CHAPTER 5

Effect of SHI irradiation on $\gamma$-In$_2$Se$_3$ thin films
Chapter 5

Abstract

This chapter deals with the effect of 90 MeV Si ions on $\gamma$-In$_2$Se$_3$ thin films. Study proved that the optical band gap of indium selenide can be enhanced using SHI irradiation without any considerable variation in structural and electrical properties. The increase in optical band gap was attributed to the annihilation of localized defect bands, near the conduction and valence band edges, on irradiation. It was observed that the sample, which had negative photoconductivity, exhibited positive photoconductivity, after irradiation.
Chapter 5
5.1 Introduction

Indium selenide is a compound semiconductor, having direct band gap and belonging to III-VI group, which attracted researchers mainly due to its potential application in photovoltaic as well as in electro and photo-memory devices [1, 2]. Even though single crystal silicon solar cells are dominating the market, there is a focused attention towards compound semiconductor based solar cells because of the high cost and technology involved in the process of silicon solar cells. Among the compound semiconductors, indium selenide has made its mark in this field because of its application as window layer, absorber layer as well as a precursor for the preparation of copper indium selenide/copper indium gallium selenide based solar cells [3]. For photovoltaic device fabrication, one prefers crystalline and photoconductive samples, having low resistance. Abdinov and Kyazym-zade reported that InSe can exhibit negative photoconductivity [4]. Later we reported that γ-In$_2$Se$_3$ could also exhibit the same behaviour even at room temperature [5]. This can adversely affect the performance of the solar cell. Hence it is very important to study the photoconductivity of these films before switching on to solar cell fabrication.

Negative photoconductivity (NPC) of a semiconductor is defined as decrease in the conductivity under illumination. Ultimate reason for NPC is the combined effect of (i) trapping of photo excited carriers (electrons in n-type) (ii) destruction of minority carriers (holes in n-type) at recombination center followed by (iii) capture of electrons in the conduction band by the recombination center, during illumination [5]. Electron traps can adversely affect the photoconductivity. Removal of these traps will allow photo-generated carriers to reach conduction band, thereby enhancing the photoconductivity.

In$_2$Se$_3$ exists at least in five different phases such as α, β, γ, δ and κ with different structural and optical properties [6]. Depending upon the optical band gap of the film, it can be used as a window layer (CIS/In$_2$Se$_3$) [7] or absorber
layer (CdS/In$_2$Se$_3$) [4, 8] in solar cells. Gordillo et al. reported efficiency of 8.3% in CIS/In$_2$Se$_3$ solar cell with an open circuit voltage ($V_{oc}$) of 0.45 V and a fill factor of 0.6 [7]. They reduced the thickness of the In$_2$Se$_3$ film from 1µm to ~70 nm, to increase the band gap from 1.75 eV to 3 eV, to use it as a window layer [7]. This resulted in the increase of short circuit current density ($J_{sc}$), at the cost of the open circuit voltage $V_{oc}$. Optical band gap of indium selenide can be varied by altering the thickness [7] and also by varying annealing temperature [9]. But variation of thickness and annealing temperature can affect other properties of the film like sheet resistance [9, 10, 11], which can increase several orders. Hence a technique that is capable of altering the optical band gap of the material, without affecting its other important properties has great significance especially, from the point of view of technological applications.

It has been reported earlier that single phase film can be prepared using SHI irradiation [12]. Effects of SHI irradiation in metals, semiconductors and insulators are entirely different. It is more sensitive to insulators than to metals and semiconductors [13, 14]. It can create point defects, columnar defects, amorphous track or a perturbed atomic distribution along its path as they pass through the material [15, 16]. SHI irradiations were used for controlled manipulation of optical, electrical and structural properties of materials [17, 18, 19]. SHI can also anneal out defects up to certain fluence, beyond which it creates defects in materials [20, 21]. In the present work, we used SHI to increase the photoconductivity and optical band gap of In$_2$Se$_3$ for the first time, without considerable variation in structural and electrical properties.

5.2 Experiment

Thin films of indium selenide were prepared by annealing In/Se bilayer systems, at different temperatures ranging from 100 °C to 400 °C, for duration of one hour, maintaining the pressure at 2x10$^{-5}$ mbar. Thin films of selenium (150 nm thick) were first deposited on glass substrate using chemical bath deposition.
technique [22], over which indium layer of thickness 56 nm was deposited with the help of resistive heating technique (using molybdenum boat) at a pressure of 2x10^5 mbar during evaporation.

