Vacuum Evaporated In$_2$S$_3$ Buffer Layer for Cu(In,Ga)Se$_2$ Thin-Film Solar Cell

A dissertation submitted to the

EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE (ETH)

ZÜRICH

for the degree of

DOCTOR OF SCIENCE

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Zurich, 2010
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Abstract

The high efficiency Cu(In,Ga)Se$_2$ (CIGS) based thin-film solar cells have been demonstrated by various groups across the globe. These high efficiency solar cells consist of chemical bath deposited (CBD) CdS buffer layer which in turn causes some concerns, ecological one being at the top, when it comes to industrial production of solar modules. In$_2$S$_3$ is one of the most promising candidates for substituting CdS in CIGS solar cell technology. With the prime focus on vacuum based deposition of In$_2$S$_3$ as an alternative to CBD buffer layer in CIGS solar cells, the research was aimed at the characterization of solar cells and In$_2$S$_3$ buffer layer grown by employing different deposition techniques.

The approach towards the set targets of current work began with the investigation of chemical and structural properties of In$_2$S$_3$ source materials used for depositing In$_2$S$_3$ buffer layer on different substrates. In order to ensure the reproducibility of the results, the chemical and microstructural stability of In$_2$S$_3$ source materials over extended period of evaporation have been studied. A significant degree of chemical disorder and microstructural inhomogeneity was detected in In$_2$S$_3$ source material. The chemical composition of the buffer layers as a function of source materials evaporation periods was determined. As a result of non-stoichiometry in the source material, the layers were found to be sulfur deficient. The effect of evaporation behavior of two different source materials on the solar cell performance was determined.
The growth and properties of thermally evaporated In$_2$S$_3$ buffer layer were investigated using various thin-film characterization techniques. Focusing on in-situ annealing treatment after buffer deposition step, extensive efforts were made to optimize the process parameters related to buffer layer deposition. As a result of set of optimization experiments, a 14.1% (without antireflection coating) efficient solar cell was realized on soda-lime-glass (SLG) substrate.

A non-vacuum in-line deposition compatible ultrasonic spray pyrolysis (USP) technique was also employed to grow In$_2$S$_3$ buffer layer. A direct comparison among the properties of USP-In$_2$S$_3$ layers with thermally evaporated layer was performed. The USP layers were found to be contained with impurities originating from precursor solution. The USP-dry technique led to growth of a polycrystalline tetragonal $\beta$-In$_2$S$_3$ layer whereas, as-deposited Thermal- and USP-wet layer In$_2$S$_3$ layer were found to be amorphous. Owing to unoptimized deposition conditions of USP-wet method, the existence of microvoids was detected in the layer.

Our research on thermally evaporated indium sulfide buffer revealed the growth of non-stoichiometry layer. With an objective of growing stoichiometric In$_2$S$_3$ layer, the flash evaporation technique was employed. An in-depth investigation of optical, chemical, structural and morphological characteristics of flash evaporated buffer layer was carried out during the course of this work. Based on the studies on layer characteristics, a layer growth model has been successfully proposed. The solar cells were developed with Flash-In$_2$S$_3$ buffer layers and their performances were compared with CBD-CdS reference devices. The elemental interdiffusion across window/buffer and buffer/CIGS interfaces giving rise to electronic effects was found to play a key role in determining the solar cell performance.

The scientific knowledge and understanding gained on thermally evaporated In$_2$S$_3$ buffer layer was then transferred to development of flexible solar cell on polyimide foils. With an initial aim to raise the conversion efficiency to an appreciable value, the research was primarily directed on the tailoring of the buffer deposition steps by introducing an intermediate CIGS surface
treatment prior to In$_2$S$_3$ deposition. A beneficial effect of air annealing of the complete device was observed and a maximum efficiency of 10.1% was achieved.
Zusammenfassung  (Abstract in German)


Um die gesteckten Ziele der Arbeit zu erreichen wurde mit der Untersuchung chemischer und struktureller Eigenschaften des In$_2$S$_3$- Ausgangsmaterials begonnen. Um die Reproduzierbarkeit der Schichten zu sichern wurde die chemische und mikrostrukturelle Stabilität des In$_2$S$_3$- Quellenmaterials über lange Verdampfungszeiten untersucht. Eine signifikante chemische Veränderung und mikrostrukturelle Inhomogenität wurde dabei festgestellt. Die chemische Zusammensetzung der Pufferschichten als Funktion der Verdampfungsdauer des Ausgangsmaterials wurde bestimmt.

Die Abweichung von der Stöchiometrie im Quellenmaterial bewirkte eine Schwefelarmut in den aufgedampften Schichten. Unterschiedliche Eigenschaften während der Verdampfung von
Zusammenfassung (Abstract in German)


Neben vakuumbasierten Depositionsmethoden wurden auch \( \text{In}_2\text{S}_3 \)-Schichten mit vakuumfreier, mit in-line-Produktion kompatibler, Ultraschall-Spraypyrolyse (USP) deponiert, die USP-Schichten wurden direkt mit vakuumverdampften Schichten verglichen. In den USP-Schichten wurden Kontaminationen nachgewiesen, deren Ursprung in den Ausgangslösungen der chemischen Reaktion liegen. Der trockene USP-Prozess führte zum Wachstum einer polykristallinen tetragonalen \( \beta \)-\( \text{In}_2\text{S}_3 \)-Schicht, während die Schichten aus thermischer Verdampfung sowie aus dem nassen USP-Prozess amorph waren. Mikroskopische Leerräume in den mit nassem USP-Prozess hergestellten Schichten konnten nachgewiesen werden. Diese haben ihren Ursprung in nichtoptimierten Prozessbedingungen während der Beschichtung.

Unsere Forschung auf dem Gebiet thermisch verdampfter Indiumsulfid- Pufferschichten zeigte das Wachstum nichtstöchiometrischer Schichten. Mit dem Ziel stöchiometrische \( \text{In}_2\text{S}_3 \)-Schichten zu wachsen wurde ein Flash-Verdampfungsprozess eingeführt. Eine tiefgehende Untersuchung der optischen, chemischen, strukturellen und morphologischen Charakteristika der flash- verdampften Pufferschichten wurde im Laufe dieser Arbeit durchgeführt. Basierend auf den genannten Untersuchungen wurde erfolgreich ein Modell des Schichtenwachstums eingeführt. CIGS-Solarzellen mit flash-verdampfter \( \text{In}_2\text{S}_3 \)-Pufferschicht wurden entwickelt und mit CBD- CdS-gepufferten Referenzzellen verglichen. Die Interdiffusion von Elementen über die Frontkontakt- Pufferschicht- und Pufferschicht-
Absorbergrenzflächen, resultierend in tiefgehenden elektronischen Effekten, wurde als wichtiges Element für die Leistung der Solarzelle bestimmt.

Das während der Untersuchung von thermisch verdampften In$_2$S$_3$-Schichten gewonnene Wissen und Verständnis wurde dann auf die Entwicklung flexibler Solarzellen auf Polyimidfolien übertragen. Mit dem Ziel, die Effizienz auf einen annehmbaren Wert zu bringen, wurde das Hauptaugenmerk auf die Anpassung des CIGS-Absorbers an die Pufferschichtdeposition gelegt, indem eine Oberflächenbehandlung vor der In$_2$S$_3$-Deposition eingeführt wurde. Ein Annealingschritt in Raumluft zeigte eine Verbesserung der Solarzelle und Effizienzen bis zu 10.1% wurden erreicht.
Chapter 1

Introduction

1.1 Solar Cell Technology

1.1.1 Historical Background

A solar cell is an electronic device which converts the solar energy directly into electrical energy in form of electricity. The function of solar cell is based on the photovoltaic effect in which the photon absorption by semiconductor in solar cell leads to generation of electron and hole resulting in a net voltage buildup between two electrodes of the device. The effect dates back to 1839 when Alexandre Edmond Becquerel observed the creation of voltage between two electrodes immersed in an electrolytic solution on exposure to light [1]. Charles Fritts is credited for demonstrating working solar cell for the first time in 1893. With 1% conversion efficiency, the solar cell was based on selenium semiconductor. The research in solar cell gradually advanced until Polish scientist J. Czochralski developed a method of growth of single-crystal silicon in 1918. Year 1954 witnessed the start of an era when interest in solar cell received a dramatic and significant momentum with the development of Si single crystal p-n junction solar cell yielding an efficiency of nearly 6% [2]. The solar cell technological development has
taken a large leap since then and the current technological advances and scientific knowledge have enabled scientists develop solar cells with efficiency as high as 42% [3,4]. With 85% marketshare, crystalline Si based solar cells are leader in the solar cell photovoltaic market [5].

1.1.2 Thin-film Solar Cells

The current high performance solar cells are either multijunction solar cells or crystalline Si based cells. The material usage, fabrication steps and other technological inputs render higher cost-per-watt to these classes of solar cells. On the other hand, thin-film technologies offer substantial cost benefit over traditional wafer-based crystalline Si and multijunction solar cell due to lower material usage, fewer processing steps, and simpler device processing and manufacturing technology for large-area modules. Further to these advantages, thin film solar cells can be developed on flexible substrate giving them a winning edge over wafer based and other class of rigid solar cells. For cost-per-watt point of view, the choice of any given technology is governed by the highest achievable efficiency, ease of manufacturing, reliability, availability of materials, and environmental sensitivity and thus thin-film solar cell technology has immense potential to become economically viable and widely accepted technology of the future. The current thin-film solar cell technology encompasses amorphous silicon, cadmium telluride (CdTe), and ternary and multinary copper indium selenide (CIS) and copper indium gallium diselenide (CIGS), and dye-based and organic solar cells. Figure 1.1 shows the technological development of solar cells over last three decades.

1.2 Cu(In,Ga)Se$_2$ Thin-Film Solar Cells

The chalcogenide Cu(In,Ga)Se$_2$ referred as CIGS are multinary alloys of CuInSe$_2$ and CuGaSe$_2$ ternary compound semiconductors. The CIGS-based thin-film solar cells are regarded as one of the most promising candidates for low-cost generation of solar
1.2. Cu(In,Ga)Se\textsubscript{2} Thin-Film Solar Cells

Figure 1.1: Historical evolution of best efficiency laboratory solar cell. (Source: National Renewable Energy Lab (NREL – Kazmerski and Zweibel))

electricity because of their high efficiency and excellent intrinsic stability in terrestrial as well as space applications \cite{6,7}. The highest efficiencies demonstrated with CIGS absorbers, 14% by Würth Solar, Germany on large area (60×120 cm\textsuperscript{2}) module \cite{8} and 19.9% on small area (0.419 cm\textsuperscript{2}) cell by National Renewable Energy Laboratory (NREL), USA \cite{9}, are well above the efficiencies attained by its conterpart CdTe or a-Si-based multi-junction solar cells and modules in thin-film solar cell family. Recently, an efficiency over 20% was achieved by researchers at Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW), Germany \cite{10}.

Thin-film solar cells can be grown on rigid (glass) as well as on flexible (metal or polymer foils) substrate. Flexible solar cells based on CIGS, CdTe, a-Si and TiO\textsubscript{2}-dye based organic materials have been developed on different types of substrates. Considering the industrial production of large area module, a remarkable advantage of flexible solar cell over one developed on glass substrate is that flexible cell can be developed in a roll-to-roll process which has huge potential to reduce the manufac-
turing cost and increase the throughput dramatically. Hence, from point of view of cost-reduction, high throughput and ease of implementation of end product at the demand site, there is a considerable interest in development of flexible solar module. Various research groups worldwide have used Ti, stainless steel and polyimide foils as substrate to develop the flexible solar cells [11–14]. The highest CIGS solar cell efficiencies of 17.4% on Ti foil, 17.7% on zirconia sheet and 14.1% on polyimide film have been achieved using CdS as buffer layer [15,16]. A highly efficient, 17.9%, flexible solar cell on Ti-foil with chemically grown ZnS(O,OH) buffer layer has been demonstrated by Yagioka et al. [17]. Recently, Chirila et al. successfully demonstrated a 16.9% efficient champion solar cell developed on polyimide substrate [18].

1.3 Buffer Layers in CIGS Technology

1.3.1 CdS Buffer Layer

The most efficient CIGS solar cell developed to date consists of CdS buffer layer grown by a non-vacuum method called chemical bath deposition (CBD). The CBD results in growth of a homogeneous and continuous layer of CdS with an excellent coverage of underlying CIGS absorber and offers beneficial chemical and electronic effects leading to enhanced solar cell properties [19–24]. In fact, the CBD-CdS is known to undergo a pseudoepitaxial growth with CIGS layer showing epitaxial correlation between (112) planes of CIGS and (111) cubic or (002) hexagonal CdS planes [21,25]. The CIGS substrate when immersed in chemical bath for CdS deposition, receives surface etching treatment resulting in removal of native oxides and hence favoring epitaxial growth of CdS layer on fresh CIGS surface. Abou-Ras et al. made a comparative study of CdS buffer layer grown by CBD and vacuum based physical vapor deposition (PVD) and demonstrated the superiority of CBD-CdS over PVD-CdS [26]. To date, CBD-CdS/CIGS device holds the pride of being most efficient solar cell in CIGS solar cell technology [10,18].
1.3. Buffer Layers in CIGS Technology

1.3.2 Alternative Buffer Layers

Although CBD-CdS buffer layer in CIGS technology yields the best performance, it is not fully accepted as the material of choice for industrial production of large area solar modules due to following reasons:

- ecological concerns due to use of Cd element \[27\]
- CBD has low process yield that leads to a large volume of Cd containing waste
- disposal of waste and byproduct of CBD-CdS adds to manufacturing cost
- CBD is incompatible to in-line production of solar cells and breaks vacuum sequences in the complete processing of solar cell device which is by and large vacuum based
- owing to low band gap of CdS (2.4 eV), lower fraction of photons are available for CIGS absorber this leads to loss of current in blue region of solar spectrum and hence limits the solar cell performance

Therefore, both from material as well as deposition technique point of views, there exists a great demand to replace chemical bath deposition method with a vacuum based in-line compatible method and CdS with a material that offers similar or better properties than CdS does.

