Surface Modification and Irradiation Strength of InP and GaP

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Abstract

The surface modifications of irradiated Indium phosphide and Gallium phosphide irradiated with 100 MeV Fe^{9+} ions have been investigated by Spectroscopic Ellipsometry, Ultraviolet-visible-near infrared spectroscopy, Atomic force microscopy and Rutherford Backscattering Spectroscopy. The optical parameters like refractive index, absorption coefficient in the surface region investigated by spectroscopic ellipsometry is found to change slightly in comparison with non-irradiated samples. The decrease in optical band gap of InP and GaP after irradiation is associated with presence of irradiation induced defect levels in the band gap region. AFM study revealed the presence of nano-sized structure on the surface of the irradiated InP and GaP.

Keywords: Ion irradiation, Spectroscopic Ellipsometry, Rutherford Backscattering, Atomic force microscopy.

Introduction

Ion irradiation is a process by which energetic ions can be introduced into a single crystal substrate in order to change its structural, optical and electrical properties [1-2]. The depth to which the energetic ions (dopants) are implanted primarily depends on the energy of the ion beam. Ions with energies typically above 1 MeV/amu, ion velocity is comparable or higher than the Bohr electron velocity. Such ions are referred as Swift Heavy Ions (SHI). Typically at these energies, electronic energy loss is about two orders of magnitudes higher than the nuclear energy loss. Such a large electronic energy loss brings out various changes in materials. There is a threshold of electronic energy loss beyond which the creation of columnar defect or latent track occurs in the materials. This threshold energy varies from material to material.

Swift heavy ions during its passage through the material creates a cylindrical high temperature zone, which can even reach the molten state (beyond certain threshold of electronic energy loss) during temperature spikes of the time duration of the order of pico second. The material within the cylindrical region and / or the surrounding may experience very high pressure. It may be due to Coulomb explosion and / or thermal spike. The material undergoes phase transition in nano cylindrical zone due to this high temperature and / or high-pressure conditions. As an irradiated ion slows down and comes to rest, it makes many violent collisions with lattice atoms, displacing them from their lattice sites and produces lattice disorder and radiation damage in the target material. A wide spectrum of defects and defect impurity interactions evolve within the irradiated layer. Vacancies and interstitials, which are created during irradiation, recombine as well as produce complex defects such as clusters, voids and dislocations. The irradiation of indium phosphide / gallium phosphide single crystal with swift (Au, Kr, Xe, Yb etc.) ions of any kind produces the disorder in the surface region as well deep inside the wafer [3-8]. Damage

formations in indium phosphide due to high electronic excitation by swift Kr and Xe ions have been studied by cross section transmission electron microscopy and Rutherford back scattering spectrometry [3]. Rutherford back scattering spectrometry and transmission electron microscopy studies of single crystal indium phosphide irradiated with 250 MeV Xe ions with fluences 5 x 10^{12} to 1 x 10^{14} cm^{-2} showed that the surface layer of indium phosphide remain defect free but discontinuous amorphous tracks developed beneath the surface [4]. Atomic force microscopy studies of single crystal indium phosphide irradiated with 100 MeV Au^{8+} ions with fluences varied from 1 x 10^{12} to 1 x 10^{14} cm^{-2} have shown that the surface roughness depends on the substrate temperature during the irradiation [5]. Damage evolution and track formation in crystalline InP and GaAs during swift Kr and Xe ion irradiation were studied by the cross–section transmission electron microscopy, Rutherford backscattering spectrometry and selective chemical etching microscopy techniques [6]. The irradiation of single crystalline indium phosphide with swift Xe and Au ions with different fluences (5 x 10^{12} to 3 x 10^{14} cm^{-2}) showed the formation of thin crystalline surface layer within the few tens of nanometer [7]. Damage evaluation of indium phosphide single crystals irradiated with 593 MeV Au^{8+} ions at room temperature reveal the surface modification of indium phosphide due to electronic energy deposition [8]. In general, swift heavy ion irradiation of indium phosphide / gallium phosphide in the electronic stopping regime causes the formation of small-size defects, i.e., simple point defects and point defect clusters. In addition to the simple defects, more complex elongated defect such as ion tracks are formed due to high electronic energy loss in the above threshold electronic regime and within a limited range of irradiation temperatures. The present study aims a comparative study of surface modification of 100 MeV $^{56}Fe^{9+}$ ions irradiated InP and GaP. Spectroscopy ellipsometry, Atomic force microscopy, Ultraviolet-visible-near infrared spectroscopy and Rutherford backscattering techniques have been used to investigate the surface and near surface modification of the 100 MeV $^{56}Fe^{9+}$ ions irradiated InP and GaP. Figures 1(a) and 1(b) show the variation of electronic energy loss and nuclear energy loss of 100 MeV ^{56}Fe ions with depth from the surface in InP and GaP, respectively. It is clear from the figure that the nuclear energy loss is very less in the surface region where as electronic energy loss is very large (about two order of magnitude higher). Figuers 2 (a) and 2 (b) displays the number of vacancies produced per unit depth per ion versus depth inside of the InP and GaP target material, respectively. The simulation has been performed using Monto Carlo simulation program, *Stopping and Ranges of Ions in Matter*, (SRIM-2003) [1]. Therefore the irradiation induced defects in the surface region is not expected much in 100 MeV 56Fe ion irradiated InP and GaP.

