Chapter 2

Indium Sulfide: A Review

2.1 Introduction

Indium sulfide (In$_2$S$_3$) is an important material for optoelectronic and photovoltaic applications and is a promising candidate for many technological applications due to its stability, wider band gap and photoconductive behavior [1]. This material is also having interesting photoluminescence properties [2], and hence finds large number of applications in optoelectronic devices [3]. It can be used as an effective nontoxic substitute for cadmium sulfide (CdS) in Cu(In,Ga)Se$_2$ based solar cells. This material not only eliminates toxic cadmium but also improve light transmission in the blue wavelength region on having band gap wider than that of CdS.

![Fig. 2.1 Crystal structure of In$_2$S$_3$](image)

(Indium atoms are in red colour and sulfur in blue colour)
The physical properties and structure of indium sulfide [Fig. 2.1] thin films are given below.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Colour</td>
<td>Yellow</td>
</tr>
<tr>
<td>Appearance</td>
<td>Crystalline solid</td>
</tr>
<tr>
<td>Melting Point</td>
<td>1050ºC</td>
</tr>
<tr>
<td>Density</td>
<td>4450 kg/m³</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>$a = b = 7.619 \text{ Å}$ and $c = 32.329 \text{ Å}$</td>
</tr>
</tbody>
</table>

2.2 Structure of In$_2$S$_3$

The structure of $\beta$-In$_2$S$_3$ has been determined by Hahn and Klinger [4] and was refined by Rooymans [5] and King [6].

Hahn and Klinger ascribed to it the cubic structure of a disordered cation deficient spinel. The structure of $\beta$-In$_2$S$_3$ has been studied by Rooymans using an x-ray powder technique. The powder pattern contained a large number of weak reflections which were attributed to a super-lattice based on a cation-deficient spinel structure. Rooymans found that the super-cell was body-centred tetragonal with $a = a'/\sqrt{2} = 7.62 \text{ Å}$ and $c = 3a' = 32.32 \text{ Å}$, $a'$ being the parameter of the spinel-type cell from which the structure was derived. The absence of $00l$ reflections with $l \neq 4n$ ($n$ being an integer), and the assumption that the structure is essentially that of a spinel with 4 tetrahedrally coordinated cation vacancies per super-cell, suggested the four vacancies to be located at the equivalent positions of the $4_1$ screw axes of the space group. However, Rooymans also mentioned that the structure might possibly have a lower symmetry because of the observation of a weak reflection at about $3.6 \text{ Å}$ which was not reconcilable with a tetragonal lattice.
In order to maintain stoichiometry of $\text{In}_2\text{S}_3$, all interstices in the complete spinel are not occupied (occupancy of complete interstices would result in composition $\text{In}_3\text{S}_4$). This can be expressed by saying that vacancies are present in the lattice of tetrahedral interstices of the spinel structure. These vacancies are ordered along rows which are parallel to the close packed sulfur rows in the $\{111\}$ planes [5]. As a result of the ordering, the cubic symmetry is lost making the crystal tetragonal with $c/a = 3$. The unit cell contains in fact three unit cells of the normal spinel, the $[001]$ direction of the tetragonal lattice coinciding with one of the cube directions of the basic spinel. Thus the tetragonal unit cell was supposed to be formed by the superposition of three spinel blocks; a four-fold screw axis appeared as the result of indium vacancy ordering.

R.S Becker et al interpreted the ordered modification of $\beta$-$\text{In}_2\text{S}_3$ as a quasi-ternary compound consisting of In, S and ‘vacancies’. Here eight of the twelve tetrahedral sites are occupied by indium and other four are empty (the latter are ordered). All octahedral sites are occupied by In and could be written as $\text{In}_6(\text{In}_2\square)\text{S}_{12}$, where $\square$ indicates vacancies and parenthesis describes tetrahedral site [11]. J. Goodyear and G. A. Steigmann reported the twinning of the cation deficient spinel structure during redistribution of the tetrahedrally occupied sites [7].

C. Haas made theoretical predictions on phase transitions based on Landau’s theory. Theoretically the transition was assumed to be first order [8]. H. Hatwell et al [9] owing to the observations in polarized light proposed that the lattice of tetrahedral indium ions undergoes some kind of "melting", [i.e. disordering], at $420 \, ^\circ \text{C}$ [The actual melting point is $1100 \, ^\circ \text{C}$], whereas a second transition was noted at $750 \, ^\circ \text{C}$. This second transition is presumably associated with the disordering of the octahedral indium ions. J. Van Landyut et al [10] reported that the indium ions in tetrahedral interstices disorder at $420 \, ^\circ \text{C}$ whereas the indium ions in octahedral interstices disorder at $780 \, ^\circ \text{C}$. The order-disorder process was observed in the electron
microscope and different types of interfaces resulting from the ordering of indium ions (or indium vacancies) were studied.

Three well defined modifications of In$_2$S$_3$ have been reported in the literature. The cubic $\alpha$-form [4] is stable above 693 K and crystallizes in the defect spinel structure ($a = 10.77 \text{ Å}$). The stable room temperature phase is $\beta$-In$_2$S$_3$ [5]. A third modification ($\gamma$-In$_2$S$_3$) with trigonal symmetry has been reported above 1047 K [10].

2.3 Preparation Techniques

Variety of preparation techniques were reported for this material and some of them are discussed below.

2.3.1. Indium sulfide crystals

In$_2$S$_3$ crystals of $\alpha$, $\beta$ and $\gamma$ form were synthesized by Diehl et al [12]. Ampoule was charged with elements of indium and sulfur in quantities corresponding to the stoichiometric composition. They found that growth temperature of 800ºC and sulfur vapour pressure of 4 atm were required to prevent dissociation of In$_2$S$_3$ and to maintain stoichiometry. This was achieved by adding 80 mg of extra sulfur in a volume of 25 cm$^3$. Iodine was used as the transport agent.

Kaito et al [13] prepared single crystals of $\beta$- In$_2$S$_3$ by the reaction of indium metal and sulfur vapour. Sulfur vapour was obtained by evaporating sulfur powder from quartz boat while Indium was evaporated from nichrom boat. $\beta$ In$_2$S$_3$ particles grew as single crystal octahedra.

In$_2$S$_3$ crystals were grown by direct melting of stoichiometric mixtures of the components [14]. Stoichiometric quantities of high purity indium and sulfur were reacted in evacuated double-wall sealed silica tubes. Temperature of the furnace was raised to 800ºC in first step and then up to 1150ºC. Molten mixtures were held at this temperature for three days with occasional stirring for homogenization. The samples
were then cooled to about 10 K below the melting point (1050 °C) and were kept at this temperature for a week. Two methods were used to cool the sample. In the first one, the tube was pulled out of the furnace progressively achieving a cooling rate of 0.5 K/h. Large surfaces of ordered crystals were obtained in this way. The second method of sample preparation consisted of rapid quenching of the ingot into ice water. Disordered crystals with random distribution of cation vacancies were produced by this procedure. Annealing in vacuum, to avoid oxidation, was performed for duration of three months at 400°C just below the transformation temperature (420 °C) between α and β-\(\text{In}_2\text{S}_3\) modifications.

A novel layered indium sulfide material consisting of corner and edge shared \(\text{InS}_4\) tetrahedra were synthesized under solvothermal conditions by Cahill et al [49]. DPA-\(\text{InS-SB}_3\) was synthesized by reacting elemental In and elemental S with the organic structure directing agent dypropylamine in the approximate molar ratio 1:2.3:3.5. Reactant slurries were sealed in pyrex tubes and held static at 180°C under autogenous pressures for five days. The resultant product, a white powder, was then washed with ethanol and water and allowed to dry in air. Large single crystals up to 0.2 mm on edge were obtained. Qualitative electron probe microanalysis revealed the presence of In, S and N. The In-S bond lengths range from 2.42 to 2.534 Å with an average of 2.432 Å. Gorai et al [57] has also reported synthesis of Indium sulfide using a convenient solvothermal route. The X-ray diffraction analysis confirmed that 180 °C was the optimum temperature for the preparation. Scanning electron microscopic images showed that morphological patterns of the samples varied depending on the growth conditions.

2.3.2 Indium Sulfide Powder

Amorphous indium sulfide powder was prepared at relatively low temperatures (50 °C) from inorganic salts [16] using the reaction between acidified
(pH = 1.3) solution of indium chloride and sodium hydrosulfide (NaHS). Indium sulfide powder prepared by this process exhibited glass transition at 330 °C and a crystallization exotherm on heating at 390 °C in a DSC.

β-In₂S₃ powder with particles having an average size of 13 nm and spherical shape was successfully prepared through the hydrothermal treatment of an acidic sol (pH = 3) from indium trichloride and sodium sulfide at 140 °C [3]. Hydrothermal treatment of alkaline sol gave amorphous In₂S₃ powder. The effects of temperature, time and the pH value of the solution on the formation of nanocrystalline β-In₂S₃ powder were investigated. Results showed that hydrothermal treatment of an acidic sol (pH = 3) at 140°C for 6 to 12 h was the optimum condition for crystallization of amorphous In₂S₃.

Bulk indium sulfide was prepared by passing H₂S gas through a solution of indium chloride in water [39]. The precipitate, orange in colour, was washed several times with distilled water and then dried in desiccators. The powder thus formed was then vacuum deposited on different faces of rock salt, on the cleavage face of mica, polycrystalline NaCl tablets and also on the glass substrates at temperatures varying from 25 to 450°C. X-ray diffraction showed that the material consisted of predominantly α phase of In₂S₃ mixed with little amount of β phase. The deposits were of β variety at high temperatures.

A novel in situ oxidation-sulfurization growth route via a self purification process was developed to synthesize β-In₂S₃ dendrites by Xiong et al [55]. The precursor of InSb dendrites was firstly obtained using “sonochemical coreduction” route. Subsequently, the mixtures of InSb dendrites (0.473 g, 2 mmol), CS₂ (0.18 mL, 3 mmol), NaOH (0.72 g, 18 mmol) and 30% H₂O₂ (0.60 mL, 6 mmol) were loaded into a 50 mL teflone-lined autoclave, which was then filled with distilled water up to 90% of the total volume. The autoclave was sealed and maintained at 180°C for 24 h and was then cooled to room temperature naturally. Precipitate was filtered off,
washed with distilled water and absolute ethanol for several times, and then dried in vacuum at 60°C for 4 h. The product obtained was pure In$_2$S$_3$.

### 2.3.3 Indium Sulfide Thin Films

#### 2.3.3.1 Thermal Evaporation

Indium monosulfide thin films were prepared by Seyam [17] by thermal evaporation onto quartz and glass substrates held at 473 K during deposition process. Deposition rate was held at 10 nm/sec keeping the pressure at 10$^{-6}$ Torr. InS granules (99.999% pure) were evaporated. The films obtained were amorphous, and stoichiometric.

Stoichiometric thin films of In$_2$S$_3$ were prepared using thermal evaporation technique for the first time by Shazly et al [18]. The ‘as deposited’ films were amorphous and crystallinity was built in on annealing at 423 K. The crystal structure, as determined by both x-ray and electron diffraction, showed that tetragonal films of β-In$_2$S$_3$ phase were obtained. The degree of crystallinity increased with increasing either the film thickness or the annealing temperature.

Indium sulfide was synthesized and deposited by single source vacuum thermal evaporation method on glass substrates by A. Timoumi et al [19]. The X-ray diffraction analysis confirmed initial amorphous nature of the deposited InS film and phase transition into crystalline In$_2$S$_3$ occurred upon annealing in free air for 2 hr at a substrate temperature of 250 °C. Optical constants of the films were obtained from the analysis of the transmission and reflectance spectral data over the wavelength range of 300–1800 nm. Films annealed at 250 °C for 2 h show a good homogeneity with 80% transmission. Analysis of the optical absorption data of the deposited films revealed optical direct band gap energy in the range of 2.0–2.2 eV.

A. Timoumi et al also reported the effect of subsequent annealing of films deposited by single source vacuum thermal evaporation in nitrogen and free air atmosphere from 250 to 350 °C for different durations [20]. Experimental parameters
were adjusted in order to optimize the annealing conditions and to obtain high band

gap energy at low deposition temperature, as required for photovoltaic applications.

X-ray diffraction analysis revealed the initial amorphous nature of deposited In–S thin

films and the phase transition into crystalline In$_2$S$_3$ upon thermal annealing. Films had

an optical direct band gap of energy about 2.2 eV. Annealing temperature of 350 °C

for 60 min in air atmosphere was the optimal condition.

Use of single source evaporation for the deposition of compound

semiconductor films often leads to highly non-stoichiometric films. This was because

of the decomposition of the solid when heated in vacuum and/or of preferential

evaporation of the components. To avoid these difficulties George et al deposited

indium sulfide by reactive evaporation of indium in a sulfur atmosphere by [21]. They

used a glass crucible placed in a canonical basket of molybdenum wire to evaporate

sulfur and a molybdenum boat to evaporate indium. The substrate (micro glass slides)
temperature was varied between room temperature and 600 K. The source to substrate
distance was 15 cm and the deposition rate was around 20 to 30 nm/min. Films

showed \( \beta \)-In$_2$S$_3$ phase. They optimized the substrate temperature to be 425 ± 50 K ie,
the films were smoother, had good transmission and the refractive index approached
that of the bulk value at this temperature. They also found that this was in good
agreement with the concept of critical optimization of Vincett [22]. He concluded
from many experimental results that, when the substrate temperature approached
about 0.33 of the boiling point of the material, the film qualities (surface smoothness,
optical transmission, carrier mobility etc) improved considerably. Also the bulk
diffusion was large at these temperatures, which helped the filling of gaps created by
the evaporation of amorphous or disordered materials.

\( \beta \)-In$_2$S$_3$ films were obtained by solid-state reaction, induced by annealing for
half an hour under constant argon flow, between the constituents sequentially
deposited in thin layers by vacuum thermal evaporation [48]. The films obtained after
annealing at 623, 673 and 723 K were crystallized in $\beta$-In$_2$S$_3$ tetragonal structure without any preferential orientation. XPS study proved that the films were contaminated by oxygen during annealing. This contamination increased slightly with the annealing temperature but the oxygen atomic percentage never exceeded 3% in the samples annealed at 623 and 673 K. To obtain In$_2$S$_3$ films with the best crystalline properties and the best purity, the optimum temperature has been found to be 673 K.

