Chapter 3

Growth of β-Indium Sulfide Buffer Layer by Two Stage Process
In photovoltaic thin film cells, the rectifying contact is between p-type absorber layer and the n-type buffer layer. Maintaining a high-quality pn junction was observed to be a critical factor for device efficiency. The transport properties of heterojunctions strongly depend on interface characteristics such as potential barrier height, interface state and band discontinuities. The aim of the buffer layer is to realize the junction with absorber.

The essential characteristics of a typical buffer layer are, it should

- be n-type for carrier separation,
- be resistive with a high coverage efficiency
- act as physical barrier against short circuits between the electrodes of the cell
3.1 Introduction

The semiconducting compounds of $A_{2}^{III}B_{3}^{VI}$ family, where $A$ is In or Ga and $B$ is S or Se have attracted particular interest in recent years due to their promising technological applications as buffer layer in solar cells. Indium sulfide ($In_2S_3$) can be used as an effective replacement for CdS in Cu(In, Ga)Se$_2$ based solar cells [1]. Though the highest conversion efficiency in thin film solar cells has been reported for Cu (In, Ga)Se$_2$ with a CdS buffer layer, there is great importance in replacing CdS with cadmium free buffer layer, for environmental reasons and possible gains in efficiency associated with an increase of the short circuit current. To avoid toxic heavy-metal Cd containing waste in the module production, a Cd free, less toxic buffer layer is desirable. Wide band gap (>2.5 eV) of $In_2S_3$ thin films suggests it can act as a better buffer layer with improved light emission in the blue region than CdS having band gap 2.4 eV. It is reported that Cu(In, Ga)Se$_2$ solar cell prepared with chemical bath deposited $In_2S_3$ as a buffer layer has efficiencies (16.4%) near to those obtained by device made with a standard CdS buffer layer [2]. The ternary indium sulfide compounds like CuInS$_2$ with an improved photosensitivity and $In_{2-x}Ga_xS_3$ offering a possibility to tailor the band gap are attractive materials for photovoltaic and optoelectronic devices [3]. $In_2S_3$ thin films can also be used as the precursor for the preparation of CuInS$_2$, which is one of the most widely used absorber layer in solar cells [4]. In the present work, the preparation and characterization of indium sulfide thin films as buffer layers for solar cell application is described.
3.2 Material Properties of In$_2$S$_3$

3.2.1 Crystallographic structure

Indium Sulfide (In$_2$S$_3$) is a kind of III-VI$_3$ materials which crystallize in cubic or hexagonal closed packed structure, same as II-VI compounds upon the replacement of the divalent cation by the trivalent In. As one third of the cation site remains empty, it causes a defect structure [5]. According to the Joint Committee on Powder Diffraction Standards (JCPDS), three major crystal modifications are known for In$_2$S$_3$ [6-10]. The low temperature metastable $\alpha$ form has a cubic structure with the lattice constant $a$ of 5.358 Å. It is a cubic closed packed structure of sulfur, where 70% of the In atoms are randomly distributed on octahedral sites and the rest remain in tetrahedral sites [11]. $\alpha$ form transforms irreversibly at 360°C to the $\beta$ form having a defect spinal lattice ($a = 10.73$ Å) in which eight of the tetrahedral sites are occupied by In, where as four are randomly left empty [12]. Thus the chemical formula of $\beta$-In$_2$S$_3$ could be written as [In(t)$_{2/3}$] In$_2$(o)S$_4$ where (t), (o) and $\Box$ represent tetrahedral, octahedral and vacant sites respectively. Under certain conditions, a high ordering of this vacancy at the tetrahedral sites occurs, establishing a tetragonal super cell containing spinel blocks along the c-axis [13-14]. This phase transition from the tetragonal structure to the less ordered $\beta$ form takes place at 420°C [11, 15]. In the temperature range between 750 and 800°C the $\beta$ In$_2$S$_3$ is reversibly transformed to $\gamma$ In$_2$S$_3$, which has a layered structure with a hexagonal unit cell ($a = 3.85$ Å, $c = 9.15$ Å). Of the three modifications, $\beta$-In$_2$S$_3$ is the stable form with tetragonal structure [16]. Besides these there is a high pressure $\varepsilon$ phase, which is rhombohedral ($a = 6.0561$ Å and $c = 17.5$ Å) [17].
The structure of the β modification is related to the spinel lattice. The cation vacancies are randomly located on either the octahedral sites only or on both types of sites. A model of ordered vacancies within a super structure of tetragonal symmetry was proposed by Rooymans [18]. The unit cell consists of three spinel cubes stacked along the c-axis. By rotating the a-and b-axis through 45° a smaller unit cell can be obtained, which belongs to a body centered tetragonal Bravis-lattice with the parameters: a = b = 7.62Å and c = 32.32 Å. This reduced unit cell contains 24-spinel type octahedral sites, which are all occupied by indium atoms. Of the 12 tetrahedral sites, normally occupied in the spinel, only 8 are occupied by indium whereas 4 remain empty (Fig.3.1). These 4 vacancies per unit cell are ordered along a fourfold screw axis of symbol 41 parallel to the c-axis. The ordered modification can therefore be interpreted as a
quasi-ternary compound consisting of In, S and vacancies or even as a quasi-quaternary one, when the difference between two types of the cation sites is taken into account.