There are numerous reports on various alternative buffer layers grown by a variety of deposition methods \[28\] \[39\]. Various research laboratories worldwide have studied In$_2$S$_3$, In(OH)$_x$S$_y$, In$_2$Se$_3$, ZnO, InZnSe$_x$, ZnS, ZnSe, (Zn,Mg)O, SnO$_2$, and SnS$_2$ as an alternative buffer layer to standard CdS \[40\]. The buffer layer deposition methods such as PVD, CBD, spray pyrolysis, atomic layer deposition (ALD), chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD), ion layer gas reaction (ILGAR), modulated flux deposition (MFD) electrodeposition and sputtering have been employed to grow a range of buffer layers for CIGS solar cells \[35, 39, 41, 53\].
1.3.3 \( \text{In}_2\text{S}_3 \) Buffer Layer

\( \text{In}_2\text{S}_3 \) single crystal

\( \text{In}_2\text{S}_3 \) is a III-VI compound semiconductor which crystallizes into three allotropic forms namely, \( \alpha-\text{In}_2\text{S}_3 \), \( \beta-\text{In}_2\text{S}_3 \) and \( \gamma-\text{In}_2\text{S}_3 \) \[54\]. The hexagonal \( \gamma \)- phase is a high temperature phase and is stable above 750°C. The spinel-like tetragonal \( \beta-\text{In}_2\text{S}_3 \) is the most stable room temperature phase and has dark-red appearance. The cubic \( \alpha-\text{In}_2\text{S}_3 \) may also be stable at room temperature depending upon its method of synthesis. Figure \[1.2\] shows the phase diagram of In-S system. The crystal structure of \( \alpha \)- and \( \beta \)- phases can be understood with the help of spinel \([\text{Al}_2\text{MgO}_4]\) chemical formula in which Al occupies octahedral sites and tetrahedral sites are filled by Mg atoms. However, in case of \( \text{In}_2\text{S}_3 \) the normal scheme of occupancy of voids by atoms is somewhat disobeyed in such a manner that one third of tetrahedral sites remain unoccupied and it can be represented with following crystal formula: \([\text{In}_2]_{\text{Oh}}[\text{In}_2/\text{3} \Delta_1/\text{3}]_{\text{Td}}\text{S}_1/\text{2}\) where, \( \Delta \) is unoccupied cite, Td is tetragonal and Oh is octahedral cite \[55\].

The statistical distribution of tetrahedral cationic voids leads to formation of cubic lattice of \( \alpha-\text{In}_2\text{S}_3 \) phase and when ordering of voids takes place along c-axis, tetragonal lattice structure of \( \beta-\text{In}_2\text{S}_3 \) phase results. Since, one third of tetrahedral sites in \( \alpha \)- and \( \beta-\text{In}_2\text{S}_3 \) remain empty, the compound is intrinsically defective and is readily addressed as defect \( \text{In}_2\text{S}_3 \) structure. Owing to ordered distribution of voids (vacancies), the structure of \( \beta-\text{In}_2\text{S}_3 \) is described as a quadratic super cell consisting of three spinel blocks stacked along c-axis and hence is represented by \([\text{In}_6]_{\text{Oh}}[\text{In}_2\Delta]_{\text{Td}}\text{S}_12\) \[58\]. The resulting lattice parameters and crystal structures \( \beta \)- and other phases of In-S are listed in Tab. \[1.1\] The crystal structure of \( \beta-\text{In}_2\text{S}_3 \) is shown in Fig. \[1.3\]

\( \text{In}_2\text{S}_3 \) thin film

Among different buffer layers studied, \( \text{In}_2\text{S}_3 \) and its derivatives (\( \text{In(OH}_x\text{S}_y \)), \( \text{In(OH)}_3 \)) are one of the most promising candidates as replacement to CdS buffer layer. The larger band gap
Figure 1.2: Phase diagram of In-S \cite{56,57}.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Lattice constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-In$_2$S$_3$</td>
<td>cubic</td>
<td>$a$=0.761 $b$=0.3224</td>
</tr>
<tr>
<td>$\beta$-In$_2$S$_3$</td>
<td>tetragonal</td>
<td>$a$=1.074</td>
</tr>
<tr>
<td>$\gamma$-In$_2$S$_3$</td>
<td>hexagonal</td>
<td>$a$=0.3800 $b$=0.9044</td>
</tr>
<tr>
<td>$\alpha$-InS</td>
<td>orthorhombic</td>
<td>$a$=0.4442 $b$=1.0642 $c$=0.3939</td>
</tr>
<tr>
<td>In$_6$S$_7$</td>
<td>monoclinic</td>
<td>$a$=0.9090 $b$=0.3887 $c$=1.7705</td>
</tr>
</tbody>
</table>

High pressure phase
$\epsilon$-In$_2$S$_3$ | rhombohedral | $a$=0.6975 $\alpha$=56.1° $\beta$=108.2° |

Table 1.1: Chemical phases and crystal structure of In-S compounds \cite{56}.

of In$_2$S$_3$ than that of CdS (2.4eV) makes it more transparent in blue region of solar spectrum than CdS. The reduced absorption
(loss) results in an enhanced spectral response of the CIGS solar cell leading to gain in device current. It has been shown that the performance of CIGS solar cell buffered with In$_2$S$_3$ layer depends on the buffer deposition technique and post-deposition annealing treatments \cite{35,39,41,45,49,52,53}. Thus, by employ-
ing a suitable deposition process the properties of In$_2$S$_3$ can possibly be tailored accordingly.

Various groups have prepared In$_2$S$_3$ layers by different methods such as CBD [43], ALD [45], ILGAR [39], reactive evaporation [32], thermal evaporation [31,49,59] and MFD [60]. Out of these, In$_2$S$_3$ buffer layers deposited by ALD produced a record efficiency of 16.4% on a small area of 0.1 cm$^2$ [45] and a module efficiency of 12.9% was achieved on an area of 30×30 cm$^2$ [61]. Despite the encouraging results obtained from CIGS solar cell with ALD-In$_2$S$_3$, ALD is slow, batch-to-batch process and expansive to upscale for large area module production. On the other hand, PVD being vacuum based, fast, low-cost, in-line deposition compatible and easily up-scalable technique holds its industrial importance and acceptance over non-vacuum chemical methods. The most efficient cell with vacuum evaporated In$_2$S$_3$ buffer layer was demonstrated by Strohm et al. in 2005 [49]. Recently, Pistor et al. produced a 15.2% efficient solar cell consisting of thermally evaporated In$_2$S$_3$ buffer layer [62]. Table 1.2 surveys the recent progress made and the champion cell efficiencies obtained using In$_2$S$_3$ buffer layer grown by various techniques in different research laboratories.

The energy band diagrams of the solar cell devices buffered with CdS and In$_2$S$_3$ layer are shown in Fig. 1.4a and b. The energy level corresponding to conduction band, valance band

<table>
<thead>
<tr>
<th>Deposition technique</th>
<th>Substrate</th>
<th>efficiency (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBD</td>
<td></td>
<td>15.7</td>
<td>Hariskos et al. [43]</td>
</tr>
<tr>
<td>ALD</td>
<td></td>
<td>16.4</td>
<td>Naghavi et al. [45]</td>
</tr>
<tr>
<td>Sputtering</td>
<td></td>
<td>12.2</td>
<td>Hariskos et al. [35]</td>
</tr>
<tr>
<td>Spray-ILGAR</td>
<td>SLG</td>
<td>14.7</td>
<td>Allsop et al. [63]</td>
</tr>
<tr>
<td>Evaporation</td>
<td></td>
<td>14.8</td>
<td>Strohm et al. [49]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.1</td>
<td>Verma et al. [64]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.2</td>
<td>Pistor et al. [62]</td>
</tr>
<tr>
<td>Polyimide</td>
<td></td>
<td>10.1</td>
<td>Verma et al. [65]</td>
</tr>
</tbody>
</table>

Table 1.2: State-of-the-art solar cell efficiencies with In$_2$S$_3$ buffer layer grown by different methods.
Figure 1.4: Band diagrams of CdS-CIGS and In$_2$S$_3$-CIGS solar cells [49].

and Fermi level are denoted by $E_C$, $E_V$ and $E_F$, respectively. $\phi^n_b$, $\phi^p_b$ represent energy barriers for electrons and holes, respectively. The symbols (1) and (2) are indicative of shift in the valence band position as induced by Cu depletion from CIGS.
The dominance of a specific recombination process (interface, space charge region or bulk) strongly depends on the CIGS surface finish with respect of Cu concentration. Turcu et al. [66] investigated the recombination processes prevailing in the CdS/CIGSSe devices with respect to Cu concentration and presented the band alignment of the devices. The bulk recombination was found to be the dominant recombination mechanism for Cu-poor composition whereas Cu-rich CIGS favored the interface recombination. For high efficiency CdS/CIGS solar cells, CIGS surface type inversion caused by Cu-depletion from CIGS has been reported in the literature [67]. There are reports on the formation of ordered vacancy compound at CIGS surface as a consequence of Cu-depletion from CIGS to buffer layer [68, 69]. The Cu-diffusion in turn increases the potential barrier for holes ($\phi_p^h$) by 0.2eV which is high enough to prevent the holes recombining with photogenerated electrons at CdS/CIGS interface (Fig. 1.4a) and thus minimizing the possibility of interface recombination. The numerical simulations confirmed the existence of conduction band spike at CdS/CIGS heterojunction emphasizing its effects on the cell performance [70]. On the other hand, the electron affinity considerations in case of CIGS and In$_2$S$_3$ suggest the presence of conduction band cliff at In$_2$S$_3$/CIGS interface [71] making interface as the dominant recombination path. The numerical simulations performed on CIGS solar cells with alternative buffer layer (Zn(Oh,S) and In(OH$_x$S$_y$)) by Nguyen et al. [72] demonstrated that the acceptor-like defect states at ZnO/In$_2$S$_3$ interface strongly affect the solar cell characteristics by inducing band bending due to CIGS surface type inversion. Strohm et al. [49] further confirmed the critical role of acceptor-like defect states present at ZnO/In$_2$S$_3$ interface on the solar cell performance and indicated interface recombination as the dominant recombination mechanism (Fig. 1.4b). The presence of conduction band cliff in case of alternative buffer layer (e.g. In$_2$S$_3$, Zn(OH,S), and In(OH$_x$S$_y$)) and CIGS junction have been reported by several researchers revealing interface as the dominant recombination path [49, 71, 75].
1.4 Scope of Thesis

Realizing the immense potential of vacuum based PVD-In$_2$S$_3$ buffer layer as a substitute to CBD-CdS buffer layer in CIGS solar cell technology, the research was focused on the vacuum deposition of In$_2$S$_3$ buffer layer. The goal was approached by characterizing the In$_2$S$_3$ source material. Two different types of In$_2$S$_3$ powders were investigated studying the impact of their evaporation behavior on the solar cell performance. After selecting a source material for evaporation of In$_2$S$_3$ buffer layers for solar cell applications, its optical, morphological, chemical and structural properties were investigated in detail. With an aim of obtaining reproducible and consistent solar cell performance, sets of experiments were performed to determine the optimum process parameters for development of high efficiency PVD-In$_2$S$_3$/CIGS solar cells. A comparative study of properties of In$_2$S$_3$ buffer layers grown by in-line deposition compatible buffer deposition methods; vacuum based thermal evaporation and non-vacuum ultrasonic spray pyrolysis was carried out. The photovoltaic properties of the devices with In$_2$S$_3$ buffer layer grown by thermal evaporation and ultrasonic spray pyrolysis methods were compared.

The occurrence of non-stoichiometry was identified in thermally evaporated In$_2$S$_3$ buffer layer. We attempted to address the issue of non-stoichiometry by exploiting flash evaporation technique. An extensive study on the growth and properties of flash evaporated In$_2$S$_3$ buffer layer was carried out using various thin film characterization techniques. Based on the material analysis of Flash-In$_2$S$_3$ layers, a layer growth model was proposed. The solar cell performances of Flash-In$_2$S$_3$/CIGS devices with respect to flash rates were analyzed and compared with CBD-CdS/CIGS reference solar cells.

