CHAPTER 4

Low temperature material synthesis and ion beam mixing of In/Se bilayer systems using swift heavy ion irradiation
CHAPTER 4

Part A

Online interface mixing study using swift heavy ions: An attempt
Abstract

This part of the chapter summarises the attempt to study on-line/in-situ ion beam mixing between In/Se bilayer system using ‘Rutherford Backscattering Spectroscopy’ with the help of 40 MeV silicon ions. Deviating from conventional RBS using 3 MeV He ions, 40 MeV Si ions was used to study the mixing between In/Se bilayer system. On-line RBS study revealed the existence of threshold fluence required for mixing to take place between In and Se. Conventional RBS study carried out using 3 MeV He ions proved that mixing between In and Se takes place at a fluence of $1 \times 10^{13}$ ions/cm$^2$. 


4.1 Introduction

Rutherford backscattering spectroscopy (RBS) is one of the most useful tools to study the mixing between bilayer systems induced by low energy (of the order of few hundred keV) and high energy (greater than few tens of MeV) heavy ion irradiations [1]. It can also provide information about the composition of multi-elemental samples, thickness of thin films, depth-profile of elements and can also be used to identify unknown elements in the material [2]. In modern conventional RBS analysis, a collimated beam of energetic ions, usually He or H ions of energy 2-3 MeV, will be used to impinge on the sample at off normal incidence (incident angle less than 10 degree, to avoid channeling). The backscattered ions from the sample are usually detected with the help of particle detector (normally a Si surface barrier detector). The signal is further amplified, shaped and finally analysed using a multi-channel analyser, to obtain the RBS spectra. Main advantages of RBS are that it is fast, simple, easy and non-destructive. Major weaknesses of this technique are the following: this is not sensitive to lighter elements, has poor mass resolution for heavier elements and not able to provide information on the chemical state of the element. In order to overcome these difficulties several techniques were developed. By using non-Rutherford elastic scattering, we can increase sensitivity towards lighter elements such as C, N and O. In this technique, the energy of the probing ions was decreased so as to increase the scattering cross-section from the lighter elements. Resonant scattering was also employed to increase the scattering cross section, thereby enhancing the sensitivity of lighter elements. Cameron [3] and Mezey et al. [4] demonstrated investigation of O composition in thin oxide layers. In these cases, in addition to the coulombic force, nuclear force is also involved in the scattering. To improve mass resolution for heavier elements, heavier ions with higher energies were used as probe beam [5]. This technique improved the depth resolution also.

High energy heavy ions (swift heavy ions), which are having velocities
comparable to the innermost orbital electrons (~ 2.2x10^8 cm/sec), lose energy to the material in two ways, (i) electronic energy loss (dE/dx)_e, (ii) nuclear energy loss (dE/dx)_n. Electronic energy loss is a secondary process in which the projectile ions first impart their energy to the lattice electrons and this energy is dissipated to the lattice through electron-phonon interactions. But in the case of nuclear energy loss, the ions give energy directly to the atomic nuclei via elastic collisions. However for swift heavy ions, the nuclear energy is very much negligible as compared to the electronic energy loss. Swift heavy ions can create point defects [6], columnar defects, an amorphous track or a perturbed atomic distribution along its path [7] and even an interface mixing, if it is passing through a layered system [8, 9]. Swift heavy ions are now intensively used by material scientists for modifying optical, electrical and structural properties of materials [10, 11, 12]. It is also used for interface mixing [8, 9], novel phase formation [13] and for material characterizations such as ‘elastic recoil detection analysis (ERDA)’ [14]. Ion beam mixing using swift heavy ions was first demonstrated by Dufour et al. [15] in 1993. Since then, several studies have been carried out in different systems such as metal/metal [16, 17], metal/semiconductor [18, 15, 19], metal/insulator [20] and metal/semi-metal [21]. On-line mixing study using elastic recoil detection analysis (ERDA) with 230 MeV Au ions in CuO/glass interface was demonstrated by Avasthi et al. [14]. In the present study, on-line mixing between In/Se interface using backscattering spectroscopy was attempted with 40 MeV Si ions.

4.2 Experiment

Thin film of selenium with thickness ~ 150 nm (measured using stylus thickness profiler Dektak6) was first deposited on to a glass substrate, using chemical bath deposition technique [22], over which 56 nm of In was vacuum evaporated (resistive heating) from Mo boat at a pressure of 2x10^-5 mbar. Thickness of In was controlled using a quartz crystal monitor. These samples were then loaded in the ladder which is attached to a goniometer in ‘general purpose scattering
chamber (GPSC) at Inter University Accelerator Centre, New Delhi. A collimated beam of 40 MeV Si ions with 2 mm diameter was allowed to fall on the sample at an angle of 45° to the sample normal and the scattered ions were detected at an angle 90° to the backscattering geometry (Fig. 4.1). The scattered ions were analysed with ‘Si surface barrier’ detector located about 20 cm from the target [at solid angle 5.7 msr]. Energy resolution of the detector was 20 keV. Experiment was conducted at a pressure of $2 \times 10^{-6}$ mbar. System calibration was done using the backscattering signals from Si wafer and In, and found each channel corresponding to energy of 7.48 keV. The electrical pulses generated in the detector was amplified, shaped and finally analysed by a multi-channel analyzer (MCA). MCA is an electronic system which converts the electrical pulses to digital signals, sorts and displays the signal on the screen in the form of ‘counts’ versus ‘channel number’ scale. During the backscattering experiment, the beam current was kept constant at 12 nA.

![Figure 4.1: Schematic arrangement of backscattering geometry of He ions from the sample. $\theta$ is the backscattering angle.](image_url)
Backscattered ions were recorded for five different doses, ranging from $1 \times 10^{11}$ to $1 \times 10^{13}$ ions. In/Se bilayer system was also irradiated using 40 MeV Si ions with a fluence of $1 \times 10^{13}$ ions/cm$^2$ at room temperature over an area of 1 cm$^2$ (by using an electromagnetic scanner). X-ray diffraction measurements on pristine and irradiated samples were carried out by varying 2$\theta$ from 10° to 60° with Cu K$_\alpha$ radiation ($\lambda = 1.5405$ Å), employing Rigaku (D.Max.C) X-ray diffractometer. RBS measurements were done with the help of 3 MV Pelletron accelerator (Model - 9SDH2). 3 MeV He$^{2+}$ ions were used for RBS measurement, with an angle of incidence 10°. A silicon surface barrier detector, placed at 160° in back scattering geometry, detected the scattered ions. Detector resolution was 20 keV and solid angle was 1msr. RBS analysis was performed with GISA simulation [23].

### 4.3 Principle of Rutherford backscattering technique

RBS spectroscopy is a simple technique which analyses the energy of the backscattered ions from material and obtains information about various aspects of the sample. As the energetic projectile ion pass through the material, it looses energy along the path and is scattered back by collisions with the atoms in the material. The collisions between the projectile ions and the target atom can be described as elastic collisions between two isolated particles. The energy of the projectile after collision, $E$ can be expressed in terms of energy before collision $E_o$ in terms of kinematic factor $K$ as [24],

$$E = K \times E_o \quad (4.1)$$

where $K$ is expressed as,

$$K = \frac{\left[1 - ((M_1 / M_2) \sin \theta)^2 + \cos \theta \right]^2}{\left[1 - ((M_1 / M_2) \sin \theta)^2 \right]^{3/2}} \quad (4.2)$$

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where $M_1$ and $M_2$ are the masses of projectile and target atom respectively, and $\theta$ the scattering angle. At this angle the scattered ions are detected by a solid state detector that subtends a small solid angle $\Omega$. From the known values of $M_1$, $E_o$ and $\theta$ one could identify the unknown element in the material with mass $M_2$. The number of counts, $[A]$ registered by the detector is given as,

$$A = Q \cdot \Omega \cdot N \cdot t \cdot \sigma(E_o, \theta)$$

(4.3)

where ‘$Q$’ is the number of ions incident on the sample, ‘$N$’ the density of the atoms in the material, ‘$t$’ the thickness of the sample and $\sigma(E_o, \theta)$ the scattering cross section for scattering into a solid angle $\Omega$ at a scattering angle $\theta$. It is given as,

$$\sigma(E_o, \theta) = \left( \frac{Z_1 Z_2 e^2}{4 E_o} \right)^2 \frac{4}{\sin^2 \theta} \cdot K$$

(4.4)

where $Z_1$ and $Z_2$ are the atomic numbers of the projectile ion and the target atom respectively. The equation 4.3 shows that from the known values of $Z_1$, $Z_2$, $\Omega$, $E_o$, $\theta$ and numbers of incident ($Q$) and detected ions ($A$), we can get the density ($N \cdot t$) of the material. From this, we can measure thickness of the material. If the material is a compound with elements A and B in the atomic ratio $A_m B_n$, the backscattering spectra would record two signals corresponding to the heavy atom A and the light atom B, as sketched in figure 4.2. Using equation 4.3, we can find the composition of the compound $A_m B_n$ as,

$$m = \left[ \frac{A_A}{\sigma_A(E_o, \theta)} \right] \frac{A_B}{\sigma_B(E_o, \theta)}$$

(4.5)
where $A_A$ and $A_B$ are the area under the curves corresponding to element A and B respectively and $\sigma_A(E_o, \theta)$, $\sigma_B(E_o, \theta)$ are the scattering cross-section of elements A and B respectively, which can be calculated using equation 4.4.

