Ion irradiation induced effects on the optical properties of polymers: a possible correlation with the energy loss profile

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Abstract. In the present study, the samples of CR-39 (monomer composition C₁₂H₁₈O₇) have been implanted with 100keV Ar⁺ and Kr⁺ ions to different fluencies ranging from 5x10¹⁴ to 1x10¹⁶ ions/cm². Further, these samples were subjected to UV-Visible, FTIR and Raman spectroscopic techniques to reveal the change in the optical behaviour of the samples in terms of induced structural changes in the polymer as a result of ion irradiation. The observed decrease in optical energy gap and increase in refractive index of the material under study after irradiation to Ar⁺ and Kr⁺ ions at the same energy have been tried to explain in terms of the energy loss profile along the trajectory of the respective ions. These studies are quite important towards the development of new materials with desired properties besides their fundamental importance.

1. Introduction
Polymeric materials have gained much importance in different fields of science and technology [1-8]. This is because of the good mechanical strength, high flexibility, good optical response etc. provided by these materials. It is well documented that the properties of the polymers can be modified to the desired extent through various means like chemical doping, irradiation, heat treatment, implantation etc. [8-15]. Among these, ion-implantation is quite promising towards the improvement of surface and near surface properties rather affecting the whole bulk. The ion implantation in polymers results in various effects such as ionization, displacing atoms, sputtering, carbonization, production of free radicals etc. [6-7, 14-22]. These structural modifications occurring in the ion implanted polymers may produce new electronic levels in the forbidden gap of the electronic band structure, thus, providing opportunities for the use of ion implantation in producing special materials for photonic applications. Especially, the ion implantation induced tailoring of optical energy gap and refractive index of transparent polymers is of great importance for the use of these materials in the fabrication of photonic device like optical waveguide, optical filters etc.[4-7, 21-22]. It is thus important to study optical properties of ion beam modified transparent polymers in a systematic manner for their utility in various optical devices.
Among the broad variety of available polymers, Poly(allyl diglycol carbonate), also known as CR-39, is considered an outstanding material. This polymer is highly transparent (over 90%) in the visible range and almost opaque in the ultraviolet region of electromagnetic spectrum. Further, it is very light weight polymer having refractive index comparable to that of crown glass. All these make it an excellent material for use in eye lenses, sunglasses, waveguides etc. [6-7, 23-26].

In the present work, the samples of CR-39 have been subjected to 100 keV Kr\(^+\) and Ar\(^+\) ion implantation. Some studies on the effect of ion implantation in CR-39 are available in the literature [6-7, 26-28], but from different point of view. We have carried out a systematic study on the effect of 100 keV Kr\(^+\) and Ar\(^+\) ion implantation on the optical energy gap and refractive index of CR-39 polymer and simultaneously tried to explain the observed changes in terms of the energy loss profile along the trajectory of the respective ions. Finally, FTIR and Raman spectroscopy have been used to correlate the observed results to the induced structural changes.

2. Experimental

The samples of area 15x15 mm\(^2\) were cut from the bulk sheets of CR-39 (monomer composition C\(_{10}\)H\(_{18}\)O\(_3\)) with thickness 250 micron, procured from TASTRAK, Bristol, England. These samples were irradiated at room temperature and under high vacuum (~ 1x10\(^{-6}\) torr) with 100 keV Ar\(^+\) and Kr\(^+\) ions to the fluences ranging from 1x10\(^{14}\) to 1.0x10\(^{16}\) ions/cm\(^2\) utilizing the Low Energy Ion Beam Facility (LEIBF) available at Inter-University Accelerator Centre (IUAC), New Delhi, India. The beam current density was kept below 1 µA/cm\(^2\) in order to avoid the thermal degradation of the samples. The energy loss profile along the trajectory of the implanted ions was found using SRIM code (version 2008.04) [29].