Experimental Details:

Single crystal InP and GaP samples were irradiated with 100 MeV $^{56}Fe^{9+}$ ions for ion fluences 1x10^{12} and 1x10^{13} cm^{-2} at Inter University Accelerator Centre (IUAC), New Delhi. Ion beam scanning was used to irradiate the whole sample surface in a uniform way. In order to prevent the heating during irradiation, the beam current was held at 3–4 pnA (particle nano-ampere) and the sample was mounted on the copper target ladder with silver paste giving a good thermal conduction between them. After irradiation, the samples were cleaned in electronic grade Trichloroethylene, Acetone and Methanol and rinsed in de-ionized water.

The Spectroscopic Ellipsometry measurements were performed using generalized Ellipsometer with rotating polarizer with model M-2000™, J.A. Woollam Co. The data was acquired at fixed incident angle in the energy range from 1.2 eV to 5 eV. Ultraviolet-visible-near infrared (UV-VIS-NIR)

transmittance spectra of non-irradiated and samples irradiated with 100 MeV $^{56}Fe^{9+}$ ions for ion fluences of 1 x 10^{12} and 1 x 10^{13} cm^{-2} were recorded in the spectral region 200 nm to 1600 nm using a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer. The surface morphology of non-irradiated samples and samples irradiated with different ion fluences were examined using atomic force microscopy from Digital Instruments (Nanoscope-III) with silicon nitride tip under ambient conditions in the tapping mode. Rutherford backscattering experiment has been done using 1.7 million volt Pelletron accelerator in backscattering geometry.

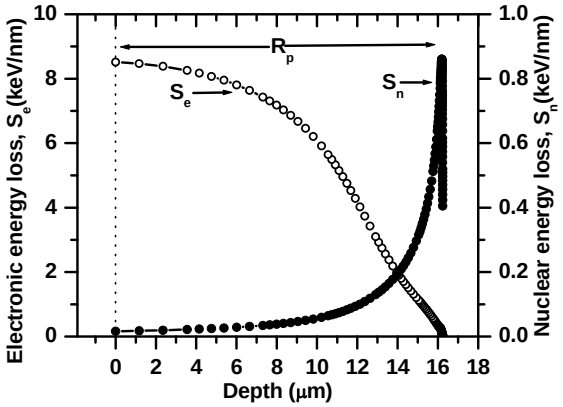


Figure 1(a): Variation of electronic energy loss and nuclear energy loss of 100 MeV 56Fe ion incidents on indium phosphide with depth from the surface, estimated by SRIM.