Thickness of the films was measured employing stylus thickness profiler (Model – Dektak 6M). The samples annealed at different temperatures [100, 150, 200, 300 and 400°C] were named as IS100, IS150, IS200, IS300 and IS400 respectively. These samples were later irradiated using Si ions of energy 90 MeV (from 15UD Pelletron accelerator) having fluence of 2x10^{13} ions/cm^2 at room temperature, over an area of 1 cm^2, by using an electromagnetic scanner. Range of 90 MeV Si in In\textsubscript{2}Se\textsubscript{3} is about 22 µm (calculated using TRIM code 95) [23], so that it passed through the film and got embedded in the substrate.

X-ray diffraction (XRD) patterns were recorded in the range of 2θ, 10° - 60° using Cu Kα radiation (λ=1.5405 Å) employing Rigaku (D.Max.C) X-ray diffractometer. Optical absorption spectra were recorded using UV-VIS-NIR spectrophotometer (Hitachi U-3410) in the range 400 to 900 nm. For photoluminescence (PL) measurements, samples were loaded in a closed cycle liquid He cryostat (Model - CSS 100/202, Make – Janis research Inc. USA) and cooled up to 10 K. Here the temperature was measured and controlled using a “Lakeshore autotuning” temperature controller. Continuous beam of wavelength 488 nm, from an Ar\textsuperscript{+}-ion laser, (Make – Melles Griot, Model: 35-LAL-415-230; Power: 150 mW) was used as the excitation source. Focused beam of excitation intensity 214 mW/cm\textsuperscript{2} was used and the emission spectra were recorded employing spectrometer USB 2000 (Technosource International INC.).

Dark and photo conductivity of the samples were measured using a ‘source measuring unit’ (SMU-123X KEITHLEY) in the voltage range 0-5 V at room temperature. The two electrodes were patches of silver paint of size 0.6 x 0.2 cm\textsuperscript{2}, with a distance of 0.6 cm between them. Output from the sample was taken using magnanin wires, connected to the electrodes. A halogen lamp (output
power of 60 mW/cm²) was used to illuminate the samples. The illumination time was approximately 60 s. Photoconductivity was measured after illuminating for 60 s. Low temperature photoconductivity measurements were performed by using a closed cycle liquid helium cryostat (Model-REF-396/D22, Make-Helix Technology Corporation, USA), along with “Lakeshore321 autotuning” temperature controller.

5.3 Results and discussion

5.3.1 X-ray diffraction analysis

Figure 5.1 shows the XRD pattern of samples annealed at different temperatures, ranging from 100 °C to 400 °C. Formation of γ-In₂Se₃ was confirmed even at 100 °C, through the peak at 29.76 degree, corresponding to (201) plane [JCPDS card: 40-1407]. Unreacted indium was also present in this sample. Annealing at 150 °C resulted in the complete diffusion of In into Se lattice [Fig. 5.1, IS150] resulting in the formation of β-In₂Se₃ along (110) plane [2θ = 45.18; JCPDS card: 72-1470]. Diffusion of In into Se resulted in crystallization of Se along (100) plane [confirmed by the peak at 23.27; JCPDS card: 6-0362]. This type of behaviour was reported earlier in In/Se bilayer system [9]. In the case of IS200 and IS300 films, indium mono-selenide (InSe) phase [along (006) plane; peak at 22.69; JCPDS card: 27-0244] was formed along with γ-In₂Se₃. However temperature of 400 °C was required for the formation of single-phase γ-In₂Se₃ along (006) and (111) planes [JCPDS card: 40-1407]. The average grain size of the samples was calculated using Debye Scherrer’s formula [24] (see section 1.10.2), and the results are tabulated in table 5.1.
Figure 5.1: XRD pattern of In$_2$Se$_3$ samples prepared at different annealing temperatures from 100 °C to 400 °C
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Table 5.1: Average grain size of the samples before and after irradiation. Crystal structure of $\beta$-$\text{In}_2\text{Se}_3$, $\gamma$-$\text{In}_2\text{Se}_3$ and InSe were rhombohedral, hexagonal defect wurtzite and hexagonal layered structure respectively.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>un-irradiated samples</th>
<th>Irradiated samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2\theta$</td>
<td>FWHM</td>
</tr>
<tr>
<td>IS100</td>
<td>29.76</td>
<td>0.43</td>
</tr>
<tr>
<td>IS150</td>
<td>45.18</td>
<td>0.61</td>
</tr>
<tr>
<td>IS200</td>
<td>22.69</td>
<td>0.63</td>
</tr>
<tr>
<td>IS300</td>
<td>27.83</td>
<td>0.57</td>
</tr>
<tr>
<td>IS400</td>
<td>27.65</td>
<td>0.17</td>
</tr>
</tbody>
</table>