2.3.3.2 Plasma-Assisted Co-Evaporation (PACE)

Sreenivas Kosaraju et al reported the development of plasma-assisted co-evaporation (PACE) for the formation of $\beta$-In$_2$S$_3$ thin films [47]. Indium was supplied by conventional thermal evaporation, while the chalcogen gas precursor (H$_2$S) was activated using inductively coupled plasma (ICP) source. With the help of optical emission spectroscopy and mass spectrometry it was shown that the ICP effectively dissociated H$_2$S, producing atomic sulfur. Transport modeling was used to quantify the flux distributions of the co-evaporated metal and the plasma-generated species impinging the substrate. Model predictions were validated by measurements of deposition rate and film properties. Substantial improvements in both materials utilization and substrate temperature reduction were realized with respect to conventional co-evaporation. $\beta$-In$_2$S$_3$ was formed at a temperature of 100 °C and the quality was a strong function of S/In ratio. The grain size decreased and the optical band gap increased as the substrate temperature was reduced.

2.3.3.3 Chemical Bath Deposition

Thin films of In$_2$S$_3$ were prepared by chemical precipitation onto glass substrates by Kitaev and Dvounin [24]. These films were amorphous regardless of their thickness (150 to 400 nm) and crystallized when heated to 773 K in vacuum.

R. Bayón et al used simple and low cost CBD technique for the preparation of indium hydroxy sulfide films [25]. Thin films of In (OH)$_x$S$_y$ were prepared from an
acidic bath (pH = 2.2-2.5) containing indium (III) chloride, acetic acid (AcOH) and thioacetamide (TA). Indium (III) chloride concentration was kept constant (0.025 M) while that of [TA] was varied from 0.05 M to 0.5 M and [AcOH] from 0 M to 0.3 M [bath temperature -70ºC]. Formation of In$_2$S$_3$ films was based on the slow release of In$^{3+}$ and S$^{2-}$ ions in an acidic medium and their subsequent condensation on the substrates when the ionic product exceeded the solubility product. Sulfide ions were provided by the hydrogen sulfide, produced during the thioacetamide hydrolysis, in dilute acid solutions. Finally the hydrogen sulfide dissociated to give rise the sulfide ions needed for the In$_2$S$_3$ precipitation. Acetic acid was added to the reaction mixture either to reduce the pH, which would favor the TA hydrolysis and avoid the formation of hydrolyzed species, or to complex the In$^{3+}$ ions. Thickness of the films was 1800 Å after deposition of about 45 min. From XPS characterization, they proved that the films were mainly composed of indium hydroxyl sulfide, indium oxide and indium sulfate having absorbed on the surface, some contaminant species from the solution and also CO$_2$ from air. Samples annealed in air were found to have greater oxygen concentration. The unannealed samples had more than 80% indium hydroxy sulfide in their composition. Molecular formula of the as deposited film was close to In (OH) S.

They investigated the structure and surface morphology of CBD indium hydroxy sulfide thin films and found that films were polycrystalline and their structure depended on deposition conditions [26]. When low TA and AcOH concentrations were used, In$_5$S$_4$ was obtained; nevertheless, as these concentrations were increased, films were composed of mixture of cubic $\alpha$- and $\beta$-In$_2$S$_3$ phases. The film composition obtained by energy-dispersive X-ray analysis (EDS) showed that samples were sulfur deficient (S/In ratios between 0.5 and 1.2). Surface morphology of the films suggested two different growth mechanisms. Which one took place seemed to be related to reactant concentrations, especially to AcOH concentration.

This group also probed reaction mechanism and kinetics of the chemical bath deposited In(OH)$_x$S$_y$ thin films [27]. They studied solution chemistry of InCl$_3$–
CH₂CSNH₂–CH₃COOH (InCl₃–TA–HAcO) system and the species distribution diagrams, solubility and precipitation curves. At an acidic pH (1–4), the (InCl₃–TA–HAcO) solution contains mainly indium–chloro-complexes and In(OH)₃ precipitation is not expected when HAcO is added. Kinetic calculations based on TA hydrolysis showed that indium hydroxide–sulfide(In(OH)ₓSᵧ) precipitation took place through a mechanism faster than TA hydrolysis, probably a direct reaction between TA and any indium–chloro-complex, leading to different products depending on the pH of the deposition solution.

Temperature of the bath and the concentration of the reactants were important parameters for films deposited using CBD. In₂S₃ thin films were successfully deposited using CBD technique by Lokhande et al [28]. The chemicals used were indium sulfate (In₂(SO₄)₃), 80% hydrazine hydrate, thioacetamide, triethanolamine (TEA) and ammonium chloride (NH₄Cl). For the deposition of In₂S₃ thin films, 10 ml of indium sulfate solution was taken in a glass vessel to which 1 ml of 7.4 M TEA and 10 ml of NH₄Cl solutions were added successively. Under continuous stirring, 0.2 ml of hydrazine hydrate (80%) was mixed and the reactant vessel was kept in a constant temperature water bath (± 0.5°C). When the appropriate temperature (25 to 70°C) was attained, 10 ml of thioacetamide solution was added to the bath. The resultant solution was transparent, which was stirred with a magnetic stirrer for a few seconds and cleaned glass substrates were immersed into it vertically. The solution colour changed to lemon yellow and finally to bright yellow. The presence of In(OH)₃ in the deposition bath was unavoidable due to the aqueous nature of the bath. For In₂S₃ films concentrations of the reactants taken in the solution were 0.1 M indium sulfate, 0.5 M thioacetamide, 1.4 M NH₄Cl, 14.7 M TEA and 80% hydrazine hydrate. Temperature increase favored homogeneous precipitation and lower film thickness. Samples deposited on FTO (F doped tin oxide) exhibited better crystallinity. Presence of oxygen in the film had been detected using RBS.
Indium sulfide thin films were deposited using CBD technique from aqueous solution containing InCl$_3$ and thioacetamide [29]. The pH of fresh solution was 3.1 and it could be adjusted by adding HCl to the reaction bath. Temperature of the bath was 50-90ºC and the reaction time was varied between 5 and 600 min to achieve required film thickness. The deposits consisted of nano-sized particles of $\beta$-In$_2$S$_3$ or its mixture with $\alpha$-In$_2$S$_3$ as found by crystallographic study and TEM. EDAX and XPS analysis revealed presence of excess sulfur in the film. Chemical bath Deposition of indium sulfide thin films from aqueous mixtures containing indium chloride and thioacetamide under the two extreme reaction conditions 30 and 70ºC was examined by Yamaguchi et al [30]. X-ray analysis of the films indicated the formation of amorphous indium hydroxysulfide in the early stage, followed by the formation of nanocrystalline indium sulfide in the late stage of the film growth. The films deposited at 30ºC had a “cauli-flower-like” morphology, whereas the fibrous structure was obtained at 70ºC.

Properties of thermal-annealed In$_2$S$_3$ films prepared by using CBD technique were presented by M. G. Sandoval-Paz et al [31]. Polycrystalline In$_2$S$_3$ films were grown on glass substrates by means of this technique and were subsequently thermal-annealed in an Ar atmosphere at temperatures from 200 to 450 ºC. Experimental results showed that the as-deposited films were composed of a mixture of both cubic $\alpha$ and $\beta$ crystalline phases, with some fraction of tetragonal phase. Thermal annealing of the films caused the conversion of the cubic crystalline phases to the tetragonal $\beta$ one and crystalline reorientation of the latter phase. Two energy band gaps were determined for all the films: one indirect and the other direct at higher energy. Structural modifications of the films were accompanied by changes in the two energy band gaps of the films. Annealing treatment of $\beta$-In$_2$S$_3$ thin films grown on glass substrate during $t_D=60$ min, and in nitrogen at 400 ºC for 1 hr resulted in the
formation of well crystallized samples with cubic structure and preferential orientation along (610) [32].

N. Barreau et al compared the properties of indium sulfide thin films prepared using Chemical Bath Deposition (CBD) and Physical Vapor Deposition (PVD) and the influence of the synthesis conditions on the physico-chemical, optical and electrical properties were discussed [23]. In CBD, the deposition took place in aqueous solution containing indium chloride (InCl₃) and thioacetamide (CH₃CSNH₂). Temperature of the bath was 345 K. Substrates were immersed vertically in the stirred solution.

In PVD deposition of the constituents was carried out by vacuum thermal evaporation at a pressure of 5 x 10⁻⁴ Pa with the purities of indium and sulfur maintained at 99.99 and 99.98% respectively. In order to obtain films, indium and sulfur layers were sequentially deposited, their thickness and evaporation rate being controlled in situ by an rf quartz monitor. [S/In ratio was ≥ 3]. Structure obtained from this process was then annealed in a tubular oven for 30 min under a constant argon flow of 0.6 dm³/min. They studied films annealed at five different temperatures 523, 573, 623, 673 and 723 K. The threshold temperature was found to be 623 K. Above this temperature, the films were wholly crystallized.

From the XPS analysis, they found that, for PVD deposited films, there was partial bond formation between In and S even before annealing. Film, after annealing, contained oxygen and Na in the bulk while there was no such contamination before annealing. However the films were amorphous, with large amount of excess sulfur. Best β- In₂S₃ thin films were obtained with heat treatment at 673 K. They had the same crystallization as those annealed at 723 K and they were lightly contaminated as those obtained at 623 K.

The CBD films were sulfur deficient and there was more oxygen than sulfur
in the film with the oxygen compensating sulfur deficiency. The major difference between the two kinds of films was in their crystalline properties; crystalline property of PVD film was far better than that of CBD.

2.3.3.4 Successive Ionic Layer Adsorption and Reaction (SILAR)

SILAR technique was used by Sankapal et al to deposit indium sulfide thin films [33]. This was achieved using indium sulfate (In$_2$(SO$_4$)$_3$) and thioacetamide solutions. Temperature of deposition was 25-70°C and deposition time was 4-5 hours. The films were 0.2 µm thick. Films deposited on glass substrates showed poor crystallinity, but those on FTO samples were crystalline. TEM analysis revealed that the initial growth of film on glass substrate was the $\gamma$ phase of In$_2$S$_3$ with particle size ranging from 20 - 40 Å. Presence of oxygen was detected by RBS analysis.

R. S. Mane and C. D. Lokhande used the versatile and simple SILAR method to deposit indium sulfide (In$_2$S$_3$) thin films [34]. Optical band gap of the In$_2$S$_3$ thin films was 2.3 eV. Films were highly resistive with resistivity of the order of $10^5$ Ω cm. Utilization of triethanolamine and hydrazine hydrate complexed indium sulphate and sodium sulfide as precursors, resulted in nanocrystalline In$_2$S$_3$ thin films [35] and the optical band gap was found to be 2.7 eV.

Post-deposition annealing effects on In$_2$S$_3$ thin films deposited using SILAR technique was reported by R. Ranjith et al [36]. Samples were prepared by varying dipping and rinsing time, and those prepared at room temperature were found to be amorphous in nature. However, peaks corresponding to $\beta$-In$_2$S$_3$ were observed on annealing at 400 °C. Grain size increased with increase in the dipping times, either in the precursor solutions or in water. Band gap decreased considerably for samples annealed at 400 °C in vacuum.
2.3.3.5 Photochemical deposition technique (PCD)

Kumaresan et al deposited indium sulfide thin films by photochemical deposition technique (PCD) [37]. The \( \text{S}_2\text{O}_3^{2-} \) ions present in the solution absorb UV radiation and release S according to the following equation:

\[
\text{S}_2\text{O}_3^{2-} + h\nu = \text{S} + \text{SO}_3^{2-}
\]

This spontaneous release of S in a more acidic medium takes place according to the equation:

\[
\text{S}_2\text{O}_3^{2-} + 2 \text{H}^+ = \text{S} + \text{H}_2\text{SO}_3
\]

Also the \( \text{S}_2\text{O}_3^{2-} \) ions get excited by absorbing the UV radiation and release electrons according to the equations:

\[
2\text{S}_2\text{O}_3^{2-} + h\nu = \text{S}_4\text{O}_6^{2-} + 2e^-
\]

\[
\text{SO}_3^{2-} + \text{S}_2\text{O}_3^{2-} + h\nu = \text{S}_3\text{O}_6^{2-} + 2e^-
\]

Sulfur atoms and electrons combine with the \( \text{In}^+ \) metal ions present in the solution of \( \text{In}_2(\text{SO}_4)_3 \) to form InS according to the relation:

\[
\text{In}^+ + \text{S} + e^- = \text{InS}
\]

The as-deposited InS films were amorphous in nature and phase transition to crystalline \( \text{In}_2\text{S}_3 \) occurred upon annealing at 500°C. Raman analysis of the as-deposited film confirmed the formation of In-S phase. The films had 3 \( \mu \)m thickness over a deposition period of 90 min. Thickness decreased to 1 \( \mu \)m upon annealing at 500°C. Presence of oxygen in the film was detected using AES analysis and the sulfur to oxygen ratio was 6:1. Even after annealing at 500°C, oxygen was present in the film and there was a possibility for the formation of \( \text{In}_2\text{S}_{3.33}\text{O}_3 \) and the S to O ratio was about 9:1. The as-deposited films did not show clear absorption edge, possibly because of the amorphous nature of the film, while on annealing, clear absorption edge was observed. Annealed samples exhibited a direct band gap of 2.1 eV.
2.3.3.6 Electrosynthesis

A new approach for the electro-synthesis of indium sulfide thin films (In$_2$S$_3$) was described by Tacconi et al [38]. Electrosynthesis using sulfur modified gold electrode and alternative exposure to indium and sulfur ion containing aqueous bath consisted of four steps (a) A polycrystalline gold surface was first modified with a sulfur layer (b) indium was placed onto this layer forming indium sulfide (c) indium continues to deposit atop the indium sulfide layer (d) transfer back to a sulfide ion containing bath resulted in the sulfurization of the residual indium sites. In$_2$(SO$_4$)$_3$ was used as the indium containing electrolyte and Na$_2$SO$_4$ as sulfur containing medium. Raman active modes present at 235, 268 and 309 cm$^{-1}$ indicated presence of the $\beta$-In$_2$S$_3$ defect spinel structure. Combined cyclic voltammetry and electrochemical quartz crystal microgravimetry scans demonstrated the veracity of this film growth approach. Photo-electrochemical measurements in a polysulfide redox medium showed that the In$_2$S$_3$ layers thus grown were photoactive and behave as an n-type semiconductor.