In order to study the optical properties, the virgin and the ion implanted samples were subjected to UV-Visible transmission and reflection studies by using Shimadzu Double beam Double Monochromator UV-VIS Spectrophotometer (UV-2550) in the wavelength range 190–900 nm with a resolution of 0.4 nm. The FTIR and Raman studies were carried out using the Shimadzu IR-Affinity-I, FTIR Spectrometer equipped with Pike, ATR-MAX-II accessory (Ge crystal) and Jobin-Yvon Raman spectrometer (He-Ne laser with \(\lambda=632.8\)nm) respectively.

3. Results and discussions

3.1. UV-visible studies

Before determining the optical energy gap and refractive index behaviour of the virgin- and ion-implanted samples, the recorded the UV–visible transmission (T) and reflection (R) spectra were taken into account the reflection losses at the surface using the method described in our earlier work [21].

3.1.1. UV-visible Absorption behaviour

The absorption behaviour of Ar\(^+\) and Kr\(^+\) implanted samples along with virgin CR-39 sample has been presented in figure 1. This figure clearly indicates the increase in absorption intensity and red shifting of the absorption edge with the increase in implantation dose. Further, the changes in absorption behaviour found to be more pronounced in case of Ar\(^+\) implantation as compared to Kr\(^+\) implantation in CR-39 polymer.

3.1.2. Determination of Optical Energy Gap

For the determination of optical energy gap (E\(_{\text{opt}}\)) of virgin and ion implanted samples of CR-39 polymer, the absorption data corresponding to the fundamental absorption edge (Figure 1) as a function of wavelength (\(\lambda\)) have been considered [6, 12-14]. The data have been plotted in the form of (ah\(^{1/2}\)) as a function of photon energy (hv) and presented in figure 2. From the intercepts of these plots on hv axis, the values of E\(_{\text{opt}}\) have been determined and are presented in table 1. This table depicts a clear-cut reduction in the value of E\(_{\text{opt}}\) with the increase in ion fluence in case of both the ions. The value of E\(_{\text{opt}}\) which was ~3.70 eV for virgin CR-39 has been reduced to ~2.54 eV and 1.90 eV at a dose of 1x10\(^{16}\) ions/cm\(^2\) for Kr\(^+\) and Ar\(^+\) ions respectively.

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Figure 1. UV-Visible absorption spectra of Ar$^+$ and Kr$^+$ ion implanted CR-39 polymer.

Figure 2. Plots for the determination of optical energy gap for virgin as well as Kr$^+$ and Ar$^+$ ions implanted CR-39 samples.

Table 1. The optical energy gap ($E_{OPT}$) values for virgin as well as Kr$^+$ and Ar$^+$ ion implanted CR-39 samples.

| Ion fluence (ions/cm$^2$) | Kr$^+$ Implanted samples | Ar$^+$ Implanted samples |
|---------------------------|--------------------------|--------------------------|
| 0                         | 3.70 ± 0.01              | 3.70 ± 0.01              |
| 1x10$^{15}$               | 2.90 ± 0.02              | 2.48 ± 0.01              |
| 5x10$^{15}$               | 2.65 ± 0.01              | 2.32 ± 0.02              |
| 1x10$^{16}$               | 2.54 ± 0.01              | 1.90 ± 0.03              |

3.1.3. Determination of Refractive Index

The refractive index (n) values for virgin as well as Kr$^+$ and Ar$^+$ ion implanted CR-39 samples have been determined at different wavelengths using the relation [12, 21]

$$n = \left\{ \frac{4r}{(r-1)^2} - K^2 \right\}^{1/2} - \frac{r+1}{r-1}$$

where $K = \alpha \lambda / 4\pi$, is the extinction coefficient with $\alpha$ as the absorption coefficient at wavelength $\lambda$ and $r$ is the reflection coefficient at the air-surface interface at the same wavelength.