As the ion passes through the material, it loses energy by scattering. Hence the energy of the scattered ion depends on the kinematic factor as well as on the depth from the sample surface where the scattering occurs. The projectile ions lose energy to reach a particular depth and after scattering, it again loses energy to come out of the sample. Thus backscattered ions contain the information about the depth also. Figure 4.2 shows the schematic picture of backscattering spectra of ions of mass $M_1$ from a compound thin film containing two different masses $M_2$ and $M_3$, deposited on a low-mass ($M_4$) elemental substrate ($M_2 > M_3 > M_4$). Energies of the backscattered ions from various depths and various atoms are marked by arrows.

![Schematic picture of RBS spectrum from a bilayer system with mass M2 and M3 on a substrate with mass M4 (M2 > M3 > M4), using He ions of energy Eo with mass M1.](image)

**Figure 4.2.** Schematic picture of RBS spectrum from a bilayer system with mass $M_2$ and $M_3$ on a substrate with mass $M_4$ ($M_2 > M_3 > M_4$), using He ions of energy $E_o$ with mass $M_1$. 

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4.4 Discussion

Ion beam mixing (IBM) is one of the tools for synthesis of compounds using low energy ions [25] and the compound phases, in general, are achievable at relatively lower temperature in the process of ion beam mixing [18]. Advantage of IBM using high energy (≥ 1 MeV/amu) heavy ions (known as swift heavy ions -SHI) over low energy ion mixing is that, the fluence required for mixing is about 10^{13} ions/cm^2 to 10^{14} ions/cm^2, which is two to three orders of magnitude smaller, compared to low energy ion induced mixing [18]. IBM by high energy heavy ions was first demonstrated by Dufour et al. [15] and after that there has been intense research, to find the cause of mixing induced by swift heavy ions in different systems such as metal/metal, metal/Semiconductor, metal/insulator interfaces. Different techniques such as ERDA [14] X-ray reflectivity [20, 26], X-ray photoelectron spectroscopy (XPS) [21], cross sectional transmission electron microscopy (XTEM) [9], cross sectional scanning electron microscopy (XSEM) [27], GXRD [28, 29], Mössbauer spectroscopy [30], Auger electron spectroscopy (AES) [32] and Rutherford backscattering spectroscopy were used to detect the interface mixing in the specimen. Among these, most commonly used technique is RBS because of its simplicity in analysis and nondestructive nature. It can also give depth-wise information. The techniques mentioned above such as XPS and AES, employ ion sputtering to remove the surface layer to get the depth-wise information, whereas XTEM needs sample preparation on grids and XSEM needs a metal coating (Au) over the sample, destroying the sample.

To study IBM by conventional RBS measurements, we have to again load the samples in a scattering chamber. The pressure inside the chamber is of the order of 1x10^{-6} mbar., created by pumping with the help of a turbo molecular pump. Again, we have to get He ions of energy 2-3 MeV from a particle accelerator. All these equipments are very expensive and the experiment consumes time also. If the RBS measurements can be done during the irradiation experiment itself using SHI, one can avoid using the ‘million-dollar’ experimental set-up required.
for conventional RBS. This can save the precious time too. For online RBS measurements, we require few additional geometrical arrangements of detectors and analyzing equipments.

In the present study, the samples were analysed using online RBS with 40 MeV Si ions. Geometries of angle of incidence (45°) of the ion beam and the scattering angle (90°) are displayed in the schematic picture (Fig. 4.1). In/Se bilayer was irradiated using 40 MeV Si ions of different doses, ranging from $1 \times 10^{11}$ ions to $1 \times 10^{13}$ ions and backscattered ions were detected using a ‘Si surface barrier detector’ and the backscattering spectra were recorded. Figure 4.3 shows the backscattering (BS) spectra of In/Se system irradiated with different doses of $3 \times 10^{12}$ to $6 \times 10^{12}$ ions. We could not find any mixing between In and Se until a dose of $6 \times 10^{12}$ ions was used as evidence from the spectra.

![Figure 4.3: Rutherford backscattering spectra of In/Se bilayer system recorded using 40 MeV Si ions with a dose of $3 \times 10^{12}$ and $6 \times 10^{12}$ ions.](image)

Figure 4.4 shows the result of BS analysis with doses $1 \times 10^{11}$ and $1 \times 10^{13}$ ions. In
this, one could find mixing between In and Se layers. We can observe from the BS spectra recorded with $1 \times 10^{13}$ ions that, the counts of In and Se peaks reduced and Se peak shifted towards higher energy side or higher channel number. This represents the mixing between In and Se layers. This study also revealed that the threshold fluence required for mixing to take place between In and Se was around $1 \times 10^{13}$ ions/cm$^2$ for 40 MeV Si ions.

Figure 4.4: Rutherford backscattering spectra of In/Se bilayer system recorded using 40 MeV Si ions with a dose of $1 \times 10^{11}$ and $1 \times 10^{13}$ ions.

Figure 4.5 shows the RBS spectra of pristine and irradiated In/Se system (fluence $1 \times 10^{13}$ ions/cm$^2$) recorded by conventional RBS using He ions of energy 3 MeV. The spectra revealed the mixing between In and Se layers. We can observe an increase in full width at half maximum (FWHM) of both the Se and In peaks on irradiation with $1 \times 10^{13}$ ions/cm$^2$. FWHM of Se and In were increased to 17 keV and 27 keV from 16 keV and 20 keV respectively. Also a
shift towards the higher energy edge [or channel number] of Se peak and a shift
towards the low energy edge or channel number by the In peak clearly shows the
mixing between In and Se layers.

![Rutherford backscattering spectra](image)

**Figure 4.5:** Rutherford backscattering spectra of unirradiated and irradiated (using 40 MeV Si ions of fluence $1 \times 10^{13}$ ions/cm$^2$) In/Se bilayer system recorded using 3 MeV He$^{2+}$ ions.

From the RBS spectra (Fig. 4.4 and Fig. 4.5) recorded using 40 MeV Si ions and 3 MeV He ions respectively, one could observe that the mass resolution of the spectra recorded using 40 MeV Si ions was higher than that with 3 MeV He ions. In the case of spectra recorded using 3 MeV He ions, the peaks of In and Se were separated only by 60 channels (one channel = 2.94 keV); but with 40 MeV Si ions, the peaks were separated by 845 channels (one channel = 7.48 keV). This shows the resolution is greater for the spectra, recorded using 40 MeV Si ions. When one uses heavier ions with higher energies, there is enhancement of the scattering cross section, leading to higher mass resolution [33]. The geometry of angle of incidence of probing ions and the scattering
angle plays a good role in enhancing the depth resolution. Here we have selected an angle of incidence as 45° and scattering angle 90° (Fig. 4.1). Increasing the angle of incidence increases the total path length that a particle traverses in the sample to reach the detector after scattering. The increase in total path length can greatly improve the effective depth resolution.

Figure 4.6: XRD pattern of (a) un-irradiated and (b) In/Se system irradiated with 40 MeV Si ions of fluence 1.05x10^{13} ions/cm².

Figure 4.6 (a) and (b) show the X-ray diffraction (XRD) pattern of In/Se system before and after irradiation. We can only observe the peak, corresponding to Indium, having reflection at 2θ = 33.65 from (112) plane. On irradiation with 40 MeV Si ions, an increase in peak intensity and reduction of FWHM of the In peak was observed from 0.28 to 0.25. It is to be noted that no compound formation was observed on irradiation even though we have observed mixing
between In and Se layers from RBS measurements.

Ion beam mixing in the electronic energy regime can be explained using two different models, namely (i) Coulomb-explosion model [35, 36, 37] and (ii) thermal spike model [37, 38, 39]. According to Coulomb-explosion model, as swift heavy ions passes through the material, it losses energy to the electrons in the material, by exciting the electrons and ionizing the atom. This leads to ionized cylindrical zone along the path of the ions, with a strong electronic deficiency in the centre. This creates electrostatic repulsion between the positively charged atoms in the centre resulting in an explosion-like atomic motion perpendicular to the path of ions [40]. This can lead to the formation of core with reduced atomic density, surrounded by a densified shell. This is an unstable state and the atoms try to regain or collapse back to the central part. But in the absence of recrystallisation process, there will be a highly perturbed or even amorphous latent nuclear track of few nanometers in diameter. In the case of metals and semi-metals, the conduction electrons smear out the excitation and ionization of atoms and in fact, possibility of Coulomb-explosion can be ruled out in the case of metals. Thus the ‘thermal spike model’ is used to explain IBM in metals and semiconductors [41, 42].

According to ‘thermal spike model’ the energy transferred by the SHI to the lattice electrons will be imparted to the lattice via electron-phonon coupling. This results in the heating of the lattice and generation of ‘Gaussian like’ temperature profile around the ions path. If the electronic energy deposited by the SHI is sufficiently high, the temperature can rise above the melting point of the material and cylindrical molten track of few nanometers can be formed. After few tens of picoseconds, rapid quenching of the melt to ambient temperature occurs. Mixing between bilayer can occur by inter-diffusion through the molten track, if the interface of the two materials in contact melted during irradiation. It was proposed that the essential condition for the mixing to take place through the interface is that, the interface of the two layers should be in a
transient molten state [43, 7].

40 MeV Si ions lose about 5.42 keV/nm and 4.13 keV/nm as electronic energy loss in In and Se respectively [calculated using TRIM] [44]. We have observed that the threshold fluence for the mixing to take place between In/Se is around $1 \times 10^{13}$ ions/cm$^2$. This can be explained in the following way: if the electronic energy deposited by SHI is above the threshold energy required to make the material molten, it creates molten tracks of few nanometer diameters (track formation occurs only if the material dependent threshold electronic energy is exceeded). As the fluence increases the track density or number of tracks increase, and overlapping of these tracks results in a uniform mixing at the interface [19].