2.3.3.7 Atomic layer deposition

Thin films of In$_2$S$_3$ were deposited on soda lime glass and SnO$_2$ coated glass using indium acetyl acetonate and H$_2$S precursors by atomic layer deposition (ALD), a sequential deposition technique allowing the formation of dense and homogeneous films [41]. ALD is based on alternate saturative surface reactions. Each precursor is pulsed into the reaction chamber alternately, one at a time, and the pulses are separated by inert gas purging periods. With properly chosen growth conditions, the reactions are surface saturated and the film growth is thereby self limiting. In that case, each ALD cycle deposits maximum one monolayer of the desired material. However the amount of material deposited per cycle depends on the temperature, precursor combination and the reactive sites on the surface and therefore only rarely is
a full monolayer growth per cycle obtained. The required thickness can be obtained simply by repeating these ALD cycles. The precursors must be volatile and thermally stable up to the reaction temperature. They should chemisorb on the surface and react rapidly at the absorbed state with the other precursors. To obtain In$_2$S$_3$, the pulsing orders were

1. indium acetyl acetonate 0.7 s
2. nitrogen (purge 1) 1 s
3. hydrogen sulfide 0.5 s
4. nitrogen (purge 2) 0.8 s

The surface chemical reactions were

Step 1  Indium pulse

\[
2 \text{In(CH}_3\text{COCHCOCH}_3)\text{)}_3 (g) + \text{surface} \rightarrow 2 \text{In(CH}_3\text{COCHCOCH}_3)\text{)}_3 (\text{adsorbed})
\]

Step 2 Sulfur pulse

\[
3\text{H}_2\text{S} (g) + 2 \text{In(CH}_3\text{COCHCOCH}_3)\text{)}_3 (\text{adsorbed}) \rightarrow \text{In}_2\text{S}_3 + 6 \text{CH}_3\text{COCH}_2\text{COCH}_3
\]

In a temperature window between 130 and 260ºC, a maximum growth rate of about 0.7 Å per cycle was obtained at 180ºC.

Yousfi et al [42] also employed Atomic Layer Deposition (ALD) for depositing In$_2$S$_3$ thin films. Depositions were carried out in an ALD machine. Indium sulfide layers were prepared from indium acetylacetonate at 130ºC and hydrogen sulfide. Deposition temperature was approximately 150-160ºC. The purging gas was nitrogen with 300/500/300/500 ms. Composition measurements were made using RBS technique, on film deposited on silicon substrates. In/S ratio was found to be 0.66 indicating the film to be In$_2$S$_3$. As the composition of the films did not change with annealing, they related the high band gap value to structural effects like quantum size effects.

Asikainen et al described the growth of In$_2$S$_3$ thin films by Atomic Layer Epitaxy (ALE) [50]. InCl$_3$ and H$_2$S were employed as the reactants. Nitrogen was used as the carrier and purging gas. The reactor pressure was about 10 mbar. InCl$_3$
was evaporated inside the reactor from a crucible held at 275°C. H₂S flow rate was 9 cm³/min. The films were deposited on glass substrates at 300-400°C. The films were cooled to about 200°C under nitrogen flow before removing from the reactor. The highest growth rate obtained was 1.4 Å/cycle at 300°C. Resulting films were polycrystalline β-In₂S₃. SEM analysis showed that the film consisted of densely packed particles with a diameter of about 100-150 nm. RBS analysis revealed the composition of the film grown at 300°C as In₀.₄₀S₀.₅₇Cl₀.₀₃.

2.3.3.8. Metal Organic Chemical Vapor Deposition (MOCVD)

Indium sulfide films were prepared using MOCVD by Barron [43]. The majority of studies have employed the thiolate compounds prepared from the parent trialkyl indium:

\[
\text{InR₃ + HSR}′ \rightarrow \frac{1}{2}[(R)₂\text{In(R}′)]₂ + \text{RH}
\]

\[
\text{InMe₃ + 2HS}′\text{Bu} \rightarrow \frac{1}{2}[(\text{BuS})(\text{Me})\text{In(S}′\text{Bu})]₂ + \text{BuH}
\]

Films grown using either \([(\text{Bu})₂\text{In(S}′\text{Bu})]₂ or \([(\text{nBu})₂\text{In(S}′\text{Bu})]₂ as the precursor at each of the temperatures 300, 350 and 400°C were essentially independent of the precursor in terms of morphology and phase present. The micro-structural features and chemical composition of the deposited films were, however, observed to have significant dependence on the deposition temperature. Films deposited from methyl substituted precursor \([(\text{Me})₂\text{In(S}′\text{Bu})]₂ exhibited marked difference from those grown using either \([(\text{Bu})₂\text{In(S}′\text{Bu})]₂ or \([(\text{nBu})₂\text{In(S}′\text{Bu})]₂. Films deposited from the methyl precursor at 400°C yielded a crystalline diffraction pattern.

Single-source organo-metallic chemical vapour deposition was reported by R. Nomura et al using Bu″In(SPr)₂ as the precursor molecule [46]. Tetragonal β-In₂S₃ thin layers with strongly preferred (103) growth orientation were obtained on Si(111) and quartz substrates at a substrate temperature \(T_{\text{sub}}\) of 300–400°C. β-In₂S₃ thin films
thus obtained were photo-responsive, with optical band gap energies and dark conductivity estimated as 1.98 eV and $2.0 \times 10^{-4}$ S cm$^{-1}$ respectively.

P. O. Brien et al [44] reported cubic $\alpha$-In$_2$S$_3$ deposited on glass, GaAs(100) and InP(111) by low-pressure metal-organic chemical vapour deposition (LP-MOCVD), using novel air-stable precursors of general formulae In(S$_2$CNMeR)$_3$ [where R=n-Butyl (compound (1)), n-Hexyl (compound (2))]. The predominant phase in all films grown was found to be $\alpha$-In$_2$S$_3$, regardless of substrate or growth temperature. Andrew N. MacInnes et al also reported deposition of indium sulfide films using MOCVD which yielded amorphous films of stoichiometry which turned crystalline ($\beta$-In$_2$S$_3$) upon annealing [45].

### 2.3.3.9 Modulated flux deposition

Indium sulfide thin films had been prepared by a novel modulated flux deposition technique [53]. Experimental parameters were adjusted to obtain high band gap and low absorption material at low deposition temperature as required for photovoltaic applications. Films were deposited in a ‘home-made’ evaporation chamber containing a rotating holder that transported standard soda-lime glass substrates cyclically around three different areas: indium source beam, heating lamps and reactive sulfur region. Parameters that had been controlled in the film deposition were the evaporation source temperatures, the substrate temperature and the angular velocity of the rotating substrate holder. Substrates were rotated at 30 rev/min and maintained at 200ºC. Samples showed tetragonal $\beta$-In$_2$S$_3$ phase. Layer thickness did not affect the crystalline phase, but influenced the average crystallite size.

C. Guillén et al also reported that indium sulfide thin films were prepared using a ‘novel modulated flux deposition’ procedure. All samples showed tetragonal $\beta$-In$_2$S$_3$ structure with random or preferential (103) plane orientation, depending mainly on the sulfur availability during the growth process. The sulfur availability was
optimized to achieve smooth surfaces and low scattering/absorption in the films. The average crystallite size decreased and the energy gap increased as the layer thickness decreased from 250 to 60 nm. Energy gap values of 3.02 eV was obtained for the thinnest In$_2$S$_3$ films.

Indium sulfide (In$_2$S$_3$) polycrystalline thin films were deposited on amorphous glass substrates employing modulated flux deposition (MFD) by C. Sanz et al [54]. Influence of different deposition parameters (elemental sources temperatures, substrate temperature, and substrate angular velocity) was studied. All the samples had tetragonal structure ($\beta$-In$_2$S$_3$) with high (103) preferential orientation. Optimized samples showed good coverage and small-grain homogeneous microstructure. A direct optical transition was observed, suggesting band gap energy ($E_g$) of 2.75 eV for 100-nm-thick films.

B. Asenjo et al reported indium sulfide (In$_2$S$_3$) thin films deposited on amorphous glass, glass coated by tin oxide (TCO) and crystalline silicon substrates by two different methods: modulated flux deposition (MFD) and CBD [62]. In$_2$S$_3$ films prepared using MFD were more compact and having homogeneous surface than those prepared using CBD. Films deposited employing CBD contained indium oxide in their composition and exhibited higher absorption edge values when deposited on glass.

### 2.3.3.10 Electrochemical deposition

The electrochemical deposition of In$_2$S$_3$ from an aqueous solution of In$_2$(SO$_4$)$_3$ and Na$_2$SO$_3$ was reported by B. Asenjo et al. In$_2$S$_3$ films with good adherence and uniformity were obtained by cycling the potential in the range for cathodic deposition of In and S [59]. A secondary In$_2$O$_3$ phase was detected in thin films, possibly arising from reduction of residual oxygen in solution and/or by an electrochemically induced precipitation reaction.
2.3.3.11 Spin Coating

In$_2$S$_3$ colloidal thin films with various thicknesses were prepared by the spin coating method [60]. In this work interestingly band gap of the thin films depended on the thickness and decreased with heat treatment. Dependence of the band gap on the thickness and heat treatment was explained well using the ‘size quantization effect’ of In$_2$S$_3$ colloidal particles in the film. In$_2$S$_3$ colloidal thin films prepared on wide gap semiconductors such as TiO$_2$ and ZnO showed an anodic photocurrent under visible light irradiation.

2.3.3.12 Chemical Spray Pyrolysis (CSP)

CSP is a simple and cost effective method for the fabrication of In$_2$S$_3$ thin films. This technique is used in the present work due to its low cost and its adaptability for large area deposition. Review of the earlier works done on indium sulfide films prepared using spray technique is given below.

Indium sulfide films deposited on glass substrate by spray method was studied by Bouguila et al [67]. In$_2$S$_3$ was formed from the chemical reaction

$$2\text{InCl}_3 + 3\text{CS(NH}_2)_2 + 6\text{H}_2\text{O} \rightarrow \text{In}_2\text{S}_3 + 3\text{CO}_2 + 6\text{NH}_4\text{Cl}$$

X-ray diffraction showed that In$_2$S$_3$ was the main phase present in these films and that the structure and the allotropic form of this phase were affected by substrate temperature. Analysis of the layers by SEM and AFM revealed that best crystallinity and homogeneity were obtained for the substrate temperature 613 K.

In$_2$S$_x$ thin films grown using spray solution composition from $x = 2.0$ to $x = 3.9$ was studied by Kim et al [66]. Films exhibited $\beta$-In$_2$S$_3$ phase with tetragonal structure. They also found that the band gap increased from 2.15 eV to 2.43 eV on increasing the $x$ composition.

Bhira et al prepared In$_2$S$_3$ thin films using spray pyrolysis technique. Films were deposited on pyrex glass by spraying a solution of $10^{-3}$ M indium chloride and $2\times10^{-3}$ M thiourea [1]. Here substrate temperature was kept at 340°C. They used
nitrogen as ‘carrier gas’ keeping the solution and gas flow rates at 2 cm$^3$/min and 4 l/min. Well crystallized films showed β-In$_2$S$_3$ phase with preferential orientation along (400) plane. Microanalysis of the films pointed out a deficit of chalcogen (46%) and using XPS analysis, they confirmed that this deficit was compensated by oxygen bonded to indium, in addition to that as a surface contaminant. They detected traces of chlorine also in the bulk of the sample. Photoconductivity measurements were carried out within the range of wavelengths in the visible spectrum at different modulation frequencies and bias voltages ranging from 5 to 300 Hz and from 3 to 25 V respectively. They observed a fast increase of photocurrent signal toward 2 eV connected with a progressive decrease in the high absorption region. They attributed this to the presence of trap centers at the grain boundaries or to the presence of structural defects or secondary phases in the film. The response increased with increase in illumination time and bias voltage. They found out the mean absorption edge from the photocurrent measurements using Devore’s model [64]. Band gap value (2.05 eV) was found to be in close agreement with that obtained from optical absorption measurements (2.08 eV).

InS films with composition close to that of In$_2$S$_3$, prepared using airless spray technique was studied by Kamoun et al [65]. Samples were prepared with different In/S ratio. They observed broadening and/or shift of the short wavelength absorption edge for smaller In/S values which was ascribed to the presence of secondary phases and to a more disordered structure. They performed spectroscopic ellipsometric measurements over the 0.5eV to 4 eV spectral ranges. It was found that the refractive index ($n$) and absorption coefficient ($\alpha$) decreased with increase in In/S value. Annealing of the films at high temperature (500ºC) resulted in strong decrease in the value of both $n$ and $\alpha$ which was explained by an improvement in sample crystallinity, while annealing at rather low temperatures (300ºC) had little effect on the optical constants.
Teny et al had done an extensive study on indium sulfide films deposited using this technique. Indium sulfide thin films prepared using chloride based precursor solutions showed $\beta$-In$_2$S$_3$ phase with preferential orientation along (220) plane [68]. Indium sulfide thin films were prepared systematically, by varying the In/S ratio in the spray solution as well as the substrate temperatures. Band gap was found to be 2.67 eV for In/S ratio 2/3. XPS analysis of the samples revealed presence of oxygen as just the surface contamination only [for a thickness of ~ 100 Å] for the samples prepared using solution having higher sulfur concentration. They could get good control over the stoichiometry of the films by varying the substrate temperature or In/S ratio in the film. Samples having In/S ratio 1.2/8 showed maximum photosensitivity ($\Delta I/I_0 = 949.97$). However these were highly resistive. On increasing the indium concentration resistivity as well as photosensitivity of the samples decreased. Teny et al had also studied the post annealing effects on indium sulfide thin films prepared using spray pyrolysis [69]. Films were annealed in vacuum at 300 and 400 °C. Annealing did not affect the optical properties of the film much, but the resistivity of the films drastically decreased while grain size increased. It was observed through these studies that In$_2$S$_3$ thin films have potential use as buffer layer in photovoltaic heterojunction devices.

Ratheesh et al studied the SHI induced modifications in spray pyrolysed $\beta$-In$_2$S$_3$ thin films [70]. In this work the films, were irradiated using 100 MeV Au ions with different fluences. XRD analysis showed that, on irradiation, crystallinity became poor. Mean crystallite size decreased from 17 nm to 10 nm, as the fluence increased up to $3 \times 10^{12}$ ions/cm$^2$. XRD pattern revealed that, for ion fluence $1 \times 10^{13}$ ions/cm$^2$, the sample became amorphous. However, when ion fluence increased to $3 \times 10^{13}$ ions/cm$^2$, recrystallization was observed and the grain size also increased to 16.5 nm. A red shift in absorption edge was observed in the case of irradiated samples.
Preparation of indium sulfide thin films employing spray pyrolysis using a new precursor [indium nitrate] was done by Teny et al [71]. In this work, Indium nitrate and thiourea were used as the precursor solutions. Samples having In/S ratio 2/3 showed better crystallinity with the band gap of 2.66 eV. XPS analysis of the sample proved the formation of indium sulfide. It was also observed that In/S ratio in the initial precursor solution determined the composition as well as electrical properties of the films. Maximum photosensitivity was observed for the sample prepared using solution having In/S ratio 2/4.