3.2.2 Optical Properties

Most of the group II–VI materials are direct band gap semiconductors with high optical absorption and emission coefficients (the exceptions are HgSe and HgTe which are semimetals). \( \beta \)-In\(_2\)S\(_3\) is an n–type semiconductor with a direct band gap of 2 to 2.3 eV [19, 20]. These values are too small for an application as buffer layer in solar cells. Several values greater than 2.3 eV have also been reported in literature. The In\(_2\)S\(_3\) films deposited by Atomic Layer Epitaxy (ALE) [21] show a band gap of 3.3 eV, which is reduced to 2.25 eV on annealing. Barreau et al has studied a widening in band gap by the increase in oxygen content in the prepared film [22]. In another work Barreau observed the increase in band gap is also due to sodium content in the film. Their explanation is that sodium increases the ionicity of the tetrahedral cationic sulfur bonds which increases the optical band gap [23]. The blue shift of the optical transmission has been explained by Kim et al [24] with the interpretation that the broadening is due to excess of sulfur in the film. Yoshida et al and Yasaki et al have explained the broadening of optical band gap of the In\(_2\)S\(_3\) by quantum size effect [14, 25]. Band tails observed in the optical spectra of vacuum deposited In\(_2\)S\(_3\) thin films after the air annealing. It could be considered as films defects created by the thermal evaporation process [26]. The broadening or shift of the short wavelength absorption of In\(_2\)S\(_3\) thin films were also explained by the presence of secondary phases and disordered structure [27].
3.2.3 Electrical Properties

Electrical studies on single crystals of $\text{In}_2\text{S}_3$ grown by chemical vapor transport and freeze gradient technique show a resistivity 30–1000 $\Omega$cm. The 3% excess sulfur incorporation in these crystals increases the resistivity to 20 $K\Omega$-cm [22]. The same results were observed by Rehwald and Harbeke [28]. Their experiments also showed that the annealing of $\text{In}_2\text{S}_3$ samples in air or vacuum at temperatures around 150°C for 2 hours results in a decrease of resistivity by more than an order of magnitude. Bessergenev et al have studied the effect of the substitution of sulfur by oxygen in the $\beta$-$\text{In}_2\text{S}_3$ films, which induces an increase in conductivity [29]. Conductivity is found to be increase with sodium content. When sodium is introduced in the crystalline matrix, it creates a disorder by the non periodic occupation of the tetrahedral sites and it can explain the increase of electrical conductivity [29]. Barreau et al showed that when the sodium content increases after particular value, it tends to total filling of the tetrahedral sites, leading to a perfectly ordered material having a very low electrical conductivity [30]. The introduction of oxygen in the thin films can also increase the conductivity by approximately two orders. The introduction of oxygen in the thin films can modify the properties of grain boundaries, which induce an increase in conductivity of the films [22].

3.2.4 Morphological Properties

Sulfur composition in excess of the stoichiometric value in spray pyrolysed $\text{In}_2\text{S}_3$ films causes an increase in $a$ and $c$ parameters [24]. The surface studies show that $\text{In}_2\text{S}_3$ prepared by chemical bath deposition at room temperature has a cauliflower-like morphology while films deposited at higher temperature resulted in fibrous structure [31]. Yahmadia et al observed some fibre structure along
with large lumps due to the presence of In$_6$S$_7$ phase [32]. Yoshida et al have reported a significant variation in surface morphology with the reaction temperature [33].