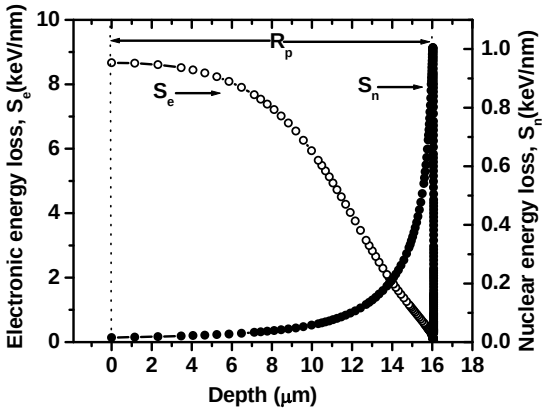


Figure 1(b): Variation of electronic energy loss and nuclear energy loss of 100 MeV 56Fe ion incidents on gallium phosphide with depth from the surface, estimated by SRIM.

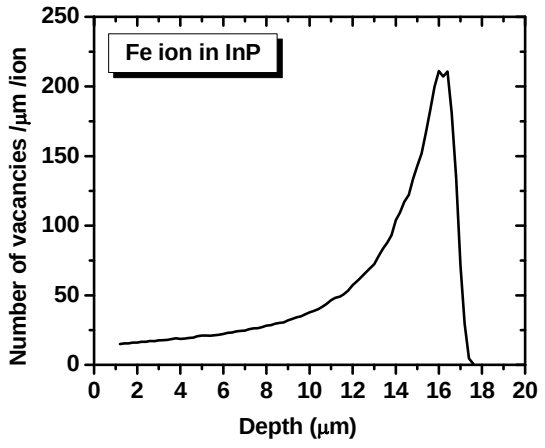


Figure 2(a): Variation of vacancy as a function of depth produced by 100 MeV 56Fe ions in indium phosphide.

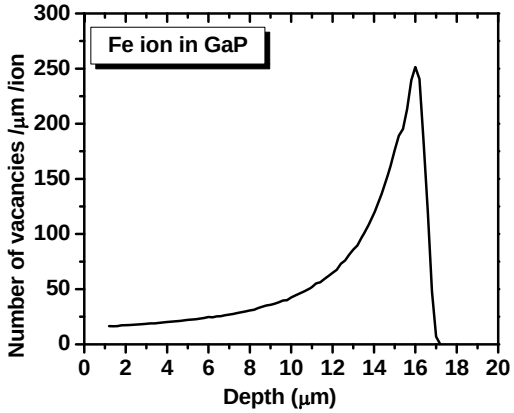


Figure 2(b): Variation of vacancy as a function of depth produced by 100 MeV 56Fe ions in gallium phosphide.

Results and Discussions:

The spectroscopic ellipsometry is one of the most adopted measuring methods in analyzing the optical properties of materials in the surface region. Ellipsometry measures the changes in the polarization state of light upon reflection from a sample surface at oblique incidence. Changes in polarization state of light typically expressed in terms of two values (ellipsometric angles) called Psi (Ψ) and Delta (Δ). These represent an amplitude ratio and relative phase shift between p and s-components of the polarized light which are induced by reflection from the sample surface. These parameters are used to determine the complex index of refraction. The real part of complex index of refraction is the conventional refractive index, n, and imaginary part is called the extinction coefficient, k. The extinction coefficient is directly related to the absorption coefficient, α, of the medium as given by equation,

$$\alpha = \frac{2\pi k}{\lambda} \quad \text{----------} \quad (1)$$

Figures 3(a) and 3(b) shows the variation of refractive index of 100 MeV $^{56}Fe^{9+}$ ion irradiated InP and GaP samples, respectively. The refractive index of the irradiated InP samples decreased slightly with increase in ion fluence. Whereas the refractive index of both irradiated GaP samples is almost same but less than the non-irradiated GaP. Figure 4(a) and 4(b) shows the variation of extinction coefficient of 100 MeV $^{56}Fe^{9+}$ ion irradiated InP and GaP samples, respectively. The extinction coefficient/absorption coefficient increased slightly with increase in ion fluence for irradiated InP. Whereas the extinction coefficient/absorption coefficient of both irradiated GaP samples is almost same but slightly more than the non-irradiated GaP. The decrease in refractive index and increase in absorption coefficient/extinction coefficient of irradiated samples may be due to presence of defects/disorder in the surface region.