Indium sulfide (In$_2$S$_3$) thin films were prepared through the spray pyrolysis (SP) technique using indium acetate and N-N dimethyl thiourea as precursor compounds [72]. Samples prepared at different temperatures and atomic ratio of In to S in the starting solution, were characterized using several techniques. X-ray diffraction studies indicated that the preparation temperature ($T_p$) affects the crystallinity of the deposited materials as well as the optoelectronic properties. For (In/S)$_{sol}=1/8$, the optical band gap ($E_g$) increased from 2.2 up to 2.67 eV when $T_p$ increased from 250 to 450 °C. For (In/S)$_{sol}=1$ and $T_p=450$ °C, the deposited material showed $n$-type electrical conductivity with a resistivity [in dark condition] of 1 (Ωcm)$^{-1}$, and $E_g=2.04$ eV.

### 2.3.3.13 Spray Ion Layer Gas Reaction Technique (Spray-ILGAR)

N.A. Allosop et al reported a new technique for the preparation of indium sulfide thin films on large area [73]. The was claimed to be a modification of the ILGAR technique used to prepare chalcogenide thin films. These samples were having high suitability for buffer layer applications in chalcopyrite solar cells. The process involved cyclical spray deposition of an indium containing precursor layer followed by its conversion to sulfide using hydrogen sulfide gas. Analysis of the deposition revealed that the indium chloride based precursor was transported via the vapor phase from the spray droplets to the substrate surface.
2.3.3.14. Miscellaneous methods

\( \text{In}_2\text{S}_3 \) films were grown using indium (III) isopropyl xanthate, \( \text{In} (\text{S}_2\text{COC}_3\text{H}_7-\text{iso})_3 \), a readily available chelate, which volatized when heated in vacuum and yielded \( \beta\)-\( \text{In}_2\text{S}_3 \) when thermally decomposed in an inert atmosphere \[51\]. Resistivity of \( \text{In}_2\text{S}_3 \) films (~ 200 nm thick) increased from \( 10^{-1} \) to \( 5 \times 10^2 \) \( \Omega \)-cm as the deposition temperature was raised from 230 to 450\(^\circ\)C. It was suggested that the lower resistivity of films deposited at lower temperatures might be due to a higher degree of disordering in the structure of \( \text{In}_2\text{S}_3 \). Analysis of film composition using AES revealed presence of \text{In}, \text{S} and \text{O}. The average ratios were \( I_\text{S}/I_\text{In} = 3 \) and \( I_\text{O}/I_\text{In} = 0.55 \). Triangular features were seen from SEM analysis, which were indicative of film growth along (111) direction.

Rahana et al has prepared \( \beta\)-\( \text{In}_2\text{S}_3 \) films on glass and on quartz substrates by rapid heating of metallic indium films in \( \text{H}_2\text{S} \) atmosphere \[58\]. Effect of sulfurization temperature and time on the growth of \( \beta\)-\( \text{In}_2\text{S}_3 \) films were investigated in this work. Highly oriented single-phase \( \beta\)-\( \text{In}_2\text{S}_3 \) films were grown by the sulfurization technique. A high photo-response was obtained for films prepared at a sulfurizing temperature of 600 \(^\circ\)C.

Herrero et al prepared thin films by chalcogenization of electroplated metallic indium films onto Ti substrates, in a flowing stream of \( \text{H}_2\text{S} \), at about 350\(^\circ\)C for 1 hour with a pretreatment of 3 hour at 130\(^\circ\)C \[15\]. X-ray diffraction patterns showed that \( \beta\)-\( \text{In}_2\text{S}_3 \) thin films were grown with good crystallinity. This material in a photo-electrochemical cell with polysulfide solution, showed low dark current, a noticeable photocurrent characteristic of n-type semiconductors. Photostability tests of the semiconductor in aqueous polysulfide showed that it was photo-degraded, and from the band scheme of \( \text{In}_2\text{S}_3 \) it was inferred that the photo-corrosion was a kinetic process and that its stability in this electrolyte was, at least thermodynamically possible.
Growth of indium sulfide by deposition of indium onto MoS₂ surface was studied [56]. Topotactical growth of indium sulfide at the initial stages of the film growth had been observed. From the electron microscopic images of the film, it was found that by the increment of In₂S₃ particle size, InS was also produced. On increasing the film thickness to more than 20 nm, indium crystals predominantly grew.

2.4. Nano Indium Sulfide

Semiconductor nanoparticles (NPs) offer a rich palette of optical, electronic, and catalytic properties, which can be tuned by their size. Their uniqueness, as compared to the bulk materials, stems from their large surface area and size quantization effect. [74, 75, 76] For the past decade, a large variety of semiconductors have been prepared in nanocrystalline form. Among others, metal chalcogenides are the materials for which the quantum confinement effect is most pronounced. Properties of NPs (quantum dots) have been extensively investigated for the II-VI class of compounds (CdS, CdSe, etc.) [77]. All nanocrystalline materials usually have 1:1 or greater stoichiometric ratio of metal atoms to atoms of chalcogenide in the unit cell. There are a large number of other semiconductors for which the total number of chalcogen atoms in the unit cell is greater than the number of metal atoms, such as MoS₂, WS₂, ReS₂, FeS₂, Sb₂S₃, In₂S₃, Bi₂S₃, with special optical, mechanical, and catalytic properties. For most of them, the nanocrystalline form was reported only in the presence of polymers [78-83] or in a physically constrained environment, such as porous solids and reverse micelles, where the growth of the NPs is arrested by the phase boundaries [84,85].

In addition to properties mentioned above, In₂S₃ has mainly three more special qualities making it an interesting candidate for both fundamental and practical aspects of NP research [86]:

52
1. In$_2$S$_3$ is a rare case of ordered crystalline material with a large amount of vacancies. Owing to tetragonal sites formed by incompletely coordinated sulfur atoms, indium sulfide can serve as a host for a number of metal ions to form semiconducting and/or magnetic materials [87, 88, 89] Doping In$_2$S$_3$ produces materials with exceptional optical, electrical, and magnetic properties, which can be adjusted not only by the NP diameter, but also by the concentration of the guest ion.[90, 91] This is in contrast to II-VI NPs, which tend to expel guest ions.[92, 93]

2. Unlike most of the semiconductors currently being used for nanocolloids, In$_2$S$_3$ and related materials display both direct and indirect conduction-to-valence band transitions, which can be observed by different modalities of UV-vis spectroscopy at 2.0-2.2 and 1.0-1.1 eV, respectively. This opens the door for the investigation of the effect of quantum confinement on direct and indirect excitonic transitions.

3. In$_2$S$_3$ NP bioconjugates can have medical applications such as cancer diagnosis.

Several authors have reported nanostructured indium sulfide obtained by different deposition techniques.

Uniform nanocrystalline $\beta$-In$_2$S$_3$ powders were prepared using organothermal synthesis by S. H. Yu et al [94]. The reaction was

$$2 \text{InCl}_3 + 3 \text{Na}_2\text{S}_3 \xrightarrow{\text{solvent}} \text{In}_2\text{S}_3 + 6 \text{NaCl} + 6 \text{S}$$

This was conducted in a glove box filled with argon gas. Toluene and 1, 2-dimethoxyethane (DME) were used as the solvents. An appropriate amount of analytical grade InCl$_3$ and 0.01M of Na$_2$S$_3$ were added into a teflone-lined autoclave of 100 ml capacity, which was filled with organic solvent up to 80% of the total volume. The air dissolved in the solution was driven off by passing argon gas through it. The autoclave was sealed and maintained at 140°C for 12 hours and cooled to room temperature.
naturally. The yellow precipitate was filtered and washed respectively with CS₂, acetone, distilled water and absolute ethanol several times to remove the byproducts of S, NaCl and other impurities. The product was then dried under vacuum at 80°C for 4 hours. The broad nature of diffraction peaks indicated formation of nanocrystalline β-In₂S₃. They found that the particle size of nanocrystalline β-In₂S₃ could be controlled by choosing different solvents. Particle size in Toluene was smaller than that in DME (8 and 16 nm respectively). They also studied the influence of water content, organothermal time and temperature on the samples. No evidence for organic impurities in the samples was obtained from IR spectrum.

Qichun Zhang et al have reported two-dimensional indium sulfide framework constructed from penta supertetrahedral p1 and supertetrahedral t2 clusters [95]. They could construct new open-framework indium sulfide (\([\text{In}_{10}\text{S}_{24}\text{H}_{2}]^{10-}\)) from penta supertetrahedral sulfide clusters (\([\text{In}_8\text{S}_{17}\text{H}_{9}]^{9-}\) P1) and supertetrahedral sulfide clusters (\([\text{In}_4\text{S}_{10}\text{H}_{7}]^{7-}\) T2) through hydrothermal synthesis. The P1 cluster reported consisted of only trivalent ions (In³⁺) and was the only known example of tetrahedral clusters with a core sulfur site bonded to four trivalent ions. Each P1 cluster was joined to three T2 clusters (vice versa) to form an infinite two-dimensional sheet stacked along the crystallographic c-axis. The UV-vis diffuse reflectance spectrum showed this material to be a wide band gap semiconductor.

Mohammmad Afzaal et al could obtain indium sulfide nanorods from single-source precursor [96]. Thin films comprised of In₂S₃ nanorods had been prepared on glass substrates by metal-organic chemical vapour deposition using [Et₂In (S₂CNMe′Bu)] without either template or catalyst.

Changhao Liang et al [97] utilized a high temperature approach for the mass production of ultra-long, straight silica nanotubes and indium sulfide filled cable-like structures by heating Si wafer and In₂S₃ powder under a stream of hydrogen/argon gases at 950 °C. Transmission electron microscopy, scanning electron microscopy and
X-ray diffraction analysis demonstrated the formation of hollow cylindrical amorphous silica tubes with lengths up to hundreds of micrometers and outer diameters in the range of 70 to 300 nm, silica tubes encapsulating indium sulfide nanorods with a cubic structure and S-filled silica tubes with high sensitivity to a focused electron beam.

Koichi Yamaguchi et al [30] reported chemical bath deposition of indium sulfide thin films from aqueous mixtures containing indium chloride and thioacetamide under the two extreme reaction conditions, namely, at 30 and 70 °C. The films deposited at 30 °C had a ‘cauliflower-like’ morphology, whereas the fibrous structure was observed at 70 °C.

Anuja et al could realize indium sulfide (In$_2$S$_3$) micro- and nanorods by sulfurization of electrodeposited metal indium layers at room temperature [99]. From XRD and TEM observations, it was concluded that the In$_2$S$_3$ nanorods and microrods had ~50 nm and ~0.5 µm diameter, respectively. A plausible top-growth mechanism was proposed for the formation of the nanorods in which the hydroxide layer was found to play an important role. The micro- and nanorods showed optical band gap of ~2.2 and ~2.54 eV, respectively.

This group also reported surfactant assisted synthesis of In$_2$S$_3$ dendrites and their characterization [100]. Partially crystalline indium sulfide dendrites were obtained via precipitation in presence of CTAB. In absence of CTAB, crude self-assembly of particles was observed. With increasing CTAB concentration and aging time of the solutions, particles were found to self-assemble in a progressive manner to extended hierarchical dendrites. Unlike in commonly known cases where dendrites are unstable but well crystallized; partially crystallized particles can also self-assemble to well-formed dendrites especially when assisted by the surfactant molecules. X-ray analysis and TEM studies confirmed the partially crystallized nature of the samples. Optical properties of the dendrites were found to show quantum confinement effects.
A template-free route to the preparation of hollow In$_2$S$_3$ nanospheres was demonstrated by Xuebo Cao et al [101]. This was achieved by solvothermally treating solid In$_2$S$_3$ spheres comprised of small particles at 180 °C, for 24 h. The well crystalline hollow nanospheres had diameter in the range 40–70 nm and an average wall thickness of 7 nm. Hollow In$_2$S$_3$ nanospheres showed an intense absorption between 318 and 512 nm, which was blue-shifted to shorter wavelengths relative to that of bulk In$_2$S$_3$. Hollow In$_2$S$_3$ nanospheres also exhibit a strong photoluminescence. The green band, centered 518 nm, was due to the band-band transitions and the orange emission centered at 624 nm originates from the indium interstitial defect. These hollow In$_2$S$_3$ nanospheres could be used as a distinctive multicolored phosphor and material for producing photo electrochemical devices.

D.P. Dutta et al accounted the preparation of nanocrystalline indium sulfide (In$_2$S$_3$) by a two-step process [102]. The first step involved metathesis reaction of trimethyl indium ether adduct (Me$_3$In·OEt$_2$) with 1,2-ethanedithiol (HSCH$_2$CH$_2$SH), resulting in the formation of a polymeric precursor. In the second step, these precursor complexes were pyrolysed in furnace under flowing nitrogen atmosphere where they undergo thermo-destruction to yield nanometer-sized particles of indium sulfide. The average size of the nanoparticles ranged from 20 to 22 nm.

Paz Vaqueiro [103] has reported solvothermal synthesis and characterization of new one-dimensional indium sulfides: [C$_{10}$N$_4$H$_{26}$]$_{0.5}$[InS$_2$]. Two new main group metal sulfides were prepared solvothermally in the presence of 1,4-bis(3-aminopropyl) piperazine and their crystal structures determined by single-crystal X-ray diffraction.

S. Gorai and S. Chaudhuri could synthesize β-indium sulfide (In$_2$S$_3$) submicron particles with cage-like network structures via the sonochemical route [104]. Time for ultrasonic treatment of the alcoholic solution of indium chloride and thioacetamide was found to be the prime factor for the formation of a cage-like network structure.
This group has also reported the synthesis of In$_2$S$_3$–SiO$_2$ nanocomposite films (with molar ratios of In$_2$S$_3$:SiO$_2$ = 15:85, 10:90 and 5:95) on quartz substrates by sol–gel method [105]. Highly confined nanoparticles of In$_2$S$_3$ (radius $\approx$ 1.8–7 nm) were obtained in SiO$_2$ matrix, indicating SiO$_2$ to be a good capping agent for the nanoparticles.

Yujie Xiong et al report a novel in situ oxidization–sulfurization growth route via a self-purification process to synthesize $\beta$-In$_2$S$_3$ dendrites [106]. It was found that the product was pure In$_2$S$_3$ with strong quantum confinement of the excitonic transition expected for the In$_2$S$_3$ dendrites.

$\beta$-In$_2$S$_3$ powder with particles having an average size of 13 nm and spherical shape, had been successfully prepared by S.Yu et al through the hydrothermal treatment of a sol from indium trichloride and sodium sulfide at 140°C [3].

$\beta$-In$_2$S$_3$ nanofibers were successfully synthesized by Xiaoyi Zhu et al via a hydrothermal method with AAO membrane as a template at 150 °C for 15 h [108]. XRD patterns indicated perfect crystallization of $\beta$-In$_2$S$_3$. SEM images proved the presence of nanofibers grown up from the channel ends of the AAO template. TEM images confirmed that the nanofibers had high aspect ratio of ca. 40–50 and diameters of about 10 nm. Room temperature photoluminescence (PL) spectrum of the $\beta$-In$_2$S$_3$ nanofibers indicated its potential applications in light-emission devices.