4.5 Conclusion

Deviating from conventional RBS where one uses He ions of energy 3 MeV, we made an attempt to study IBM using 40 MeV Si ions for recording the backscattering spectra. By online RBS measurements using 40 MeV Si ions, threshold fluence for mixing to take place between In/Se bilayer systems was found out. Use of high energy heavy ions provided better mass and depth resolution. Online IBM study enabled us to get the information about the mixing very quickly and hence we could avoid the entire experimental techniques used to study the IBM induced by swift heavy ions. Threshold fluence for mixing to take place between In/Se bilayer systems was found to be $1 \times 10^{13}$ ions/cm$^2$ for 40 MeV Si ions. Conventional RBS spectra recorded using 3 MeV He ions proved the mixing between In/Se bilayer.
CHAPTER 4

Part B

Single-phase InSe formation using SHI irradiation and low temperature annealing
Chapter 4
Abstract

This part summarises the formation of single phase indium selenide at lower annealing temperature induced by 40 MeV Si ion irradiation. In/Se bilayer system was irradiated using 40 MeV Si ions and annealed at different temperatures. In the case of irradiated sample single phase indium selenide formation occurs at much lower annealing temperature as compared to the un-irradiated sample. The low temperature compound formation is explained as the inter mixing of the atoms through the damages created during SHI irradiation.
4.6 Introduction

Indium selenide (InSe) is a III-VI compound semiconductor, having direct band gap of 1.3 eV, which has been widely studied recently, due to its potential application as an absorber layer in photovoltaic devices [45, 46, 47]. This is mainly because of its high absorption coefficient as well as optimum energy band gap, suitable for solar energy conversion [48]. Various methods such as electrodeposition [49], flash evaporation [50], sequential evaporation [51] and co-evaporation of In and Se [52] are used to prepare thin films of this material. Usually it is difficult to produce single-phase indium selenide due to the co-existence of different phases together [53]. This difficulty is evident from the narrowness of the formation range of InSe in the phase diagram of the In-Se system [52] and there are different stoichiometric compounds such as InSe, In₄Se₃, In₆Se₇, In₂Se₃ [52, 54, 55, 56] for these two elements.

Indium monoselenide (InSe) is a layered compound [57]. The absence of dangling bonds on the surface layer (001) makes it a potential material for heterojunction devices [54, 58]. Band gap of InSe is 1.3eV, which again makes it an attractive material for solar energy conversion as an absorber layer in solar cells.

It was shown by us that single phase indium selenide films is formed only at 400°C [59]. In general, large number of studies was carried out to reduce the synthesis temperature of compound semiconductors. It is because; the substrates that are used as the backing should have the capability of withstanding high synthesis temperatures. This also restricts their application to device fabrication. Ion beam mixing (IBM) is one of the techniques by which one could obtain compound phases at relatively lower temperature and/or even at room temperature without any post annealing treatment. Novel phases of compounds with required properties can also obtained using IBM.
SHI transfers energy to the target, mostly by electronic excitation, (electronic energy loss, $S_e$) causing point defects [60], columnar defects or a perturbed atomic distribution [7]. In this case, the energy lost by the incident ions due to nuclear energy loss ($S_n$) is usually negligible. Above a certain threshold of $S_e$, electronic excitations induce atomic displacements in majority of materials. This can lead to mixing at the interface, if it is passing through a layered system [8, 61]. SHI irradiation can produce defects at the interface [62]. Thereafter, rearrangement of the interfacial atoms and/or short-range diffusion can cause mixing of the two components. In some cases, the latter is aided by post irradiation annealing [63, 64], during which nucleation and phase growth can occur. In the present work, the compound formation in irradiated and un-irradiated In/Se bilayer system, annealed at different temperatures, were investigated using X-ray diffraction (XRD) and optical absorption techniques.

4.7 Experiment

Thin films of selenium with thickness 150 nm were deposited on glass substrates using chemical bath deposition technique [22], over which 40 nm of In was deposited by resistive heating [pressure $\approx 2 \times 10^{-5}$ mbar], with Mo boat as the heating source. Thickness of the film was measured using stylus thickness profiler. In/Se system was irradiated using 40MeV Si ions in an area of 1cm$^2$ with a fluence of $1 \times 10^{13}$ ions/cm$^2$ using the 15UD Pelletron accelerator. An electromagnetic scanner was used to scan the ion beam over this area. Range of 40MeV Si ions was such that these got deposited deep into the substrate, at a depth of more than 10$\mu$m. The electronic energy loss ($dE/dx$)$_e$, for In and Se were 5.42 keV/\(\mu\)m and 4.13 keV/\(\mu\)m respectively for 40MeV Si ions, calculated using TRIM [44]. Irradiated samples were annealed at 50 °C and 100 °C while the unirradiated samples were annealed from 50 °C to 400 °C for one hour. Both annealings were at a pressure of $2 \times 10^{-5}$ mbar. Before annealing the unirradiated samples at higher temperatures ($\geq 100$ °C), these were kept at 50 °C (at a pressure of $2 \times 10^{-5}$ mbar.) for 1 hour. The irradiated samples, annealed at 50 °C
and 100 °C, were named as I IS50 and I IS100 and unirradiated samples annealed at 50 °C, 100 °C, 300 °C and 400 °C were named as U IS50, U IS100, U IS300 and U IS400 respectively. The RBS spectra of unirradiated and irradiated samples were recorded using 3 MeV He\(^{3+}\) ions. 3 MV Pelletron accelerator at Institute of Physics, Bhubaneswar, India was used for generating the 3 MeV He ions. XRD studies were done in the range 2θ = 10° to 60°, using Cu K\(_{\alpha}\) (\(\lambda = 1.5405\) Å) radiation employing Rigaku (D.Max.C) X-ray diffractometer. Optical band gaps were measured from absorption spectra recorded in the range 400nm to 900nm by employing UV-VIS-NIR spectrophotometer (Model: Hitachi U-3410).

### 4.8 Result and discussion

#### 4.8.1 Rutherford backscattering analysis

Figure 4.7 shows the RBS spectra of pristine (unirradiated) and irradiated In/Se bilayer system (irradiated with 40 MeV Si ions of fluence \(1 \times 10^{13}\) ions/cm\(^2\)). The peak at higher channel number corresponds to indium and that of lower channel number corresponds to the selenium in the bilayer system. One could see that on irradiation with 40 MeV Si ions of fluence \(1 \times 10^{13}\) ions/cm\(^2\), the lower channel number edge of the indium peak shifted towards left (towards lower channel number) and that of higher channel number edge of selenium peak shifted towards right (towards higher channel number). This is due to the migration or diffusion of indium and selenium atoms across the interface during ion beam irradiation.

On diffusion of In atoms into Se layer, the energy of the ions backscattered from In atoms from the Se layer would be less (channel number is a measure of energy of backscattered ions). Also, the energy of the backscattered ions from In layer will be higher with respect to that from the Se layer. This is the reason for the shift of lower channel number edge of In peak to lower channel number and
higher channel number edge of Se peak to higher channel number. Thus we have observed ion beam mixing between In and Se layers. Explanation for mixing between In and Se layer was discussed in detail in the previous section 4.2.4.

**Figure 4.7:** RBS spectra of un-irradiated and In/Se system irradiated with 40 MeV Si ions of fluence $1 \times 10^{13}$ ions/cm$^2$.

### 4.8.2 X-ray diffraction analysis

Figure 4.8(a) and (b) show the XRD pattern of In/Se bilayer system before and after irradiation with 40 MeV Si ions of fluence $1 \times 10^{13}$ ions/cm$^2$. The XRD peak at $2\theta=33.59$ was corresponding to the elemental indium in the In/Se bilayer (JCPDS number: 05-0653). Even though we have observed mixing between In and Se layer at a fluence of $1 \times 10^{13}$ ions/cm$^2$ (Fig. 4.7), no compound formation was observed from the XRD analysis in as irradiated system (Fig. 4.7(b)). One could observe only a decrease in FWHM of In peak at $2\theta=33.59$ degree, from
0.28 to 0.25. This might be due to the clustering of In on the surface due to 40 MeV Si ion irradiation.

Figure 4.8: XRD pattern of In/Se system (a) pristine (b) irradiated with 40 MeV Si ions of fluence $1 \times 10^{13}$ ions/cm$^2$ (c) irradiated sample annealed at 50$^\circ$C for 1hr. (d) unirradiated sample annealed at 50$^\circ$C for 1hr. (e) irradiated sample annealed at 100$^\circ$C for 1hr. and (f) un-irradiated sample annealed at 100$^\circ$C for 1hr. (g) 300$^\circ$C (h) 400$^\circ$C respectively.

No compound formation occurred in as-irradiated In/Se system (Fig. 4.8(b)). Annealing the irradiated sample at 50 $^\circ$C for one hour resulted in the formation
of In$_2$Se$_3$ and InSe phases, resulting in the peaks at $2\theta=29.39$ and 21.27 degree respectively (Fig. 4.8(c)). Moreover, the XRD results indicated that pure indium phase was very much reduced and this might be probably due to the good mixing taking place in irradiated annealed sample. In the case of U IS50, indium selenide formed with less vigor and there was only In$_2$Se$_3$ phase. From XRD pattern (Fig. 4.8(d)) it was also clear that there was large amount of unreacted In in U IS50. Annealing the sample I IS50 again at 100°C for one hour, resulted in formation of InSe only having orientation along (006) with less crystallinity (Fig. 4.8(e)). It was very clear that In$_2$Se$_3$ phase was almost fully lost after second annealing. In the case of U IS100, still there was mixed phase of In$_2$Se$_3$ and InSe (Fig. 4.8(f)).