3.3 Processing Techniques for Indium Sulfide Thin Films

A wide range of preparation methods exist to grow In$_2$S$_3$ thin films. The deposition method has generally a large impact on the resulting film properties as well as on the production costs. In$_2$S$_3$ thin films are currently being deposited using both wet and dry processes. Prominent among them are Low Pressure Metal-Organic Chemical Vapour Deposition (MOVCD) [34], Atomic Layer Chemical Deposition (ALCVD) [1], Spray Pyrolysis [35,36] Chemical Bath Deposition (CBD) [37], Atomic Layer Epitaxy (ALE) [3,38,39], photochemical deposition [40], annealing of elemental layers [41], evaporating metal onto molybdenite [42], and Physical Vapor Deposition (PVD) [23,43], sulfurisation of metallic electroplated indium [44] etc.

CBD is relatively inexpensive, simple and convenient for large area deposition [45]. Using this method, deposition of In$_2$S$_3$ thin films from a bath containing indium salt and thioacetamide as sulfide ion source has been reported [46,47]. The CIGS based solar cell prepared with CBD In$_2$S$_3$ as a buffer layer have reached the efficiencies (15.7%) [48].

Attempts have been made to deposit In$_2$S$_3$ thin films by using successive ionic layer adsorption and reaction (SILAR) method [49]. This method is mainly based on immersion of the substrate into separate cation and anion precursor solutions and rinsing between every immersion with ion exchanged water.
ALCVD is based on the surface reaction of the precursors. Main advantage is it allows the deposition of highly homogenous thin films and layer thickness growth control. A solar conversion efficiency of 13.5% has been obtained on small area device with indium sulfide buffer layer by ALCVD [21]. Naghavi et al. [2] recently demonstrated an efficiency of 16.4%, which is the record for CIGS using indium sulfide. They employed an atomic layer deposition (ALCVD) process using indium acetylacetonate and hydrogen sulfide (H₂S) for In₂S₃ window layer synthesis, with best results obtained at 220°C substrate temperature. Although ALCVD has produced the best devices to date, the deposition rate is slow and the reagents are expensive.

With respect to industrial integration, the high vacuum techniques are most attractive. Researchers have examined PVD by sequentially evaporating indium and elemental sulfur [3, 11]. Its main advantage is easy control over growth rate through its various preparative parameters. However, an additional annealing step was required to form high-quality indium sulfide. Annealing temperature is a critical constraint on In₂S₃ window layer deposition, as excessive temperature results in copper diffusion and decreased solar cell performance [50, 51].

In the present investigation we aimed to combine high vacuum evaporation with rapid thermal processing (RTP) for chalcogenisation. The precursor preparation by vacuum evaporation followed by chalcogenisation called the two-step processes are pursued due to their superior potential for industrial production. By the introduction of rapid thermal processing the annealing time could be reduced from 3 h to 45 minutes.

The chalcogenisation was carried out at various annealing temperatures ranging from 250°C to 600°C in the presence of H₂S which resulted in the sulfurisation
of indium film to yield indium sulfide. The In$_2$S$_3$ film characterization including structural, optical, and electrical and composition is presented.

3.4 Experimental Details

Thin films of Indium were coated on the glass and amorphous silica substrates by the vacuum thermal evaporation technique. High purity Indium (99.999%) was evaporated from molybdenum boat at a pressure of $3 \times 10^{-5}$ m bar. Thickness of indium layer 4000 Å was monitored using a quartz digital thickness monitor. The deposition rate was around 1 Å per second.

![Figure 3.2. The thermal cycle used for Rapid 2 process.](image)

Indium films prepared at room temperature were found to be less adhesive. A substrate temperature of 75°C was maintained during indium deposition for better adhesion. The sulfurisation was done at different temperatures. Initially, the In$_2$S$_3$ films were prepared by heating the indium films from room temperature to
set temperature under H$_2$S atmosphere. It took around 30-45 minutes to reach the set temperature. The slow heating of indium films to set temperature resulted in the evaporation of indium and hence the films obtained were very thin. To minimize the indium loss, the metallic precursors were introduced rapidly into the furnace in the presence of H$_2$S, which has already attained the set temperature, and the sulfurisation was carried out for 3 hrs. After the sulfurisation samples were allowed to remain in the furnace itself till it cools to room temperature which took around nine hours. This cycle was named as Rapid 9. Rapid indicates the fast heating rate (30 to 70 sec to reach the set temperature) and the 9 indicates the removal of samples after 9 hours. In an another thermal cycle named Rapid 2 the samples were allowed to cool naturally for 2 hours in the furnace after 3 hours sulfurisation and then they were taken out from the surface which prevented the large loss of indium during the cooling to room temperature. This thermal circle is represented graphically in figure 3.2. The sulfurisation carried out for different temperatures varying from 250°C to 600°C.