Shaohua Shen and Liejin Guo have presented the structural, textural and photocatalytic properties of quantum-sized In$_2$S$_3$-sensitized Ti-MCM-41 prepared by ion-exchange and sulfurization methods [109]. In$_2$S$_3$ nanocrystallites were successfully encapsulated into the mesopores of Ti-MCM-41 by a two-step method involving ion-exchange and sulfurization. The In$_2$S$_3$ nanocrystallites inside the Ti-MCM-41 host showed a significant blue-shift in the UV-vis absorption spectra. Under irradiation using visible light, the composite material showed much higher photocatalytic activity for hydrogen evolution than bulk In$_2$S$_3$. It can be explained by the effective charge-separation in the quantum-sized In$_2$S$_3$-sensitized Ti-MCM-41.
2.5 Characterization

Structural, optical and electrical properties of indium sulfide prepared through different methods were characterized using different techniques.

2.5.1 Structure and growth

Crystal structure of In$_2$S$_3$ thin films obtained by the chemical vapor deposition from the volatile complex compounds [indium (III) isopropyl xanthate and indium (III) diethyl dithiocarbonate] was studied with the help of synchrotron radiation diffraction [110]. High photon beam intensity (3x10$^{10}$ photons/mm$^2$s) and high angular resolution (0.02º) of the reflexes made it possible to study weak reflexes to analyze the phase composition of the samples in more detail, to determine the size of the particles and to evaluate stress at the microscopic level. They showed that the films obtained at $T= 230^\circ$C crystallized as cubic $\alpha$-In$_2$S$_3$. At the deposition temperature $T > 250^\circ$C, the films crystallized in the tetragonal $\beta$ phase. Annealing of the films synthesized at 230$^\circ$C, lead to $\beta$-In$_2$S$_3$ phase formation as well. Size of the particles increased as the deposition temperature increased. Values of the inter-planar spacing $d$, for close packed planes, were almost the same for all the samples deposited at temperatures, in the range, 230 - 370$^\circ$C and practically did not depend on crystal modification, deposition temperature and thickness of the samples. They also showed that microstress decreased after annealing or for higher deposition temperatures. For the sample deposited at 430$^\circ$C, splitting of the reflex (5,0,15) was observed, which could be explained as a monoclinic or hexagonal distortion of $\beta$-In$_2$S$_3$.

Powder neutron and X-ray diffraction data for indium sulfide were reported by N. S. Rampersad et al [111]. The lattice parameters obtained from a Rietveld refinement for the neutron data are: $a=7.5937$ (6) Å; $c=32.352$ (3) Å; $V=1865.6$ (3) Å$^3$ and for X-ray data are: $a=7.6172$ (1) Å; $c=32.3307$ (8) Å; $V=1875.86$ (6) Å$^3$. The crystal system was taken to be tetragonal (space group I4$_1$/amd).
Growth of indium (III) sulfide thin films from aqueous thioacetamide (TA)–In(III) solution was monitored with a quartz crystal microbalance (QCM) [112]. It was found that growth of the film consists of parallel deposition of In$_2$S$_3$ and In$_2$O$_3$. Both the processes were induced by sulfide anions ($S^{2-}$) produced after decomposition of thioacetamide. In$_2$S$_3$ was deposited by precipitation of crystallites formed in the bulk solution. When the solutions were stirred, this reaction was hindered due to the disruption of the nucleation centres.

Amlouk et al [129] showed that acoustic techniques, more specifically acoustic signature $V(z)$, are very powerful non-destructive methods to characterize $\beta$-In$_2$S$_3$ thin films prepared using CSP technique. Young’s modulus of the order of 443 GPa, was consistent with the assumption of the $\beta$-In$_2$S$_3$ material to be in ceramics group. Acoustic microscopy study revealed the possibility of presence of surface and bulk defects in this thin film.

In almost all the reports the crystal structure of $\beta$-In$_2$S$_3$ is analyzed with the help of X-ray diffraction technique. The crystal structure is found to depend on different deposition parameters and post deposition treatments. The crystal structure of annealed $\beta$-In$_2$S$_3$ thin films with different thickness was investigated by X-ray diffraction technique [113]. Lattice parameters, crystallite size and microstrain were calculated. It was found that the lattice parameters were independent on film thickness, while annealing in an increase of these parameters. Crystallite size increased with the increase of the film thickness and annealing temperature. In all cases, the microstrain decreased gradually with the increase in both film thickness and annealing temperatures.

### 2.5.2 Optical

The first optical measurements of In$_2$S$_3$ were reported by Kauer and Rabenau [114]. Investigations by Bube and McCarroll [115] and Gilles et al [116] were mainly concerned with photoconduction in indium sulfide. Garlick et al [117] reported on the
IR emission and luminescence properties. Rehwald and Harbeke [118] reported on the electrical and optical properties. All the studies were done on single crystals or polycrystalline bulk materials. For $\beta$-In$_2$S$_3$ the absorption edge was mainly due to direct transitions [119] and weak indirect transition was also reported [118].

George et al [21] calculated refractive index from the optical transmission spectra of the samples prepared using reactive evaporation of indium in sulfur atmosphere. They used the method given by Manifacier et al [120]. The value was found to be 2.56. Band gap was found to be 2.01 eV corresponding to a direct forbidden transition. They attributed the unresolved absorption peaks just before the onset of band-to-band transition from the plot of $\alpha$ vs $\nu$ as due to different energy levels (sulfur vacancies) in the forbidden gap to which transition may take place.

Indium monosulfide thin films prepared using thermal evaporation by Seyam [17] exhibited absorption coefficient of the order of $10^5$ cm$^{-1}$ and the band gap was 1.94 eV. He calculated the refractive index ($n$) and extinction coefficient ($k$) from the transmittance and reflectance spectra and the values were estimated to be 2.2 and 2.3 respectively. The high frequency dielectric constant was calculated from the plot of $(n^2-1)^{-1}$ vs $\lambda^{-1}$ and the value was found to be 5.76.

Optical band gap ($E_g$) of indium sulfide thin films prepared using CBD technique by Lokhande et al [28] was found to be 2.75 eV. The ‘as prepared’ samples were photoactive as observed from Time Resolved Microwave Conductivity (TMRC) studies. The same value of band gap was obtained for SILAR samples also [33]. Band gap value could be tuned between 2.3 and 2.7 eV by changing the reaction temperature or pH of the aqueous chemical bath as shown by Yoshida et al [29]. Variation of $E_g$ values was discussed in terms of the change of chemical composition, crystal modification and crystal size.

Refractive indices of the films prepared using Atomic Layer Epitaxy was found to be of the order of 2.5-2.7 and the band gap was 2.3 eV [50]. Samples were
highly resistive and they showed photo response when exposed to daylight. The photo response was reversible and fast.

Barreau et al studied the optical properties of In$_2$S$_3$ thin films grown using PVD [122]. Optical properties of indium sulfide thin film depended on their synthesis process and composition. High homogeneity and excellent surface state of the films were confirmed by the presence of interference fringes on transmission and reflectivity spectra. Band gap was found to be independent of the annealing temperature and the value was about 2.8 eV, higher than that of β-In$_2$S$_3$ single crystal, due to the presence of oxygen in the film. Refractive index ($n$) and the extinction coefficient ($k$) were also found to be independent of annealing temperature. The values were in the range 2.1 - 2.8 and 0.01 – 0.3 for wavelengths in the range 250 nm to 2500 nm.

Absorption onset indicated a band gap value above 2.5 eV for indium sulfide thin films, prepared using a novel modulated flux deposition technique [53]. Energy band gap increased for indium sulfide layers of lower thickness, which was related to a reduction of the average crystallite size of the films.

ALD In$_2$S$_3$ thin films, deposited by Yousfi et al [42] were amorphous and the band gap was approximately 3.3 eV which was much greater than that of the bulk value. Band gap reduced to 2.25 eV after annealing, while those deposited by Naghavi et al [41] were crystallized in tetragonal form with band gap values of about 2.7 eV. Quantum size effect was considered as the possible reason for wide band gap. A shift of 0.7 eV was expected for grain size of about 3 nm.

Mane et al deposited indium sulfide thin films by SILAR technique using indium chloride and sodium sulfide as cation and anion source in an aqueous medium [123]. The films were amorphous. Optical band gap was 2.3 eV and the films were highly resistive [~ 10$^5$ Ω-cm].
Optical band gap of the prepared by rapid heating of metallic indium films in H₂S atmosphere [58] was found to vary from 1.9 to 2.5 eV when the sulfurization temperature was varied from 300 to 600 °C or by increasing the sulfurization time. Indium sulfide thin films were prepared using Spray-ILGAR process an indirect bandgap of 2.2 eV [73].

Bhira et al. found out the mean absorption edge from the photocurrent measurements using Devore’s model [64] for samples prepared using spray pyrolysis technique on pyrex glass by spraying a solution of 10⁻³ M indium chloride and 2x10⁻³ M thiourea [1]. Band gap value (2.05 eV) was found to be in close agreement with that obtained from optical absorption measurements (2.08 eV). In₂S₃ thin films grown using spray solution composition from x = 2.0 to x = 3.9 was studied by Kim et al [66]. Films exhibited β-In₂S₃ phase with tetragonal structure. They also found that the band gap increased from 2.15 eV to 2.43 eV on increasing the x composition. Teny et al reported bandgap of be 2.67 eV for In/S ratio 2/3 for indium sulfide thin films prepared using chloride based precursor solutions. Indium sulfide thin films prepared through the spray pyrolysis (SP) technique using indium acetate and N-N dimethyl thiourea as precursor compounds [72] showed that the optical band gap (E_g) increased from 2.2 up to 2.67 eV for (In/S)_mol=1/8, when T_p increased from 250 to 450 °C. New precursor indium nitrate gave crystalline indium sulfide films having band gap of 2.66 eV [71].

For indium sulfide polycrystalline thin films deposited on amorphous glass substrate employing modulated flux deposition direct optical transition was observed, suggesting band gap energy (E_g) of 2.75 eV for 100-nm-thick films.

Electro reflectance measurements on indium sulfide grown from indium melt was done by T. Nishimo et al [124]. Electro reflectance spectra of InS grown from In melt was measured in the photon energy range from 2.0 to 4.0 eV. The spectra revealed structures associated with the E₀ fundamental edge due to direct transitions and some higher interband transition edges. Analysis of the E₀ structure indicated
characteristic features of low-field electro reflectance spectra which enabled to
determine the direct band gap of this material.

Widening of bandgap is usually observed in indium sulfide thin films. Some
authors attribute the widening of band gap of indium sulfide films to quantum size
effect [125] while some authors explained this due to excess sulfur [66]. Recently
presence of oxygen and sodium were also reported to increase the band gap markedly
[23]. Optical band gap varied from 2.1 eV to 2.9 eV for samples, which contained 8.5
at% oxygen as reported by Barreau et al [121]. They found that the electronic
structure of indium sulfide was very much disturbed due to the presence of even a few
oxygen atoms that substituted sulfur in the crystalline matrix, which induced the high
increase of optical band gap. Electrical conductivity of the oxygen containing samples
was found to be greater by approximately 2 orders than that of pure In2S3 films. They
attributed this effect to the modification of the properties of the grains or their grain
boundaries when oxygen was introduced in the films. The films showed n-type
conductivity indicating that the introduction of oxygen did not change the type of
majority carriers.

Temperature dependence of band gap of β-In2S3 thin films was studied by
Kambas et al [119]. They found that the transition was direct and the E\textsubscript{g} dependence
on T was linear. Band gap increased with decrease in temperature and the value was
found to be 2 eV at room temperature.

Optical properties annealed β-In2S3 thin films with different thickness were
studied in the spectral range from 400 to 2500 nm to determine the optical constants
(n and k), the high frequency dielectric constant, ε\textsubscript{\infty}, the lattice dielectric constant, ε\textsubscript{L},
and the energy gap [113]. The optical constants were found to be independent on film
thickness in the range from 200 to 630 nm. High frequency dielectric and lattice
dielectric constants of the as-deposited films increased on annealing. The energy gap
for the as-deposited In\textsubscript{2}S\textsubscript{3} was found to be 2.60 eV and increased to 2.70 and 2.75 eV
by annealing at 423 and 473 K for 1 h, respectively
Band gap of PVD $\beta$-In$_2$S$_3$ films increased with annealing temperature until 623 K, whereas for higher annealing temperature, the absorption threshold was stable [23]. Band gap was found to be in the range, 2.8 eV to 2.9 eV, which was greater than that of earlier reports. They observed that, when oxygen was introduced into the films, the band gap values were far higher than that of the single crystals. The wide band gap of PVD films was attributed to the presence of In-O bonds. Substitution of indium by Na was also found to increase the band gap. When heating rate was increased, the band gap was not as broad, because of the fast crystallization. They found that oxygen contamination had a positive effect to obtain layers with properties matching well with the specification of solar cell buffer layers.

PL spectra of InS single crystals were investigated in the wavelength region 477.5-860 nm and in the temperature range 8.5-293 K [126]. There were three PL bands centered at 605 nm, 626 nm and 820 nm. The first two bands were due to radiative transitions from the donor level at 0.01 eV below the bottom of the conduction band to the valence band and from the donor level at 0.06 eV below the bottom of the conduction band to the acceptor level at 0.12 eV above the top of the valence band respectively.

PL study done by R. Jayakrishnan et al on $\beta$-In$_2$S$_3$ thin films prepared using CSP technique revealed presence of two emission bands (named A and B) with peaks at 568nm and 663nm [2]. Based on the PL peak energy dependence on composition the A-band emission was found to be due to transition from sulphur vacancy (0.43eV) to Indium vacancy (0.1eV ), ($V_S$-$V_{In}$), and the B-band was assigned to be due to transition from Indium interstitial, [acting as donor level 59meV] to oxygen replacing sulphur vacancy level (0.82eV above the valence band). Dependence of FWHM and PL peak energy on temperature of both the bands confirmed the assignments.

Fifteen normal modes of vibrations were observed for $\beta$-In$_2$S$_3$ dendrites from Raman spectra, which exactly correspond to those given by a sample of $\beta$-In$_2$S$_3$ with
unpolarised light [55]. The sample showed strong quantum confinement of excitonic transition, which was expected for In$_2$S$_3$ dendrites. Under PL excitation at 330 nm, the In$_2$S$_3$ dendrites emitted blue light at 358 nm, which clearly indicated the existence of electronic transition at particular wavelength (358 nm), and was stronger than in the bulk In$_2$S$_3$.

Temperature dependence of the Raman-active mode frequencies in indium sulfide was measured in the range from 10 to 300 K [127]. Temperature dependence of the $A_g$ intralayer optical modes showed that Raman frequency shift resulted from the change of harmonic frequency with volume expansion and anharmonic coupling to phonons of other branches. The pure-temperature contribution (phonon–phonon coupling) was due to three- and four-phonon processes.