Average grain size of the samples was calculated using Debye Scherrer’s formula $d = (0.9 \lambda / \beta \cos \theta)$ [65] (See section 1.10.2). Average grain size of I IS100 was ~11nm ($2\theta = 21.35$, FWHM = 0.727) and that of U IS100 was 20nm ($2\theta = 30.54$). We could see that in U IS300 (Fig. 4.8(g)) both InSe and In$_2$Se$_3$ existed and in U IS400 (Fig.4.8 (h)) there was only $\gamma$-In$_2$Se$_3$, with preferential orientation along (006) plane.

For irradiated sample, we obtained indium selenide at lower temperature compared to the unirradiated sample. This might be due to the enhancement in mixing. The defects (or atomic displacements which build up on either side of the interface) generated due to SHI irradiation were largely immobile. When sufficient thermal energy was supplied to the system, the atomic mobility through the defects, and across the interface enhanced [18, 62]. Even though we were getting indium selenide as a result of annealing at 100°C in unirradiated system, it was multi-phased. Even after annealing at 300°C both InSe and In$_2$Se$_3$ existed (Fig. 4.8(g)). Single phase In$_2$Se$_3$ was obtained only after 400°C annealing (Fig. 4.8(h)). Thus it was observed that annealing at 400°C was required to eliminate InSe phase in un-irradiated system.
4.8.3 Optical absorption study

Optical absorption spectra were recorded in the wavelength range 400-900 nm. In the case of U IS400 and I IS100, there was only one absorption edge. But for all other samples, in addition to the strong absorption in the range 700-850 nm, there was another absorption in the range 500-600 nm. This might be due to the existence or presence of multi-phases of indium selenide in the film. XRD analysis proved the presence of InSe phase in the unirradiated samples prepared up to an annealing temperature of 300 °C.

According to the theory of optical interband absorption in solids, at the absorption edge, the absorption coefficient $[\alpha]$ varies with the photon energy $h\nu$ and this is governed by the expression [66] $a h\nu = A (h\nu - E_g)^n$, where $A$ is a constant and $E_g$ is the optical energy gap and $n$ is an index with value $\frac{1}{2}$ for the direct and 2 for in-direct allowed transitions. Figure 4.9 depicts the $(a h\nu)^2$ versus $h\nu$ graph of I IS100 and U IS100, whereas figure 6.10 shows that of U IS300 and U IS400 respectively. For U IS100 ($E_g = 1.61$ eV and $1.85$ eV) and U IS300 ($E_g = 1.69$ eV and $2.04$ eV) we could observe two band gaps corresponding to the mixed phases existing in those samples. Of these, the lower value was that of InSe while higher value was that of In$_2$Se$_3$. But in the case of U IS400, there was only one absorption edge corresponding to $E_g = 2.48$ eV. However irradiated sample exhibited single absorption edge ($E_g = 1.55$ eV) just after annealing at 100 °C, which proved that the indium selenide formed with only one phase (InSe) in the case of irradiated system. X-ray diffraction study also showed only the presence of InSe phase (Fig. 4.8 (e)). Thus in the case of irradiated system, only an annealing at the temperature of 100 °C was required to obtain single-phase InSe film. This proved that SHI irradiation was assisting the formation of single phase InSe at lower annealing temperature. From figure 4.9 and figure 4.10, it was clear that for multi-phased film, there were two band gaps and for single phase film, there was only one band gap.
Optical band gap of InSe film was 1.3eV [52], but in I IS100 band gap is 1.55eV. This might be due to the smaller grain size of the film. Because of the smaller grain size (~11nm) of the film, effective band gap may be larger than the
real value due to ‘quantum size effect’ [67]. The average crystallite size can be estimated using the following equation [67].

\[
E_{gn} = \left[ E_{gb}^2 + \frac{2\hbar^2 E_{gb} (\pi / R)^2}{m^*} \right]^{1/2}
\]

Where \( E_{gn} \) and \( E_{gb} \) are the nanocrystalline and bulk semiconductor band gap, \( R \) is the particle radius and \( m^* (= 0.13m_o) \) the effective electron mass in InSe (\( m_o \) is the electronic rest mass) [68]. The average crystalline size calculated using this expression was 9.4 nm, which was in agreement with the experimental value (11nm). Another interesting observation was the phase transition of indium selenide from \( \text{In}_2\text{Se}_3 \) (hexagonal) to InSe (rhombohedral), taking place due to annealing at 100°C in the irradiated sample.

4.9 Conclusion

Single phase indium selenide can be obtained at low temperature, using ion beam mixing followed by vacuum annealing at 100°C, whereas in the un-irradiated system, single phase film was obtained only through annealing at 400°C for one hour. In/Se bilayer system irradiated using 40 MeV Si ions showed binary compound formation at lower temperature in comparison with the unirradiated sample. Again a phase transition was observed from \( \text{In}_2\text{Se}_3 \) (hexagonal) to InSe (rhombohedral) in the irradiated sample, annealed at 100°C. Swift heavy ion irradiation resulted in better atomic mixing across the interface, leading to compound formation at lower temperature and phase transition. Swift heavy ion irradiation on In/Se bilayer system followed by annealing favours InSe phase.
CHAPTER 4

Part C

Ion beam mixing in In/Se bilayer system at different electronic energy regime
Chapter 4
Abstract

This part of the chapter elucidates the effects of inter-layer mixing between In/Se bilayer system at different electronic energy regimes. The irradiation study indicated the dependence of threshold fluence and energy of swift heavy ions required for interlayer mixing to take place between In/Se bilayer systems. Threshold fluence for mixing to take place between In/Se bilayer system was found out for 100 MeV Ag, 80 MeV Ni and 90 MeV Si ions. Optical absorption study depicted that the band gap of indium selenide can be tuned/ varied with the help of swift heavy ion irradiation followed by 100°C annealing.
4.10 Introduction

Ion beam mixing (IBM) is one of the tools used for synthesis of compound semiconductors, silicides, metal alloys at relatively low temperature [13, 69, 70, 71]. Using IBM novel phases of materials can be attained with required properties [72-76]. IBM with low energy ion beams (with few hundreds of keV energy) has been widely studied and used to form both equilibrium and metastable phases [77-79]. The ion beam, with this energy range loses energy of the order of keV/nucleon, to the target material through nuclear interaction with the target material (elastic collision). The atomic transport mechanism at the interface by low energy ion beams (few hundred keV energy) is explained as ‘collision cascades’ formed at the interface due to the atomic migration across the interface as a result of elastic collisions between projectile ions and target atoms [80, 81]. When the energy transferred to the target atoms exceed the displacement threshold of 20-50 eV, the atoms are pushed from their lattice positions and may collide with other target atoms [82]. In this manner a recoil cascade is initiated where thousands of atoms are relocated by a single ion [83]. If the recoil cascade overlaps with the interface of a layered system, this should result in atomic mixing in the vicinity of interface [84]. Fluence of the order of 1x10^{17} ions/cm^2 was required to obtain this type of mixing using low energy ions.

SHI’s were used extensively for material modification, material synthesis, metal silicides and IBM [13, 28, 62]. The advantage of using high energy heavy ions which lose energy to the target material of the order of few MeV/nucleon is that it causes mixing with relatively low fluence (1x10^{13} ions/cm^2), i.e. 2-3 orders less than that of low energy ions [15, 26, 30]. In this case the energy loss is predominantly by inelastic collision with the target material, i.e. the energy loss by nuclear energy loss (by elastic collision, few eV/nm) is very negligible as compared to that of electronic energy loss, which is of the order of few tens of keV/nm. In this case, the mixing is explained using ‘thermal spike model’
(discussed in section 4.2.4), in which the diffusion of atoms takes place at the interface through the molten interface. Essential condition for mixing to take place between the interfaces is that the two materials forming the interface should be in molten state, induced by SHI irradiation. But later it was proposed that if one of the materials got melted due to sudden rise of temperature induced by the dissipation of energy by SHI [85], to attain equilibrium, the molten material transfers its heat to the material in contact. If the heat transferred by the material is higher than the melting point of the material making the interface, the material in contact will also melt and mixing occurs though this molten phase.