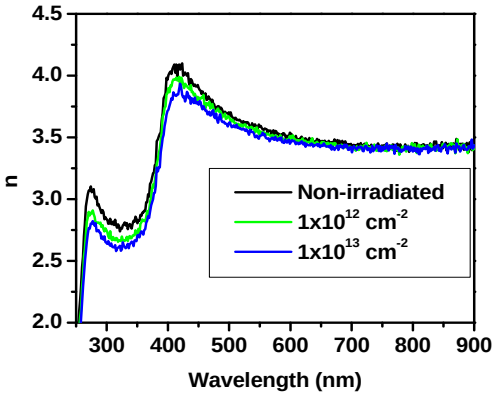


Figure 3(a). Refractive index of non-irradiated and 100 MeV Fe9+ ion irradiated InP.

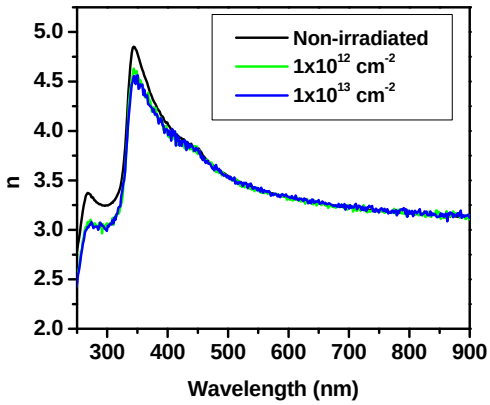


Figure 3(b). Refractive index of non-irradiated and 100 MeV Fe9+ ion irradiated GaP.

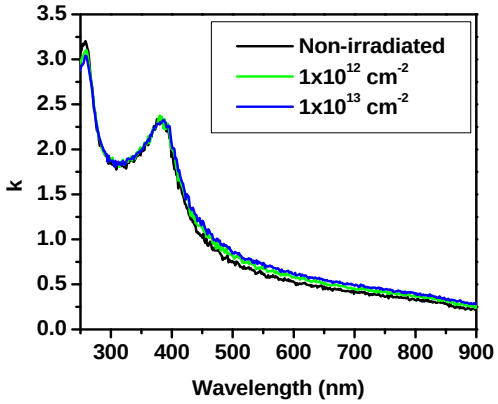


Figure 4(a). Extinction coefficient of non-irradiated and 100 MeV Fe9+ ion irradiated InP.

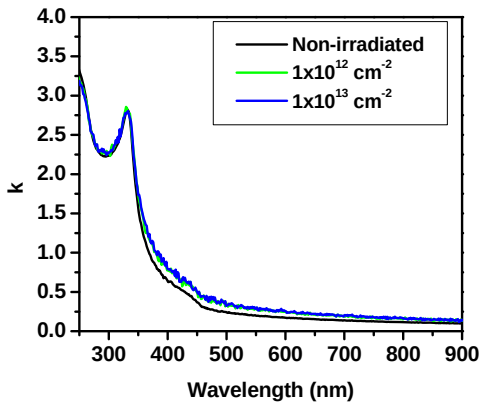


Figure 4(b). Extinction coefficient of non-irradiated and 100 MeV Fe^{9+} ion irradiated GaP.

As the nuclear energy loss of 100 MeV ^{56}Fe ions is two order of magnitude less than the electronic energy loss in InP (Fig.1(a)) and GaP (Fig.1(b)). Also the concentration of the vacancy created by 100 MeV ^{56}Fe ions in InP (Fig.2(a)) and GaP (Fig.2(b)) is very small. The increase in absorption coefficient may be associated with the point defects created in the surface region of irradiated InP and GaP after ion irradiation. The concentration of these defects is not sufficient and hence irradiated surfaces are almost similar to non-irradiated surface.

