4.1 General

The present work has been aimed at exploring the low energy argon ion irradiation induced surface structuring in PP, PC and PET polymers. The morphological evolution of surfaces in these polymers has been investigated using Atomic Force Microscopy (AFM). Raman Spectroscopic studies have been performed to correlate the observed morphological transformation in the irradiated polymeric specimens with that of structural alterations in the irradiated specimens. The behavior of implanted argon ions (retained dose and projected range) as well as elemental composition in the post-irradiated specimens has been examined utilizing Rutherford backscattering spectrometry (RBS) as a result of oblique argon ion irradiation. UV-Visible spectroscopic technique analyzed the modifications in transmission, reflectivity and refractive index in these irradiated specimens. The alterations in surface structure, composition, depth profile, roughness, morphology and optical parameters of pre- and post- irradiated polymeric specimens have been analyzed using these characterization techniques qualitatively. The major results of the present study and the conclusions drawn from this work are summarized in section 4.2 and 4.3 respectively. The scope of the future work is presented in section 4.4.

4.2 Summary

A single step methodology for creation of nano patterns using argon ion beams on polymeric surfaces has been presented for first time. For this, the samples of size 2×2 cm² were cut from the commercially available flat polished sheets of PP, PC and PET polymers. These polymeric specimens have been irradiated with 40 keV Ar⁺ ions
with different fluences of $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$, $2.5 \times 10^{16}$ Ar$^+$ cm$^{-2}$ and $5 \times 10^{16}$ Ar$^+$ cm$^{-2}$ at varying off normal incidences of $30^\circ$, $40^\circ$ and $50^\circ$.

AFM studies explored the self-organized morphological evolution on surfaces of irradiated PP, PC and PET specimens under different irradiation parameters (angle of incidence and ion fluence). The structural alterations as a result of low energy argon ion irradiation have been investigated using Raman and UV-Visible spectroscopic techniques. In addition, the retained argon fluence and projected range has been estimated utilizing Rutherford Backscattering spectroscopy. Utilizing the results of these characterization techniques, correlation has been made between the observed self-organized morphological evolution with that of structural alterations induced in polymeric structure as a result of argon ion irradiation.

**Effect of oblique argon ion irradiation on Polypropylene (PP)**

- Atomic force microscopy has been used to explore the effect of various irradiation parameters on the topographical evolution of PP specimens. It has been observed that in case of PP ion beam irradiation at oblique incidence of $30^\circ$ resulted in formation of ripple like features with wavelength~2$\mu$m and amplitude~15 nm over the PP surface at ion fluence of $1 \times 10^{16}$ ions cm$^{-2}$. The continuous irradiation of these surfaces with higher fluence of $2.5 \times 10^{16}$ ions cm$^{-2}$ and $5 \times 10^{16}$ ions cm$^{-2}$ led to suppression of these features. Furthermore, increase in oblique incidence to $40^\circ$ caused the distortion of these ripples structures. With increase in ion fluence at same incidence, these ripple features start disintegrating into dot like structures and finally at highest angle of incidence ($50^\circ$) sharp dot like features evolved randomly over the surface. While at highest ion fluence of $5 \times 10^{16}$ ions cm$^{-2}$ nano-dot morphology got uniformly distributed over the whole of PP surface with average size~60±23 nm.

Thus it can be concluded that oblique ion beam irradiation of PP surfaces resulted in formation of ripple like features at lower incidences which slowly transforms into dot like structures with increase in ion incidence. This formation of ripples is attributed to sufficient energy deposition by incident ions at lower incidences to stimulate ripple features [1-3]. While increase in oblique incidence restricts the energy deposition only to near surface leading to collision cascades [4-7] and hence appearance of carbon clusters in form of nano dots.
Raman Spectroscopic studies have been performed to correlate the observed morphological transformation in the irradiated polymeric specimens with that of structural modifications. Raman studies investigated that after argon ion irradiation the fundamental structure of PP specimen has been modified completely. Moreover with increase in ion fluence from $1 \times 10^{16}$ ions cm$^{-2}$ to $5 \times 10^{16}$ ions cm$^{-2}$ a broadband feature appeared in the Raman spectra at all incidences. This feature latter deconvoluted separately into D and G bands. The formation of these bands at highest ion fluence was attributed to the irradiation induced disordering of PP specimens as a result of formation of dense carbon clusters beneath the polymeric surface. The disordering parameter in form of $I_D/I_G$ ratio has been estimated and found to increase with increase in angle of incidence which pointed toward the organization of carbon clusters with increase in ion fluence [8-13]. These Raman findings supports the formation of carbon clusters which appear in the form of nano dots investigated through AFM studies at highest ion fluence of $5 \times 10^{16}$ ions cm$^{-2}$.