The know-how gained on thermally evaporated In$_2$S$_3$ buffer and solar cell developed on glass substrate was transferred onto flexible solar cell developed on polyimide foils. With an initial focus on attaining an appreciable efficiency values, the research was primarily focused on finding the suitable process steps associated with processing of the complete solar cell.
Chapter 2

Solar Cell Development and Characterization Techniques

For the development of Cu(In,Ga)Se$_2$ solar cell, a sequence of thin film deposition methods was applied. Figure 2.1 illustrates the schematic cross-section image of CIGS solar cell describing stack of various thin layers contributing to the complete solar cell device. The chapter discusses various thin film deposition techniques employed for the development of the complete device and various solar cell & materials characterization techniques used.

2.1 Solar Cell: Layer Structure

Two kinds of CIGS solar cells were developed and studied in this work. Depending upon the substrate chosen, the stack structure of the solar cell can be represented as:

1. ZnO:Al/$i$-ZnO/buffer/CIGS/Mo/soda-lime-glass
2. ZnO:Al/i-ZnO/buffer/CIGS/Mo/polyimide

With the above cell structure, we employed chemical bath deposited CdS buffer layer in fabrication of reference cell and different vacuum and non-vacuum techniques for the development of In$_2$S$_3$/CIGS solar cells. The schematic cross-section of the complete solar cell device depicting various layers present in the solar cell structure is presented in Fig. 2.1.

2.2 Solar Cell Processing

This section presents a detailed description of various steps involved in the development a complete CIGS solar cell.

2.2.1 Substrate

We start with a 3mm thick SLG (area: $5 \times 5 \text{ cm}^2$) or 12.5$\mu$m thick polyimide ($5 \times 5 \text{ cm}^2$) substrate. An ultrasonic cleaning of the substrate is performed sequentially in deionized water, VLSI grade isopropanol and acetone solutions for several minutes (10-15 min). After chemical cleaning, the substrate is dried with the help of dry N$_2$ gas flash.

The high efficiency solar cells require CIGS growth temperature of $\approx 550^\circ \text{C}$ which is below the softening point ($\approx 700^\circ \text{C}$) of the SLG. Moreover, SiO$_2$ being the backbone of SLG also contains alkali oxides such as Na$_2$O and K$_2$O. The sodium oxide present in the substrate act as the source of Na impurity in CIGS layer which has beneficial effect on the solar cell performance [76]. The most important effect of the SLG substrate on CIGS film growth is that it supplies sodium to the growing chalcopyrite material. The sodium diffuses through the Mo back contact to CIGS and the resulting microstructure of CIGS is clearly influenced by the presence of Na with larger grains and a higher degree of preferred orientation with the (112) axis perpendicular to the substrate [77].
2.2. Solar Cell Processing

Owing to their light weight and flexibility, metal (titanium and steel) or plastic (polyimide) foils have advantages over glass substrates. The high thermal expansion coefficient and inferior high-temperature susceptibility of polyimide foils are major challenges unlike its SLG counterpart. Also, polyimide is Na free material, thus an external source of Na is needed for the growth of high quality CIGS layer.

Figure 2.1: Schematic cross-section image of CIGS solar cell developed in this work. The curved arrows denote the incident light on the solar cell.
2.2.2 Molybdenum Back Contact

Mo layer of \( \approx 1 \mu \text{m} \) is deposited by dc-sputtering technique on the substrate in a vacuum chamber at a base pressure of \( \approx 1 \times 10^{-5} \) mbar. The desired thickness of Mo layer is mainly governed by sheet resistance of Mo layer which is \( \approx 0.5 \Omega/\text{sq} \). A careful selection of sputtering parameters minimizes the mechanical stress induced in the Mo layer which is mainly responsible for poor adhesion [78] with SLG substrate. Wada et al. found the existence of MoSe\(_2\) interfacial layer between Mo and CIGS and its beneficial effects on the solar cell performance was reported indicating the formation of quasi-ohmic contact with CIGS layer [79].

2.2.3 CIGS Layer Growth

The most efficient CIGS solar cells to date consist of CIGS absorber layer grown by a well defined scheme of evaporation of constituent elements Cu, In, Ga, and Se onto a heated substrate. The basic concept of growth process was developed by Gabor et al. [80] and is known as a “3-stage” process. Modification in the 3-stage process have been applied by several groups worldwide.

Our baseline in-house 3-stage CIGS growth process is schematically depicted in Fig. 2.2. For CIGS growth, the vapor flux of constituent elements are controlled by regulating the temperatures of the source effusion cells. A constant flux (overpressure) of Se vapor is maintained all through the CIGS deposition process. During the 1\(^{st}\) stage at substrate temperature of 400°C, the coevaporation of elements In and Ga is carried out for 16 min keeping Ga atomic fraction \( (x=\frac{[Ga]}{[In]+[Ga]}) \) constant at 0.3. Once 1\(^{st}\) stage is over, the sample remains exposed to Se vapor for 30 sec in the absence of flux of other elements before starting the 2\(^{nd}\) stage. During the interval between end of 1\(^{st}\) and beginning of 2\(^{nd}\) stage, the substrate temperature is ramped up with a heating rate of 20°C/min so that substrate temperature at the start of 2\(^{nd}\) stage reaches to 570°C. Then the 2\(^{nd}\) stage starts with the deposition of Cu which is evaporated with a constant rate for 20 min. During the Cu evaporation pe-
2.2. Solar Cell Processing

Figure 2.2: Schematic presentation of our “in-house” baseline 3-stage process for growth of CIGS layer on SGL (solid line) or on polyimide (dashed line) substrates.

In case of flexible polyimide substrate\(^1\) the deposition scheme is followed as described above except the maximum substrate temperature which is maintained at 450°C. As soon as the 3\(^{rd}\)

\(^1\)The dotted profile shown in Fig. 2.2 illustrates the CIGS growth process steps followed in case of polyimide substrate.
stage finishes, the substrate is cooled down from 450°C to 100°C at cooling rate of 20°C/min with termination of Se vapor exposure at the substrate temperature of 300°C. With simultaneous heating from 100°C to 400°C at heating rate of 20°C/min, the sample is exposed to NaF vapor for 20min which results in formation of a ≈30nm thin NaF layer on the CIGS surface (see sec. 2.2.1 for the role of Na in CIGS layer). NaF flux is then switched off and sample is subjected to an annealing treatment for 20min at 400°C. The annealing treatment is known as post-deposition treatment (PDT). After 20min of PDT, the sample is cooled down to 100°C at cooling rate of 20°C/min followed by switching off the substrate heater. All the steps described above are in-situ performed in the same vacuum chamber. The details description of CIGS growth processes and PDT can be found in Ph.D. Thesis of D. Rudmann [76].

Figure 2.3a and 2.3b show the SEM cross-section micrographs of a typical CIGS solar cell developed on SLG and flexible polyimide substrate, respectively, in our laboratory. As noticeable in the figure, the CIGS grain growth strongly depends on the substrate which is directly linked to Na supply to CIGS during growth as described in sec. 2.2.1. Easy Na diffusion from SLG to CIGS results in growth of continuous grains normal to substrate plane with grains as large as layer thickness (Fig. 2.3a). Whereas, in case of Na-free polyimide substrate (Fig. 2.3b), externally supplied Na through PDT significantly affect the grain growth leading to small and discontinuous grains with large density of grain boundary defect.

2.2.4 Buffer Layer

With a prime focus on vacuum evaporated In$_2$S$_3$ buffer layer, we also fabricated solar cells with chemical bath deposited CdS buffer layer serving as a reference solar cell.
2.2. Solar Cell Processing

Figure 2.3: SEM cross-section micrographs of solar cell developed on glass (a) and polyimide (b) substrates.
Chapter 2. Solar Cell and Characterization Tools

Chemical bath deposition of CdS buffer layer

The chemical bath deposition of CdS buffer layer was performed by taking 15ml of $1.8 \times 10^{-3}$M cadmium acetate (Cd(CH$_3$COO)$_2$), 10ml of 0.024M thiourea (SC(NH$_2$)$_2$), and 25ml of 1.13M NH$_3$ dissolved in 200ml of deionized H$_2$O. The sample holder carrying the sample is immersed into the beaker containing the precursor solution. The beaker is then immersed into a chemical bath kept at 70°C. The immersion time of 15min results in formation of $\approx 50$nm thin layer of CdS on the substrate. The underlying overall chemical reaction can be expressed as [22]:

$$[Cd(NH_3)_4]^{2+} + SC(NH_2)_2 + 2OH^- \rightarrow CdS + CH_2N_2 + 4NH_3 + 2H_2O.$$ (2.1)

Reactants (Cd(CH$_3$COO)$_2$) and (SC(NH$_2$)$_2$) act as source of Cd and sulfur, respectively.

Thermally evaporated In$_2$S$_3$ buffer layer

Thermal evaporation of In$_2$S$_3$ buffer layer was carried out in a vacuum chamber at base pressure of $1 \times 10^{-6}$mbar. The compound source In$_2$S$_3$, in powder form, was filled in a graphite crucible which is subjected to resistive heating in a vacuum chamber. After attaining desired evaporation rate, the substrate is exposed to evaporation flux of source vapor by opening the substrate shutter so that a desired thickness of buffer layer is deposited on the substrate. The deposition rate and layer thickness are monitored and controlled with the help of quartz crystal monitor. The buffer layer acts as n-type junction partner with p-type CIGS absorber layer.

2.2.5 Window Layer

The transparent conducting oxides (TCO) are highly desired in optoelectronic and photovoltaic industry. There are primarily three kinds of TCOs which find their wide share of applications:
2.2. Solar Cell Processing

SnO$_2$, In$_2$O$_3$:Sn (ITO) and ZnO. The high temperature deposition requirements in case of SnO$_2$ makes it unsuitable for CIGS solar cell application where device tends to degrade above 200-250°C. The higher material cost of ITO discourages its use over ZnO. In the present work, the buffer layer deposition step is followed by sequential deposition of $i$-ZnO and Al:ZnO layer by rf-sputtering technique. The bottom layer in bilayer structure of $i$-ZnO/Al:ZnO is called window layer in CIGS solar cell terminology and top Al:ZnO layer is termed as front contact. Typical thicknesses of $\approx 50$nm and $\approx 250$nm for $i$-ZnO and Al:ZnO layers, respectively were deposited by r.f.-sputtering.

2.2.6 Ni-Al Metal Grid

In order to enhance the carrier collection from the solar cell device, the cell is completed by depositing a metal grid of Ni of $\approx 30$nm followed by evaporation of $\approx 2$µm of Al metal. The deposition of metal grid was carried out by e-beam evaporation technique.

2.2.7 Patterning

Following the above steps of deposition of contributing layers in a complete solar cell device, we finally end up with a cell area of $\approx 5 \times 5$ cm$^2$. The patterning of such a large cell is done by mechanical scribing so that sub-cells of desired area are obtained. In the present work, the sub-cell areas of 0.3 cm$^2$ and 0.6 cm$^2$ were defined my mechanical scribing of cells developed on glass and polyimide substrates. Figure 2.4 shows the image of a CIGS solar cell grown on 5×5 cm$^2$ substrate and patterned into 32 sub-cells of 0.6 cm$^2$ area.
2.3 Characterization Techniques

2.3.1 Energy Dispersive X-ray analysis

The chemical compositions of In$_2$S$_3$ source materials and CIGS layers were determined by energy dispersive X-ray analysis (EDX) technique. The specimens were probed at acceleration voltage of 20 kV in a Tracor EDX system attached to scanning electron microscope at Thin Film Physics Group, Technopark, ETH Zurich, Switzerland.

Figure 2.4: Photographic view of CIGS solar cell developed in our laboratory.
2.3. Characterization Techniques

2.3.2 Scanning Electron Microscope

The microstructural (plan and cross-section) investigations of the samples were carried out using scanning electron microscope (SEM) obtained from Jeol and in CrossBeam NVision 40 from Carl Zeiss SMT equipped with field-emission gun in Nonmetallic Inorganic Materials Group of the Department of Materials at the ETH Zurich, Switzerland.

2.3.3 X-ray Diffraction

The structural (crystalline or amorphous) and chemical (phase identification) study of the samples were performed using X-ray diffraction (XRD) technique using Siemens D5000 diffractometer with Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ Å) at Nonmetallic Inorganic Materials Group of the Department of Materials at the ETH Zurich, Switzerland. Grazing angle x-ray diffraction (GA-XRD) investigations were carried out at grazing angle of 3° using ARL X’TRA Thermoelectron x-ray diffractrometer at Indian Institute of Technology Kanpur, Kanpur, India.

2.3.4 Optical Transmission and Reflection

The optical transmission and reflection spectra were measured using a UV/VIS/NI spectrophotometer (Cary 5000, Varian) at Thin Film Physics Group, Technopark, ETH Zurich, Switzerland.