In both experiments the obtained films were considerably thinner than assumed. Also, since the main aim of the two stage process is making the cost of fabrication less, another thermal cycle was tried to make the time consumption less. In this thermal cycle the metallic precursors were introduced rapidly into the furnace at the set temperature in the presence of H$_2$S. The duration of sulfurisation was varied from 10 minutes to 3 hours keeping the sulfurisation temperature at 300°C. The samples were rapidly withdrawn from the furnace to minimize the indium loss. The sulfurisation of indium films for 45 minutes and above resulted in single phase β-In$_2$S$_3$. The thickness of the films found decreases with the increase in sulfurisation time. So further chalcogenisation experiments were carried out keeping the sulfurisation time constant for 45
minutes but for various sulfurisation temperatures ranging from 250°C to 600°C. This thermal cycle was named Rapid 45 since sulfurisation duration was fixed as 45 minutes. The numeric (Rapid 45) here indicate sulfurisation time and the cooling and heating by introducing and removing the samples from the furnace, whereas in Rapid 2 and Rapid 9 the numeric indicates the natural cooling time of the samples within the furnace.

The thickness of the In$_2$S$_3$ was measured by using gravimetric method using a sensitive microbalance. Precursor indium film thickness was measured using a quartz thickness monitor. The In$_2$S$_3$ films were further characterized by studying the structural, morphological, optical and electrical properties by X-ray diffractometer, Scanning Electron Microscopy (SEM), UV-VIS-NIR spectrophotometer and I-V measurement system respectively. The crystal structure, lattice strain, lattice parameters, absorption coefficient, conductivity, band gap and resistivity were obtained from these studies. Composition of the films was analysed using Energy Dispersive X-ray analysis (EDX). For electrical characterisation two silver electrodes in planar geometry were used as electrodes.

3.5 Results and Discussions

3.5.1 Crystal structure and composition

The X-Ray diffraction patterns of In$_2$S$_3$ films prepared in different processes were analyzed. It has been observed from XRD that there is no formation of indium oxide in the films. The XRD spectra of samples prepared by the Rapid 2 Process are shown in figure 3.3.
The XRD spectra show the presence of InS peak (111) along with In$_2$S$_3$ phase for lower sulfurisation temperature (<400°C). As the sulfurisation temperature is increased it has been observed that the intensity of (111) plane corresponding to InS phase along with the other In$_2$S$_3$ diffraction peak increases. The films obtained were a mixture of InS and In$_2$S$_3$ upto a sulfurisation temperature of 350°C. No peaks corresponding to InS was observed when the sulfurisation was carried at 400°C and above. Single phase In$_2$S$_3$ was obtained by Rapid 2 process when the temperature was 400°C and above.
Figure 3.4 XRD pattern of β-In$_2$S$_3$ films prepared in Rapid 9 process at different sulfurising temperature.