Raman spectra of InS single crystals was studied at different hydrostatic pressures up to 1.2 GPa [128]. Mode-Grüneisen parameters were obtained for Raman-active normal modes. It was shown that the variations observed in Raman spectra with growing pressure could be interpreted from the standpoint of the structural phase transition $D^{12}_{2h} \rightarrow D^{17}_{4h}$ in InS as the hydrostatic pressure continues to increase. The transition pressure was evaluated at $(7 \pm 1)$ GPa.

IR reflectivity of In$_2$S$_3$ crystals was studied and higher reflectivity was observed for quenched sample at low frequencies [14]. The peaks for the annealed samples were sharper and well resolved. There were 12 reflectivity bands for polarized light having $E \perp c$ case and eight bands for $E \parallel c$ case.

### 2.5.3. Electrical

The electrical property of single crystal indium sulfide was studied by Rehwald et al [118]. The range of electrical resistivity and Hall coefficient at room temperature and its variance with temperature was presented. When these parameters were low, it changed slightly with temperature or even remained constant down to
liquid nitrogen temperature, whereas higher values had strong dependence on temperature. By heat and sulfur vapour treatment, it was demonstrated that this large variation had its origin in the deviations from stoichiometric composition of the material. The nearly exponential dependence of the measured Hall mobility on temperature, observed in specimens of high resistivity, was explained by different scattering mechanisms for electrons and hole in the same temperature region. All crystals were found to be n-type, regardless of doping during growth. Impurities, which otherwise produce p-type conductivity in similar materials, did not have the effect of changing the sign of charge carriers in In$_2$S$_3$. The main effect on concentration and sign of charge carriers come from the deficiency in sulfur, which could not be completely avoided during growth. The cation vacancies, forming a constituent of the lattice due to the chemical formula, were assumed to be mainly ordered in indium sulfide. The small fractions of disordered cations and cation vacancies acted as donors and acceptors nearly compensating each other. Their difference in concentration was determined by the lack of sulfur. They also suggested that high resistivity material might be useful as a photoconductor.

Gilles et al [116] studied the photoconduction in In$_2$S$_3$ prepared by the direct synthesis under a pressure of sulfur of the order of 5 to 10 atmospheres. They found that under an illumination of nearly 1000 lux, conductivity of this material increased by five orders of magnitude. Traces of copper increased the photosensitivity of the compound markedly. Diffusion length was found to be of the order of few millimeters. They observed a correlation between the reciprocal of the diffusion length and the photosensitivity of copper doped samples: the maximum photocurrent was obtained in samples where the reciprocal of the diffusion length was a maximum. From the thermal analysis, they found two-phase transitions in indium sulfide. The first one was in the temperature range between 414°C and 421°C while the second one was around 738°C. Thermal activation energy was determined from the measurements
of resistivity as a function of temperature and was found to be 0.56 eV below first transition point and 0.63 eV above 420°C.

Electrical properties In₂S₃ thin films deposited by ALD [41] had been addressed by using impedance measurements on semiconductor-electrolyte junctions. The films were n-type with doping concentration around 10^{16}-10^{17} cm⁻³ and possessed good blocking behaviour under reverse bias. The doping concentration increased with increase in the deposition temperature. Their flat band potential was close to -1.1 V versus MSE.

George et al [21] also found that for samples prepared using reactive evaporation of indium in sulfur atmosphere above a substrate temperature of 350 K were low resistive and indium made good ohmic contact to these films while films prepared below this temperature showed high resistivity and indium did not make ohmic contact to these films. From the temperature dependant resistance measurements of these films, the activation energy for electronic conduction was obtained as 0.26 ± 0.02 eV.

Both dark electrical resistivity and thermoelectric power (Seebeck coefficient S) were measured for films prepared using thermal evaporation technique, the measurements were carried out before and after annealing [13]. Dark electrical resistivity decreased exponentially with increasing film thickness. Resistivity decreased after annealing also. Thermoelectric power of all films decreased on increasing the sample temperature. The films showed n-type conduction. Existence of two distinct activation energies ΔE₁ and ΔE₂ belongs to two types of level: a shallow level of ΔE₁ = 0.319 eV before annealing and ΔE₁ = 0.166 eV after annealing and deep level of ΔE₂ = 0.61 eV for as deposited films and ΔE₂ = 0.515 eV for annealed films. The deep level was also detected by the ‘space charge limited current’ technique and the trap density was found to be 3.92 x 10^{22} m⁻³. The decrease in ΔE₁
for the shallow levels as a result of annealing indicated that these levels were structure defect levels.

Dark resistivity of Indium monosulfide thin films prepared using thermal evaporation was reported by Seyam [17]. The dark resistivity of the samples decreased with increasing temperature and film thickness. Thermal activation energy of the charge carriers, from the electrical resistivity measurements, was found to be 0.84 eV. Density of charge carriers was found to be $10^{21}$ m$^{-3}$ from the space charge limited current analysis.

Thermally stimulated current measurements were carried out on as grown n-InS single crystals having orthorhombic structure in the temperature range 10-125 K by Gasanly et al [131]. They identified four trap levels located at 20, 35, 60 and 130 meV and suggested that these levels in undoped layered crystals might be associated with structural defects and/or unintentional impurities. Trap parameters were determined by curve fitting method, peak shape method and initial rise method and found that they agreed well with each other. The re-trapping process was negligible for these levels, as confirmed by the good agreement between the experimental results and the theoretical predictions of the model that assumed slow re-trapping.

Defect characterization of the semiconducting thin films of $\beta$-In$_2$S$_3$ was done by Rupa et al using thermally stimulated conductivity studies and this work revealed four trap levels with activation energies 0.1 eV, 0.26 eV, 0.43 eV and 0.82 eV in the band gap of this material [132]. Variation of their prominence was studied with different stoichiometric ratios of In:S. Samples with lower In concentration showed the presence and prominence of Indium Vacancy (0.1 eV). Irrespective of the variation of In:S concentration ratio, chlorine impurity level (0.26 eV) and sulphur vacancy (0.43 eV) existed in almost all the samples. A high temperature defect level attributed to the replacement of sulphur by oxygen is also detected at 0.82 eV. Variation in the prominence of these traps with rate of heating and duration of
illumination was also observed. It is relevant from the observation that no single trap gained prominence, as the material possessed a multiple distribution of traps rather than a single trap. But the trap level at 0.82 eV was prominent in all measurements and was not affected by the change in heating rate. Effect of re-trapping of the carriers by the traps was also detected. Comparing the capture cross sections of these levels with the earlier theoretical results the authors concluded three centers (0.1 eV, 0.266 eV and 0.43 eV) to be coulomb repulsing while the fourth one (at 0.82 eV) to be a neutral center, which is mostly responsible for the electrical property of $\beta$-In$_2$S$_3$.

2.6 Doping in In$_2$S$_3$

High-temperature modification of In$_2$S$_3$ called $\gamma$-In$_2$S$_3$, (which exist above 754 °C), was stabilized at room temperature by replacing about 5 to 10% of the In atoms by the elements As, Sb or Bi [12]. Single crystals of In$_2$S$_3$ is doped with As ($\gamma$-In$_2$S$_3$ (As)) (red, hexagonal plates up to 1.5 cm$^2$, P m1, a = 3.800 ± 0.001 Å, c = 9.044 ± 0.005 Å) formed a layer structure in a closed system by iodine transport in the presence of As$_2$S$_3$ vapor. From the measured As$_2$S$_3$ equilibrium pressures over $\gamma$-In$_2$S$_3$ (As) and the thermodynamics of the vapor transport of In$_2$S$_3$ with iodine, the optimal growth conditions were derived. Crystals of In$_2$S$_3$ is doped with Sb ($\gamma$-In$_2$S$_3$ (Sb)) were also prepared in a similar way. The compositions of these materials were In$_{1.9}$As$_{0.1}$S$_3$ and In$_{1.8}$Sb$_{0.2}$S$_3$. These were characterized by measuring absorption spectra, thermoelectric power and temperature dependence of the conductivity between 20 and 500 °C. Both were n-type semiconductors. The phase diagram As$_2$S$_3$-In$_2$S$_3$, which was evaluated using DTA, indicated that $\gamma$-In$_2$S$_3$ (As) is soluble in molten As$_2$S$_3$. Single crystals were obtained by cooling solution of 7 mole% In$_2$S$_3$ from 850 to 300 °C. The potential of As$_2$S$_3$ as the flux for other sulfide materials is emphasized.

A variety of differently doped samples of In$_2$S$_3$ were prepared by chemical vapor phase transport (CVT) and gradient freeze techniques by Becker et al [11]. For
CVT, I₂ was used as the transport agent. X-ray diffraction of pure, tin doped, samples with excess sulfur and those with P and InP doping were shown to be single-phase β-In₂S₃. They found that if a sample with excess sulfur, having n- and p-type responses, was heated at 750°C for 0.5 hour, the resistivity dropped by ~ 5 orders of magnitude and the n- and p-type responses were then replaced solely by the n-type response. The result was explained by the removal of S giving excess interstitial In donors. Doping of phosphorous and indium phosphide resulted in a weak p- response but n-response was also present. In the case of Sn doping, low resistance n-type material resulted. Whether this was due to true Sn⁴⁺ substitution for In³⁺ or whether Sn disrupted the lattice order such that the concentration of interstitial In was greater than In vacancies was not known.

Studies of conduction mechanism in single crystal β-In₂S₃ [118] showed that the conductivity is always n-type and p-type is not observed when the samples are doped with copper or cadmium. Becker [11] obtained p-response when single crystals were prepared with an excess of sulfur or InP, but n- response was also present.

β-In₂S₃ and β-In₂S₃:Co²⁺ (cobalt doped β-In₂S₃) single crystals were produced using chemical transport reaction method employing ZnCl₂+I₂ as a transport agent by Choe et al [134]. For In₂S₃ single crystal, In₂S₃ powder (purity 99.999%), 15 mol% of excess sulfur (purity 99.999%) and 5 mol% of ZnS (purity 99.999%) were used as starting materials. For β-In₂S₃:Co²⁺ single crystal, 2 mol% of Co (purity 99.99%) was added to the starting materials. Temperatures of the growth and source-zones were maintained at 670°C and 830°C respectively for 7 days. Dimension of the single crystals were approximately 6 x 5 x 3 mm³ and they crystallized into tetragonal structure. Optical absorption spectra were measured in the temperature range 5 K to 300 K. At 290 K, they obtained an indirect optical energy band gap of 2.24 eV for β-In₂S₃ and 1.814 eV for β-In₂S₃:Co²⁺ while the direct energy band gap was 2.639 eV for β-In₂S₃ and 2.175 eV for β-In₂S₃:Co²⁺. Three groups of impurity optical absorption peaks for β-In₂S₃:Co²⁺ single crystal were observed in the wavelength ranges of 675-
830 nm, 1300- 1900 nm and 2800- 3200 nm. These peaks could be attributed to the electron transition between the energy levels of Co$^{2+}$ ions sited in the Td symmetry point. Polycrystalline thin films of Co-doped In$_2$S$_3$ were grown by the spray pyrolysis method and flash evaporation method [135]. The optical absorption spectra of these thin films were investigated in the wavelength region from 500 to 2500 nm at 298 K.

Kim et al has reported the preparation of CoIn$_2$S$_{3+x}$ thin films [136] by spraying a solution prepared by dissolving CoCl$_2$, InCl$_3$ and thiourea in solvent composed of methanol and distilled water (ratio of 1:1) to give 0.2 molar solutions of each solute, and then by mixing these solutions in appropriate volume ratio to give the desired x composition. An additional 20% in volume of thiourea solution compensated for the loss of sulfur caused by vapourisation. Rate of spray was 6 ml/min and the substrate was maintained at 270°C. They found that, $\beta$-In$_2$S$_3$ thin films were grown over the range $x = 0$ to 0.4 and amorphous thin films over the range 0.6 to 1. Band gap was found to be decreasing with increasing x composition. The samples showed impurity absorption corresponding to wavelengths 695 nm, 750 nm and 802 nm. Intensities of these peaks increased with increasing x composition and they found that the Cobalt atoms in Co$_x$In$_2$S$_{3+x}$ existed as Co$^{2+}$ ions.

Kim et al also found that, as Cobalt was introduced into In$_2$S$_3$ single crystals, the structural defects were decreased [137]. The Cobalt atoms were located at the Td symmetry site of the $\beta$-In$_2$S$_3$ host lattice as Co$^{2+}$ ion. Three peaks at 752 nm, 802 nm and 825 nm in the absorption spectrum of Co doped crystals were ascribed to Cobalt impurities. The photo acoustic spectrum of $\beta$-In$_2$S$_3$:Co$^{2+}$ crystal, when compared with that of $\beta$-In$_2$S$_3$ single crystal in the wavelength region 500 to 2500 nm, possessed four peaks at 650, 760, 1700 and 2130 nm. First peak was ascribed to crystal defect and the rest to Cobalt impurities. Photoconductivity spectra of $\beta$-In$_2$S$_3$ single crystal at 286 K showed a broad peak centered at 663 nm and a tail in the long wavelength region. As ambient temperature decreased to 28 K, the broad peak also appeared at 626 nm and
the tailing phenomenon in the long wavelength region was not reduced. Photoconductivity spectrum of $\beta$-$\text{In}_{2}\text{S}_{3}$:Co$^{2+}$ single crystal at 284 K had two peaks centered at 620 and 705 nm. The long wavelength tail in the spectrum was reduced when compared to that of $\beta$-$\text{In}_{2}\text{S}_{3}$ single crystals. When the temperature was reduced to 21 K, the spectrum showed two peaks at 585 and 655 nm and the tail in the long wavelength region was rapidly reduced.

Structural and optical properties of $\text{In}_{2-2x}\text{Al}_{2x}\text{S}_{3-3y}\text{O}_{3y}$ alloys obtained by the spray pyrolysis technique were studied by L. Bhira et al [138]. X-ray diffraction (XRD) showed well crystallized films preferentially oriented towards (4 0 0) direction corresponding to $\beta$-$\text{In}_{2}\text{S}_{3}$ phase for low compositions ($x \leq 0.2$); for $x > 0.2$, the structure became amorphous as confirmed by scanning electron microscopy (SEM). Moreover, microanalysis and X-ray photoelectron spectroscopy (XPS) measurements detected oxygen in the films, present in $\text{Al}_{2}\text{O}_{3}$ and $\text{In}_{2}\text{O}_{3}$ oxides and $\text{Al(OH)}_{3}$ hydroxides forms. The study of the absorption coefficient of thin layers versus incident light energy revealed that the value of the band gap energy increased with the composition $x$ according to a parabolic profile.