In order to study the irradiation induced defects in InP and GaP, ultraviolet-visible-near infrared (UV-VIS-NIR) transmittance spectra of non-irradiated and irradiated samples irradiated with 100 MeV $^{56}Fe^{9+}$ ions for ion fluences of 1 x 10^{12} and 1 x 10^{13} cm^{-2} were recorded in the spectral region 200 nm to 1600 nm. Figure 5(a) and 5(b) show the transmittance spectra of 100 MeV iron ion irradiated InP and GaP, respectivity. The transmission spectra shown in figures 5(a)-5(b) exhibits two effects: first, transmission intensity tends to decrease and second; absorption edge (minimum or zero transmission) shift towards the higher wavelength (red shift). This result may be due to swift heavy ion induce defects in the indium phosphide/gallium phosphide which absorbs incident light and reduces the transmission intensity. The red shift of absorption edge indicates the decrease in the optical band-bap energy of the solid.

To estimate the optical band gap (E_g) of InP, α^2 versus photon energy ($h\nu$) graphs (Figure 6(a)) and for GaP, $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) graphs (Figure 6(b)) of non-irradiated and sample irradiated for ion fluences 1 x 10^{12} cm^{-2} were plotted. The straight-line portion extrapolated to $\alpha^2 = 0$ or $(\alpha h\nu)^{1/2}=0$ gives the optical band gap of InP or GaP. The values of optical band gap of the sample irradiated for ion fluence 1 x 10^{12} was found to be 1.253 eV and 2.140 eV, respectively for InP and GaP. Whereas the corresponding estimates of non-irradiated InP and GaP was 1.281 and 2.20 eV, respectively.

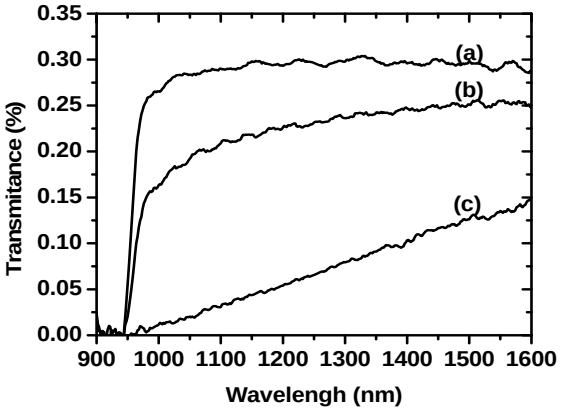


Figure 5(a). Variation of transmission as a function of wavelength of indium phosphide samples; (a) non-irradiated and irradiated with 100 MeV $^{56}Fe^{9+}$ ions for ion fluence of (b) 1 x 10^{12} and (c) 1 x 10^{13} cm^{-2}.

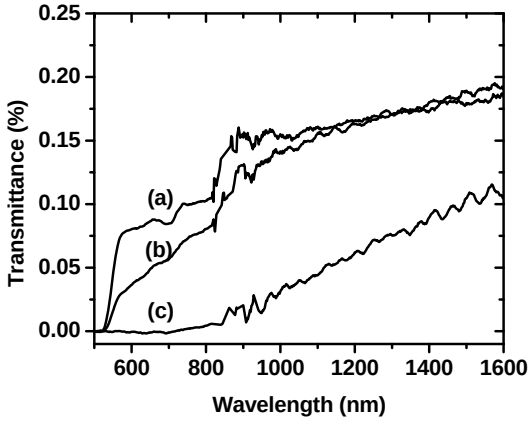


Figure 5(b). Variation of transmission as a function of wavelength of gallium phosphide samples; (a) non-irradiated and irradiated with 100 MeV $^{56}Fe^{9+}$ ions for ion fluence of (b) 1 x 10^{12} and (c) 1 x 10^{13} cm^{-2}.