The variation of the refractive index as a function of ion dose, at wavelengths 400 and 600 nm, has been presented in figure 3. From this figure, it is clear that the value of refractive index which remains
almost ~1.56 for virgin sample has been found to be increased to ~2.00 and ~2.40 at the wavelengths 400 and 600 nm respectively, for the sample implanted at the dose of $1 \times 10^{16}$ ions/cm$^2$ with Kr$^+$ ions. Further, for samples implanted at $1 \times 10^{16}$ ions/cm$^2$ with Ar$^+$ ions, the value of refractive index has been found to increase to ~2.15 and 2.50 at the wavelengths 400 and 600 nm respectively.

The observed changes in optical parameters of Kr$^+$ and Ar$^+$ implanted CR-39 may be attributed to the formation of cross-linked and conjugated carbonaceous network in the near surface region of the implanted polymer [6-7, 14-17].

![Figure 3. Variation of refractive index with ion dose, for virgin as well as Kr$^+$ and Ar$^+$ ion implanted CR-39 samples, at wavelengths 400 and 600 nm.](image)

### 3.1.4. Relative comparison

A comparison between the observed values of various optical parameters (Table 1 & Figure 3) clearly indicates that the extent of changes produced in the case of Ar$^+$ implanted CR-39 is more pronounced as compared to Kr$^+$ implantation in CR-39. This may be explained on the basis of the spurs (a region of discrete energy loss by the ion along its trajectory) formed during the penetration of the implanted ions within the polymeric material [30].

For most of the polymers, the spur energy lies within an average value of 30 - 40 eV, which is sufficient to create the ion or radical pairs [7, 30]. The spur separation can be calculated after dividing the spur energy by the Linear Energy Transfer (LET). Therefore, a change in LET leads to a change in the spur separation. For low LET, the spurs are widely separated, while for increased LET the spurs are closely separated, resulting in the increased possibility of cross-linking. A separation of about 2 nm between the two adjoining spurs is sufficient for cross-linking. Further, the creation of closely spaced spurs is dominated in case of electronic energy loss in comparison to nuclear energy loss, by the penetrating ions in the implanted region [30].

Figure 4 presents the electronic LET plotted against penetration depth for 100 keV Kr$^+$ and Ar$^+$ ions in CR-39, as calculated through SRIM simulation for 1000 ions [29]. Figure 5 presents the profile of the separation between two adjoining spurs at different penetration depths corresponding to electronic LET (Figure 4). From this figure, it is clear that the spurs of separation ~0.03 – 2.0 nm and 0.05 – 2.0 nm are formed up to a penetration depth of ~140 and 200 nm in CR-39 after implantation to Kr$^+$ and Ar$^+$ ions respectively. Since, the spur separation up to ~2.0 nm favours cross-linking, therefore, it can be concluded that the effect of cross-linking is extended up to a larger thickness of the implanted sample in case of Ar$^+$ ions as compared to Kr$^+$ ion implantation.
Figure 4. SRIM calculated electronic LET for 100 keV Kr\(^+\) and Ar\(^+\) ions in CR-39 polymer as a function of penetration depth.

Figure 5. Separation between the Spurs formed as a result of 100 keV Kr\(^+\) and Ar\(^+\) ion implantation in CR-39 polymer, as a function of penetration depth.

3.2. Structural studies

3.2.1. FTIR

The FTIR-ATR spectra (recorded with Ge crystal) of virgin as well as Kr\(^+\) and Ar\(^+\) ion implanted sample of CR-39 have been presented in figure 6. In the spectrum for virgin sample, a number of peaks and bands at positions 783, 1007, 1255, 1394, 1526, 1742, 2308, 3615 and 3726 cm\(^{-1}\) have been observed. The identification of these bands has been made on the basis of data available in the literature and is in line with the monomer structure of CR-39 polymer [26, 31-32].

Figure 6. FTIR-ATR spectra of virgin- and ion-implanted CR-39 polymer.