Rutherford backscattering spectrometry has been performed to estimate the effect of oblique argon ion irradiation on elemental composition in the specimens. RBS studies show an increment in the carbon concentration for all the Ar$^+$ implanted specimens. It has been found that after argon ion irradiation the carbon and argon concentration decreases in the PP specimens with increase in off normal incidence from 30° to 50° at ion fluence of $5 \times 10^{16}$ Ar$^+$ cm$^{-2}$. The behaviour of implanted argon ions (retained dose and projected range) in PP specimens has been examined. The shift in carbon edge and argon peak position to higher channel number w.r.t. ion incidence was attributed to the ion beam sputtering induced out diffusion of these atoms and hence causes the Amorphization and argon deposition near to the surface of irradiated specimen. The variation in the carbon edge of the implanted PP surface as compared to the un-implanted one indicates towards the carbon enriched surface layer in the implanted polymer which confirms the formation of carbonaceous network [14-20].

UV-Visible spectroscopy has been employed to explore the effect of various oblique incidences and ion fluences on structure of PP polymer.
• The optical transmission has been observed to decline drastically after argon ion beam treatment. Further decrease in transmission observed at lower oblique incidences has been attributed to the significant damage created inside the polymeric matrix which results in formation of absorbing centers (carbon rich domains) at this incidence [21-22]. The increase in ion fluence from 1x10^{16} ions cm^{-2} to 5x10^{16} ions cm^{-2} also led to appreciable decline in transparency which has been recognized due to conjugation of these carbon rich domains [23].

• The specular reflectivity of PP specimens has been observed to increase drastically after argon ion irradiation. With increase in oblique incidence from 30° to 50° reflectivity has been improved further which has been attributed to the formation of valence electrons and free radicals near the surface as a result of argon ion irradiation [24-26]. Further increase in the specular reflectivity with increase in ion fluence from 1x10^{16} ions cm^{-2} to 5x10^{16} ions cm^{-2} was attributed to formation of hydrogenated amorphous carbon and hence supports our previous studies.

• The refractive index has been estimated at different wavelength and found to increase in irradiated PP specimens as an effect of oblique argon ion irradiation.

> Theoretical estimations in term of B-H coefficients have been realized. For given experimental conditions, \( \Gamma_x \) and \( \Gamma_y \) have been found to be positive with \( \Gamma_x > \Gamma_y \). It has been observed that with increase in ion incidence, \( \Gamma_y \) approached to \( \Gamma_x \) and hence elucidated the conversion of ripple morphology into nano-dot morphology in irradiated PP polymer. Power spectral density (PSD) deduced from the AFM micrographs provided the information about the dominating mechanisms behind the morphological evolution. The observed slope of PSD spectra at 30° oblique incidence and at various ion fluences revealed \( k^{-2} \) dependence which is characteristic behavior value of ballistic drift induced smoothing mechanism. While PSD slope at higher incidences (i.e. at 40° & 50°) has been observed to be of \( k^{-4} \) dependence which pointed out that the effective ion-induced surface diffusion (ESD) came into picture at higher incidences [27-28].
Chapter 4: Summary, Conclusions and Scope of Future Work

Effect of oblique argon ion irradiation on Polycarbonate (PC)

- Atomic force microscopic analysis of PC specimens revealed the formation of random nano structures over its surface irradiated with ion fluence of $1 \times 10^{16}$ ions cm$^{-2}$ at oblique incidence of 30°. These random structures have fragmented into dot like structures with increase in ion fluence to $2.5 \times 10^{16}$ ions cm$^{-2}$ with an average size 34±14 nm. While increase in ion fluence to $5 \times 10^{16}$ ions cm$^{-2}$ resulted in agglomeration of these structures. Further, shift in oblique incidence to higher incidence of 40° led to dot like features with an average size 29±9 nm at ion fluence of $1 \times 10^{16}$ ions cm$^{-2}$. While increase in ion fluence to $2.5 \times 10^{16}$ ions cm$^{-2}$ resulted in random topography which converts into some ripple like morphology with increase in sputtering time. Increase in oblique incidence to 50° didn’t result in any defined dot or ripple morphology. Thus, it can be concluded that 40 keV oblique ion beam irradiation resulted in evolution of nano dot like structures only for a few combinations of ion incidence angle & ion fluence ruling out the possibility of ripple features over PC specimens. This experimental finding is attributed to the aromatic nature of this polymer which hinders the formation of rippled patterns at chosen experimental conditions.