2.3.5 Spectroscopic Ellipsometry

Ellipsometric measurements were performed using a phase modulated spectroscopic ellipsometer (UVISEL, Horiba Jobin Yvon) at 70° angle of incidence in a wide spectral range of 280-1650 nm. The measurements were performed by Mr. Debjit Datta at Department of Physics, Indian Institute of Technology Kanpur, Kanpur, India.
2.3.6 Raman Spectroscopy

The structural properties of the samples were further investigated with the help of Raman spectroscopy measurements performed using a He–Ne laser (\( \lambda = 632.817 \) nm) with 10\( \times \) objective lens at Loughborough University, Loughborough, United Kingdom and Empa, Dübendorf, Switzerland.

2.3.7 Rutherford Backscattering and Elastic Recoil Detection Analysis

The chemical composition of the samples were determined using Rutherford backscattering (RBS) [2 MeV, He\(^+\) ions] and Elastic recoil detection analysis (ERDA) [12 MeV, \( ^{127}\text{I} \) ion] techniques performed with a 6 MV tandem accelerator. The RBS and ERDA measurements were done by Dr. Max Döbeli at PSI/ETH Laboratory for Ion Beam Physics, ETH Zurich.

2.3.8 Current-Voltage Characteristic

The current-voltage (\( I-V \)) characteristic of the solar cell was recorded under simulated AM1.5 global illumination condition at cell temperature of \( \approx 25^\circ \)C. The Current density-voltage (\( J-V \)) was determined by dividing measured solar cell current (\( I \)) by solar cell area. The bias voltage (\( V \)) dependent current-density (\( J \)) from a solar cell device under illuminated condition can be expressed as:

\[
J(V) = J_0 \left( e^{\frac{q(V-R_sJ)}{AK_BT}} - 1 \right) + \frac{V - R_sJ}{R_p} - J_{ph} \quad (2.2)
\]

---

\(^2\)AM stands for Air Mass. AM1.5 denotes the solar radiation reaching at the earth’s surface when the sun is positioned at 42\(^\circ\) from the normal resulting in actual path length of sunlight being 1.5 times the normal path length. Under these conditions, the irradiated powder density is 1000 W/m\(^2\). The term ‘global’ indicates the direct as well as diffused irradiation.
where, $J_0$ is saturation current density, $q$ is elementary charge, $k_B$ is Boltzmann constant and $T$ is absolute temperature, $A$ is diode ideality factor, and $J_{ph}$ is photocurrent density.

Figure 2.5 shows a typical $J-V$ characteristic of a solar cell under illuminated condition. The performance of a solar cell is determined by measuring its electrical parameters commonly known as photovoltaic (PV) parameters of a solar cell. The most important and significant parameters are defined as follows.

**Figure 2.5:** $J-V$ characteristic of a solar cell under AM1.5G illuminated condition.

- **Short-circuit current ($J_{sc}$):** current density at zero bias voltage applied to solar cell.
- **Open-circuit voltage ($V_{oc}$):** bias voltage when no current is delivered by a solar cell.
- **Maximum power density ($P_{max}$):** is maximum power density derived by a solar cell and is defined by $P_{max} = J_{max} \cdot V_{max}$.
- **Fill factor (FF):** is defined as; $FF = \frac{P_{max}}{J_{sc} \cdot V_{oc}} = \frac{J_{max} \cdot V_{max}}{J_{sc} \cdot V_{oc}}$. FF
is a measure of how well the \( J-V \) characteristic of a solar cell resembles a perfect square shape in \( J-V \) plane.

- **Efficiency (\( \eta \))**: denotes the performance of solar cell and is defined as what percentage of incident solar powder density (\( P_i \)) is converted into maximum power density (\( P_{max} \)) delivered by a solar cell. Mathematically,
  \[
  \eta = \frac{P_{max}}{P_i} = \frac{J_{max} \cdot V_{max}}{P_i} = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_i}.
  \]

- **\( R_p \)**: series resistance.

- **\( R_s \)**: shunt resistance.

### 2.3.9 Quantum Efficiency

The quantum efficiency (QE) of the solar cell is the ratio of the number of charge carriers collected by a solar cell to number of incident photons at a given wavelength. The quantum efficiency determines the wavelength dependent current profile of the solar cell over the entire spectrum. Obviously, not all the incident photons are absorbed by solar cell and some fraction is lost in optical reflection and transmission phenomena. The solar cell community commonly deals with external and internal quantum efficiencies to characterize the solar cells. The external quantum efficiency refers to collection of carriers under the effect of incident light on the solar cell and thus encompasses the impact of optical reflection loss. The internal quantum efficiency accounts for the carrier collection under the effect photons absorbed by the solar cell.
Chapter 3

Characterization of \( \text{In}_2\text{S}_3 \) Source Material

The chapter gives a detailed microstructural and chemical analysis of the \( \text{In}_2\text{S}_3 \) source materials used for depositing buffer layer on a substrate and for making solar cells. The source materials were characterized as a function of time of deposition. The solar cells performances were compared with respect to buffer layer evaporated from two different source materials. The analysis led to make a choice over two different \( \text{In}_2\text{S}_3 \) source materials.

3.1 \( \text{In}_2\text{S}_3 \) Powders

The phase diagram of In-S system suggests \( \text{In}_2\text{S}_3 \) phase separation into \( \text{In}_2\text{S} \) and S \[57\] leading to formation of sulfur deficient film at evaporation temperature of \( \approx 750^\circ \text{C} \) \[49\]. There were few reports on the non-stoichiometry observed in indium sulfide buffer layer, however a detailed analysis of the source materials was lacking in the literature at the time of start of this work. This motivated us to investigate the properties of the very source material used for the deposition of \( \text{In}_2\text{S}_3 \) buffer layers. As a first step towards the development of solar cells with
vacuum deposited In$_2$S$_3$ buffer layer and its growth and properties, the initial research was aimed at the characterization of the very source materials. Two different types of In$_2$S$_3$ powders named as Powder-A (99.99% metal basis) and Powder-B (99.999% metal basis) procured from suppliers Sigma Aldrich and Alfa Aesar, respectively, were used for depositing In$_2$S$_3$ layer on different substrates by thermal evaporation technique. The Powder-A with finer particles size ($\approx 2 \mu m$) and narrower particle size distribution was dark-red in color. On the other hand, the Powder-B (light red color) was coarser (particle size 5-10 $\mu m$) than Powder-A with a relatively larger distribution in particle size. Figure 3.1 and Fig. 3.2 show the SEM micrographs of as-received Powder-A and Powder-B, respectively. The microstructural disparity in as-received powders may be due to different methods of preparation used by suppliers. In order to carry out the deposition, the required amount of powder was filled in a graphite crucible which is heated to 720-740$^\circ$C with a well defined heating profile (heat ramp). The deposition was performed at a base pressure of $\approx 1 \times 10^{-6}$ mbar. After attaining a desired evaporation rate the substrate shutter was opened and layer of desired thickness was deposited on the substrate.

Figure 3.1: SEM micrograph of as-received Powder-A.
3.2 Microstructural and Chemical Analysis of Source Material

The source materials subjected to various evaporation periods were studied by SEM and EDX. As a firsthand observation, the source powders (-A and -B) changed into consolidated mass (lump) after an evaporation run. The colors of Powder-A and -B changed into brick-red and ash-gray, respectively. The microstructural evolution of the source material as a function of time of evaporation was studied. Figure 3.3 and Fig. 3.4 present the SEM micrographs of both source powders after 4 min of evaporation. Apparently, the microstructure of Powder-B changed significantly (Fig. 3.2 and 3.4) after a small period of evaporation (4 min). However, a relatively small change in microstructure, before and after evaporation (Fig. 3.1 and 3.3), was observed in Powder-A. Figure 3.5 illustrates the microstructural evolution of Powder-B acquired at different positions on the sample after 3 min and 70 min of deposition time. As indicated in Fig. 3.5a, the presence of well structured gains was most commonly observed feature in Powder-B.

The evaporation period dependent composition of the Powder-A and Powder-B derived from EDX measurements performed at
different positions on the samples is shown in Fig. 3.6. Apart from microstructural contrast, a noticeable difference between two powders was the degree of sulfur loss (S-loss) from the source material. Interestingly, the compositional non-uniformity was observed in the Powder-B in as-received state followed by a significant S-loss even after a very short period of evaporation (3min). Whereas, the Powder-A was found to be chemically
3.2. SEM and EDX Analysis of Source Material

Figure 3.5: Microstructural features of Powder-B acquired from different positions on the sample after 3 min a) and b), and 70 min c) of evaporation time.

Figure 3.6: Powder-A and -B composition derived from EDX measurements at different positions on the sample.
Chapter 3. \textit{In}_2\textit{S}_3 Source Material

stable showing relatively small deviation in In/S ratio from 2/3 even after 15min of evaporation period.

According to the phase diagram of In-S system (Fig. 1.2), the \textit{In}_2\textit{S}_3 dissociates into S and \textit{In}_2\textit{S}_{2.8} leading to sulfur deficiency in the source material \cite{57}. Dissociation of \textit{In}_2\textit{S}_3(s) into \textit{In}_2\textit{S}(g) and \textit{S}_2(g) constituents and occurrence of \textit{congruent} dissociation in slightly \textit{sulfur-poor} indium sulfide material was reposted by Miller et al. \cite{82,83}. Additionally, a large difference in the partial pressure of dissociated constituents (p(\textit{In}_2\textit{S}) \approx 10^3 \cdot p(\textit{S}_2)) may further favor sulfur to escape from the material \cite{84}. Thus, the loss of sulfur from the bulk of material may lead to a significant compositional shift in indium sulfide powder. Consequently, the stoichiometry of evaporated buffer layers might not be same as in the source material and it may also subsequently change with successive deposition runs. Quantitatively, in contrast to Powder-A, S-loss from Powder-B was high and non-uniform regions of different In/S ratios were determined at different positions in the lump. It is expected that the part of source material which is close to the wall of evaporation crucible might behave in a considerably different manner than the part in the middle. The microstructural and chemical disparity observed in Powder-A and -B may be attributed to the difference in their methods of synthesis, which leads to a large difference in two materials in as-received state with respect to microstructure (Fig. 3.1 and 3.2) and chemical composition (t\textit{\_deposition} =0 min in Fig. 3.6). Notably, after 4 min of evaporation of Powder-B, the presence of In (large particle visible in SEM micrograph in Fig. 3.5b) was detected in EDX spectra. The compositional investigation by EDX also indicated the oxidation of \textit{In}_2\textit{S}_3 into \textit{In}_2\textit{O}_3 after 70 min of deposition as shown in Fig. 3.5c. The Powder-B was further characterized by XRD technique to identify the phase present in the material. Figure 3.7 shows the XRD patterns of Powder-B after 4 min of evaporation. The tetragonal \textit{\beta}-\textit{In}_2\textit{S}_3 was identified as the main phase with concomitant presence of cubic \textit{In}_2\textit{O}_3 phase in the material.
3.3. In$_2$S$_3$ Buffer Layer

3.3.1 Chemical Composition

The effect of stoichiometric deviation observed in the source powders (-A and -B), as a result of thermal evaporation, on the layer composition was studied. The layer composition as a function of time of deposition was determined by RBS measurements. The layers evaporated from a given powder were grown on three Si(111) substrates in a single evaporation run in such a way that each substrate is exposed to evaporation flux for a fixed period of deposition of 5 min. This deposition step is followed by next two consecutive steps so that indium sulfide layers of same thickness get deposited on three Si substrates successively in a single evaporation run.

Fig. 3.8 shows the RBS spectra of the layers evaporated from two powders (-A and -B) on Si(111) substrate for a period of 15 min with 5 min of deposition step. The layer composition
Chapter 3. \(\text{In}_2\text{S}_3\) Source Material

3.2 Source Material

3.2.1 RBS Spectra

Figure 3.8: \textit{RBS spectra of indium sulfide layers evaporated from Powder-A and -B.}

Extracted from RBS investigation is presented in Fig. 3.9. As indicated in the Fig. 3.9, the layers were found to be sulfur deficient. The Zn impurity in the layer evaporated from Powder-B originated from external source and should be disregarded. It can be inferred from Fig. 3.9 that the degree of off-stoichiometry in buffer layer deposited from Powder-B was larger than that from Powder-A which can be associated to different degree of S-loss in two powders. The results presented in this section are in accordance with the earlier discussion in section 3.2 which suggested the growth of non-stoichiometric layer as a consequence of thermal evaporation of \(\text{In}_2\text{S}_3\) source material.

3.3.2 Optical Transmission

\(\text{In}_2\text{S}_3\) layers of thickness \(\approx 30\text{nm}\) were deposited on SLG substrate from two different powders. The optical transmission of the layers were recorded in the wavelength region of 300-1100 nm. The layers deposited from two powders were found to be 70-
3.4. Solar Cell Performance

90% transparent in wavelength region below 500nm (Fig. 3.10). A large decrease in optical transmission suggests the band gap edge lying at \( \approx 600\text{nm} \). The photons with energies larger than the bang gap of \( \text{In}_2\text{S}_3 \) layer are absorbed leading to sudden drop in transmission as implied by Fig 3.10. The wavelength dependent optical transmission profiles of the layers were found to be similar with slight different in magnitude originating from difference in layer thicknesses.