Since, the present FTIR-ATR measurement was carried out by employing the Ge crystal that provides the structural information up to a depth of ~600 nm which is much larger than the thickness of the implanted layer (~140 nm for Kr\(^+\) ions and ~200 nm for Ar\(^+\) ions in CR-39 polymer), therefore the
recorded spectrum is expected to reveal both the characteristic bands of virgin and the important features of implanted layer [7]. A careful investigation of the ATR spectrum (Figure 6) of the sample implanted with Kr⁺ and Ar⁺ ions at the dose of 1x10¹⁶ ions/cm², clearly indicates the reduction in the absorption intensity and broadening of all the important characteristic bands which were observed in case of virgin sample in the region ~700-4000 cm⁻¹. Such behaviour may be due to the formation of carbonized layer in the near surface region as an effect of implantation [7]. Further, the appearance of a new band in the region ~1600 – 1800 cm⁻¹ and centered at position 1727 cm⁻¹ can be attributed to the formation of a system of conjugated bonds in the thin surface layer of CR-39 after implantation [31-32].

3.2.2. Raman

The FTIR-ATR spectra discussed in previous section though give an indication of the formation of conjugated carbonaceous material in the implanted region but a more conclusive idea about the carbonization can be drawn on the basis of Raman analysis [7]. Figure 7 presents the Raman spectrum of virgin CR-39 polymer. Like IR spectrum, various characteristic peaks and bands have been observed in the Raman spectrum of virgin CR-39 polymer and again the identification of these peaks and bands has been done on the basis of data available in literature [32-34].

The Raman spectra for the sample implanted with Kr⁺ and Ar⁺ at the dose of 1x10¹⁶ ions/cm² (Figure 8), clearly shows the disappearance of characteristic features which were observed in virgin sample and the appearance of two new broad bands in the wavenumber region 1000-2000 cm⁻¹. For Kr⁺ ion implantation, the Lorentzian fitting among these two bands depicts their centers at positions ~1357 cm⁻¹ and 1580 cm⁻¹, which mark the presence of D and G bands of carbonaceous materials respectively [7, 14-15, 21]. For Ar⁺ ion implantation, the Lorentzian fitting among these two bands depicts their centers at positions 1351 cm⁻¹ and 1578 cm⁻¹, with their intensity ratio (I_D/I_G) ~1.2. The intensity ratio (I_D/I_G) in case of Kr⁺ found to be ~1.3. Further, very small features of characteristic bands of virgin CR-39 found to appear along with the D and G bands in case of Kr⁺ implantation. This may be due to the smaller penetration depth of Kr⁺ ions in CR-39 as compared to the penetration depth of Ar⁺ ions. Thus, Raman analysis supports the results that the effects produced by Ar⁺ ion implantation are more prominent as compared to that produced by Kr⁺ ion implantation. Similar trends have also been observed by our group in a study of N⁺ and Ar⁺ ions implantation in PMMA polymer [21], where the effects produced by N⁺ ion implantation are found to more prominent as compared to that produced by Ar⁺ ion implantation.

![Figure 7. Raman spectra of virgin CR-39.](image)

![Figure 8. Raman spectra of Kr⁺ and Ar⁺ ion-implanted CR-39.](image)
4. Conclusions
In the present work, the optical behaviour of CR-39 polymer exposed to 100keV Ar$^+$ and Kr$^+$ ions has been studied through UV-visible spectroscopic technique. From this study, it has been observed that the values of optical energy gap decreases while the values of refractive index increases with the increase in ion implantation dose. It has also been observed that the changes in optical parameters are more pronounced in case of Ar$^+$ implantation as compared to Kr$^+$ ions implantation in CR-39. This fact has been explained on the basis of energy loss profile along the trajectory of the respective ions and it has been inferred that the changes induced also depends upon the implanted ion and its depth of penetration. Further, all the observed changes have been well correlated with the structural changes through FTIR and Raman spectroscopy. Such studies are quite important towards the development of new materials with desired properties besides their fundamental importance.

5. References

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