Figure 3.4 is the XRD spectra of films prepared under Process Rapid 9. Contrary to Rapid 2 process Rapid 9 shows single phase In$_2$S$_3$ even at low sulfurisation temperature. The slow cooling to room temperature in Rapid 9 process might be giving sufficient time for conversion of InS phase to In$_2$S$_3$. The InS initially formed at low sulfurisation temperature (as evident in the XRD of Rapid 2 process) [52] is being converted to In$_2$S$_3$ on the prolonged annealing when the samples are allowed to cool to room temperature in the furnace.
The crystallinity of the films was also studied for the Rapid 45 samples. The sulfurisation of the indium films at 300°C in H₂S atmosphere for 10 minutes yielded only a single (0012) peak of β-In₂S₃ and showed poor crystallinity (Fig. 3.5). The films obtained by 30-minutes sulfurisation at 300°C showed two major diffraction peaks (109) and (103) of β-In₂S₃ along with (111) peak of InS phase. This may be because the duration of sulfurisation was insufficient for the complete conversion of InS to In₂S₃. Another diffraction peak (003) corresponding to In₆S₇ was also present, but it disappeared on annealing the samples in air for 30 minutes.
Single phase $\text{In}_2\text{S}_3$ was obtained when the sulfurisation time was 45 minutes at 300°C. For the films obtained by the sulfurisation for 45 minutes and 1 hour showed the prominent peak corresponding to (109) plane of $\text{In}_2\text{S}_3$ while the films sulfurised for 2 hours and 3 hours showed the preferred orientation of (103) plane (Fig. 3.6). However no peaks corresponding to InS or any other impurity phase was observed when the sulfurisation time was 45 minutes and above. Hence for further studies varying sulfurisation temperature, the sulfurisation time was fixed as 45 minutes.
The XRD pattern of In$_2$S$_3$ films prepared at different sulfurisation temperature for 45 minutes is shown in figure 3.7. X-ray diffraction studies show that sulfurisation of indium films at 300°C and above result in single-phase β-In$_2$S$_3$. When the films were sulfurised at 600°C, highly oriented In$_2$S$_3$ films were obtained (Fig. 3.8).

These films show (h 0 3h) peaks with small value of Full Width at Half Maximum for (103) peak (FWHM=0.264). These films show only (h 0 3h) reflections while the other films, which were prepared at lower sulfurisation temperature showed an orientation along (109) plane.
Grain size of the indium sulfide thin films were calculated using the Scherrer's formula $t = 0.9\lambda / (\beta \cos \theta)$ where $\lambda$ is the wavelength of the X-rays used, $\beta$ is the full width at half maximum (FWHM) in radians for a particular peak and $\theta$ is the Bragg angle [53]. The grain size was found to be in the range of 20-30 nm irrespective of the process adopted for the sulfurisation. The lattice constants of the films were calculated and the calculated values of $a$ and $c$ ($a = 7.8$ Å and $c = 32.61$ Å) are comparable with values for $\beta$-In$_2$S$_3$ crystals ($a = 7.619$ Å and $c = 32.329$ Å) [7]. However the lattice parameters for the film are found to be slightly higher than that of the crystals. This may be due to excess sulfur (as
shown by EDX) percent in the films, which occupy the interstitial position of defect spinal structure causing lattice expansion.

S/In ratio of the prepared films has been calculated by the EDX measurement. All the films prepared have been found to have excess sulfur. It is observed that S/In ratio increases with increase of sulfurisation temperature upto 400°C and then it decreases (Fig. 3.9). The film sulfurised at 350°C has an S/In ratio 1.58 that is nearly stoichiometric.

![Figure 3.9: Variation of S/In ratio of In₂S₃ films with sulfurisation temperature.](image)

The morphology of the indium sulfide thin films was examined by the Scanning Electron Microscope (SEM). The visual appearance suggests an outer rough surface of spherically structured grains for films sulfurised below 400°C for
the films prepared by rapid 2 and 9 cycles. The higher sulfurisation temperature (>400°C) resulted in randomly distributed needle like particles covering the whole film surface (Fig. 3.10). Also the surfaces are found to be more orderly and closely packed for samples that were cooled to room temperature (9 hours) in the furnace itself. The grains are seen as spherically

Figure 3.10 Surface SEM of β-In$_2$S$_3$ thin films sulphurised at 600°C
a) Rapid 2 process, b) Rapid 9 process
structured for the films prepared by rapid 45 also, when the sulfurisation temperature is 350°C. As the sulfurisation temperature increases to 400°C the surfaces are found to be more orderly and closely packed (Fig. 3.11).

![Surface SEM of β-In₂S₃ thin films prepared by Rapid 45 process.](image)

**Figure 3.11** Surface SEM of β-In₂S₃ thin films prepared by Rapid 45 process,  
a) sulfurised 350°C  b) sulfurised at 400°C

Films obtained are found to be formed of clusters when the sulfurisation temperatures are 500°C and 600°C (Fig. 3.12).
3.5.2 Optical Characterizations

The optical energy gaps of $\beta$-$\text{In}_2\text{S}_3$ thin films were obtained from the optical transmission spectra in the wavelength range 300 to 2000 nm. The absorption
coefficient $\alpha$ was deduced from the transmission spectra using the relation $I = I_0 e^{-\alpha t}$ where 't' is the thickness of the film.