### 4.11 Experiment

In/Se bilayer systems were deposited over glass substrate. Thickness of Se was 150 nm and that of In was 40 nm. These samples were irradiated using 90 MeV Si, 80 MeV Ni and 100 MeV Ag ions with fluences ranging from $1 \times 10^{12}$ to $1 \times 10^{14}$ ions/cm$^2$. Irradiation was done over an area of 1 cm$^2$, with the help of an electromagnetic scanner, which scanned the ion beam of 1 mm diameter. Stable current of 4 nA, 9 nA and 4 nA were obtained from 15UD Pelletron accelerator (at IUAC, New Delhi) for 90 MeV Si, 80 MeV Ni and 100 MeV Ag ions respectively. RBS analysis was performed on the irradiated sample using 3 MeV He$^3$ ions. For generating 3 MeV He ions, 3 MV Pelletron accelerator at Institute of Physics, Bhubaneswar, was used. Si surface barrier detector of 20 keV resolutions, kept at a scattering angle 170°, detected the backscattered ions. Angle of incidence was kept at 10° to avoid channeling. The surface morphology of the samples was studied with a ‘Veeco Digital Nanoscope IIIa SPM’. X-ray diffraction study was done to detect compound formation. Optical absorption study was done to determine the optical band gap of the samples.
4.12 Results and Discussion:

4.12.1 Rutherford backscattering analysis

(a) Irradiation using 100 MeV Ag ions

Figure 4.11(a) shows the RBS spectra of un-irradiated and irradiated In/Se bilayer system with a 100 MeV Ag ions of fluence $1 \times 10^{12}$ ions/cm$^2$. We can observe a shift in the Se peak to lower channel number. But the lower channel number edge of the In peak does not show any shift. The full width at half maximum of both Se and In peak also does not show any increase. Hence one could not find any mixing between the bilayer systems. But, as the fluence increased to $6 \times 10^{12}$ ions/cm$^2$ one could see the mixing between In and Se [Fig. 4.11(b)]. The lower channel number edge of the In peak (marked A), shifted towards still lower channel side. This proved the mixing between In and Se layers starting at a fluence of $6 \times 10^{12}$ ions/cm$^2$. As the fluence increased to $1 \times 10^{13}$ ions/cm$^2$, mixing between In and Se layers also increased further [Fig. 4.11(c)]. For 100 MeV Ag ions, the electronic energy loss is 17.75 keV/nm and 13.32 keV/nm in In and Se respectively (calculated using TRIM code 1995). From this study, we could observe that the threshold fluence for mixing to take place between In and Se layers is around $6 \times 10^{12}$ ions/cm$^2$. Beyond this fluence, the mixing increased with increase in ion fluence.
Figure 4.11: RBS spectra of un-irradiated and irradiated In/Se systems, with different fluences of 100 MeV Ag ions, (a) 1x10^{12} (b) 6x10^{12} and (c) 1x10^{13} ions/cm^2.

(b) Irradiation using 80 MeV Ni ions:

In the case of irradiation using 80 MeV Ni, the electronic energy loss was 12.03 keV/nm and 9.15 keV/nm on In and Se layers respectively (calculated using TRIM code 1995). Hence the mixing between the bilayer was expected to take place at higher fluence, since more ions were required for the overlapping of molten tracks. This ultimately resulted in uniform mixing at the interface [19]. Fluence ranging from 1x10^{12} ions/cm^2 to 1x10^{14} ions/cm^2 was used for irradiation using 80 MeV Ni ions. RBS study revealed that there was no mixing between the In/Se bilayer system up to a fluence of 6x10^{12} ions/cm^2. As the
fluence increased to $1\times10^{13}$ ions/cm$^2$, mixing between In and Se layers was observed (Fig. 4.12). Beyond this fluence, the mixing increased with increase in ion fluence (Fig. 4.12). This proved that the threshold fluence for mixing to take place with 80 MeV Ni was around $1\times10^{13}$ ions/cm$^2$. In comparison with the case of 100 MeV Ag ions, an additional fluence of the order of $\sim 4\times10^{12}$ was required to get mixing between In and Se, in the case of 80 MeV Ni ions.

![RBS spectra of un-irradiated (pristine) and irradiated In/Se systems, with fluencies $1\times10^{13}$ and $1\times10^{14}$ ions/cm$^2$ of 80 MeV Ni ions.](image)

**Figure 4.12:** RBS spectra of un-irradiated (pristine) and irradiated In/Se systems, with fluencies $1\times10^{13}$ and $1\times10^{14}$ ions/cm$^2$ of 80 MeV Ni ions.

(c) Irradiation using 90 MeV Si

Figure 4.13 shows the RBS spectra of In/Se system irradiated using 90 MeV Si ions. In this study using 90 MeV Si ions fluences ranging from $3\times10^{12}$ ions/cm$^2$
to $1 \times 10^{14}$ ions/cm$^2$ were used for irradiation. 90 MeV Si ions lost about 4.67 keV/nm and 3.45 keV/nm as electronic energy loss in In and Se layers respectively [TRIM code 1995]. This was very much less as compared to the electronic energy loss of 100 MeV Ag and 80 MeV Ni ions. Hence we could not find any kind of mixing between In/Se bilayer up to a fluence of $3 \times 10^{13}$ ions/cm$^2$. Figure 4.13 (a) and (b) depicts the RBS spectra of In/Se system irradiated with 90 MeV Si of fluence $1 \times 10^{13}$ ions/cm$^2$ and $3 \times 10^{13}$ ions/cm$^2$. One could not find any mixing between the bilayer systems. The full width at half maximum (FWHM) of both In and Se peaks did not show any increase, proving that there was no mixing taking place on irradiation with a fluence of $3 \times 10^{13}$ ions/cm$^2$.
ions/cm². But as the fluence increased to 1×10^{14} ions/cm², one could see mixing between In and Se layer [Fig. 4.13(c)]. The FWHM of the Se layer and In layer increased while the height of the both peak decreased. FWHM of Se peak increased from 18.7 to 20.9 and that of In peak increased from 13.5 to 14.9 respectively for unirradiated and In/Se system irradiated with a fluence of 1×10^{14} ions/cm². This showed that mixing occurred during irradiation with a fluence of 1×10^{14} ions/cm². One could also observe a small shift in higher channel number edge of Se peak towards right.

From RBS analysis of In/Se system irradiated using SHI of different electronic energy regimes with different ion fluences, one could get clear evidence that for different electronic energy regimes, there existed a threshold fluence for mixing to take place between the bilayer system. It can be observed from the RBS spectra [Figure 4.11(c), 4.12 and 4.13(b)] that at a fluence of 1×10^{13} ions/cm², the mixing between In and Se was decreasing with decrease in the electronic energy deposition. That is, we obtained more mixing in 100 MeV Ag than with 80 MeV Ni ions and very low mixing was observed for the samples irradiated with 90 MeV Si. A similar type of interface mixing with different electronic energy regime was demonstrated by Kraft et al. in which they showed the mixing of ZnO/SiO₂ using 200 MeV Xe, 260 MeV Kr and 100 MeV Ar [43]. They found that mixing was higher in the case of 200 MeV Xe than 260 MeV Kr. Again for 100 MeV Ar, there was comparatively very low mixing between ZnO/SiO₂ layers. [Electronic energy loss of 200 MeV Xe ions in ZnO/SiO₂ system is 27/15.4 keV/nm; for 260 MeV Kr ions this is 18.1/10.1 keV/nm and that of 100 MeV Ar ions is 7.7/4.3 keV/nm respectively]. This revealed the dependence of electronic energy loss on the phenomena of ion beam mixing. One more thing to be noted is the dependence of fluence and the electronic energy deposited by the ions. In the case of In/Se bilayer system, one could see that only a fluence of ~ 6×10^{12} ion/cm² was required to probe mixing between In and Se. whereas a fluence of ~ 1×10^{13} ions/cm² was required in the case of 80
MeV Ni ions. But fluence of almost \( \approx 1 \times 10^{14} \) ions/cm\(^2\) was required with that of 90 MeV Si ions.

Mixing between the bilayer under dense electronic energy regime (or using SHI irradiation) is explained with the ‘thermal spike model’ [41, 42] (as explained in section 4.2.4). According to this model, as the ions pass through the material, if the energy of the ions are sufficiently high, it increases the lattice temperature. If the temperature rise is above the melting point of the material, material melts and a transient molten track forms. Mixing between the layers occurs across the interface by inter-diffusion of the atoms through the molten track. In our case, we observed mixing between In and Se with 90 MeV Si ions which deposited about 4.67 keV/nm and 3.45 keV/nm energy to In and Se respectively. This proved that the threshold energy for creating molten transient tracks in In and Se was about 4.67 keV/nm and 3.45 keV/nm respectively. But higher fluence of about \( 1 \times 10^{14} \) ions/cm\(^2\) was required, which was more than one order higher than that of 100 MeV Ag ions, for mixing to take place between In and Se.

Swift heavy ions pass through the material, creating molten cylindrical tracks of few nano-meters along the path, if the energy is sufficiently high. Till now, lots of studies has been carried out, experimentally and theoretically, and found that ion track radius (cylindrical molten track radius) was dependent on electronic energy deposition [85, 86, 87]. Track radius increased with electronic energy deposition [88]. Toulemonde et al. [88] found, in the case of a-Ge, a-Si and in Fe\(_{86}\)B\(_{15}\) that radius of molten track increased with increase in electronic energy deposition. As the fluence increased, the ion tracks with few nanometer size overlapped and a uniform mixing occurred. In the case of ions which deposit less energy, the molten track radius will be small. Hence higher fluence was required for mixing to take place. But for ions with higher energy deposition, the track radius will be high and one can obtain mixing with lower fluence. This might be the reason why we have obtained mixing between In and Se with lower fluence for 100 MeV Ag ions as compared with 80 MeV Ni and 90 MeV Si ions.
Similar result with low fluence was reported by Kraft et al. in which they observed mixing between ZnO/SiO$_2$ at a fluence of $4.2 \times 10^{15}$ ions/cm$^2$ when they used 200 MeV Xe ions [43], whereas a fluence of $5.7 \times 10^{15}$ ions/cm$^2$ was required with 260 MeV Kr ions.

4.12.2 Atomic Force Microscopy (AFM) analysis

SHI induced modification in surface morphology of In/Se system was studied using AFM. By using AFM one could get the information of the deformation/changes of the surface occurred during SHI irradiation [89, 90]. SHI induced ditch and dick formation [91] and plastic flow of the materials [90] were observed and was attributed due to the macroscopic momentum transfer from ion beam to the target material [92]. The mechanism of surface modification due to these processes, however, is far from clear.