- Raman studies reveal the alterations in chemical bonding and structure of irradiated PC specimen. It has been observed that ion beam induces comparatively lesser destruction in this polymer as compared to PP. Most of the fundamental bands got diminish as a result of argon ion irradiation. The effect has been observed to be more pronounced at higher ion fluences. Further at 30° oblique incidence disorder D and graphitic G band have appeared. This finding has been attributed to the damage creation in terms of carbon clustering at this incidence. It also has been observed that disordering parameter in term of intensity ratio of D & G bands decreased with increase in ion fluence which confirms the clustering of carbon atoms on the surface of irradiated PC specimens [10-11]. AFM studies also reveal the formation of these random nano structures at this incidence. Thus our Raman findings support the morphological evolution investigated through AFM analysis.

- RBS studies estimated the change in surface elemental composition and shift in carbon & oxygen edge to the higher channel number w.r.t. ion incidence. Also, argon peak position has been found to be shifted to higher channel number with
increase in oblique ion incidence. This finding is attributed to the out diffusion of these atoms resulting in argon deposition near to the surface in irradiated PC specimens. The shifting of carbon edge in the implanted PC surface indicates towards the evolution of carbon enriched surface layer as result of ion beam irradiation induced carbonaceous network [15-17]. Thus the estimation of near surface carbonization as a result of ion implantation using RBS studies supports our Raman findings.

- UV-Visible spectroscopy has been carried out to reveal the structural alterations due to argon ion irradiation.
  - A drastic decline in optical transparency as an effect of argon ion beam treatment at various oblique incidences and fluences. The transmission has been observed to decline further with decrease in oblique incidences which was attributed to the significant damage created inside the polymeric matrix at this incidence. The increase in ion fluence resulted in further decline in transmission but in this case decline in optical transparency was small as comparison to that observed in case of PP specimen.
  - The specular reflectivity has been observed to increase after argon ion irradiation. This increase has been attributed to the formation of excess number of valence electrons over the polymeric surface as result of argon ion irradiation. The radical enhancement in reflectivity has been observed with increase in ion fluence from $1 \times 10^{16}$ ions cm$^{-2}$ to $5 \times 10^{16}$ ions cm$^{-2}$ due to creation of sufficient disordered species beneath the polymeric surface [24-25].
  - The refractive index has been observed to increase after argon ion irradiation.

- B-H coefficients $\Gamma_x$ & $\Gamma_y$ in case of PC didn’t deviate much from each other. Instead they have been observed to approach each other with increase in oblique incidence. Hence it has been investigated that present experimental conditions ruled out the emergence of ripple like patterns for the symmetry reasons and allowed only the formation of nano-dots.
Effect of oblique argon ion irradiation on Polyethylene terephthalate (PET)

- AFM analysis of PET specimens irradiated with $1 \times 10^{16}$ ions cm$^{-2}$ at $30^\circ$ oblique incidence resulted in formation of hillocks over its surfaces which disappears with increase in ion fluence. At $40^\circ$ incidence, ion beam sputtering induced pits over the PET surface which first transforms into some random features with increase in ion fluence to $2.5 \times 10^{16}$ ions cm$^{-2}$ and finally to fractal like structures at ion fluence of $5 \times 10^{16}$ ions cm$^{-2}$. With further increase in oblique incidence of $50^\circ$, ripple like features started evolving at higher ion fluences of $2.5 \times 10^{16}$ ions cm$^{-2}$ and $5 \times 10^{16}$ ions cm$^{-2}$ which indicates the early evolution stage of ripples over PET surfaces. Thus it can be concluded that in case of PET also, aromatic structure hindered the formation of ripple patterns at lower incidences while increase in incidence resulted in formation of some wavy features and has been recognized as early stage of ripple evolution.

- Raman spectroscopy also has been performed to investigate the effect of low energy oblique argon beam irradiation on the PET specimen. It has been investigated that intensity of most of the fundamental bands of the polymer has been reduced. The decline has been observed to be more pronounced at lower oblique incidence i.e. $30^\circ$. This finding was attributed to the higher projected range at this incidence which allowed incident ions to deposit sufficient energy to cause polymeric chain scissioning [19].

- UV-Visible transmission spectroscopy has been employed to study the effect of argon ion beam treatment at various oblique incidences and ion fluences on the polymeric structure. These studies revealed the significant decline in transmission. The transmission has been observed to decline further with decrease in oblique incidences which was attributed to the significant damage created inside the polymeric matrix at this incidence. The increase in ion fluence resulted in further decline in transmission but in this case decline in optical transparency was small as comparison to that observed in case of PP specimen.

- The specular reflectivity with respect to wavelength at different fluences at varying oblique incidences have been plotted and observed to increase after oblique argon ion irradiation. This increase has been attributed to the formation