3.4 Solar Cell Performance: Selection of \( \text{In}_2\text{S}_3 \) Material

CIGS solar cells buffered with \( \text{In}_2\text{S}_3 \) layers evaporated from two source powders (-A and -B) were fabricated and characterized by measuring their J-V characteristics presented in Fig. 3.11. The solar cell device with CdS buffer layer was used as reference cell to compare the quality of \( \text{In}_2\text{S}_3 \) buffered solar cell. The PV
parameters of the solar cells are listed in Tab. 3.1. The higher

<table>
<thead>
<tr>
<th>Powder</th>
<th>$\eta$ (%)</th>
<th>FF (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
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<tbody>
<tr>
<td>-A</td>
<td>8.6</td>
<td>55</td>
<td>570</td>
<td>27.4</td>
</tr>
<tr>
<td>CdS-Ref.</td>
<td>11.9</td>
<td>67.2</td>
<td>591</td>
<td>30</td>
</tr>
<tr>
<td>-B</td>
<td>11.6</td>
<td>62</td>
<td>654</td>
<td>28.6</td>
</tr>
<tr>
<td>CdS-Ref.</td>
<td>12.4</td>
<td>67.4</td>
<td>627</td>
<td>29.4</td>
</tr>
</tbody>
</table>

**Table 3.1:** PV parameters of solar cells with $\approx 30$nm thin $\text{In}_2\text{S}_3$ layer evaporated from Powder-A and Powder-B and their respective CdS reference cell.

efficiency of solar cell with Powder-B buffer layer than cell with buffer layer evaporated from Powder-A was mainly due to higher FF and $V_{oc}$. It should be recalled from section 3.2 that the loss of sulfur from $\text{In}_2\text{S}_3$ source powders (-A and -B) was detected. The amount of sulfur escaped from source Powder-B was higher than that from Powder-A.

**Figure 3.10:** Optical transmission of $\approx 30$nm thick $\text{In}_2\text{S}_3$ layer evaporated from Powder-A and Powder-B.
3.4. Solar Cell Performance

Nakada et al. reported the beneficial effects of sulfurization of CIGS layer on the solar cell performance \[85,86\]. They identified the increase in cell efficiency mainly due to increase in $V_{oc}$ and FF. The formation of Cu(In,Ga)(Se,S)$_2$ surface layer was detected in low angle XRD characterization of the CIGS layer after a certain period of sulfurization. The incorporation of S (substituting Se) in CIGS film helped reducing recombination losses due to passivation of deep trap states \[87\], responsible for recombination losses in space charge region. A marked presence of Cu(In,Ga)(Se,S)$_2$ surface layer as a result of post-CIGS growth In$_2$S$_3$ evaporation has been experimentally confirmed with S substituting Se atoms \[86\]. Moreover, the sulfur incorporation in CIGS widens the band gap of the surface absorber layer leading to increased transmission at short wavelength in the space charge region \[85\].

Due to very high S-loss in Powder-B, it is highly probable that sulfur may get incorporated in CIGS surface layer causing sulfurization of CIGS surface which may result in gain in device performance. The effect is expected to be more pronounced in case of Powder-B which suffers from larger S-loss than for Powder-A due to their evaporation behavior discussed in section \[3.2\]. In the present case of solar cells with evaporated In$_2$S$_3$ buffer layer, very high $V_{oc}$ and FF (similar to CdS reference cell) was obtained from device with buffer layer evaporated from Powder-B \[Tab. 3.1\]. Although $V_{oc}$ of CdS reference device corresponding to Powder-A In$_2$S$_3$ device was found to be lower than $V_{oc}$ of CdS device corresponding to Powder-B In$_2$S$_3$ device, a distinct increase in $V_{oc}$ in Powder-B device was noticed. In addition to improvement in solar cell performance with use of Powder-B, from experimental point of view, the handling (avoidance of spilling of source powder out of evaporation crucible during evaporation run) of Powder-B during evaporation was easier than that of Powder-A. Thus, based on the solar cell results discussed above and ease of handling of source powder during evaporation, we selected Powder-B as In$_2$S$_3$ source materials for further studies.
3.5 Conclusion

The thermal evaporation of $\text{In}_2\text{S}_3$ layers was carried out using two different types of $\text{In}_2\text{S}_3$ source powders obtained from different suppliers. With microstructural homogeneity and small loss of sulfur from source material over a given period of deposition, the Powder-A was found to be chemically more stable than Powder-B. On the other hand, accompanied with a larger degree of microstructural inhomogeneity than that observed in Powder-A, the Powder-B suffered from substantial amount of sulfur loss with successive deposition runs. The buffer layers deposited from Powder-A and Powder-B were found to be sulfur deficient. The compositional evolution of buffer layers with period of depositions revealed that the layer evaporated from chemically more unstable powder (B) showed larger deviation from $\text{In}_2\text{S}_3$ stoichiometry than that determined in case of buffer layer evaporated from Powder-A. The superior performance of solar cell with $\text{In}_2\text{S}_3$ buffer layer deposited from Powder-B was
attributed to sulfurization of CIGS surface during In$_2$S$_3$ evaporation that resulted in increased FF and $V_{oc}$. 
Chapter 4

Solar Cells Buffered with Thermally Evaporated In$_2$S$_3$ Layers

The thermal evaporation technique was used to deposit In$_2$S$_3$ layers on different substrates. The morphological, optical, chemical and structural properties of evaporated In$_2$S$_3$ buffer layer relevant for photovoltaic applications have been investigated. The effect of post-buffer deposition air annealing treatment on solar cell performance was studied. A highly efficient solar cell yielding conversion efficiency of 14.1\% was developed.

4.1 Properties of Thermally Evaporated In$_2$S$_3$ Buffer Layer

Our research on thermally evaporated In$_2$S$_3$ buffer layers observed a headstart once the choice over source material was made. The efforts were focused on the investigation of opti-
4.1.1 Layer Morphology

The surface morphology of the In$_2$S$_3$ layers deposited on SLG substrate was studied by AFM technique. Figures 4.1a, 4.1b and 4.1c show the AFM micrographs of as-deposited, air-annealed for 10 min at 200°C and 400°C, respectively, In$_2$S$_3$ layers.

A uniform and continuous growth of In$_2$S$_3$ layer was observed (4.1a). The change in morphology indicated the onset of crystallization of as-deposited amorphous (Fig. 4.9) layer after air annealing treatment at 200°C for 10 min (Fig. 4.1b). A uniform grain growth of the layer over the entire surface of the substrate occurred after air annealing at 400°C (Fig. 4.1c). Obviously, the surface roughness of the film increased with rise in the annealing temperature which resulted in reduced reflection from air annealed films as shown in Fig. 4.2. The root-mean-square roughness before and after annealing was estimated to be 2.1 nm and 6.4 nm, respectively.

4.1.2 Optical Properties

Transmission and reflection

The optical transmission and reflection spectra of In$_2$S$_3$ layers were recorded in the wavelength region of 300-1500nm and are shown in Fig. 4.2. The as-deposited layers were found to be 60-85% transparent in 600-1500 nm wavelength region. A slight increase in transmission and decrease in reflection was observed after air annealing at 200°C. The air annealing of the layer at higher temperature such as at 400°C led to further increase in transmission and decrease in reflection. As shown in Fig. 4.1, the morphological studies revealed the grain growth after air annealing treatment resulting in roughening of layer surface and
4.1. Properties of In$_2$S$_3$ Layers

Figure 4.1: AFM micrographs of thermally grown In$_2$S$_3$ buffer layers, as-deposited (a), air annealed for 10 min at 200°C (b), 400°C (c).
hence lowering in optical reflection. The blue shift in the transmission spectra of layer after air annealing at 400°C suggested the increase in band gap.

![Figure 4.2: Transmission and reflection characteristics of thermally evaporated In$_2$S$_3$ buffer layer.](image)

**Energy band gap**

In addition to increase in transmission accompanied by decrease in reflection, the optical absorption edge was observed to shift to low wavelength region indicating an increase in band gap as a results of air annealing. According to Ref. [88], the absorption coefficient ($\alpha$) can be expressed as,

\[ \alpha(E) = A \frac{(E - E_g)^m}{E} \quad (4.1) \]

where $E$ is photon energy, $A$ and $m$ are constants and depend on the type of transitions taking place in the film and $E_g$ is the band gap. The constant $m$ can be 1/2, 2, 3/2 and
4.1. Properties of In$_2$S$_3$ Layers

3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. Using Lambeer-Beer’s Law, the absorption coefficient ($\alpha$) can be expressed in terms of transmission and reflection of the layer by using,

$$\alpha(\lambda) \approx -\frac{1}{t} \ln \left[ \frac{T(\lambda)}{(1 - R(\lambda))^2} \right]$$

(4.2)

where, $T(\lambda)$ and $R(\lambda)$ are wavelength ($\lambda$) dependent transmitted and reflected intensity, respectively. There are numerous reports on the optical characterization of In$_2$S$_3$ layer and the occurrence of direct [34, 89–91] and indirect [29, 37, 92, 93] transition has been reported by various authors. In the present study, we used a formulation described in Ref. [94] to determine the type of optical transition ($m$). The band gap of the layer was calculated using eq. 4.2. The value of $m$ was found to be $\approx 0.5$ indicating direct band-to-band transition taking place in the layers. The $E_g$ of layer was calculated by plotting $(\alpha \cdot E)^2$ against photon energy ($E$) as shown in Fig. 4.3.

![Figure 4.3: Plots of $(\alpha \cdot E)^2$ vs. photon energy of thermally evaporated In$_2$S$_3$ layer.](image)
Clearly, the band gap of layers increased with increase in annealing temperature. Table 4.1 lists the band gap values of the layer before and after air annealing treatment.

<table>
<thead>
<tr>
<th>Band gap (eV)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>as-deposited</td>
<td>2.53 ±0.077</td>
</tr>
<tr>
<td>air annealed for 10min at:</td>
<td></td>
</tr>
<tr>
<td>200°C</td>
<td>2.56 ±0.072</td>
</tr>
<tr>
<td>400°C</td>
<td>2.72 ±0.074</td>
</tr>
</tbody>
</table>

**Table 4.1:** Energy band gap of In$_2$S$_3$ layer before and after air annealing.

The inclusion of oxygen impurity in crystalline matrix of In$_2$S$_3$ has been studied by Barreau et al. [34,95]. It was found that the presence of oxygen in spinel-like structure of In$_2$S$_3$ causes lattice compression giving rise to band gap widening of β-In$_{2-x}$S$_3$−$x$O$_3x$ layer with 0≤x≤0.15. The band gap of the film increases with increase in amount of oxygen impurity in In$_2$S$_3$ until a certain at%. For x > 0.15, In$_2$O$_3$ phase separates out from the parent In$_2$S$_3$−$3x$O$_3x$ compound. The band gap increment from 2.1 eV to as high as 2.9 eV has been determined for oxygen containing In$_2$S$_3$ films [95]. Owing to the presence of In vacancies ($V_{In}$) as *intrinsic point defect* in the lattice of In$_2$S$_3$, Na can readily diffuse into defect In$_2$S$_3$ matrix [55]. A similar effect, as in case of oxygen containing In$_2$S$_3$ layers, of band gap widening in In$_2$S$_3$ layer contaminated with Na impurity has been observed [96].

The band gap increase with air-annealing temperature in the present study may be due to inclusion of oxygen into In$_2$S$_3$ layers. Moreover, the layers are also expected to be contaminated with Na which can readily diffuse into In$_2$S$_3$ defect structure from SLG substrate. Thus, increase in band gap with rise in annealing temperature can be attributed to oxygen and Na inclusion in In$_2$S$_3$ layer as a result of air annealing.
4.1. Properties of In$_2$S$_3$ Layers

Optical constants

Spectroscopic ellipsometry\footnote{The detailed theoretical description of Spectroscopic Ellipsometry is beyond the scope of this thesis. The author has tried to include some theoretical aspects to support the results presented in this chapter. The reader is advised to go through the references \textsuperscript{97,100} for further details.} technique was used for precise determination of optical constants of In$_2$S$_3$ layers. The model fitting for ellipsometric analysis was performed using Marquardt-Levenberg fitting technique for minimization of the mean square error given by:

$$
\chi^2 = \frac{1}{2M - P} \sum_{i=1}^{M} \left\{ (I_s^{exp}(\lambda) - I_s^{cal}(\lambda))^2 + (I_c^{exp}(\lambda) - I_c^{cal}(\lambda))^2 \right\} \tag{4.3}
$$

where, $M$ and $P$ are the total number of experimental data points and model parameters, respectively. The fitting raw data $[I_s(\lambda)$ and $I_c(\lambda)]$ determine the signal detected by the ellipsometer given by:

$$
I(\lambda) = I_0(\lambda) + I_s(\lambda)\sin\delta(t) + I_c(\lambda)\cos\delta(t) \tag{4.4}
$$

where, $\delta(t)$ is the induced phase shift by modulator in the ellipsometric setup and $I_0(\lambda)$ is a function of the ellipsometric angles and the angles of the polarizer, analyzer, and the modulator from the plane of incidence. In our experimental setup, the polarizer, analyzer, and the modulator angles were configured to set $I_0(\lambda) \approx 1.0$.