XRD patterns of the irradiated samples are depicted in figure 5.2. On irradiation with Si ions [90 MeV], the unreacted indium in IS100 got mixed with Se lattice, leading to the formation of indium mono-selenide (InSe) along with $\gamma$-$\text{In}_2\text{Se}_3$. Irradiating IS150 resulted in the elimination of $\gamma$-$\text{In}_2\text{Se}_3$ and $\beta$-$\text{In}_2\text{Se}_3$ phases completely, leading to the formation of single phase InSe. SHI induced single phase InSe formation was earlier reported in which we used 40MeV Si ions for irradiation [12]. But, in the case of IS200 and IS300, the irradiation favoured growth of $\gamma$-$\text{In}_2\text{Se}_3$ only, which was evident from the XRD spectra (Fig. 5.2). Average grain size of the irradiated samples is tabulated in table 5.1. It showed that 90 MeV Si ions of fluence $2\times10^{13}$ ions/cm$^2$ did not cause any amorphisation in $\gamma$-$\text{In}_2\text{Se}_3$ thin films. Moreover it increased the average grain size of the samples except IS300. IS300 did not show any considerable variation in the average grain size. Increase in the average grain size of the crystallites also indicated the reduction in the density of grain boundaries present in the samples upon irradiation. XRD patterns (Fig. 5.1 and 5.2) of all the samples (irradiated
and un-irradiated) showed a broad X-ray scattering background at $2\theta \sim 25^\circ$. This broad hump might be due to the backscattering from the glass substrate. Since our samples were only $\sim$206 nm thick, there is a possibility of background scattering from the glass substrate.

![Figure 5.2](image)

**Figure 5.2:** XRD pattern of samples irradiated by 90 MeV Si ion with a fluence of $2\times10^{13}$ ions/cm$^2$.

XRD analysis showed that, irradiation using 90 MeV Si ions, eliminated secondary phase from indium selenide thin films. 90 MeV Si ions lose about $\sim$ 4 keV/nm energy to In$_2$Se$_3$ as electronic energy loss ($S_e$) and about $3.5\times10^3$ keV/nm as nuclear energy loss $S_n$, calculated using TRIM code 95 [23]. $S_n$ is negligible as compared to $S_e$ and causes very little effects on In$_2$Se$_3$ films.
Electronic energy loss of ~ 4 keV/nm in In$_2$Se$_3$ might not be sufficient for amorphisation of these films. However, this is sufficient to increase the average grain size of the samples [Table 5.1]. Swift heavy ions transferred energy to the lattice via electron – phonon interaction, according to thermal spike model [25]. The energy lost by the SHI is mostly converted into the kinetic energy of the electrons, in the target material. This energy is dissipated to the lattice, via electron – phonon coupling, resulting in heating up of lattice. If the electronic energy deposited is sufficiently high, the temperature may rise above the melting point of the material and a molten cylinder, of diameter some nanometers, is formed. This can persist up to tens of picoseconds before rapid quenching of the melt to ambient temperature, resulting in defect rich or even amorphous cylindrical latent tracks. Track formation only occurs if the threshold electronic stopping energy ($S_e$) of the material is exceeded. Previous study using 40 MeV Si ions [12], in In/Se bilayer system showed that $S_e$ (5.42 keV/nm in indium and 4.13 keV/nm in selenium) was not sufficient to produce a transient molten track in In/Se bilayer system. Hence an electronic energy 4 keV/nm of 90 MeV Si may not be sufficient to produce latent tracks in In$_2$Se$_3$ thin films. This may be the reason why we have no amorphisation even after irradiation with 90 MeV Si ions.