Figure 4.14 shows the AFM picture (5x5 µm dimension) of unirradiated and irradiated In/Se system with 100 MeV Ag ions of fluences $1 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$. One could clearly observe the variation in surface morphology induced by 100 MeV Ag ions. The unirradiated In/Se system [Fig. 4.14(a)] gives the uniform surface morphology with an RMS roughness of ~15 nm and as the fluence increased to $6 \times 10^{12}$ ions/cm$^2$ we can see clearly isolation/clustering of surface material [Fig. 4.14(b)]. More over, craters were observed between the clusters. When the fluence was increased to $1 \times 10^{13}$ ions/cm$^2$ clustering of the surface material could be clearly observed [Fig. 4.14(c)]. Piling up of material along the sides of craters could also be observed. Craters with a radius of 0.5 µm to 0.65 µm could be seen with a fluence of $1 \times 10^{13}$ ions/cm$^2$. The craters formation might be due to the explosive evaporation of material during SHI irradiation and / or due to the plastic flow of material due to tremendous electronic energy deposited during irradiation [93]. This type of crater formation was observed in different materials at high fluences. The high energy deposited
by the SHI might be breaking the bonds between the atoms, resulting in the enhancement of the mobility of atoms to form clusters of material. Clusters of different sizes, ranging from 0.5 µm to 1 µm, could be observed in the case of sample irradiated with $1 \times 10^{13}$ ions/cm$^2$.

![AFM images](image)

**Figure 4.14**: Atomic Force micrograph (AFM) of (a) un-irradiated In/Se system (b) irradiated with $6 \times 10^{12}$ ions/cm$^2$ and (c) $1 \times 10^{13}$ ions/cm$^2$ of 100 MeV Ag ions.

Figure 4.15 shows the AFM pictures of In/Se system irradiated using 80 MeV Ni. In this case, we can see that there is not much variation in surface morphology of the sample irradiated with a fluence of $1 \times 10^{13}$ ions/cm$^2$ [Fig. 4.15(a)]. As the fluence increased to $3 \times 10^{13}$ ions/cm$^2$ clustering of the surface
material along the sides of the craters can be observed [Fig. 4.15(b)]. One can also observe the clusters of different sizes here.

From the AFM study of In/Se system irradiated with different energy ions, one could find that the surface modification induced by swift heavy ions was depending on electronic energy deposition. For 100 MeV Ag ions, which deposits an energy of 17.75 keV/nm in Indium (the surface layer), lower fluence of about $6 \times 10^{12}$ ions/cm$^2$ was required, while with 80 MeV Ni, which deposits an energy of 12.03 keV/nm, a higher fluence of $\sim 3 \times 10^{13}$ ions/cm$^2$ is required to produce surface modification.

![AFM pictures of In/Se system irradiated with 80 MeV Ni ions of fluence (a) $1 \times 10^{13}$ ions/cm$^2$ and (b) $3 \times 10^{13}$ ions/cm$^2$](image)

**Figure 4.15:** AFM pictures of In/Se system irradiated with 80 MeV Ni ions of fluence (a) $1 \times 10^{13}$ ions/cm$^2$ and (b) $3 \times 10^{13}$ ions/cm$^2$

### 4.12.3 X-ray diffraction analysis

*(a) Irradiation using 100 MeV Ag ions*

Figure 4.16 shows the XRD pattern of In/Se system irradiated with different fluences ranging from $1 \times 10^{12}$ to $1 \times 10^{13}$ ions/cm$^2$. The unirradiated one (Fig.
4.16(a)), showed only the x-ray diffraction peak from elemental In and Se at $2\theta = 32.75^{\circ}$ and $2\theta = 23.36^{\circ}$ respectively. The prominent peak of In at $2\theta = 32.75^{\circ}$ (unirradiated sample) with a FWHM of 0.2684 reduced to about 0.2427 on irradiation with a fluence of $1 \times 10^{12}$ ions/cm$^2$. The decrease in FWHM of In peak reflects the enhancement in the crystallinity of In layer due to 100 MeV Ag ion irradiation. The other thing to be noted is that the Se peak vanished on irradiation. This may be due to the amorphisation of the Se layer. On increasing the fluence to $6 \times 10^{12}$ ions/cm$^2$ we could observe the formation of indium selenide compound, [In$_2$Se$_3$ phase] at $2\theta = 36.37$, 27.84 and In$_6$Se$_7$ phase at $2\theta = 20.69^{\circ}$ respectively (Fig. 4.16(c)). From RBS analysis, it became evident that at this same fluence ($6 \times 10^{12}$ ions/cm$^2$) mixing between In/Se layers took place. XRD analysis also confirmed the compound formation at this fluence without any post annealing treatment. This proved beyond doubt that the threshold fluence for indium selenide compound formation with 100 MeV Ag ions is $6 \times 10^{12}$ ions/cm$^2$. Here also we could find the presence of elemental indium in the sample. This might be due to the agglomerated / clustered indium present in the surface of the film. In this case also the FWHM of In peak decreased to a value of 0.2271. But further increase of fluence [i.e. to $1 \times 10^{13}$ ions/cm$^2$] resulted in the amorphisation of indium selenide formed (peaks of indium selenide at $2\theta = 36.37$, 27.84 and 20.69$^{\circ}$ vanished on increasing the fluence) [Fig. 4.16(d)]. But the FWHM of the In peak decreased to 0.2194. This confirmed that, in metal layer and in semiconductors, swift heavy ions behave differently. In metal (In), it is improving/ enhancing the crystallinity whereas in semiconductor (indium selenide), it is amorphising the material.
Figure 4.16: XRD pattern of In/Se system (a) un-irradiated and irradiated with 100 MeV Ag ions of fluences (b) $1 \times 10^{12}$ (c) $6 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$.

The samples were vacuum annealed at 50°C and 100°C for 1 h at the pressure of $2 \times 10^{-5}$ mbar. Figure 4.17 shows the In/Se system annealed at 50°C for 1h. In the unirradiated sample, there was unreacted Se [XRD peak at $2\theta = 23.6^\circ$] along with In$_2$Se$_3$ formed along (202) plane [XRD peak at $2\theta = 28.95^\circ$] (Fig 4. 17(a)). One could also find a new XRD peak [though faint] at $2\theta = 23.88$ for the samples irradiated with $6 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$, which was identified to be due to In$_6$Se$_7$ phase. The reflection from In$_6$Se$_7$ phase (Fig. 4.16(c)) at $2\theta = 20.69$ disappeared on annealing at 50 °C (Fig. 4.17(c)) in the case of sample irradiated with a fluence of $6 \times 10^{12}$ ions/cm$^2$. One interesting point to be noted here is that the intensity of In peak of irradiated sample is much higher than that of un-irradiated sample. In the case of unirradiated sample, the intensity of In
decreased due to the diffusion taking place between In and Se, thereby reducing the presence of elemental In. But in the case of irradiated sample the clustered In atoms present in the surface of the sample are not participating in the diffusion process. This might be the reason for the increase in the peak intensity.

Figure 4.17: XRD pattern of In/Se system (a) un-irradiated, irradiated with 100 MeV Ag ions of fluences (b) 1x10^{12} (c) 6x10^{12} and 1x10^{13} ions/cm² and annealed at 50°C for 1h.

Figure 4.18 shows the XRD pattern of the samples annealed at 100°C for 1 h. On annealing the sample at 100°C, we observed In₂Se₃ phase formation in all the samples. Again, the samples irradiated with 6x10^{12} and 1x10^{13} ions/cm² had
In$_6$Se$_7$ phase also (Fig. 4.18(c) and (d)). The sample irradiated with $6 \times 10^{12}$ ions/cm$^2$ showed the formation of InSe phase [peak at $\theta = 32.54^\circ$]. In this case the In peak completely vanished. This might be due to the complete mixing of In layer with Se to form indium selenide. In the case of sample irradiated with $1 \times 10^{13}$ ions/cm$^2$, the intensity of the InSe peak increased. This shows the increase in mixing between In and Se layers.

**Figure 4.18:** XRD pattern of In/Se system (a) un-irradiated, irradiated with 100 MeV Ag ions of fluences (b) $1 \times 10^{12}$ (c) $6 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$ and annealed at 100°C for 1h.

By RBS study, we found that the mixing between In and Se layers occurred at a fluence of $6 \times 10^{12}$ ions/cm$^2$ with 100 MeV Ag ions. During the passage of SHI,
it created defects and atomic displacements at the interface. These defects were immobile at room temperature and when we supplied enough energy by annealing at 100 °C, more atoms diffused across the interface through the defects and we obtained a complete mixing [62, 69].

(b) Irradiation using 80 MeV Ni ions.

In/Se bilayer system was irradiated using 80 MeV Ni ions of different fluences ranging from $1 \times 10^{12}$ to $1 \times 10^{14}$ ions/cm$^2$. XRD analysis showed no compound formation up to fluence of $3 \times 10^{13}$ ions/cm$^2$ (Fig. 4.19(d)). But as the fluence increased to $1 \times 10^{14}$ ions/cm$^2$ indium selenide (In$_2$Se$_3$) compound formation was observed [XRD peak at $2\theta = 39.45$] along (212) plane (Fig. 4.19(e)). The elemental In was also present in the sample.

![Figure 4.19: XRD pattern of In/Se systems (a) un-irradiated, and irradiated with 80 MeV Ni ions of fluences (b) $1 \times 10^{12}$, (c) $1 \times 10^{13}$, (d) $3 \times 10^{13}$ and (e) $1 \times 10^{14}$ ions/cm$^2$.](image)
Figure 4.20 shows the XRD pattern of the In/Se system annealed at 50 °C for 1 h. Here in the sample irradiated with a fluence of $1 \times 10^{12}$ ions/cm$^2$ itself, one could see the compound formation ($\text{In}_2\text{Se}_3$) resulting in the peak at $2\theta = 27.82$ along (006) plane. But the sample irradiated with a fluence of $3 \times 10^{12}$ ions/cm$^2$ showed $\text{In}_2\text{Se}_3$ formation [peak at $2\theta = 29.47$ corresponding to (201) plane]. Samples irradiated with higher fluence did not show any sign of crystalline compound formation. In the case of samples irradiated with higher fluence, higher order of defects and/or amorphisation might have taken place and might require more energy for crystalline indium selenide formation.

