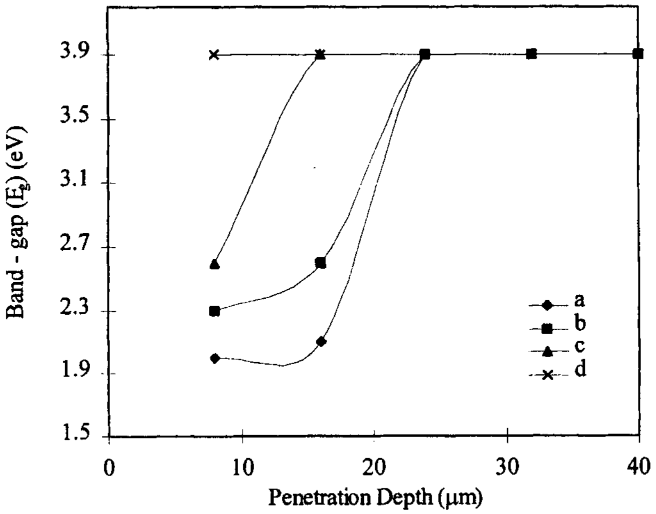

FIGURE 2 Variation in Band-gap (E_g in eV) with penetration depth of Polypropylene by four different doses [$a = 5 \times 10^{12}$ ions·cm^{-2}, $b = 2 \times 10^{12}$ ions·cm^{-2}, $c = 5 \times 10^{11}$ ions·cm^{-2}, $d = 2 \times 10^{11}$ ions·cm^{-2}] of ^{58}Ni.

TABLE I Variation of optical band-gap with fluence of ^{28}Si and ^{58}Ni in different foil thicknesses of Polyimide

Ion fluence *(ions/cm^2)*	*Foil thickness* *(μm)*	*Energy band gap $E_g(eV)$*	
		^{28}Si	*^{58}Ni*
5.0×10^{12}	50	1.9	1.6
	100	2.0	2.3
2.0×10^{12}	50	2.1	1.9
	100	2.1	2.3
5.0×10^{11}	50	2.3	2.0
	100	2.3	2.3
2.0×10^{11}	50	2.3	2.3
	100	2.3	2.3

3.2. Polyimide

The energy band-gap of pristine polymer with respect to air was found to be 2.3 eV. For the highest ion fluence of 5.0×10^{12} ions/sec of 140 MeV ^{28}Si, E_g was reduced to 1.9. The ion fluence $\approx 10^{11}$ ions/sec of ^{28}Si has almost no effect in altering the band gap in polyimide as mentioned in Table I. Similarly, in case of 100 MeV ^{58}Ni, the highest fluence of 5.0×10^{12} ions/sec of ^{58}Ni reduced the energy band-gap to 1.6 eV. The lowest dose of 2.0×10^{11} ions/sec has no effect at all in alternating E_g and in the cases of other two intermediate ion fluences, value of E_g is found to be nearly 2.0 eV. Since, the foil thickness of polyimide was 50 μm and the beam of 100 MeV ^{58}Ni could pass upto 26.8 μm, so, these effects were noticed only on the first foils of each stack.

4. CONCLUSION

As evident from the above cases, the effect of ^{58}Ni is more in altering the band-gap than that of ^{28}Si. Similarly, the change is noticed to be more for higher fluences of the same ions. This indicates that the increase in conductivity is directly dependent on the heavier ions as well as on higher dose of the same ions. As we can see from the cases of Polypropylene that the value of E_g remains almost same after a certain depth. Though it can be presumed that this constancy must be a simultaneous function of energy, dose and range of the ion beam, still further investigation is necessary to have a clear understanding of the mechanism. Again, the ion-dependent relative stability at these given four doses shows that Polyimide is more stable than Polypropylene. The presence of aromatic groups in the repeating unit of Polyimide accounts for its radiation stability.

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