To account for surface roughness and In$_2$S$_3$/SLG interface, we used a tri-layer stack model (Fig. \textsuperscript{4.4}), wherein, the bottom layer (optically infinite), middle layer, and the top layer represents the glass substrate, In$_2$S$_3$ thin film, and the In$_2$S$_3$ film roughness, respectively. Bruggeman effective medium approximation was used for the top layer comprising of dielectric functions of In$_2$S$_3$ and void ($n \approx 1$, $k \approx 0$). Thicknesses of the
middle layer and the top layer were initially estimated by multiple pre-trials in non-absorbing optical range of the In$_2$S$_3$ film (800-1650 nm). For final thickness values, presented here, the thickness parameters were estimated along with other fitting parameters of the model dielectric function.

Earlier reports on ellipsometric studies on In$_2$S$_3$ thin films either extracted the optical constants using direct inversion of the ellipsometric raw data or incorporated Classical-Oscillator and Forouhi-Bloomer model dielectric function to extract the optical parameters to generate the optical constants [101,102]. However, recent ellipsometric investigations on various thin films indicates that the choice of proper model dielectric function, in terms of the Kramer-Kronig consistency and the presence of optical band gap as a model parameter, is crucial for extraction of reliable optical parameters and the resultant optical constants [97–100].

A detailed description of the commonly used model dielectric functions such as Classical-Oscillator (CO), Forouhi-Bloomer (FB) and Tauc-Lorentz (TL) model for the analysis of thin films along with the limitations of each model can be found in Ref. [97,100]. The extinction coefficient and index of refraction derived from the FB model are given by:

\[
k(E) = \sum_{n=1}^{N} \frac{A_n (E - E_{gFB})^2}{E^2 - B_n E + C_n} \tag{4.5}
\]

\[
n(E) = \sqrt{\epsilon_\infty} + \sum_{n=1}^{N} \frac{B_{0n} E + C_{0n}}{E^2 - B_n E + C_n} \tag{4.6}
\]
where \( N \) is number of optical transitions, \( A_n, B_n, C_n \) are fitting parameters for \( n^{th} \) optical transition, \( E_{gFB} \) is the band gap energy, \( B_{0n} \) and \( C_{0n} \) are functions of \( A_n, B_n, C_n \) and \( E_{gFB} \), and \( \epsilon_\infty \) is the high frequency dielectric constant. The TL model, consistent with Kramer-Kronig relation, is based on the consideration of Tauc’s density of states above the band edge and Lorentz oscillator model for oscillating electron in optical electric field \[99\]. The imaginary part of the complex dielectric function \( (\epsilon(E)=\epsilon_r(E)+i\epsilon_i(E) \) is given by:

\[
\epsilon_i(E) = \frac{1}{E} \cdot \frac{AE_0C \left(E - E_{gTL}\right)^2}{\left(E^2 - E_0^2\right)^2 + C^2 E^2} \tag{4.7}
\]

where, \( A, E_0, C, \) and \( E_{gTL} \) are the amplitude, peak transition energy, broadening, and the optical band gap, respectively. The real part of the dielectric function is calculated by Kramers-Kronig integration of the imaginary part and is given by:

\[
\epsilon_r(E) = \epsilon_\infty + \frac{2}{\pi} p \int_{E_{gTL}}^{\infty} \frac{\Im \cdot \epsilon_i(E)}{\Im^2 - E^2} d\Im \tag{4.8}
\]

where \( p \) indicates the principle value of the integration performed for energies above the band edge and \( \epsilon_\infty \) is the core dielectric constant. Figure 4.5 presents FB and TL model fitting of ellipsometric raw data obtained from \( \text{In}_2\text{S}_3 \) thin film on SLG substrate. The optical constants derived from fitting of TL and FB models are shown in Fig. 4.6. The optical parameters extracted from FB and TL fitting are listed in Tab. 4.2.
Chapter 4. Thermally Evaporated Buffer Layer

Figure 4.5: FB and TL model fitting on the ellipsometric data acquired from In$_2$S$_3$ layers.

Table 4.2: Optical parameters of as-deposited and air-annealed (t=10min and 200°C) In$_2$S$_3$ layers obtained from FB and TL model fitting.

<table>
<thead>
<tr>
<th>Model</th>
<th>Layer</th>
<th>as-deposited</th>
<th>air-annealed</th>
</tr>
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<tbody>
<tr>
<td>Forouhi-Bloomer</td>
<td>$A_{FB}$</td>
<td>0.24±0.03</td>
<td>0.26±0.02</td>
</tr>
<tr>
<td></td>
<td>$B_{FB}$ (eV)</td>
<td>8.3±0.1</td>
<td>8.2±0.1</td>
</tr>
<tr>
<td></td>
<td>$C_{FB}$ (eV)$^2$</td>
<td>19.1±0.6</td>
<td>18.6±0.5</td>
</tr>
<tr>
<td></td>
<td>$E_{gFB}$ (eV)</td>
<td>1±0.1</td>
<td>1.38±0.09</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>$A_{TL}$ (eV)</td>
<td>128.5±3.7</td>
<td>135.2±9.8</td>
</tr>
<tr>
<td></td>
<td>$E_{0TL}$ (eV)</td>
<td>4.8±0.2</td>
<td>4.33±0.06</td>
</tr>
<tr>
<td></td>
<td>$C_{TL}$ (eV)</td>
<td>6.9±0.3</td>
<td>4.66±0.28</td>
</tr>
<tr>
<td></td>
<td>$E_{gTL}$ (eV)</td>
<td>1.85±0.03</td>
<td>1.88±0.03</td>
</tr>
</tbody>
</table>

It can be inferred from the Fig. 4.5 that an excellent fitting to ellipsometric data acquired from In$_2$S$_3$ layer was achieved by TL model. Figure 4.6 clearly indicates that application of
4.1. Properties of In$_2$S$_3$ Layers

Figure 4.6: Optical constants of In$_2$S$_3$ film derived from FB and TL model fittings.

Different model dielectric functions generates difference in the optical constant. The similar results on the suitability of TL model have been reported by Datta et al. [97,100]. Based on above discussion, the TL model was used to determine the optical constants of In$_2$S$_3$ layer in this study.

The dispersion relations with index of refraction and extinction coefficient of In$_2$S$_3$ layer deduced from TL model are shown in Fig. 4.7. The refractive index of layer annealed at 200°C for 10 min was found to be lower that that of as-deposited layer. In addition, air annealing led to a blue shift in extinction coefficient indicating an increase in band gap which is in agreement with results discussed in sec. 4.1.2. Notably, the blue shift in extinction coefficient was accompanied by lowering in its value over the entire wavelength region of measurement. The observed decrease in extinction coefficient is a suggestive of altered midgap states of In$_2$S$_3$ as a consequence of air annealing. The decrease in refractive index indicates the structural modifications taking place in the layer and as a result, the packing density reduces.
leading to relatively ordered arrangements (partial crystallinity) in the layer. The section 4.1.4 reveals that crystalline order appears in the layer after air annealing treatment.

**Figure 4.7:** Optical constants of as-deposited and air-annealed In$_2$S$_3$ layer.

Contrary to decrease in refractive index after air annealing treatment, El-Nahass et al. [103] found increase in refractive index as the layers were annealed at higher temperatures. It should be pointed out that the optical constants deduced from direction inversion of optical transmission and reflection measurements can be misleading and unreliable. This is due to negligence or (and) incorrect consideration of the effect of light scattering originating from surface roughness, grain boundaries, film thickness and compositional non-uniformity and hence these imperfections present in the layer can bring about a large difference between actual and measured values of optical constants. On the other hand, the success of ellipsometric analysis largely depends on selection of suitable multilayer stack model (representing the surface roughness and the various interfaces) and
model dielectric functions which turns out to be a more reliable method of determining the optical constants than from transmission and reflection measurements.

A similar trend, as in our case, in optical constants of airless-spray deposited $\text{In}_2\text{S}_3$ layer was reported by Kamoun et al. [104]. They varied the molar ratio $y = \frac{[\text{In}^{3+}]}{[\text{S}_2^{-}]}$ in the precursor solution in such a way that layer of different composition (stoichiometric and non-stoichiometric) were grown accordingly and studied by spectroscopic ellipsometry. It was observed that the refractive index decreases with increase in molar ratio ($y$) indicating a strong dependency of layer stoichiometry on refractive index. The refractive index of layer with near stoichiometric composition ($y$=0.6) decreased with air annealing temperature which is in accordance with change in refractive index observed in our study (Fig. 4.7). Moreover, the higher values of refractive index ($\approx$2.5) in present case than that of airless-sprayed layer ($\approx$ 2.3) in Ref. [104] implies higher density of thermally grown $\text{In}_2\text{S}_3$ layer.

Since, in addition to change in packing density, thermally grown $\text{In}_2\text{S}_3$ layer is expected to be contaminated with oxygen after annealing in air (sec. 4.1.2), the change in refractive index can be attributed to structural modification (sec. 4.1.4) and off-stoichiometry of the layer.

### 4.1.3 Microstructural Investigation

The microstructure of thermally evaporated $\text{In}_2\text{S}_3$ buffer layer on SLG substrate was investigated using SEM. Fig. 4.8 presents the microstructural evolution of layer with air annealing treatment for 10min at 200°C and 400°C. The growth of highly smooth layer is evident from Fig. 4.8a. With a small difference in microstructures of as-deposited and the layer annealed at 200°C (Fig. 4.8b), a large microstructural contrast was observed after air annealing at 400°C (Fig. 4.8c). The air annealing treatment rendered the compactness to the layers leading to a dense and continuous microstructure.
Figure 4.8: SEM plan-view of thermally evaporated $\text{In}_2\text{S}_3$ layer: as-deposited (a), air-annealed for 10min at 200°C (b) and 400°C (c).
4.1.4 Structural Properties

The layers were further characterized using XRD technique to identify the chemical phases present in as-deposited and air-annealed layers. Figure 4.9 shows the XRD patterns of layers deposited at room temperature and air annealed for 10 min at 200°C and 400°C. As apparent from figure, the as-deposited layer was found to be amorphous and crystallized into tetragonal $\beta$-In$_2$S$_3$ phase after air annealing at 200°C. The degree of crystallinity further improved after annealing at higher temperature of 400°C. The presence of In$_2$O$_3$ was also detected in the layer air-annealed at 400°C indicating phase separation of In$_2$O$_3$ taking place from In$_2$S$_3-3x$O$_{3x}$ parent matrix. This indirect measurements further supports the results discussed in sec. 4.1.2 that as a consequence of air annealing, the oxygen gets incorporated into In$_2$S$_3$ layer. The AFM, SEM and XRD investigations discussed in above suggest that recrystallization starts at air annealing temperature of 200°C. Therefore, the air
annealing temperature of 200°C was found to be an onset temperature of crystallization for thermally evaporated In$_2$S$_3$ buffer layer.

4.1.5 Chemical Composition

![RBS spectra of indium sulfide layer deposited on Si substrate.](image)

**Figure 4.10:** RBS spectra of indium sulfide layer deposited on Si substrate.

Further to results discussed in sec. 3.3.1, the RBS measurements were performed to determine the chemical composition of evaporated layer. Figure 4.10 shows the RBS spectra of the ≈60 nm thick indium sulfide layer grown on Si(111) substrate. As anticipated, the layers were found be non-stoichiometric with respect to sulfur content with overall chemical composition given by In$_2$S$_{2.8}$. The origin of non-stoichiometry in indium sulfide evaporation layer has been described in sec. 3.2 and 3.3.1.
4.2 Solar Cell Properties

The growth characteristic of In$_2$S$_3$ layers on CIGS absorber was studied by SEM. The top and cross-section SEM micrographs of In$_2$S$_3$/CIGS stack are presented in Figure 4.11a and 4.11b, respectively. Fig. 4.11a presents a comparison between microstructure of bare CIGS and In$_2$S$_3$ layer deposited on CIGS surface inferring the uniform growth of buffer layer on rough CIGS surface. No significant microstructural difference was discerned before and after In$_2$S$_3$ deposition on CIGS substrate surface suggesting conformal coverage of rough CIGS surface by In$_2$S$_3$ buffer layer. The cross-section SEM micrograph (Fig. 4.11b) revealed that In$_2$S$_3$ uniformly covered CIGS substrate with occasional discontinuity in buffer layer at large CIGS grain edges.

CIGS solar cells consisting of $\approx$30nm and $\approx$60nm thick thermally evaporated In$_2$S$_3$ buffer layer were prepared and their PV performances were compared with CBD-CdS reference cells. Owing to higher band gap of In$_2$S$_3$ film than that of CdS, the gain in $J_{sc}$ is obtained in blue region of solar spectrum which is depicted in EQE plot of cells shown in Fig. 4.12.

With emphasis on achieving higher and reproducible solar cell efficiencies, the buffer layer deposition step was optimized primarily focusing on the post-deposition annealing treatment. The solar cell performances were compared with CBD-CdS reference devices. An in-situ annealing treatment for 10 min at 100°C, 200°C and 250°C were applied after buffer layer growth on Mo coated CIGS substrate. The PV parameters of the devices are listed in Tab. 4.3. It can be inferred from table that the effect of different buffer layer thicknesses is not so pronounced on solar cell performance and $\approx$30nm thick buffer appeared to be a better choice. The results led to extend the analysis on cells with $\approx$30nm In$_2$S$_3$ buffer layer. The following discussion is thus based on cells with $\approx$30nm buffer layers.