![XRD pattern of In/Se systems](image)

**Figure 4.20:** XRD pattern of In/Se systems irradiated with 80 MeV Ni ions and annealed at 50°C for 1 h.
On annealing the sample at 100 °C, we observed compound formation in all the samples (Fig. 4.21). As we supplied sufficient energy, the atoms migrated across the interface, which resulted in the formation of crystalline In$_2$Se$_3$ and InSe phases. It was also seen that the peak of elemental In completely vanished for the sample irradiated with a fluence of 3x10$^{12}$ ions/cm$^2$ (Fig. 4.21(c)). However the sample irradiated with 3x10$^{13}$ ions/cm$^2$ showed only the reflection from InSe phase (Fig. 4.21(e)), whereas all other samples showed multi-phased indium selenide formation.

Figure 4.21 XRD pattern of In/Se systems irradiated with 80 MeV Ni ions and annealed at 100°C for 1 h.
(c) Irradiation using 90 MeV Si ions.

Different fluences ranging from $3 \times 10^{12}$ to $1 \times 10^{14}$ ions/cm$^2$ were used for irradiating the sample using 90 MeV Si ions. Figure 4.22 shows the XRD pattern of these samples. No compound formation was observed up to a fluence of $3 \times 10^{13}$ ions/cm$^2$ [Fig. 4.22(b)]. But In$_2$Se$_3$ phase was formed [peak at $2\theta = 27.71^\circ$ and $28.87^\circ$ corresponding to (006) and (201) planes respectively] with a fluence of $1 \times 10^{14}$ ions/cm$^2$ [Fig. 4.22(c)]. However elemental In and Se were also present in the sample. Thus the threshold fluence for compound formation to take place between In and Se with 90 MeV Si ions was found to be $1 \times 10^{14}$ ions/cm$^2$.

![Figure 4.22: XRD pattern of In/Se system irradiated with 90 MeV Si ions.](image)

Figure 4.23 shows the In/Se samples annealed at 50°C for 1h. No crystalline indium selenide formation was observed up to a fluence of $3 \times 10^{13}$ ions/cm$^2$. But the sample irradiated with $1 \times 10^{14}$ ions/cm$^2$ showed crystalline indium selenide phases as we observed in the irradiated case [Fig. 4.23(b)]. The FWHM of the peaks along (006) and (201) plane decreased on annealing at 50°C. This shows
that the crystallinity increased on annealing at 50 °C. But in this case also, elemental In was present in the sample, which might be the clustered In atoms present on the surface of the film.

On annealing the samples at 100 °C, one could see that the elemental In present in the sample was almost lost fully (Fig. 4.24). This might be due to the mixing taking place between In and Se, when sufficient energy was supplied. But we could see the formation of mixed phases of indium selenide (In$_2$Se$_3$ and In$_6$Se$_7$) on annealing at 100 °C [Fig. 4.24(d), (e) and (f)]. One thing again to be noted is the decrease in crystallinity. The FWHM of the peaks increased on annealing.

Figure 4.23: XRD pattern of In/Se system irradiated with 90 MeV Si ions and annealed at 50°C for 1 h.
Figure 4.24: XRD pattern of In/Se system irradiated with 90 MeV Si ions and annealed at 100°C for 1 h.

4.12.4 Optical absorption studies

(a) 100 MeV Ag ion irradiation:

Optical absorption studies of samples irradiated with 100 MeV Ag ions were carried out in the range of 400 – 900 nm. Figure 4.25 shows the absorption spectra of these samples. One can clearly observe here a blue shift in the absorption edge on increasing the irradiation fluence. Optical band gap of the
material was found out from $(\alpha \nu)^2$ versus $\nu$ plot, by extrapolating the straight portion of the plot to $\alpha = 0$ Table 4.1. There is an increase in optical band gap of the sample from 1.83 eV to 2.01 eV on irradiation with a fluence of $6 \times 10^{12}$ ions/cm$^2$ and this reveals the formation of indium selenide. In fact the XRD pattern (Fig. 4.16) proved $\text{In}_2\text{Se}_3$ formation along with $\text{In}_6\text{Se}_7$ phase. On increasing the fluence further to $1 \times 10^{13}$ ions/cm$^2$, the band gap increased to 2.25 eV. Figure 4.26 shows the $(\alpha \nu)^2$ versus $\nu$ plot of the unirradiated and the sample irradiated with a fluence of $1 \times 10^{13}$ ions/cm$^2$. From this it is clear that increase in optical band gap suggesting the formation of indium selenide phase.

![Absorption spectra of In/Se systems irradiated with different fluences of 100 MeV Ag ions.](image)

**Figure 4.25** Absorption spectra of In/Se systems irradiated with different fluences of 100 MeV Ag ions.
Table 4.1: Optical band gap of the samples irradiated using 100 MeV Ag ions

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Irradiation fluence (ions/cm²)</th>
<th>Band gap (eV)</th>
<th>As irradiated</th>
<th>Annealed at 50°C</th>
<th>Annealed at 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Un-irradiated</td>
<td>1.83</td>
<td>1.82</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>1x10¹²</td>
<td>1.88</td>
<td>1.9</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>6x10¹²</td>
<td>2.01</td>
<td>2.07</td>
<td>2.05</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>1x10¹³</td>
<td>2.25</td>
<td>2.45</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.26 $(\alpha h\nu)^2$ versus $\nu h$ plot of In/Se system, un-irradiated and irradiated with 100 MeV Ag ions of fluence $1x10^{13}$ ions/cm²

On annealing the samples at 50°C (at a pressure of $2x10^{-5}$ mbar.) for 1 h, the band gap of the samples increased further (Table 4.1). But in the case of
unirradiated sample, there was no such increase. The sample irradiated with a fluence of $1 \times 10^{13}$ ions/cm$^2$ had the maximum band gap of 2.45 eV. The increase of band gap can be due to the quantum size effect [67]. This effect often appears in amorphous materials or in material with particle size of few nanometers. But in our case, we can see the XRD pattern of In$_6$Se$_7$ phase and crystalline In layer [Fig. 4.17(d)]. The average grain size of the sample irradiated with $1 \times 10^{15}$ ions/cm$^2$ is about ~29 nm($\theta = 23.41$, FWHM = 0.2766), and thus we can rule out the increase in band gap due to quantum size effect.

When these samples were further annealed at 100°C for 1 h, the band gap further increased [Table 4.1]. A band gap of about 2.5 eV was observed for the sample irradiated with a fluence of $1 \times 10^{13}$ ions/cm$^2$. Average grain size of the samples irradiated with $6 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$ were 39 and 44 nm respectively ($\theta = 32.54$, FWHM = 0.2110 and 0.1868) and hence the possibility of increase in band gap due to quantum size can be ignored. The increase in band gap in this case can be explained by considering the annihilation of defects bands or the Urbach tale due to the irradiation followed by annealing at 100 °C.

In the case of intrinsic semiconductors, there would be no defect levels in the forbidden gap, making the absorption possible only when a photon of energy greater or equal to the band gap is incident on it, leading to band-to-band transition. But in the case of impurity semiconductors, there could be defect levels in forbidden gap, resulting in the absorption of photons with sub band gap energies too. There can also be dense localized energy states, near the valence and conduction band edges, known as ‘Urbach energy bands’, whose density decays exponentially as one moves away from valence and conduction band edges [94]. Different semiconductors, namely a-SiC [95], a-C: H [96] and even chalcogenide compounds such as CuInSe$_2$ [97] and InSe [98] exhibited Urbach tail. Urbach energy width (tail width) is a measure of disorder in the material [96].
Figure 4.27: Sketch of the assumed band structure, with dense localized energy states near band edges (a) before irradiation and (b) after irradiation and/or annealing.

Figure 4.27 shows the sketch of the assumed band structure, with dense localized energy states near band edges. Because of the presence of these states, it was very difficult to distinguish between the bottom of the conduction band and the top of the valence band with the band tails and this results in absorption even at energies much below the band gap. According to Urbach rule [99, 100], below the fundamental absorption edge, the absorption coefficient $\alpha$ varies exponentially as $\alpha = \alpha_o \exp\left(\frac{h\nu}{E_u}\right)$, where $\alpha_o$ is the characteristic parameter of the material, $h\nu$ the photon energy and $E_u$, the width of the exponential tail, known as the Urbach energy or Urbach tail energy. This region is attributed to the electronic transition between a localized band tail and an extended band [101] and represents the degree of disorder in the material. The Urbach tail width ($E_u$) can be estimated from the inverse slope of the plot $\ln(\alpha)$ versus $h\nu$ below the fundamental absorption [100]. $E_u$ of all the samples after annealing at 50°C and 100°C were calculated and tabulated in Table 4.2. On annealing (at a pressure of $2 \times 10^{-5}$ mbar.) the samples at 50°C for 1 h, the Urbach energy decreased from 1.67 eV (un-irradiated sample) to 901 meV for the sample
irradiated with a fluence $6 \times 10^{12}$ ions/cm$^2$. One could observe that the Urbach tail width decreased further on annealing at 100°C. The decrease of Urbach tail width indicated that irradiation could anneal out the disorders (localized states) in the material, which resulted in the increase of band gap of the material. Similar type of annealing out of disorders and subsequent increase of band gap was observed in In$_2$Se$_3$ by El-Shair et al. by thermal annealing at higher temperatures [99].