In our case, we observed an increase in average grain size of the samples after irradiation. This might be due to the annealing effect of SHI below the threshold $S_e$ value [21, 26]. Kamarou et al. [21] found, in the case of pre-damaged InP, that ‘damage-annealing’ dominates the ‘damage-formation’ for sub-threshold energy (using 140 MeV Kr ion). But above the threshold energy ($S_e$) (using 390MeV Xe, 150 MeV Au and 600 MeV Au ions) irradiation caused higher damage in InP and observed hardly any effect of annealing. Similar case was reported in the case of GaAs and InP in which annealing was observed at low fluence with sub threshold energy [21, 26]. Hence the increase in average grain size of the indium selenide samples was attributed to the annealing of point defects.
defects and the growth of small crystalline inclusions present in the film, leading to local crystallisation [26].

5.3.2 Optical studies

(a) Determination of band gap energy and Urbach energy

Optical absorption spectra of irradiated and unirradiated samples were recorded in the range of 400 to 900 nm. The unirradiated samples showed multiple absorptions in the ranges 650-850 nm and 500-600 nm, whereas the irradiated samples showed only one absorption each in the range 500 – 650 nm (for IS100 and IS150) and in the range 400 – 550 nm (for IS200, IS300 and IS400), respectively. Figure 5.3 shows the absorption spectra of IS100 before and after irradiation. In the case of unirradiated IS100 [Fig. 5.3(a)], clear extrinsic absorption could be seen, indicating the presence of strong levels, existing below the conduction band. But on irradiation, these levels got eliminated [Fig. 5.3(b)].

![Figure 5.3: Absorption spectra of IS100 (a) before and (b) after irradiation](image)
The optical band gap ($E_g$) of the samples was determined by extrapolating the straight line portion of $(\alpha \nu)^2$ versus $\nu$ plot to $\alpha = 0$ [27], where $\nu$ is the incident photon energy and $\alpha$ is optical absorption coefficient, determined from the absorption spectra. Extrapolating the other straight line portions of $(\alpha \nu)^2$ versus $\nu$ plot to $\alpha = 0$, gave the indications of defect levels and/or the band gap of the secondary phase present in the sample [5, 9, 27]. The optical band gap of irradiated and unirradiated samples is tabulated in table 5.2.

**Table 5.2:** Optical band gap of the samples before and after irradiation.

<table>
<thead>
<tr>
<th>SL.</th>
<th>Sample name</th>
<th>Optical band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Un-irradiated</td>
</tr>
<tr>
<td>1.</td>
<td>IS100</td>
<td>1.84eV</td>
</tr>
<tr>
<td>2.</td>
<td>IS150</td>
<td>1.81eV</td>
</tr>
<tr>
<td>3.</td>
<td>IS200</td>
<td>2eV</td>
</tr>
<tr>
<td>4.</td>
<td>IS300</td>
<td>2.04eV</td>
</tr>
<tr>
<td>5.</td>
<td>IS400</td>
<td>2eV</td>
</tr>
</tbody>
</table>

Figure 5.4 shows the $(\alpha \nu)^2$ versus $\nu$ plot of IS100 (band gap=1.84 eV). Extrapolating the straight line portions of this plot to $\alpha=0$, one could get three more activation energies 1.42 eV (level-A), 1.26eV (level-B) and 1.08 eV, corresponding to defect levels present in the forbidden energy gap in this sample. The defects at 1.42 eV and 1.26 eV were already attributed to light activated electron traps [5]. IS150 showed the band gap of $\beta$ and $\gamma$-phase present in the sample corresponding to an energy 1.7 eV and 1.81 eV respectively (Fig. 5.1, IS150) [9]. But IS200 and IS300 (with band gap=2.02 and 2.04 eV respectively) showed a defect level at 1.65 eV above the valence band (Fig. 5.5).
Figure 5.4: $(\alpha h \nu)^2$ versus $h \nu$ plot of IS100 before irradiation

Figure 5.5: $(\alpha h \nu)^2$ versus $h \nu$ plot of IS300 before irradiation. Inset shows the plot after irradiation.
Figure 5.6 depicts the optical absorption spectra of IS400. In addition to the absorption in the range 500 nm – 650 nm (2 eV; band to band absorption) this sample had an additional absorption in the range 700 nm – 850 nm [1.62 eV]. As IS400 did not show any secondary phase in XRD analysis (Fig. 5.1), this absorption might be due to the defect level, present in the sample. From $(\alpha h\nu)^2$ versus $h\nu$ plot of this sample, (inset of Fig. 5.6), the defect level was identified at 1.62 eV above the valence band. But on irradiation, the absorption spectra indicated that this defect level [at 1.62 eV] was annealed out (Fig. 5.6). An increase of band gap from 2 eV to 2.8 eV was also observed on irradiation.