The absorption edge of the $\beta$-In$_2$S$_3$ was examined using the relation given by Bardeen et al. [54]. The coefficient $\alpha$ is related to the incident photon energy $h\nu$ as $\alpha h\nu = \beta (h\nu - E_g)^n$, where $E_g$ is the energy gap and $n=1/2$ for direct transition. Figure 3.13 shows the plot of $(\alpha h\nu)^2$ as a function of the photon energy for the films sulfurised at different temperature for 45 minutes. The intercept of the linear portion on the energy axis at $(\alpha h\nu)^2$ equal to zero gives the band gap energy.

![Figure 3.13](image)

Figure 3.13 The plot of $(\alpha h\nu)^2$ vs the photon energy for $\beta$-In$_2$S$_3$ films prepared by Rapid 45 process at different temperatures.

The optical band gap measurements show that the sulfurisation temperature affects the band gap values of the films. Asikainen et al has reported the dependence of optical properties of $\beta$-In$_2$S$_3$ on the sulfurising parameter [3].
the present study the band gap of In$_2$S$_3$ films are found to be in the range of 2.37 to 2.58 eV, which depends on the sulfurisation temperature. The films sulfurised at 350°C which was nearly stoichiometric exhibit the higher band gap 2.58 eV. For the films sulfurised at 400°C and above the band gap is around 2.4 eV (Fig. 3.14), which agrees very well with values reported for β- In$_2$S$_3$ films prepared by SILAR technique [48].

![Graph: Variation of band gap of In$_2$S$_3$ films with sulfurisation temperature.](image)

**Figure 3.14** Variation of band gap of In$_2$S$_3$ films with sulfurisation temperature.

The optical band gap value of the films of In$_2$S$_3$ reported in the literature varied from 2 to 2.4 eV. Higher value of band gap (> 2.5 eV) has also been reported. This broadening of band gap in In$_2$S$_3$ films has been explained with the help of different phenomenon. Kim et. al interpreted the band gap broadening of their thin films by the presence of excess sulfur in the bulk [24]. Other possibility for
band gap broadening can be attributed to the partial substitution of oxygen for sulfur to form In$_2$S$_{3-x}$O$_x$ [22]. Their study of the optical properties has shown that the band gap is higher than that of $\beta$-In$_2$S$_3$ when they contain oxygen. In the present study the possibility of the presence of traces of oxygen cannot be ruled out, however no oxides were detected by XRD or in the EDX spectra. The higher resistivity of the films also suggests the absence of oxygen impurities in the films. Another reason reported in the literature for the band gap broadening of the $\beta$-In$_2$S$_3$ thin films is on the basis of quantum size effect [25]. Yoshida et al have shown that the grain size has an influence on the band gap [14]. Though the average grain size of the films in the present study obtained from the XRD data are ~22 nm for a sulfurisation temperature below 400°C and ~30 nm at 400°C and above, the variation of the band gap of the films with sulfurisation temperature may be attributed to the quantum size effect. The sulfurisation at temperature 400°C and above causes an increase in the grain size to 30 nm and have the band gap lower compared to films sulfurised below 400°C. Similar observation of variation of band gap on annealing has been reported by Yousfi et al [21].

**Table 3.1 Variation of thickness with sulfurisation time**

<table>
<thead>
<tr>
<th>Sulfurisation time</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 minutes</td>
<td>546.61</td>
</tr>
<tr>
<td>45 minutes</td>
<td>527.1</td>
</tr>
<tr>
<td>1 hour</td>
<td>471.2</td>
</tr>
<tr>
<td>2 hour</td>
<td>451.4</td>
</tr>
<tr>
<td>3 hour</td>
<td>419.5</td>
</tr>
</tbody>
</table>
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The thickness of the In$_2$S$_3$ films were measured gravimetrically and it was observed that the thickness of films decreased with increase in the duration of sulfurisation time. The variation of thickness with the sulfurisation time is shown in the table 3.1.

3.5.3 Electrical characterizations

i. Resistivity by two probe method

Resistivity of the samples was calculated from the slope of the current voltage characteristics. The voltage was varied from 0 to 10 V and the corresponding current through the film was noted. A thin layer of silver was used as the electrode. The linear behavior of the I-V curve confirmed that silver forms an ohmic contact with the thin films.

