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Effects of Kr^+, Ar^+ and N^+ Implantation on CR-39

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ABSTRACT: The samples of CR-39 have been implanted with 100 keV Kr^+, Ar^+ and N^+ ions at the fluence of $1x10^{16}$ ions/cm^2. The optical behaviour of the polymer after implantation has been studied through UV visible absorption, transmission and reflection spectroscopy. Due to implantation, reduction in transmittance, optical band gap and increase in refractive index for Kr^+, Ar^+ and N^+ ion implanted CR-39 samples has been observed. The optical changes are maximum for N^+ ions and minimum for Kr^+ ions, at the same implantation dose and may be due to the higher penetration depth of N^+ ions in comparison to that for Ar^+ and Kr^+ ions at the same energy. The observed trends in various optical parameters can be described on the basis of the formation of cross-linked carbonaceous structure in the implanted. The formation of such a structure may be explained on the basis of the spurs formed during the penetration of the implanted ions within the polymeric material.

Keywords: Ion implantation; absorption; optical energy gap; refractive index; spurs.

INTRODUCTION: In last few decades, a lot of research activities are being carried out related to the modification of the materials through ion beam irradiation [1-13]. At low energies, ion implantation is a versatile technique used for polymers without altering bulk substrate materials [2-7]. The enhanced use of ion implantation method for tailoring the surface structure and properties of polymers is also due to the liberty of embedding any desired amount of ions inside the polymers. The changes in physical and chemical properties due to ion implantation strongly depends upon the structure of polymers and the parameters of implantation such as ion energy, ion current, and ion fluence. One of the major objectives of such studies is to modify the properties of the materials to develop futuristic materials for device fabrication.

The energy deposited during ion implantation in polymers leads to the two main processes, i.e. chain scissioning and cross-linking, which produce large irreversible changes in physical, chemical and other properties of the polymers [1-4]. The electronic processes enhance cross-linking whereas nuclear processes enhance chain scissioning. Cross-linking and chain scissioning mechanisms were explained by the concepts of LET, ion track, and spur. The most important parameter for cross-linking is found to be linear energy transfer (LET). LET is a measure of energy deposited per unit ion path length, often expressed in SI units of eV/nm/ion or simply eV/nm. High LET tracks have a large effective radius and spurs are closed separated facilitating cross-linking, whereas, in low LET , spurs are widely separated and occur independently, often leading to chain scissioning[2]. In the present work, an attempt has been made to correlate experimentally observed optical behavior with spur formation along the penetration depth of implanted ion in CR-39. CR-39($C_{12}H_{18}O_7$) is an organic aliphatic polymer synthesized by polymerization of diethyleneglycol bis allylcarbonate (ADC) in presence of di-isopropyl peroxydicarbonate (IPP) as catalyst. Figure 1 shows monomer structure of CR-39.

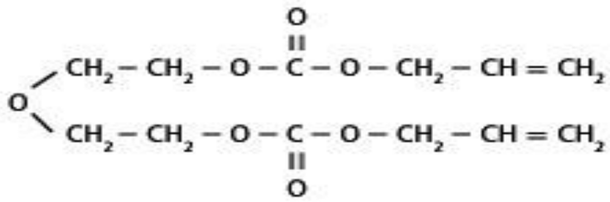

Figure1: Monomer structure of CR-39

CR-39 is highly transparent in visible region and almost opaque in the ultraviolet range which makes it an excellent substitute of glass substrate [14, 15]. It is very light weight polymer, about one half of the weight of glass. Its index of refraction is comparable to that of glass. It is largely used for the production of optical glasses, sunglasses, for the fabrication of various optical and optoelectronic devices and for nuclear track detection [1, 3, 7].

Material and characterization techniques: The samples of CR-39 of size (1.5 x 1.5 cm^2) were cut from flat sheet and irradiated at room temperature and under high vacuum (~ 10^{-6} torr) to 100 keV N^+, Ar^+, Kr^+ ions at $1x10^{16}$ ions/cm^2, utilizing the Low Energy Ion Beam Facility (LEIBF) available at Inter-University Accelerator Centre (IUAC), New Delhi, India. The beam was electrostatically scanned over the entire area of the sample for uniform implantation. The beam current density was kept below 1 μA/cm^2 to prevent the thermal degradation of the samples. The

UV-visible transmission, absorption and reflection spectra were recorded in the wavelength range 190-900 nm using Shimadzu double beam double monochromator UV-Visible spectrophotometer (UV-2550) with a resolution of 0.5 nm keeping air as reference.

RESULTS AND DISCUSSION:

UV- Visible spectroscopy: From the detailed data analysis related to the effect of 100 keV Kr^+, Ar^+ and N^+ ion implantation on the optical behaviour of CR-39, it is apparent that there is a significant change in the values of various optical parameters like transmittance, optical energy gap and refractive index of this polymer after implantation. The values of Eg for virgin and implanted samples of CR-39 were determined from the intercepts of the plots of $(ahv)^{1/2}$ versus (hv) on the hy axis using Tauc's relation [15]. The values of Eg so determined are presented in Table 1. However, the change in the magnitude of these parameters depends on the implanted ion parameters. Table 1 presents some representative data related to the change in transmittance, optical energy gap and refractive index of CR-39 after implantation to 100 keV Kr^+, Ar^+ and N^+ ions at a dose of $1x10^{16}$ ions/cm^2.