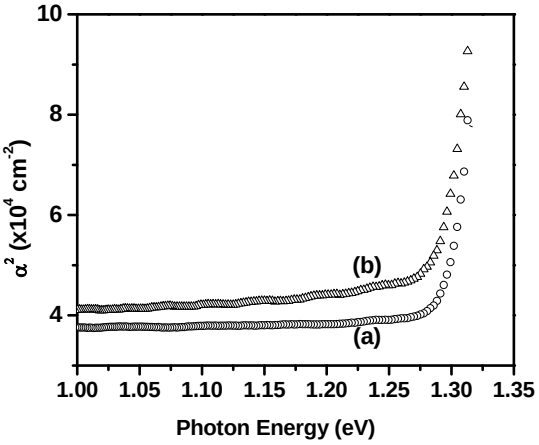


Figure 6(a). α^2 versus photon energy plots of (a) non-irradiated indium phosphide and sample irradiated with 100 MeV $^{56}Fe^{9+}$ ions for ion fluence of 1 x 10^{12} cm^{-2}.

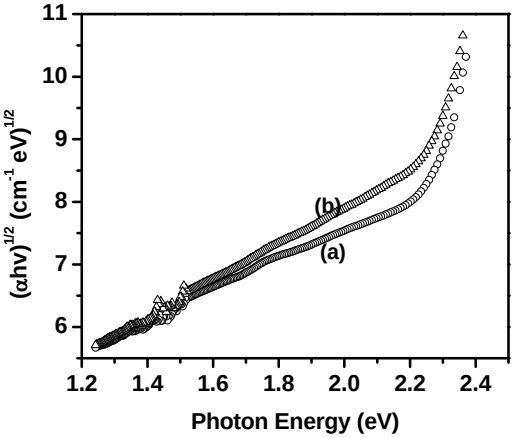
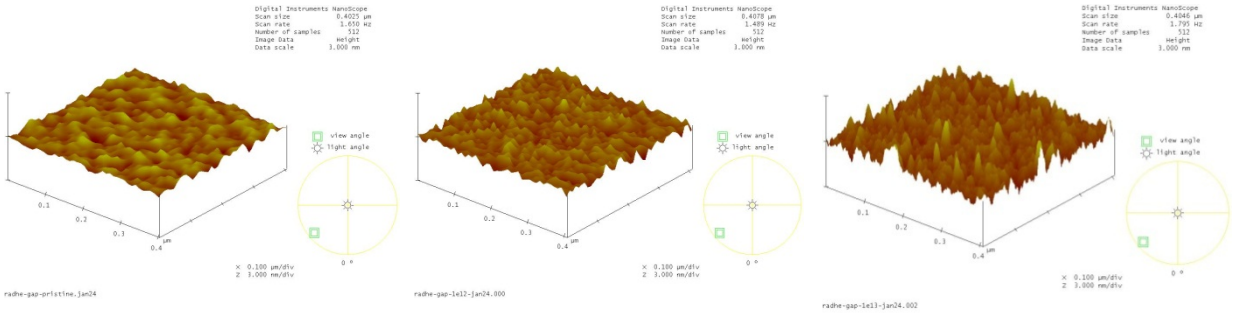


Figure 6(b). $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) plots of (a) non-irradiated gallium phosphide and sample irradiated with 100 MeV $^{56}Fe^{9+}$ ions for ion fluence of 1 x 10^{12} cm^{-2}.



(a) (b) (c)

Figure 7. Three-dimensional (400 nm x 400 nm) AFM micrographs of (a) non-irradiated gallium phosphide surfaces and irradiated with 100 MeV $^{56}Fe^{9+}$ ions for ion fluences of (b) 1 x 10^{12} cm^{-2} and (c) 1 x 10^{13} cm^{-2}.