Figure 3.15 The plot of Resistivity ($\rho$) vs. Sulfurisation Temperature.
The resistivity ($\rho$) of In$_2$S$_3$ films is found to increase with sulfurisation temperature (Fig.3.15). The low resistivity values of In$_2$S$_3$ films prepared below 400°C may be due to the presence of impurity phases or incompletion of sulfurisation. At higher sulfurisation temperature the resistivity of $\beta$-In$_2$S$_3$ films are in the range of $10^6$ $\Omega$ cm. Similar values have been obtained for ALE grown In$_2$S$_3$ films [3].

ii. Temperature Dependence of the Conductivity

The temperature dependence of the conductivity of the films was studied by measuring the variation in current I through samples at different temperatures ranging of 100K to 500K for a constant applied voltage of 12 V.

![Graph showing temperature dependence of conductivity](image-url)

**Figure 3.16:** Temperature dependence of the conductivity for the films sulfurised at 500°
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The conductivity is found to increase very slowly with temperatures in the low temperature range, but shows a rather sharp increase in the high temperature region. This is the typical behavior of a classical broad gap semiconductor. The plot of $10^3/T$ Vs $\ln \sigma$ is shown in figure 3.16.

The value of the activation energy $E_a$ is evaluated from the plot $ln(\sigma)$ vs $1000/T$ using the relation [55]

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

where $T$ is the absolute temperature and $k$ is Boltzmann’s constant.

**Figure 3.17:** The plot of $ln(\sigma T^{1/2})$ vs $T^{-1/4}$ in the temperature range 100K to 300 K
The temperature dependence of the conductivity showed two distinct activation regions, a high temperature region above 150°C with an activation energy 0.6 eV and a lower temperature region with activation energy 0.3 eV. All the \( \beta \)-In\(_2\)S\(_3\) films showed the same general trend, the change from low to high activation energy is a gradual one. The \( \ln(\sigma) \) Vs 1000/\( T \) plot is not a well fit by a straight line.

The \( \ln(\sigma T^{1/2}) \) Vs \( T^{-1/4} \) plot is more close to a straight line (Fig.3.17) suggesting a variable range hopping in more appropriate [56].

iii. Photosensitivity

Figure 3.18 shows the variation of photosensitivity with the sulfurisation temperature. Photosensitivity \( \frac{I_I - I_D}{I_D} \) is the ratio of the difference between the illuminated current and dark current to the dark current. \( I_I \) is the current through the sample under illumination; \( I_D \) is the dark current. The measurement was carried out using Source Measure Unit. The samples were illuminated using tungsten halogen lamp. It is observed that photosensitivity increased with sulfurisation temperature. Maximum photo response was obtained for the highly oriented \( \text{In}_2\text{S}_3 \) films prepared by sulfurisation at 600 °C. The increase in the photosensitivity can be attributed to the improvement in crystallinity with increase in sulfurisation temperature as indicated by XRD (Fig. 3.7 and Fig. 3.8).
The type of carriers responsible for conduction in In$_2$S$_3$ films has been determined by the hot probe method and found to be n-type.

**3.6 Conclusions**

Single phase β-In$_2$S$_3$ thin films can be obtained by sulfurising the indium films above 300°C for 45 minutes. Low sulfurisation temperature requires prolonged annealing after the sulfurisation to obtain single phase β-In$_2$S$_3$. The slow cooling of the samples sulfurised at high temperature resulted in very smooth and closely packed surface. But considering the time consumption factor and the loss of indium by long duration of process, it can be concluded that the 45 minutes is the optimum duration of sulfurisation for the fabrication of a cost effective buffer layer for solar cell. The
thickness of the In$_2$S$_3$ films decreases with increase in sulfurisation time. The resistivity of β-In$_2$S$_3$ was found to increase from $10^2$ to $10^6$ Ω cm with the increase in the sulfurisation temperature. The maximum band gap of 2.58 eV was obtained for the β-In$_2$S$_3$ sample sulfurised at 350°C, which is nearly stoichiometric. This wider band gap, n type β-In$_2$S$_3$ can be used as an alternative to toxic CdS as window layer in photovoltaics. The β-In$_2$S$_3$ thin films can be used as the precursor for the preparation of CuInS$_2$. 
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[52] Joint Committee on Powder Diffraction Standards, Card 190588