Table 1. clearly indicates that the transmittance which was ~90% in virgin sample has been found to be decreased to ~19%, 5% and 0% (at 400 nm) for 100 keV Kr^+, Ar^+ and N^+ ion implantation respectively, at the same dose of $1x10^{16}$ ions/cm^2. In the similar manner, the optical energy gap which was ~3.70 eV for virgin sample has been reduced to ~2.54, 1.90 and 1.10 eV after Kr^+, Ar^+ and N^+ ion implantation respectively. Further, the refractive index has been found to be increased from 1.56 in virgin sample to 2.00, 2.15 and 2.35 for Kr^+, Ar^+ and N^+ ion implanted CR-39 samples respectively, at the wavelength 400 nm. The observed changes are maximum for N^+ ions and minimum for Kr^+ ions, at the same implantation dose. The formation of such a structure may be explained on the basis of the spurs formed during the penetration of the implanted ions within the polymeric material [8].

Table 1: Optical parameters of CR-39 after implantation to 100 keV Kr^+, Ar^+ and N^+ ions at a dose of $1x10^{16}$ ions/cm^2

Optical parameters	Virgin sample	Implanted Samples		
		Kr^+	Ar^+	N^+
Transmission (%) At λ = 400 nm	90	19	5	0
Optical energy gap (eV)	3.70	2.54	1.90	1.10
Refractive index At λ = 400 nm	1.56	2.00	2.15	2.35

A spur is a region of discrete energy loss by the ion along its trajectory. For most of the polymers, the spur energy lies within an average value of 30 - 40 eV [1, 8], which is sufficient to create the ion or radical pairs. The spur separation can be calculated after dividing the spur energy by the Linear Energy Transfer (LET). Therefore, changing the LET means changing the spur separation or spur density. For low LET, the spurs are widely separated and occur independently, 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 as it is approximately of the same order as the intermolecular chain distance in polymers [2]. 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.

Figure 2 presents the electronic LET plotted against penetration depth for 100 keV Kr^+, Ar^+ and N^+ ions in CR-39, as calculated through SRIM simulation for 1000 ions. Figure 3 presents the profile of the separation between two adjoining spurs at different penetration depths corresponding to electronic LET (Figure 2). 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, while for N^+ ion implantation, it has been found that the spurs of separation ~0.11 – 2.0 nm are formed up to a depth of ~390 nm. Since, the spur separation up to ~2.0 nm favours cross-linking, therefore, it can be concluded that the cross-linking has occurred in case of all the three implanted ions resulting in the observed changes in various optical parameters. Since the effect of cross-linking is extended up to a larger thickness of the implanted sample in case of N^+ ions as compared to Ar^+ and Kr^+ ion implantation, therefore, the change in optical parameters like transmittance, optical energy gap and refractive index is expected to be maximum for N$^+$ and minimum for Kr$^+$ ion implantation as observed experimentally.

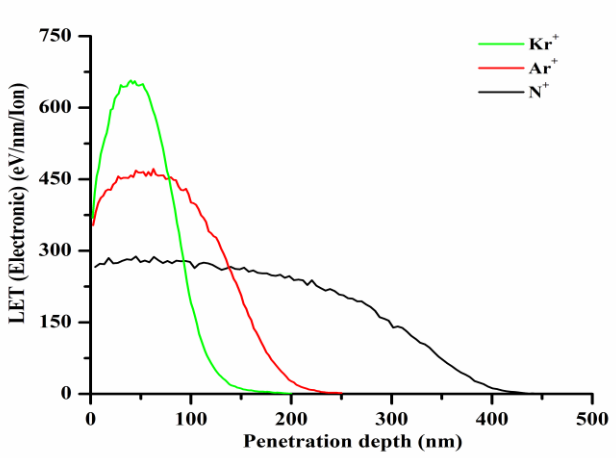

Figure 2: SRIM calculated electronic LET for 100 keV Kr$^+$, Ar$^+$ and N$^+$ ions in CR-39 polymer as a function of penetration depth

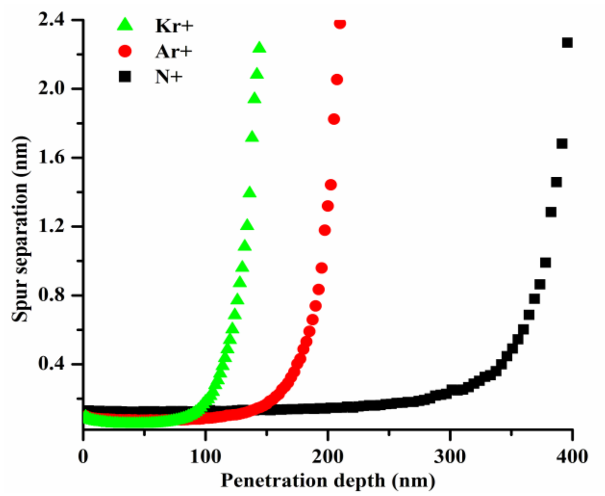

Figure 3: Separation between the Spurs formed as a result of 100 keV Kr$^+$, Ar$^+$ and N$^+$ ion implantation in CR-39 polymer, as a function of penetration depth

CONCLUSIONS: It can be concluded that the various optical parameters like transmittance, optical energy gap, refractive index etc. of CR-39 polymer can be tailored as per requirements by selecting the proper ion dose combinations. Effect of N$^+$ ion implantation on these optical parameters has been found to be more pronounced in comparison to Ar$^+$ and Kr$^+$ ion implantation, at the same energy and same implantation dose. The induced changes in these optical parameters after implantation occur as a result of the formation of cross-linked carbonaceous structure in the near surface implanted region. Electronic energy loss process by the implanted ions seems to be the dominant process for the formation of such a cross-linked structure. The pronounced effects observed in case of N$^+$ ion implantation as compared to Ar$^+$ and Kr$^+$ ions are due to the higher penetration depth of N$^+$ ions in comparison to that for Ar$^+$ and Kr$^+$ ions at the same energy.

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