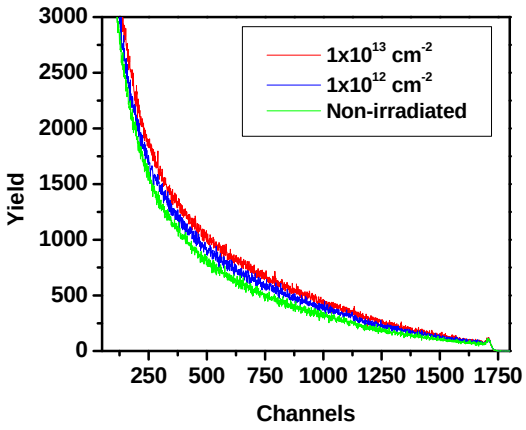


Figure 8(a). RBS/C spectra of InP irradiated with various fluences of 100 MeV $^{56}Fe^{9+}$ ions at room temperature.

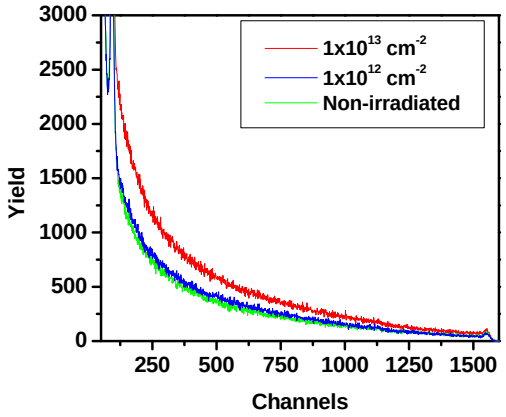


Figure 8(b). RBS/C spectra of GaP irradiated with various fluences of 100 MeV $^{56}Fe^{9+}$ ions at room temperature.

The modification in the surface morphology of InP and GaP single crystal have been studied after 100 MeV ^{56}Fe ion irradiation by Atomic Force Microscopy [9-10]. Figure 7 show the representative AFM images of 100 MeV $^{56}Fe^{9+}$ ion irradiated gallium Phosphide. AFM observations revealed the presence of nanosized structure on the surface of irradiated InP and GaP samples. Swift heavy ion during its passage through the material creates a cylindrical high temperature zone, which can even reach the molten state during temperature spike of the time duration of the order of pico second. The local temperature in the surface region may be enough to melt the lattice. The material within the cylindrical region may experience very high pressure and temperature. As a result stresses / strains are induced in the materials. These stresses will result in the flow of substrate matter out of plane of wafers and collected in heap anisotropically to form the hill type of features. The size (diameter) and density of defect clusters was found as a function of ion fluence. Root mean square (rms) surface roughnesses measured using the Nanoscope software supplied with the AFM instrument were found to increase with ion fluence. The

increase in the r.m.s. roughness is due to swift heavy ion induced mass transport phenomena through atomic displacements in the surface region [9-10].

Figure 8(a) and 8(b) shows the RBS/C spectra measured on InP and GaP respectively, after irradiation with 100 MeV $^{56}Fe^{9+}$ ions for ion fluence 1 x 10^{12} and 1 x 10^{13} cm^{-2}. The RBS spectrum was recorded using 2MeV He^{+} ions. The penetration depth of 2MeV He in InP and GaP is 6.36 µm and 6.57 µm, respectively. There for RBS give the information deep below the surface. The backscattered yield increases over the entire range with ion fluence. The increased yield values are very small in comparison with the non-irradiated sample. The increase in yield value with fluence indicates that the some amount of defects is present deep below the surface.

Conclusions

Single crystal InP and GaP have been irradiated by 100 MeV $^{56}Fe^{9+}$ ions for ion fluence 1 x 10^{12} and 1 x 10^{13} cm^{-2}. The optical properties in the surface region investigated by spectroscopy ellipsometry showed that the surface is almost similar to non-irradiated InP and GaP with some amount of defects present in the surface/near surface region. The optical band gap of irradiated InP and GaP has been reduced after ion irradiation due to the presence of defects/disorder deep in the material. The RBS study also reviled the presence of the defects deep in the irradiated material. Atomic force microscope study revealed the presence of nano-sized structure on the surface of the irradiated InP and GaP. The r.m.s surface roughness was found the increase with ion fluence due to mass transport phenomena through atomic displacements in the surface region.

References

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