Table 4.2: Urbach energy variation of samples irradiated with 100 MeV Ag ions annealed at different temperatures.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Irradiation fluence (ions/cm$^2$)</th>
<th>Urbach energy (eV)</th>
<th>Annealed at 50 °C</th>
<th>Annealed at 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Un-irradiated</td>
<td>1.67</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>$1 \times 10^{12}$</td>
<td>0.968</td>
<td>0.784</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>$6 \times 10^{12}$</td>
<td>0.901</td>
<td>0.877</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>$1 \times 10^{13}$</td>
<td>0.917</td>
<td>0.882</td>
<td></td>
</tr>
</tbody>
</table>

When we measure the optical band gap of the material, because of the band tailing, we were able to measure only the band gap $E_{g_m}$. This was very much less than the actual band gap $E_g$ of the material [Fig. 4.27]. Urbach tail width measurements on the irradiated sample revealed annealing out the localized energy bands near the band edges, indicating a reduction in $E_u$. As a result of this, conduction and valence band tail states were separated further apart in energy [Fig. 4.27(b)], which was evident from blue shift in absorption spectra [Fig. 4.25]. This might be the reason for the increase in band gap of indium selenide samples.
Optical band gap of the samples irradiated using 80 MeV Ni ions was calculated from \((\alpha h\nu)^2\) versus \(h\nu\) plot [Table 4.3]. An increase in the band gap could be observed as the irradiation fluence increased, reaching a maximum of 2.34 eV, for the sample irradiated with a fluence of \(1\times10^{14}\) ions/cm\(^2\). XRD analysis indicated (Fig. 4.20) indium selenide formation, at this fluence. This shows that the band gap of Indium selenide can be increased to 2.34 eV without any post annealing treatment. On annealing the samples at 50\(^\circ\)C and 100\(^\circ\)C for 1 h (at a pressure of \(2\times10^{-5}\) mbar.), the band gap further increased, reaching a value of about 2.88 eV for the sample irradiated with a fluence of \(1\times10^{14}\) ions/cm\(^2\). The optical band gap of the samples was tabulated in table 4.3. In this case also the increase in band gap of the samples can be explained as due to the reduction in the Urbach energy. Urbach energy of the samples were calculated and tabulated in table 4.4. From the table we can see that the Urbach energy of the samples irradiated with 80 MeV Ni ions after annealing at (50\(^\circ\)C and 100\(^\circ\)C) were less than that of the unirradiated samples. This shows that, irradiation can anneal out the defect bands present at the valence and conduction edges. We can observe an increase in Urbach energy in the case of sample irradiated with a fluence of \(3\times10^{13}\) ions/cm\(^2\) after annealing at 100\(^\circ\)C. This was also reflected in the band gap of the sample. The increase in Urbach energy might be due to the increase in planar defects in the sample [102, 103], since the sample formed is single phase InSe, which has hexagonal planar structure. Reduction in Urbach energy in InSe due to decrease of planar defects in InSe was reported earlier by us due to 40 MeV Si ions in indium selenide films [103].
Table 4.3: Optical band gap of samples irradiated with 80 MeV Ni ions

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Irradiation fluence (ions/cm²)</th>
<th>Band gap (eV)</th>
<th>As irradiated</th>
<th>Annealed at 50°C</th>
<th>Annealed at 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1x10^{12}</td>
<td>1.7</td>
<td>1.76</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>1x10^{13}</td>
<td>1.96</td>
<td>1.96</td>
<td>2.45</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>3x10^{13}</td>
<td>2.2</td>
<td>2.52</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>1x10^{14}</td>
<td>2.34</td>
<td>2.52</td>
<td>2.88</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: Showing Urbach energy of the sample irradiated with 80 MeV Ni.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Irradiation fluence (ions/cm²)</th>
<th>Urbach energy (eV)</th>
<th>Annealed at 50 °C</th>
<th>Annealed at 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Un-irradiated</td>
<td>1.67</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>1x10^{12}</td>
<td>1.04</td>
<td>0.738</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>1x10^{13}</td>
<td>0.829</td>
<td>0.811</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>3x10^{13}</td>
<td>0.896</td>
<td>0.943</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>1x10^{14}</td>
<td>0.952</td>
<td>1.01</td>
<td></td>
</tr>
</tbody>
</table>

(c) Irradiation using 90 MeV Si ions

As in the case of irradiation using 100 MeV Ag ions and 80 MeV Ni ions, the optical band gap of the material increased on irradiation with 90 MeV Si ion, followed by annealing at 50 and 100°C. Fluence used for irradiation ranges from 3x10^{12} to 1x10^{14} ions/cm². As the irradiation fluence increased, the optical band gap also increased. A maximum value of about 2.04 eV was achieved for the samples irradiated with a fluence of 1x10^{14} ions/cm² after annealing at 50°C.
When this sample was again annealed at 100°C for 1 h, the band gap reached to a value of 2.8 eV. The values of band gap are tabulated in table 4.5. Here a clear increase in optical band gap can be observed as the irradiation fluence increases. Figure 4.28 gives the $(\alpha h\nu)^2$ versus $h\nu$ plot of the samples which are irradiated with 90 MeV Si ions, with different fluences and annealed at 50°C. Figure 4.29 shows the absorption spectra of the samples irradiated with a fluence of $1\times 10^{13}$, $3\times 10^{13}$ and $1\times 10^{14}$ ions/cm$^2$ and annealed at 100°C. We can see a sharp shoulder at about 600 nm, corresponding to a strong defect level in the sample irradiated with $3\times 10^{13}$ ions/cm$^2$. As the fluence increased to $1\times 10^{14}$ ions/cm$^2$, the shoulder became broader. Also the absorption shifted towards lower wavelength indicating an increase in band gap of the material.

![Figure 4.28](image_url) (\(\alpha h\nu\))^2 versus $h\nu$ plot of In/Se system irradiated with different fluences of 90 MeV Si ions and annealed at 50°C for 1 h.
<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Irradiation fluence (ions/cm²)</th>
<th>Band gap (eV)</th>
<th>Annealed at 50 °C</th>
<th>Annealed at 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Un-irradiated</td>
<td>1.73</td>
<td></td>
<td>1.81</td>
</tr>
<tr>
<td>2.</td>
<td>3x10^{12}</td>
<td>1.83</td>
<td></td>
<td>2.55</td>
</tr>
<tr>
<td>3.</td>
<td>6x10^{12}</td>
<td>1.86</td>
<td></td>
<td>2.71</td>
</tr>
<tr>
<td>4.</td>
<td>1x10^{13}</td>
<td>1.87</td>
<td></td>
<td>2.13</td>
</tr>
<tr>
<td>5.</td>
<td>3x10^{13}</td>
<td>2.02</td>
<td></td>
<td>2.52</td>
</tr>
<tr>
<td>6.</td>
<td>1x10^{14}</td>
<td>2.04</td>
<td></td>
<td>2.8</td>
</tr>
</tbody>
</table>

Urbach energy of all the samples were calculated and tabulated in table 4.6. In the case of samples annealed at 50°C, the Urbach energy decreased as the fluence increased, showing annihilation of the defects in the samples. An increase in optical band gap was also observed [Table 4.5]. On annealing the samples at 100°C, the Urbach energy increased, i.e. on annealing, the defects in the samples increased. Interestingly the band gap of the material did not decrease. But it increased, on annealing at 100°C. In this case, the increase in band gap due to quantum size effect cannot be ruled out, since the samples obtained after 100 °C annealing was amorphous. The average grain sizes of the samples annealed at 100 °C, irradiated with fluences 6x10^{12}, 1x10^{13}, 3x10^{13} and 1x10^{14} ions/cm² were 5.2, 15, 5 and 13 nm respectively and hence the increase in band gap of the samples was attributed due to the quantum size effect.
**Figure 4.29** Absorption spectra of In/Se samples irradiated with 90 MeV Si ions and annealed at 100°C for 1 h.

**Table 4.6:** Urbach energy of the samples irradiated with 90 MeV Si ions and annealed at 50 and 100°C.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Irradiation fluence (ions/cm²)</th>
<th>Urbach energy (eV)</th>
<th>Annealed at 50 °C</th>
<th>Annealed at 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Un-irradiated</td>
<td>1.67</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>3x10^{12}</td>
<td>0.958</td>
<td>2.42</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>6x10^{12}</td>
<td>0.887</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>1x10^{13}</td>
<td>0.857</td>
<td>0.879</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>3x10^{13}</td>
<td>0.777</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>1x10^{14}</td>
<td>0.683</td>
<td>1.36</td>
<td></td>
</tr>
</tbody>
</table>
4.13 Conclusion

Threshold fluence for ion beam mixing (IBM) to take place between In/Se bilayer system was found out at different electronic energy regime. Threshold fluence for mixing using 100 MeV Ag, 80 MeV Ni and 90 MeV Si ions were \(6 \times 10^{12}\), \(1 \times 10^{13}\) and \(1 \times 10^{14}\) ions/cm\(^2\) respectively. SHI irradiation study proved that the optical band gap of indium selenide can be tuned/varied from 1.8 eV to 2.5 eV, without any post annealing treatment. With a post annealing treatment at 100\(^\circ\) C for 1 h, band gap can be enhanced up to 2.88 eV. Annihilation of the localized defect levels situated near conduction and valence band edges resulted in increase in band gap.
Chapter 4

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