$\beta$-$\text{In}_{2}\text{S}_{3}$ and $\beta$-$\text{In}_{2-x}\text{Al}_{x}\text{S}_{3}$ thin films were deposited on different substrates (pyrex glass, $\text{SnO}_{2}$/pyrex and steel) using spray pyrolysis technique at 320°C [139]. In the case of the growth on a steel substrate, crystallography of the film was good and introduction of Al did not noticeably change the spectrum. In the case of deposition on pyrex, the structure of $\beta$-$\text{In}_{2}\text{S}_{3}$ was of poor quality. Al improved the crystallinity. On $\text{SnO}_{2}$/pyrex substrate, presence of Al resulted in broader and smaller diffraction peaks. The surface structure was studied using AFM and SEM. Crystallite size increased on going from steel to $\text{SnO}_{2}$. For steel substrates, characterized by a poor structural quality and a lattice disorder, the impinging atoms strongly interacted with the surface but with little surface migration. The layers were having good stability; Work function and surface photovoltage did not change with time. They used Auger studies to get
information on the surface layer composition. They also studied effect of heat treatment and substitution of a few indium atoms by aluminium atoms to this composition. In all the cases, the work function topographies were flat and variation of $\Delta \phi$ along the surface was small indicating uniformity of the surface layer of the films.

$\text{In}_{2-2x}\text{Al}_{2x}\text{S}_{3-3y}\text{O}_{3y}$ alloys were prepared on pyrex glass substrates by spray pyrolysis technique and their photoelectrical properties were studied by Bhira et al [140]. The spraying solution contained InCl$_3$, AlCl$_3$ and CS(NH$_2$)$_2$ as starting materials. The Al/In ratio ($x$) was varied from 0 to 1. Solution and gas flow rates were kept at 2 cm$^3$/min and 4 l/min respectively. Nitrogen was used as the carrier gas and the substrate temperature was 340°C. Shape of the photoconductivity spectra $I_{ph}(\nu)$ and the variations $I_{ph}(f)$ and $I_{ph}(V)$ helped them to understand the conduction mechanism and the photo carrier recombination. For low compositions ($x \leq 0.2$), $I_{ph}(V)$ parabolic variation showed that this conduction was limited by the space charge zone in accordance with Child’s law ($I_{ph} \propto V^2$). This showed that the density of trap centers increased with the composition. As percentage of Al doping was increased, the photoconductivity measurements depended on the photo carrier recombination mechanism due to the presence of trap centers at grain boundaries. For $x \geq 0.4$, the electrical conduction followed Ohm’s law. Band gap showed a parabolic profile with $x$, varied in the range from 2.05 to 2.42 eV. For low compositions ($x = 0, 0.05, 0.1, 0.2$) the conductivity study, as a function of temperature, presented a deviation to Arrhenius law in the temperature domain 80 to 330 K. At very high temperatures, ranging from 330 to 575 K, a quasi-linear variation of $\sigma$ as a function of temperature according to Arrhenius law was observed. They found that for higher Al compositions, films were amorphous having poor electrical and photoelectrical properties.
Kulińska et al prepared Li$_x$In$_2$S$_3$ electrochemically with different amounts of Lithium ($0 \leq x \leq 0.13$) [141]. They applied Perturbed Angular Correlation (PAC) to understand the mechanisms that occur during Li insertion. PAC experiments could measure the hyperfine interaction between a radioactive probe and the Electric Field Gradient (EFG) generated by direct neighborhood at the site of the probe atom. At lower temperatures undoped material showed a strong damping of the PAC spectra while after doping (with electron donor Li) the higher concentration of mobile charge carriers repaired this damping. PAC spectra showed a new dynamic behavior, which increased with increasing Li content. They proposed that for higher temperatures ($T \geq 500$ K) migration of indium atoms from the tetrahedral site started and this was favored by the presence of empty sites in the direct neighborhood of a tetrahedral site, in contrast to the octahedral sites. They also proposed that the Li insertion lowered the threshold which confined the indium ions to the tetrahedral sites. The dynamic behavior between room temperature and 500 K was caused by the mobile Li ions, because the dynamic fraction was proportional to the Li content.

$\beta$-In$_2$S$_3$-$3x$O$_{3x}$ thin films were prepared using a dry physical process on glass substrate [121]. The temperature during the synthesis process was 473 K. Na free substrates were used to avoid diffusion of Na. They found that the films were smooth, continuous and homogeneous from SEM analysis and the grain size was 50 nm as obtained from AFM. N. Barreau et al investigated the evolution of the conduction and valence band levels with the increase in optical band gap. The results obtained are discussed first in terms of $\beta$-In$_2$S$_{3-3x}$O$_{3x}$ intrinsic property, then in terms of its application as buffer layer in Cu(InGa)Se$_2$-based solar cell. The valance band discontinuity measurements suggested that the substitution of sulphur atoms by oxygen atoms in the crystalline matrix of $\beta$-In$_2$S$_3$ has only a small influence on the position of the valence band level of the material. Robles et al.[143] had shown that the sulfur orbitals participate in both conduction and valence bands of $\beta$-In$_2$S$_3$. On the other hand, Matar et al.[144] had shown that the oxygen orbitals also contribute to
both conduction and valence bands of $\beta$-In$_2$O$_3$. Therefore, in the case of an increase of the optical band gap due to an electronic effect, both valence and conduction bands should shift, contrary to what is usually observed [142]. Robles et al. have also shown that the compression of the $\beta$-In$_2$S$_3$ lattice induced an increase in its optical band gap. In the case of the BISO thin films, we observed that the introduction of oxygen, substituted for sulfur in the crystalline matrix of $\beta$-In$_2$S$_3$, induces a decrease of its lattice parameters. [145] From these results, it seems that the increase of the optical band gap of the BISO thin films with $x$ is not due to the presence of oxygen orbitals, but instead it is simply due to the decrease of the lattice parameter induced by its introduction.

Thin films of In$_2$S$_3$ containing different quantities of sodium were synthesized by annealing at 400°C of structures composed of thin indium, sulphur and indium fluoride layers sequentially evaporated on sodium-free glass substrates [146]. They exhibited $\beta$-In$_2$S$_3$-like structure and the sodium atoms are homogeneously distributed in the whole films. To determine the structure of the material and particularly the position of the sodium atoms in the $\beta$-In$_2$S$_3$ spinel matrix, single crystal of the same compound was synthesized and then studied using XRD and transmission electron microscopy. These studies showed that the materials obtained could be described using the general formulation [In$_{16}$]$_{Oh}$[In$_{5.33-x}$Na$_x$]$_{2.66-2x}$T$_d$S$_{32}$ $(0 \leq x \leq 1.33)$, where Oh and Td, respectively, represented the octahedral and tetrahedral sites of the spinel structure. In thin film form, the maximum of sodium which could be introduced in the crystalline matrix corresponded to $x=0.9$. This new material family was named as BINS.

Optical and electrical properties of $\beta$-In$_2$S$_3$ thin films containing Na ([In$_{16}$]$_{Oh}$[In$_{5.33-x}$Na$_x$]$_{2.66-2x}$]$_{T_d}$S$_{32}$) were studied by Barreau et al [147]. Both transmission and reflectivity curves showed interference fringes, which proved the homogeneity of the morphology of the films. They found that the band gap linearly
increased from 2.1 eV (when the films were pure) to 2.95 eV (when their Na content was 8.4 at%). The electro-negativity of Na is 0.9 while that of In is 1.7. Therefore when it was substituted for indium, the sodium increased the ionicity of the tetrahedral cationic-sulfur bonds, which could be an explanation of the increase of the optical band gap. They also suggested that incorporation of Na in the tetrahedral vacant sites, attracted electrons of sulfur, inducing an increase of In-S bond length which in turn produced perturbation of the electronic structure of the material resulting in the increase of band gap. All the films had n-type conductivity. Incorporation of Na was found to increase the conductivity of In$_2$S$_3$ films. But when the Na content was increased from 0.2 at% to 5 at% the conductivity decreased, while on further increasing (above 6 at%) conductivity drastically increased.

F. Py, M. Womes et al have worked on In$_2$S$_3$ containing copper. A study of the In$_2$S$_3$---Cu$_2$S---CuS system indicated the existence of a solid solution range with the In$_2$S$_3$ vacant spinel crystal structure. An X-ray diffraction study has allowed the identification of two redox processes in the formation of solid solutions with CuS, which is a mixed valency copper sulfide, $\text{Cu}_2^{1}\text{Cu}^{11}(\text{S}_2)^2\text{S}^-$. At low CuS concentrations all copper (I) is oxidized to copper (II) and the substitution of indium (III) by copper (II) proceeds without sulphur loss. At higher CuS concentrations the redox reaction is restricted to the sulphur atoms and the substitution of indium (III) by copper (I) and copper (II) is accompanied by sulphur losses. Presence of copper in two oxidation states has been confirmed by diffuse reflectance and X-ray absorption at the Cu K edge.

### 2.7 Indium sulfide in solar cells

Naghavi et al [149,150], through a systematic study of the deposition parameters of In$_2$S$_3$ buffer layers on CIGS solar cells, achieved a high efficiency of about 16.4% without anti-reflection coating. These studies demonstrate the considerable potential in the fabrication of cadmium-free CIGS thin-film solar cells.
without the CBD method and using indium sulfide buffer layers. The highest efficiency of 16.4% has been obtained at 220 °C for a layer thickness of 30 nm. However the temperature of deposition and the thickness of the films are compromised to yield out good efficiency. Analysis of the device showed that indium sulfide layers were characterised by an improvement of the blue response of the cells compared with a standard CdS-processed cell, due to a high apparent band gap (2.7–2.8 eV), higher open-circuit voltages (up to 665 mV) and fill factor (78%). The high values of the open-circuit voltage and the fill factor of the best cells show that the interface quality between CIGS and In$_2$S$_3$ was high. Preliminary XPS measurements indicated the presence of a small amount of Cu and Na in these films, meaning that inter-diffusion processes had taken place during film formation, which is supposed to have positive role in the junction formation processes and the cell performance. For instance, indium sulfide might have acted as a sink for copper from CIGS up to a certain level at higher temperatures, which could have improved the properties of the cells. It seems that the indium sulfide buffer layers allow higher temperature device preparation compared with classical CdS.

Spiering et al presented the results of large area CIGS modules with indium sulfide (In$_2$S$_3$) as buffer layer deposited by the atomic layer chemical vapor deposition technique [152, 153]. This work is interesting regarding environmental aspects and the implementation in industrial production. Module efficiency close to 13% was realized on the area of 30x30 cm$^2$ ($\eta=12.9\%$, $V_{OC}=27.8$ V, $FF=72.6\%$, $I_{SC}=0.457$ A, aperture area: 714 cm$^2$ and 42 cells). Diffusion processes at the buffer layer interfaces, dependent on deposition temperature and post annealing, have been investigated by X-ray photoelectron spectroscopy, secondary ion mass spectrometry and sputtered neutral mass spectrometry analysis. Diffusion of Cu and Na into the buffer layer and intermixing of S and Se at the In$_2$S$_3$/CIGS interface was detected.

In yet another work Spiering et al reported lifetime measurements of these solar modules [154] which are very important for its implementation in industrial
production. The results from long-term stability testing of Cd-free devices are presented in comparison with reference devices with the CdS buffer layer. Indoor tests were performed at the ZSW laboratories, including damp heat and thermal cycling tests and the I–V performance under light soaking and under different irradiances were investigated. The outdoor testing was performed at the Widderstall solar test field in Germany. The results showed comparable stability behavior of the CIGS modules with different buffer layers and thus reinforced the qualification of In$_2$S$_3$ as buffer material for high-efficiency CIGS thin-film solar modules.

D. Hariskos et al reported Solar cells based on Cu(In,Ga)Se$_2$ by replacing the "standard buffer layer" CdS with a In$_x$(OH,S)$_y$ thin film [155]. The buffer layer was deposited using chemical bath (CBD) process using an aqueous solution containing InCl$_3$ and thioacetamide. The achieved conversion efficiency of 15.7% (active area) using the cadmium free In$_x$(OH,S)$_y$ buffer demonstrated the potential of this process as an alternative to the standard chemical bath deposition of CdS. X-ray photoemission spectroscopy measurements were performed in order to characterize the growth kinetics and the chemical composition. Influence of different concentrations of InCl$_3$ and thioacetamide in the solution on the electrical properties of the solar cells was studied by measuring the j-V characteristics and the spectral quantum efficiencies. Capacitance-voltage (C-V) measurements indicated that the high $V_{oc}$ values of devices with the novel buffer layer were correlated with narrower space charge widths and higher effective carrier concentrations in the absorber materials.

Solar cells with ALD deposited ZnO and indium sulfide layers has been investigated by E. B. Yousfi et al [42]. In situ monitoring at the monolayer level was done using quartz crystal microgravimetry (QCM), with a special focus on extrinsic doping of ZnO with Al. Cu(In,Ga)Se$_2$/In$_2$S$_3$ (ALE)/ZnO (ALE) cells present efficiencies up to 13.5%. Indium sulfide layers used in these cells were characterized by a high band-gap value (up to 3.3 eV). They possessed an ‘amorphous-like’ structure and a composition close to In$_2$S$_3$ as determined by Rutherford Back
Scattering measurements. Lowering of the band-gap and crystallization took place under annealing; they suggest that the high band-gap value of ALE indium sulfide layer to be related to the structural effects.

Indium sulfide buffer layers deposited with the help of the Spray-Ion Layer Gas Reaction (Spray-ILGAR) technique had recently been used with Cu(In,Ga)(S,Se)₂ absorbers resulting in cells with an efficiency equal to that of cadmium sulfide references was reported by Nicholas A. Allsop et al [157]. In this paper they show that cells prepared with Cu(In,Ga)Se₂ absorbers (sulfur free) having indium sulfide buffer layers reached an efficiency of 13.1% which was slightly below the efficiency of the cadmium sulfide reference. However, temperature dependant current-voltage measurements revealed that the activation energy of the dominant recombination mechanism remained unchanged from the cadmium sulfide buffered cells indicating that recombination was within the space charge region. They also reported the results of manipulating the absorber BUFFER interface between the chalcopyrite Cu (In,Ga)(S,Se)₂ absorber (CIGSSe) and the indium sulfide buffer [158]. It was shown that the deposition of a small amount of zinc sulfide at the absorber/buffer interface could be used to increase the open circuit voltage. A small but significant increase of 20 mV (up to 580 mV), as compared to the pure indium sulfide buffered cells was possible leading to an increase in the overall efficiency.