The analysis of PV dataset presented in Tab. 4.3 indicated that in-situ annealing temperature of 250°C adversely affected the solar cell characteristics. Whereas, the annealing treatment
Figure 4.11: SEM plan-view (a) and cross-section (b) of $\text{In}_2\text{S}_3$ layer deposited on CIGS substrate, inset in (a) shows the microstructure of bare CIGS.
4.2. Solar Cell Properties

Figure 4.12: Normalized external quantum efficiencies of solar cells with In$_2$S$_3$ and CdS buffer layer.

at 100°C and 200°C yielded nearly similar solar cell efficiencies. It is interesting to note that as the in-situ annealing temperature increased from 100°C to 200°C, the $J_{sc}$ increased and $V_{oc}$ dropped indicating that lower is the in-situ annealing temperature higher is $V_{oc}$ and lower is $J_{sc}$. The FF remained nearly same in both the cases.

The Cu, Na and In elemental interdiffusion across In$_2$S$_3$/CIGS interface has been reported by several research groups [45, 61, 73, 105, 108]. The migration of Cu and Na from CIGS absorber to In$_2$S$_3$ (structurally defective compound) and counter diffusion of In from In$_2$S$_3$ side to CIGS layer has been experimentally confirmed with its strong effect on the solar cell performance. As a result of elemental interdiffusion, being a strong function of temperature, the interface between two junction partners is not abrupt but is graded one. Abou-Ras et al. [105, 106] studied the ALD-In$_2$S$_3$/CIGS and PVD-In$_2$S$_3$/CIGS interface properties using high-resolution transmission electron microscopy and auxiliary techniques. In case of ALD-In$_2$S$_3$ buffer layer grown
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<table>
<thead>
<tr>
<th>T\text{annl.} (°C)</th>
<th>Buffer thickness(nm)</th>
<th>η (%)</th>
<th>FF (%)</th>
<th>V\text{oc} (mV)</th>
<th>J\text{sc} (mA.cm}^{-2} \text{)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>30</td>
<td>11.7</td>
<td>67.9</td>
<td>623</td>
<td>27.7</td>
</tr>
<tr>
<td></td>
<td>CdS-ref.</td>
<td>13.9</td>
<td>72</td>
<td>633</td>
<td>30.5</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>10.1</td>
<td>58.7</td>
<td>633</td>
<td>27.4</td>
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<td></td>
<td>CdS-ref.</td>
<td>13.5</td>
<td>73.4</td>
<td>655</td>
<td>27.9</td>
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<td>200</td>
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<td>65.4</td>
<td>587</td>
<td>29.5</td>
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<td>68.5</td>
<td>618</td>
<td>29.4</td>
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<td>657</td>
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<td>688</td>
<td>28.5</td>
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<td></td>
<td>60</td>
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<td>33.5</td>
<td>487</td>
<td>25.4</td>
</tr>
<tr>
<td></td>
<td>CdS-ref.</td>
<td>14.2</td>
<td>72.7</td>
<td>685</td>
<td>28.5</td>
</tr>
</tbody>
</table>

Table 4.3: PV parameters of In$_2$S$_3$ buffered cells receiving different in-situ annealing treatments for 10min and that of respective CBD-CdS devices.

at 210°C, a distinct orientation relationship between \{112\} and \{103\} planes of CIGS and In$_2$S$_3$ layers, respectively, was identified. However, the presence of staggered interface between In$_2$S$_3$/CIGS was detected at higher buffer deposition temperature of 240°C. Their findings implied the existence of a buried junction in CIGS layer as a result of thermally assisted elemental interdiffusion across the interface. In case of thermally evaporated In$_2$S$_3$ buffer, a significant amount of Cu diffusion in In$_2$S$_3$ layer was measured even in the layer grown at room temperature without applying any post-deposition annealing treatment. Py et al, studied the diffusion behavior of Cu in In$_2$S$_3$ system and found that Cu not only occupies the vacant In sites (V\text{In}) but also it can substitute In atoms (Cu\text{In}) \[\text{[109]}\]. Therefore, Cu diffusion from CIGS is not only favored by temperature but also there acts a net chemical potential assisting Cu migration from CIGS to In$_2$S$_3$ \[\text{[106]}\]. The Cu diffusion is further enhanced with rise in substrate temperature and post-deposition annealing of the complete device. The post-deposition annealing was found to be beneficial for achieving higher performance of cells with buffer layer grown at 20°C. Whereas, substrate tempera-
ture of 300°C during buffer deposition was found to adversely affect the PV performance of the device. This suggested that Cu migration unto a certain extent is beneficial for attaining higher conversion efficiency solar cells and beyond that limit, Cu diffusion destroys the PV performance of the device. The presence of n-type CuIn$_5$S$_8$ compounds (having high defect density) was detected by selected electron area diffraction analysis which is attributed to excess Cu diffusion from CIGS to In$_2$S$_3$ side of junction. Barreau et al. [73] studied the effect of Cu and Na diffusion on the solar cell performances. It was found that the presence of Na on CIGS surface impedes Cu migration from CIGS to In$_2$S$_3$ layer leading to lowering in $V_{oc}$ and higher $J_{sc}$. An exponential increase in amount of Na on CIGS surface with post-deposition vacuum annealing temperature was reported. It was also observed that Na and Cu diffusion strongly depended on substrate temperature during buffer layer deposition and their amount increased with increase in substrate temperature. Since Cu migration is severely hindered by presence of Na at the surface, for a given substrate temperature Na diffusion may dominate. The Cu diffusion was found to have direct impact on the effective junction width and it increased with increase in amount of Cu diffusing from CIGS to buffer layer resulting in increase in $V_{oc}$.

In our case (Tab. 4.3), the decrease in $V_{oc}$ and increase in $J_{sc}$ with rise in in-situ annealing temperature can be understood by Na and Cu diffusion taking place across In$_2$S$_3$/CIGS interface. At annealing temperature of 100°C, indicating lower surface Na concentration, Cu migration is favored resulting in higher $V_{oc}$ of the device. Cu inclusion in In$_2$S$_3$ matrix leads to lowering in band gap [108] and hence decreasing $J_{sc}$. The amount of Na diffusing from CIGS bulk to surface is expected to be higher with increase in in-situ annealing temperature and with rise in annealing temperature to 200°C, the CIGS surface may get enriched with Na therefore impeding Cu out-diffusion towards buffer layer leading to lowering in $V_{oc}$. Furthermore, the incorporation of Na in In$_2$S$_3$ causes band gap widening [55,108] and hence allows larger fraction of photons reaching CIGS absorber resulting in gain in photocurrent. With further rise in annealing temperature to 250°C, excess Cu diffusion may destroy the junc-
Chapter 4. Thermally Evaporated Buffer Layer

The signature of thermally driven elemental diffusion altering the light absorption and hence the photocurrent generation by solar cells are shown in external quantum efficiencies of solar cells in Fig. 4.13. As displayed in figure, the small change in spectral response of In$_2$S$_3$ cell in blue region in an indicating of increase in buffer layer band gap as a result of air annealing.

![Graph showing external quantum efficiency for In$_2$S$_3$/CIGS cells before and after air annealing.](image)

**Figure 4.13:** External quantum efficiencies of solar cells with In$_2$S$_3$ buffer: as-deposited and air annealed for 10 min at 200°C, and CdS reference cell.

Another set of optimization experiments were carried out omitting *in-situ* post-deposition annealing step and the buffer layer was grown at room temperature. The effect of air annealing of the complete device with In$_2$S$_3$ buffer layer was studied. Table 4.4 compares the PV parameters of as-deposited and air-annealed (5 min, 200°C) cells with ≈30 nm ≈60 nm thick In$_2$S$_3$ buffer layers. Contrary to improvement in cell performance reported by several researchers [49, 59, 106], we measured a decrease in efficiency after air annealing of complete cell mainly due to loss in $V_{oc}$ and FF with slight increase in $J_{sc}$ (Fig. 4.13).
A possible reason for cell deterioration after air annealing might be that air annealing was carried out in an oven where cells were put directly on a metal plate kept at 200°C thus subjecting them to a thermal shock within a short period of time. Following the discussion on page 62, the degradation of PV properties of cell under the effect of sudden annealing step may be attributed to thermally induced excessive elemental intermixing across In$_2$S$_3$/CIGS junction. However, as described later, due to lack of consistent results after air annealing treatment of the complete cell, no standard scheme for air annealing of the cells could be defined.

As a result of optimization experiments outlined above, the In$_2$S$_3$ buffered solar cells yielding conversion efficiencies in the range of 12.5%-13.5% were routinely developed without applying antireflection coating. It is known that a slight change in CIGS surface composition such as Ga or Cu concentration can bring about a large variation in cell performance [75,110]. Moreover, if not large, the possibility of a minor variation in the chemical composition incurred due to different growth recipes of CIGS, buffer and window layer adopted by various research groups worldwide cannot be ruled out. Hence, there may exist a large difference in reproducible and the best reported efficiencies delivered by a solar cell documented in the literature.

In the present case, the efficiency gap between 12.5% and 13.5% can be understood by a minor (or large) but unavoidable degree of process irreproducibilities associated with growth of various layers forming a complete solar cell. These irreproducibilities may originate from a) CIGS growth: elemental compositional variation during various deposition stages Fig. 2.2, b) non-stoichiometry of thermally evaporated In$_2$S$_3$ (sec. 3.3.1 and sec. 4.1.5) and c) process parameters during sputtering of $i$-ZnO/ZnO:Al deposition layer. All of these above mentioned likely causes of uncertainties have great influence on the In$_2$S$_3$ buffered solar cell performance. Couzinié-devy et al. [110] and Jacob et al. [75] confirmed the significant influence of Cu and Ga concentration in CIGS on PV performance of solar cells with In$_2$S$_3$ buffer layer. The buffer layer composition may also strongly affect the PV properties of the solar cell as reported
Table 4.4: PV properties of cells with In$_2$S$_3$ buffer layer grown at room temperature without any in-situ post-deposition treatment. The In$_2$S$_3$ cells were annealed in air for 5min at 200°C. CdS device served as reference cell.

Table 4.5: The irreproducibilities in PV performance of as-deposited solar cells with thermally evaporated In$_2$S$_3$ buffer layer.

The study revealed that In$_2$S$_3$ buffered cells yielded maximum conversion efficiency when buffer layer is grown at room temperature. No appreciable positive effect of air annealing of the complete device on In$_2$S$_3$ buffered solar cell performance was measured. However, a decrease in efficiency after air annealing of complete cell primarily due to loss in FF and $V_{oc}$ was commonly observed.

Nevertheless, a highly efficient solar cell with conversion ef-
4.2. Solar Cell Properties

...ficiency of 14.1\%, an efficiency close to CdS reference cell, was realized by depositing \( \approx 50\text{nm} \) thick In\(_2\)S\(_3\) at room temperature. The superior performance of the cell may be due to high quality of interface formed between In\(_2\)S\(_3\) and CIGS with lower chemical disorder in the layer composition. The air annealing of cell for 5min at 200\(^\circ\text{C}\) adversely affected the cell properties resulting in loss of efficiency to 13.2\%. The PV parameters and the J-V characteristics of the cells are present in Tab. 4.6 and Fig. 4.14, respectively.

![Figure 4.14: J-V characteristic of the most efficient In\(_2\)S\(_3\) buffer layer based solar cell developed in our laboratory.](image-url)
<table>
<thead>
<tr>
<th>Cell</th>
<th>$\eta$ (%)</th>
<th>FF (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA.cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-dep.</td>
<td>14.1</td>
<td>70.7</td>
<td>683</td>
<td>29.1</td>
</tr>
<tr>
<td>air-annld.</td>
<td>13.2</td>
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</tr>
<tr>
<td>CdS-ref.</td>
<td>14.2</td>
<td>72.2</td>
<td>685</td>
<td>28.5</td>
</tr>
</tbody>
</table>

Table 4.6: PV parameters of most efficient solar cell with In$_2$S$_3$ buffer layer developed in our laboratory comparing with CdS reference cell. The as-deposited In$_2$S$_3$ cell was air annealed for 5min at 200°C.