**Figure 5.6**: Absorption spectra of IS400 before and after irradiation. Inset shows $(\alpha h\nu)^2$ versus $h\nu$ plot of IS400 before irradiation.
For all the samples, irradiation caused an increase in optical band gap, with the maximum increase of about 40% in the case of IS400 (Table 5.2). One of the factors, which could affect the optical band gap, is the quantum size effect [12, 29]. If the grain size of the samples was reduced to the order of few nano meters, optical band gap should increase. But here XRD analysis revealed that, the grain size actually increased on irradiation (Table 5.1), proving that quantum size effect was to be ruled out. Hence this could be explained in the following way.

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 band gap was 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. 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 [29, 30]. Different semiconductors, namely a-SiC [32], a-C:H [33] and even chalcogenide compounds such as CuInSe₂ [34] and InSe [35] exhibited Urbach tail. Urbach energy width (tail width) is a measure of disorder in the material [33]. Figure 5.7 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 resulted in absorption spectrum, showing absorption even at energies much below the band gap [for example the absorption spectrum of IS100 in Fig. 5.3(a)]. In this figure, we could observe a broad shoulder in the range 550 nm - 650 nm, which strongly indicated the presence of dense state near the conduction band (see region marked A-B in Fig. 5.4). According to Urbach rule [28, 36], below the fundamental absorption edge, the absorption coefficient \( \alpha \) varies exponentially as \( \alpha = \alpha_0 \exp (h\nu/E_u) \), where \( \alpha_0 \) 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 [31]. This 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 [28].

Figure 5.7: Sketch of the assumed band structure with dense localized bands, (a) before and (b) after irradiation.

Figure 5.8 shows the same plot ‘$(\ln \alpha)$ versus $h\nu$’ of IS200, before and after irradiation. $E_u$ of all the samples before and after irradiation with 90MeV Si ions was calculated and tabulated (Table 5.3). One could observe that the Urbach tail width decreased for all samples except IS150, after irradiation. The decrease of Urbach tail width shows 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 [36]. Increase in Urbach tail width in the case of IS150 after
irradiation might be due to the creation of planar defects during irradiation, since InSe has a hexagonal layered structure. Abay et al. [37] observed a decrease in Urbach energy in InSe due to the reduction of planar defects. One point to be noted here is that, the samples, except IS100 and IS150, were formed with single phase γ-In$_2$Se$_3$, which has a hexagonal defect wurtzite structure [6].

![Figure 5.8: ln α versus hν plot of IS200 before and after irradiation.](image)
Table 5.3: Variation of Urbach energy with irradiation.

<table>
<thead>
<tr>
<th>Sl.</th>
<th>Sample name</th>
<th>Urbach energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before irradiation</td>
</tr>
<tr>
<td>1.</td>
<td>IS100</td>
<td>2.04eV</td>
</tr>
<tr>
<td>2.</td>
<td>IS150</td>
<td>450meV</td>
</tr>
<tr>
<td>3.</td>
<td>IS200</td>
<td>363meV</td>
</tr>
<tr>
<td>4.</td>
<td>IS300</td>
<td>400meV</td>
</tr>
<tr>
<td>5.</td>
<td>IS400</td>
<td>418meV</td>
</tr>
</tbody>
</table>

When we measured the optical band gap of the material, because of the band tailing, we were able to measure only the band gap \( E_g \). This was very much less than the actual band gap \( E_g \) of the material (Fig. 5.7(a)). Optical absorption study revealed that irradiation could anneal out defects from forbidden energy region. Urbach tail width measurements on the irradiated sample showed annealing out the localized energy bands near the band edges, which indicated a reduction in \( E_u \). As a result of this, conduction and valence band tail states were separated further apart in energy (Fig. 5.7(b)), which was evident from blue shift in absorption spectra (Fig. 5.6). This might be the reason for the increase in band gap of indium selenide samples. It is also worth mentioning here that the highest optical band gap already reported for \( \text{In}_2\text{Se}_3 \) was \(-3\text{eV}\), which is very close to the value obtained in the present study [7].