They also carried out dry and damp heat stability of chalcopyrite solar cells prepared with an indium sulfide buffer deposited by the spray-ILGAR technique [159]. These cells were subjected to dry and damp heat conditions of 85 °C and 85% humidity for 100 h without encapsulation. The resulting cell parameters were measured and compared to cells prepared using a standard cadmium sulfide layer deposited by chemical bath deposition. Two different zinc oxide window processes were used for both buffers and the effect of changing the zinc oxide process was discussed. Before the damp heat tests, using an rf-sputtered zinc oxide process the indium sulfide buffers had an efficiency equal to the cadmium sulfide buffered cells.
and on using a second rf/dc-sputtered zinc oxide process, a superior efficiency was obtained with the indium sulfide. The biggest loss in efficiency after damp heat testing was shown to arise from shunt paths at the scribe lines. The indium sulfide buffered cells degraded by only 11% under damp heat conditions when measured after rescribing. A difference between the cell efficiencies using two different zinc oxide windows highlighted the interdependence of the process steps.

S. Gall et al conducted XPS studies of Cu(In,Ga)Se$_2$ (CIGSe)/In$_2$S$_3$ structures [160]. The indium sulfide layers were grown using physical vapor deposition (PVD) in which indium and sulfur were evaporated on the substrates at a temperature $T_s$. These as-deposited thin films were then heated at 200 °C for 1 min. A 12.4% efficiency was achieved using this process. The XPS study revealed that copper diffused from the chalcopyrite absorber towards the indium sulfide layer during this synthesis process. The quantity of copper strongly depended on synthesis temperature ($T_s$); the higher $T_s$, the more was the copper diffused. This observation was correlated with the solar cell performance to conclude that a significant Cu-diffusion inhibited the formation of a high-quality junction between the Cu(In,Ga)Se$_2$ and the buffer layer.

S. Gall et al also reported the influence of sodium compounds at the Cu(In,Ga)Se$_2$/(PVD)In$_2$S$_3$ interface on solar cell properties [161]. This work dealt with indium sulfide buffer layers grown by thermal co-evaporation of elemental indium and sulfur. It was found necessary to deposit these buffer layers at low substrate temperatures in order to reach $V_{oc}$ values similar to those with (CBD) CdS. However, such deposition conditions lead to high recombination at the Cu(In,Ga)Se$_2$/indium sulfide interface. Even though the Cu(In,Ga)Se$_2$ surface was cleaned in NH$_3$ (1 M, room temperature) prior to the indium sulfide deposition, this behavior was associated to the presence of sodium carbonates/oxides at the interface. An explanation is that, despite the chemical etch, sodium carbonates/oxides remain in the air exposed Cu(In,Ga)Se$_2$ grain boundaries and can migrate towards the surface when
the Cu(In,Ga)Se₂ is heated under vacuum. These polluted interface areas acted as recombination zones and this might have lead to the inferior devices. The device performance was improved by (i.e. improve the interface quality) sulfurizing the remaining sodium carbonates/oxides. The resulting Na₂S could then leave the interface by formation of a solid solution with the indium sulfide. By adapting this buffer layer deposition process, device with an efficiency of 13.3% was realized.

Lafond et al reported investigations on In₂S₃ containing Cu and/or Na compounds [151], which were expected to be formed at the Cu(In, Ga)Se₂/In₂S₃ interface. It was observed that a solid solution NaₓCu₁₋ₓIn₅S₈ existed from CuIn₅S₈ (x=0) to NaIn₅S₈ (x= 1) with a spinel-like structure. The single crystal structure determination showed that indium, copper and sodium atoms are statistically distributed on the tetrahedral sites. XPS investigations on the CuIn₅S₈, Na₀.₅Cu₀.₅In₅S₈ and NaIn₅S₈ compounds combined with the band gap changes are mainly due to valence band maximum shift; it is moved downward when x increases from 0 to 1. These observations are confirmed by the electron structure calculations based on the density functional theory, which additionally demonstrate that the pure sodium compound has direct gap whereas the copper-containing compounds have indirect gaps.

N. Barreau et al showed the potential of In₂S₃ containing sodium (BINS) thin films which can be grown on glass substrates heated at 200 °C [162]. The films had n-type electrical conductivity and their optical band gap could be managed between 2.15 and 2.90 eV by controlling their sodium content. In the aim of realizing efficient solar cells, the physico-chemical and electrical properties of Mo/CIGS/BINS structures and solar cells were studied. An efficiency of 8.2% was been reached with a 100 nm thick BINS buffer having a band gap of 2.8 eV.

The impact of NaₓCu₁₋ₓIn₅S₈ compounds formed at the Cu(In,Ga)Se₂/In₂S₃ interface of these thin film solar cells is also discussed by Barreau et al [163] in yet another work. Structural and optical properties of NaₓCu₁₋ₓIn₅S₈ powders, with x=0,
0.25, 0.5, 0.75 and 1, are determined. It is shown that all of the samples have the same crystalline structure, which indicates the existence of a solid solution over the whole range of $x$ (i.e. 0-1). Increase of the optical band gap of these compounds is found to be linear between $x=0$ and $x=0.75$ (1.85 eV), whereas for $x=1$ (i.e. NaIn$_5$S$_8$) $E_g$ is found to be 2.40 eV, which is much higher than the value expected from the linear slope. Such an evolution shows that the copper and the sodium weigh differently on the optical properties of the material.

F. Jacob et al presented the influence of the Ga content ($x = Ga / (Ga + In)$) in the absorber on the solar cell performance for devices using (PVD) In$_2$S$_3$-based buffers [164]. For experiments with $x$ between 0 and 0.5, devices using (PVD) In$_2$S$_3$-based buffers were compared to reference devices using (CBD) CdS. Both buffers showed similar cell characteristics for narrow band gap absorbers, typically $E_{gCIGSe} < 1.1$ eV. However, the parameters of the cells buffered with (PVD) In$_2$S$_3$ are degraded when the absorber gap was widened. These evolutions were coherent with the existence of a conduction band cliff at the CIGSe/(PVD)In$_2$S$_3$ interface.

Our group reported Copper indium sulfide (CuInS$_2$)/In$_2$S$_3$ solar cells fabricated using spray pyrolysis method [165]. High short circuit current density and moderate open circuit voltage were obtained by adjusting the condition of deposition and thickness of both the layers. Consequently, a relatively high efficiency of 9.5% (active area) was obtained without any anti-reflection coating. The cell structure was ITO/CuInS$_2$/In$_2$S$_3$/Ag. We avoided the usual cyanide etching and CdS buffer layer, both toxic, for the fabrication of the cell.

K. Ernits et al presented In$_x$S$_y$ thin-film buffer layers prepared by ultrasonic spray pyrolysis in the CIGS solar cell configuration, reaching an efficiency of 8.9% [166]. Light soaking enhanced the efficiency of In$_x$S$_y$/CIGS cells primarily by improvements in fill factor and open circuit voltage.

D. Ohashi et al reported the improvement of CIGS thin-film solar cells by surface sulfurization using In$_2$S$_3$ and sulfur vapor [167]. Surface sulfurization of
Cu(In,Ga)Se₂ (CIGS) thin films was carried out using two alternative techniques that did not utilize toxic H₂S gas; a sequential evaporation of In₂S₃ after CIGS deposition and the annealing of CIGS thin films in sulfur vapor. A Cu(In,Ga) (S,Se)₂ thin layer was grown on the surface of the CIGS thin film after sulfurization using In₂S₃, whereas this layer was not observed for CIGS thin films after sulfurization using sulfur vapor, although a trace quantity of S was confirmed by AES analysis. In spite of the difference in the surface modification techniques, the cell performance and process yield of the ZnO:Al/CdS/CIGS/Mo/glass thin-film solar cells were remarkably improved by using both surface sulfurization techniques.

Solar cells of CuInS₂/In₂S₃/ZnO type are studied by B. Asenjo et al [168] as a function of the In₂S₃ buffer deposition conditions. In₂S₃ was deposited from an aqueous solution containing thioacetamide (TA), as sulfur precursor and In³⁺. In parallel, variable amounts of In₂O₃ are deposited that have an important influence on the buffer layer behavior. Higher efficiency was attained with buffer deposited at high temperature (70 °C) and [TA] (0.3 M). These conditions were characterized by short induction time, high deposition rate and low In₂O₃ content in the buffer. For films having higher In₂O₃ content (deposited at lower temperature), the efficiency of the cells decreased with buffer thickness.

K. C. Wilson et al of our group reported a novel route of preparing copper indium sulfide thin films on In₂S₃ thin films [156]. Copper indium sulfide thin films were prepared by copper diffusion into argon ion implanted In₂S₃ thin films. Copper diffusion in implanted samples enabled to prepare an In₂S₃/CuInS₂ solar cell.

The conduction band offset between the absorber and the buffer layer is an important parameter influencing conversion efficiency of solar cells. The evolution of the electronic affinity difference, \( \chi(CuIn_{0.7}Ga_{0.3}Se_2) - \chi(BISO-\beta-In_2S_3) \) containing oxygen, versus the optical band of the BISO thin film has been reported [150], from which we can observe that at the conduction band offset between BISO and
CuIn$_{0.7}$Ga$_{0.3}$Se$_2$ is well adapted when the optical band gap of the BISO thin film is between 2.50 and 2.90 eV. The value for the CBD-CdS buffer layer is also reported; its electronic affinity corresponds to a 2.70-eV BISO film. For the same conduction band offset (0.20 eV), BISO films induced less absorption losses in the blue region due to their wider band gap. BISO thin films as buffer layer may allow an improvement in the performance of high band gap Cu(InGa)Se$_2$-based solar cells due to a better conduction band offset matching.

Band alignment at the interface of the heterostructure $\beta$-In$_2$S$_3$/SnO$_2$ was studied using XPS by Bernède et al [130]. They observed that the conduction band discontinuity ($\Delta E_c$) between $\beta$-In$_2$S$_3$ and SnO$_2$ was -0.45 eV. From this value and using SnO$_2$ work function and the Cu(In$_{1-x}$Ga$_x$)Se$_2$ electronic affinity values reported in the literature, they estimated the conduction band discontinuity at the interface Cu(In$_{1-x}$Ga$_x$)Se$_2$/\$\beta$-In$_2$S$_3$ to be about 0 eV.

H. Ihara et al has carried out XPS analysis of the valence band of CdIn$_2$S$_4$ and In$_2$S$_3$ single crystals [107]. The spectrum of CdIn$_2$S$_4$ had a strong resemblance to its synthesized spectrum from the In$_2$S$_3$ and CdS spectra, which was in good agreement with the theoretical density of states (DOS). The contribution of constituent atoms to the valence band DOS in CdIn$_2$S$_4$ was corresponding to those in In$_2$S$_3$ and CdS.

A comparative photo-electrochemical study of compact In$_2$O$_3$/In$_2$S$_3$ multilayer thin films was conducted by S.S. Kale et al. [98] Indium sulfide (In$_2$S$_3$) thin films were successfully deposited using chemical bath deposition (CBD) onto indium-doped-tin-oxide (ITO) substrates from an aqueous mixture containing indium chloride and thioacetamide at 343 K. As-deposited films were annealed at 673 K to convert into In$_2$O$_3$ and were confirmed through the measurement of energy dispersive X-ray analysis (EDAX). Over In$_2$O$_3$, again In$_2$S$_3$ film was deposited using CBD to form In$_2$O$_3$/In$_2$S$_3$ bilayer, where In$_2$O$_3$ served as an effective window and/or hole blocking layer and In$_2$S$_3$ as a sensitizing layer. Enhanced photochemistry was confirmed from
photo-electrochemical (PEC) measurement, where multilayer thin films showed better performance with solar conversion efficiency ($\eta$%) of 0.17% than In$_2$O$_3$ and In$_2$S$_3$.

Nanocrystalline In$_2$S$_3$ modified In$_2$O$_3$ electrodes were prepared with sulfidation of In$_2$O$_3$ thin film electrodes under H$_2$S atmosphere by Hara et al [63]. The aqueous slurry of In$_2$O$_3$ was prepared from 2 g of commercial In$_2$O$_3$ powder, 10 µl of acetylacetone, 50 µl of Triton X-100 (as a surfactant) and distilled water (4 ml). This slurry was deposited on fluorine doped SnO$_2$ transparent conducting glass using a scotch tape as the spacer with ‘doctor blade painting’ and calcinated at 500ºC for 1 hour under air. The In$_2$O$_3$ thin films were treated under H$_2$S at 200-300ºC for 10-30 min, resulting in the formation of an In$_2$S$_3$/In$_2$O$_3$ thin film electrode. Band gap of In$_2$S$_3$ estimated from the onset of absorption spectra was 2 eV. This photo-electrochemical cell could convert visible light of 400-700 nm to electrical energy. A highly efficient incident photon to electron conversion efficiency of 33% was obtained at 410 nm. The solar conversion efficiency [$\eta$], under AM 1.5 was 0.31% with $J_{sc}$ = 3.1 mA/cm$^2$, $V_{oc}$ = 0.26 V and FF = 38%.

P. M. Sirimanne has done a comparative study of semiconductor sensitization by micro-crystals of indium sulfide on various porous wide band gap semiconductor substrates [52]. Semiconductor sensitization on various n-type wide band gap semiconductors was studied by using micro-crystals of n-type indium sulfide. The generation of an anodic photocurrent on the electrode was explained from the viewpoint of semiconductor sensitization. A very high incident photon-to-current conversion efficiency (IPCE) of more than 80% was achieved on In$_2$S$_3$/In$_2$O$_3$ electrodes in a polysulfide electrolyte. The observed values of the IPCE for In$_2$S$_3$/TiO$_2$ and In$_2$S$_3$/ZnO electrodes were rather low compared to that of In$_2$S$_3$/In$_2$O$_3$ electrodes, in the same electrolyte. Semiconductor sensitization process was not observed on In$_2$S$_3$/ZnS electrodes. A very high incident photon to current conversion efficiency of 80% was achieved at an In$_2$S$_3$/In$_2$O$_3$ electrode in a polysulfide electrolyte [40].
Conclusion

A review of the studies carried out on indium sulfide demonstrates it to be an ideal buffer layer for PV applications. It could be prepared by a variety of techniques. Simple low cost chemical methods also yield good films and the impurities like oxygen, hydroxides and Na getting incorporated during these processes finds to be beneficial in the case of indium sulfide. Doping could beneficially alter the properties of indium sulfide but only a few studies are reported in this perceptive.

Studies prove that indium sulfide buffer layers allow higher temperature device preparation compared with classical CdS. The Long term stability test qualifies In$_2$S$_3$ as buffer material for high-efficiency CIGS thin-film solar modules. The highest efficiency value reported for cell with indium sulfide is slightly lower than value achieved by using CdS buffer layer, this contradicts the expectation of better efficiency for In$_2$S$_3$ as it possesses a wider band gap. So to grab its potential fully, better optimization has to be done.
References