**(b) Photoluminescence**

Figure 5.9 shows the PL spectra of IS100 before and after irradiation. The emission at 746 nm (peak-X, Fig. 5.9) was attributed to the transition to a
recombination center 1.66 eV (level-C) below the conduction band [5, 10]. Interestingly the third activation energy (1.08 eV) obtained in IS100 from optical absorption study exactly coincides with energy between level B and level C, and hence attributed as the transition from level C to level B). The emission at 675 nm (1.84 eV) was attributed to the transition from defects below the conduction band to the defect states above the valence band (peak-Y), since the measured band gap of unirradiated IS100 was 1.84 eV (Fig. 5.4). Band gap increased from 1.84 eV to 2.02 eV and a shift in PL emission towards lower wavelength [from 675 nm to 664 nm, corresponding to energy of 1.87 eV], was also observed on irradiation. But it is to be specifically mentioned here that the emission at 1.66 eV remained without any change. This indicated that irradiation was not affecting the recombination center, while annihilation of localized states near band edges caused the shift of emission at 1.84 eV to 1.87 eV. The full width at half maximum (FWHM) of the peak-Y reduced from 85.5 nm to 47.5 nm, on irradiation. The blue-shift and the reduction of FWHM of PL peak were due to the annihilation of localized states near band edges [32, 33], which ultimately resulted in increasing optical band gap of the material. Earlier Kamboj et al reported annihilation of defects induced by 40 MeV Si ions in Se_{80-x}Te_{20}Pb_x in which an increase in band gap from 1.36 eV to 1.48 eV was also observed [38]. But Sorieul et al. [18] observed a decrease in optical band gap of α-SiC single crystals due to heavy ion irradiation (4 MeV Xe and 4 MeV Au ions) and this was attributed to the creation of localized states in the forbidden energy region. They also found that Urbach energy was increasing with the irradiation fluence. The increase of Urbach energy reflected the introduction of disorders/defects in α-SiC, which ultimately resulted in reduction of optical band gap [18]. But in our case, Si ions of energy 90 MeV, annealed out the defects/disorders in In_{2}Se_{3}, which was evident from x-ray diffraction and optical absorption studies. Urbach energy also decreased on irradiation, and this again supported our argument.
In the case of IS400, one could observe a large blue shift in absorption spectra, induced by irradiation [Fig. 5.6]. Figure 5.10 shows the PL spectra of the sample IS400 recorded at 100 K before and after irradiation. This also showed a blue-shift. The unirradiated sample showed an emission at 631 nm (1.97 eV). As the band gap of IS400 was 2 eV, the emission at 1.97 eV is attributed to the band-to-band (i.e., defect tail-to-defect tail) recombination. On irradiation, the emission was shifted to 594 nm and an additional emission at 495 nm corresponding to 2.51 eV, was also observed. Higher energy emission at 2.45 eV is reported in κ-In$_2$Se$_3$, but XRD analysis did not show any presence of κ phase [Fig. 5.2]. At higher temperatures, emission at 495 nm vanished and a broad peak at 584 nm (2.13 eV) was observed (inset of figure 5.10). Hence the shift of PL emission, from 631 nm to 584 nm, again shows the annihilation of localized states near band edges, as the cause of this shift.
In addition to the emission at 1.87 eV and 1.66 eV, two more broad emissions were observed at 611 nm and 559 nm, [corresponding to energies 2.03 eV and 2.22 eV respectively] on irradiation of IS100 (Fig. 5.9). The emission at 2.03 eV might be probably, the band-edge emission while the broad emission centered at 2.22 eV might be from the tiny amount of κ-In2Se3 phase present in the film [10]. But again XRD analysis did not show any sign of the κ phase (Fig. 5.2). Irradiation annealed out the defects present in the forbidden gap. This allowed more photo-generated carriers to reach the conduction band, which participated in the recombination process too. This might be the reason for the increase in PL intensity of the peaks X and Y [Fig. 5.9] [5]. One interesting point to be noted is
the dominance of the PL peak Y over X on irradiation. This suggested that the
destruction of minority carriers by the recombination center (at 1.66 eV) was
more in the unirradiated sample than in irradiated sample.

5.3.3 Electrical study

(a) Room temperature photoconductivity

Dark and photo conductivity of irradiated and unirradiated samples were
measured at room temperature and tabulated in table 5.4. Irradiation caused only
marginal increase in sheet resistance of the films. Increase in photosensitivity
$S$, $S = (I_L - I_D) / I_D$, (ie, the ratio of difference between photocurrent ($I_L$) and dark
current ($I_D$) to the dark current) was clearly seen for all the samples. Here we
could observe a conversion of photoconductivity/photosensitivity from negative
to positive in IS100 upon irradiation.

Table 5.4: Variation of photosensitivity and Sheet resistance before and after irradiation.

<table>
<thead>
<tr>
<th>Sl.</th>
<th>Sample name</th>
<th>Photosensitivity</th>
<th>Sheet resistance (in ohm cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Un-irradiated</td>
<td>Irradiated</td>
</tr>
<tr>
<td>1.</td>
<td>IS100</td>
<td>- 0.04</td>
<td>0.3</td>
</tr>
<tr>
<td>2.</td>
<td>IS150</td>
<td>0.11</td>
<td>1.04</td>
</tr>
<tr>
<td>3.</td>
<td>IS200</td>
<td>0.07</td>
<td>1.3</td>
</tr>
<tr>
<td>4.</td>
<td>IS300</td>
<td>0.06</td>
<td>0.22</td>
</tr>
<tr>
<td>5.</td>
<td>IS400</td>
<td>0.37</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Figure 5.11 shows the photoconductivity spectrum of IS100, before and after
irradiation. For the unirradiated sample, when the light was turned on, the
current decreased to a lower value, below the dark current and when the light
was turned off, the current increased back to the dark current. But in the case of
irradiated sample (IS100) we could observe that the conductivity was positive on illumination (Fig. 5.11(b)). From this observation, one could find that irradiation caused the photoconductivity to change from negative to positive, probably due to the annealing out of the defects, which were responsible for negative photoconductivity.

To explain the negative photoconductivity in IS100, earlier we used a model for γ-In$_2$Se$_3$ (Fig. 5.12) [chapter 3, section 3.4.4]. Blocking of excited electrons from reaching the conduction band by the levels A and B and the recombination taking place at level C were the most important processes leading to the negative photoconductivity of γ-In$_2$Se$_3$ at room temperature [5] (for more details please see chapter 3). Optical absorption study revealed the annihilation of trap levels at 1.42 eV (level A) and 1.26 eV (level B) in the case of IS100 upon irradiation. Annihilation of these trap levels A and B allowed photo-generated carriers to reach conduction band, which resulted in increasing the photosensitivity. Photoluminescence study also revealed that, on irradiating IS100 (Fig. 5.9) PL
emission peak Y dominated the peak X, which suggested that the destruction of minority carriers at recombination centre was reduced considerably on irradiation. Low photosensitivity registered for IS200 and IS300 might be due to the presence of light activated electron trap (1.65 eV) in the sample. Annealing of this trap, due to SHI irradiation, resulted in the increase of photosensitivity. Grain boundaries in the sample may also act as electron traps. Irradiation using 90 MeV Si ions increased the average grain size of the crystallites thereby reducing the density of grain boundaries. This might have helped the photo-generated carriers to survive, resulting in the increase of the photosensitivity/photoconductivity. Thus by controlled dense electronic energy deposition using SHI irradiation, one could eliminate electron traps and enhance the photoconductivity and optical band gap of $\gamma$-In$_2$Se$_3$ with a marginal increase of sheet resistance.

Figure 5.12: Band structure of IS100 before irradiation.
5.4 Conclusion

Through SHI irradiation, using 90 MeV silicon ions, one could increase optical band gap and photoconductivity of $\gamma$-In$_2$Se$_3$ without decreasing the thickness and considerable variation in resistance. Annihilation of defects, which trapped photo-excited electrons, may be the reason for increase in photoconductivity. Annealing of traps at 1.42 eV and 1.26 eV above the valence band in IS100 converted the photoconductivity from negative to positive. Optical band gap of $\gamma$-In$_2$Se$_3$ can be increased from 2 eV to 2.8 eV due to irradiation. Annihilation of localized defect levels near the band edges increased the optical band gap of the material.
Chapter 5

References

Chapter 5