4.3 Conclusion

The thermal evaporation of In$_2$S$_3$ resulted in formation of a layer with highly smooth and uniform morphology. The AFM morphology of the air-annealed layer suggested the recrystallization and grain growth induced by air annealing for 10min at 200°C leading to roughening of the surface. The numerical calculations identified the direct band-to-band transition in the layer with band gap increase with increase in annealing temperature. The spectroscopic ellipsometry study of the layer revealed the suitability of Tauc-Lorentz over Forouhi-Bloomer model, thus the optical constants based on TL model were extracted. The microstructural study revealing the formation of dense and continuous layer was in agreement with AFM investigation. Based on XRD examination, the as-deposited layer was found to be amorphous and crystallized into tetragonal $\beta$-In$_2$S$_3$ layer after air annealing at 200°C. The degree of crystallinity of the layer increased with further rise in annealing temperature and presence of In$_2$O$_3$ was also detected in the layer annealing at 400°C suggesting the occurrence of In$_2$O$_3$ phase separation from oxygen contained In$_2$S$_3$ layer. Without noticeable microstructural contrast between bare CIGS and CIGS covered with In$_2$S$_3$ layer, the buffer layer formed a dense and continuous morphology on CIGS absorber layer. The buffer layer conformally covered the CIGS surface however, occasional discontinuity at the large CIGS edges was also discerned in SEM investigation.
The post-deposition *in-situ* annealing treatment above 250°C after buffer deposition step was found to have negative effect on the solar cell performance. The solar cell with buffer layer grown at substrate temperature as room temperature was found to offer best results. A highly efficient solar cell yielding conversion efficiency of 14.1% was developed.
Chapter 5

In$_2$S$_3$ Buffer Layers Grown by Vacuum and Non-vacuum Techniques

A vacuum based thermal evaporation and a non-vacuum chemical ultrasonic spray pyrolysis techniques were employed to deposit In$_2$S$_3$ buffer layers. Two variants of ultrasonic spray pyrolysis method were used to grow the layers on SLG and CIGS/Mo/SLG substrates. The growth and properties of buffer layers deposited by three techniques were investigated. The performances of solar cells comprising of buffer layer grown by three different routes were studied and compared.

5.1 Deposition Techniques

Indium sulfide layers of 100 - 120nm thickness were grown on different substrates to study their properties relevant for photovoltaic application.
5.1.1 Thermal Evaporation

The thermal evaporation of In$_2$S$_3$ layers was carried out by evaporation of In$_2$S$_3$ compound powder (99.999% metal basis, Alfa Aesar) in a vacuum chamber at a base pressure of $\approx1\times10^{-6}$ mbar. A detailed description of thermal evaporation can be found in sec. 3.1.

5.1.2 Ultrasonic Spray Pyrolysis

The ultrasonic spray pyrolysis (USP) is a non-vacuum, low-cost, easily upscalable and in-line compatible deposition technique. Differed by physical state of constituents arriving at the substrate surface from precursor solution, two modifications of USP method namely, USP-dry and USP-wet, were used to grow In$_2$S$_3$ layers on different substrates. Figure 5.1 shows the schematic diagrams of the USP deposition setups illustrating their working principles. In case of USP-dry method (Fig. 5.1a), a chemical precursor solution is ultrasonically excited using oscillating piezo crystals to generate very small size (sub-micron) droplets. Nitrogen is used as a carrier gas to transport the chemical droplets, appearing like a fine mist, through a tube and funnel system onto the heated substrate. While in the case of USP-wet method (Fig. 5.1b), the solution droplets are generated at the tip of the spray nozzle and directed towards the heated substrate through N$_2$ carrier gas jet with higher impact velocity. The two spray methods can be differentiated by the physical (dry and wet) states of the reactants arriving at the substrate surface. The precursor carried onto the heated substrate, kept at $\approx220^\circ$C, decomposes and forms a compound on the substrate surface.

In order to form In$_2$S$_3$ layer by USP technique, the precursor solution consisting of 0.1M InCl$_3$ (99.99% from Alfa Aesar) and thiourea (($\text{NH}_2$)$_2$CS) (99.0% from Fluka) was taken and solution was dissolved in methanol solvent (HPLC grade from Fisher Scientific) so that the In/S ratio of 2/3 is attained in the final precursor solution.
5.1. Deposition Techniques

Figure 5.1: Schematic diagrams of: USP-dry (a) and USP-wet (b).
5.2 Comparative Study of Thermal-In$_2$S$_3$ and USP-In$_2$S$_3$

5.2.1 Morphology

The growth characteristics of In$_2$S$_3$ layers grown by thermal evaporation, USP-dry and USP-wet on SLG substrate were studied by AFM technique. Figure 5.2 shows the AFM micrographs of Thermal-In$_2$S$_3$ (as-deposited and air annealing at 200°C for 10min), USP-dry and USP-wet In$_2$S$_3$ layers deposited on SLG substrates.

**Figure 5.2:** AFM micrographs of thermally evaporated (as-deposited (a) and air annealed for 10min at 200°C (b)), USP-dry (c) and USP-wet In$_2$S$_3$ layers (d).

The as-deposited Thermal-In$_2$S$_3$ layer formed smooth surface morphology (Fig. 5.2a). The change in morphology after air annealing indicated a uniform grain growth over the entire surface of substrate (Fig. 5.2b). In case of the USP
layers, the layer morphology strongly depended on their deposition method. In addition to the precursor solution concentration, the substrate temperature ($\approx 220^\circ C$) strongly influences the crystallization and grain growth of the layers. Figure 5.2 and Fig. 5.2.d demonstrate the morphologies of $\text{In}_2\text{S}_3$ layers grown by USP-dry and USP-wet techniques, respectively, detailing a large morphological dissimilarity between two layers. The USP-dry layer (Fig. 5.2.c) exhibited a continuously uniform but granular surface morphology, whereas the USP-wet (Fig. 5.2.d) technique resulted in a non-uniform and inhomogeneous growth of the $\text{In}_2\text{S}_3$ layer with formation of surface "microvoids". The noticeable morphological contrast between two USP layers may be due to the inherently different nature of the physical and chemical states of the reactants arriving at the substrate that may lead to entirely different growth mechanisms and hence different morphologies. In case of USP-dry methods, the reactants arrive at the substrate surface at a relatively low velocity and tend to cover the substrate surface uniformly. Whereas, in case of USP-wet method a jet of reactants is directed towards substrate rendering high velocity to constituent atoms consequently the reactant atoms hitting the surface are more likely to undergo a back reflection event leading to formation of inhomogeneous and porous layer with presence of microvoids.

5.2.2 Microstructural Investigation

The microstructural study of $\text{In}_2\text{S}_3$ layers grown by thermal and USP techniques on CIGS surface grown on Mo coated SLG substrate were carried out by SEM. Figure 5.3 shows the respective SEM plan-view and cross-section micrographs detailing deposition method dependent microstructure and surface coverage of CIGS absorber by $\text{In}_2\text{S}_3$ layers. Coherent with results presented in the previous section 5.2.1, the thermal evaporation resulted in the growth of a continuous and uniform layer on rough CIGS surface forming a dense layer morphology (Fig. 5.3.a). The cross-section SEM image shown in Fig. 5.3.b furthered confirmed the conformal coverage of rough CIGS surface with occasional discontinuity at the large CIGS grain edges. On the other hand, USP-dry deposited layers formed its intrinsic microstruc-
ture different from that of CIGS substrate (see inset of Fig. 4.11a) forming a continuous but rough morphology. The cross-section study revealed a uniform coverage of CIGS surface by USP-dry In$_2$S$_3$ layer. In case of buffer layer deposited by USP-wet technique, we observed a non-uniform and inhomogeneous layer growth leading to formation of randomly distributed microvoids over the surface of CIGS substrate. With needle-like microstructure a porous morphology of USP-wet grown layer was detected. Moreover, the growth of a relatively thicker ($\approx$ 180nm) layer took place by USP-wet technique suggesting poor control over thickness during deposition. It should of be noted from plan-view SEM micrograph of USP-wet In$_2$S$_3$ layer that the microvoid extended deep up to CIGS surface which are potential cause of shunt paths in the solar cell with USP-wet buffer layer.

5.2.3 Optical Properties

The transmission and reflection spectra of the layers grown by Thermal-, USP-dry and USP-wet methods are shown in Fig. 5.4. The layers were found to be 60-80% transparent in the visible and near infrared region of the solar spectrum. The difference in optcial transmission and reflection behavior of three layers may originate from inherently different growth mechanisms resulting in formation of layers with varied surface morphologies, packing density, grain size etc. The higher reflection from Thermal-In$_2$S$_3$ compared to USP-In$_2$S$_3$ layers was due to growth of layer with highly smooth surface morphology as evident from Fig. 5.2a. Whereas, the rought surface of USP-In$_2$S$_3$ layer led to low reflection occurring from In$_2$S$_3$ surface. Addi-
tioanlly, the absorption edge was also found to be dependent on the method of deposition indicating different energy band gap values depending upon the deposition technique. The air annealing of Thermal-In$_2$S$_3$ layer for 10min at 200°C was found to have a small effect on optical transmission and reflection characteristic of the layer and hence on the band gap. The numerical calculation described in sec 4.1.2 were performed to determine the band gap of the layers grown by three different methods. The variation of ($\alpha$·E)$^2$ with photon energy (E) is plotted in
5.2. Thermal-In$_2$S$_3$ Vs. USP-In$_2$S$_3$

Figure 5.3: SEM micrographs of In$_2$S$_3$ layers deposited by thermal evaporation: plan-view (a) and cross-section (b); USP-dry: plan-view (c) and cross-section (d), and USP-wet: plan-view (e) and cross-section (f). The inset in (c) and (e) show the magnified images of the respective micrographs.
Fig. 5.5. Table 5.1 summarizes the band gap values numerically calculated from direct inversion of transmission and reflection data. Consistent with transmission spectra of layers shown in Fig. 5.4, the band gap of the In$_2$S$_3$ layers were found to be a function of deposition technique.

Figure 5.4: Transmission and reflection characteristics of In$_2$S$_3$ layers grown on SLG substrate by thermal evaporation, USP-dry and USP-wet techniques.

Figure 5.5: ($\alpha \cdot E$)$^2$ vs. wavelength plots of In$_2$S$_3$ layers grown by thermal evaporation, USP-dry and USP-wet techniques.
5.2. Thermal-In$_2$S$_3$ Vs. USP-In$_2$S$_3$

<table>
<thead>
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<th>Deposition technique</th>
<th>Band gap (eV)</th>
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</thead>
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</tr>
<tr>
<td>: as-deposited</td>
<td>2.53 ± 0.077</td>
</tr>
<tr>
<td>: air-annealed</td>
<td>2.56 ± 0.072</td>
</tr>
<tr>
<td>USP-dry</td>
<td>2.43 ± 0.064</td>
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<tr>
<td>USP-wet</td>
<td>2.84 ± 0.11</td>
</tr>
</tbody>
</table>

Table 5.1: Numerically calculated band gap values of In$_2$S$_3$ layers deposited by thermal evaporation, USP-dry and USP-wet techniques on SLG substrate.

5.2.4 Structural Properties

The In$_2$S$_3$ layers grown by thermal and USP techniques were characterized by XRD and Raman spectroscopic as presented in Fig. 5.6 and Fig. 5.7. The Thermal-In$_2$S$_3$ layer was found to be amorphous in as-deposited state and crystallized into $\beta$-In$_2$S$_3$ phase after air annealing treatment at 200°C. The layer grown by USP-wet method was detected to be amorphous in nature as confirmed by both XRD and Raman scattering measurements. However, the as-deposited layer by USP-dry technique was found to be polycrystalline in nature showing Bragg’s reflections according to $\beta$-In$_2$S$_3$ phase. Surprisingly, the Raman scattering did not show any signature of crystalline order in air-annealed Thermal-In$_2$S$_3$ layer which was due to instrument’s sensitivity limit. However, the Thermal-In$_2$S$_3$ layer air annealed at higher temperature (≥400) the presence of $\beta$-In$_2$S$_3$ phase was identified. The structural investigation led to an important conclusion that the layer grown by USP-dry method crystallized into tetragonal $\beta$-In$_2$S$_3$ phase and layers grown by thermal and USP-wet methods were amorphous.

5.2.5 Chemical Composition

The chemical composition of the In$_2$S$_3$ layers grown by thermal evaporation and USP methods were determined by RBS measurements. Recalling section 4.1.5 the layer grown by ther-
Figure 5.6: XRD patterns (a) and Raman spectra (b) of In$_2$S$_3$ layers grown by thermal evaporation (as-deposited, air-annealed for 10 min at 200°C) USP-dry and USP-wet techniques.
5.2. Thermal-In$_2$S$_3$ Vs. USP-In$_2$S$_3$

**Figure 5.7:** (a) RBS spectra of USP-dry layer grown from precursor solution with different In/S ratios (b) layer composition derived from RBS measurements with varied precursor composition and substrate temperature, and (c) atomic fraction of various elements present in layer determined from ERDA investigation.
nal evaporation method was found to be non-stoichiometric with respect to sulfur content with overall composition given by \( \text{In}_2\text{S}_{2.8} \) \[64\]. On the other hand, a stoichiometric growth of indium sulfide layer was obtained from USP-dry technique. Owing to intrinsic chemical route of USP method, the spray precursor solution consists of various chemical compounds containing elements In, S, C, N, O and Cl. Therefore, the layer is expected to be contaminated with some impurities. The concentration of these impurities in the layer depends on the chemical composition of the spray solution and substrate temperature during deposition \[11\]. Figure 5.7a shows the RBS spectra of the USP-dry deposited indium sulfide layers at varied precursor concentration given by In/S ratios. The chemical composition of layers grown with different molar ratios of In/S and grown at different substrate temperature were deduced from RBS measurements and are plotted in Fig. 5.7b. C, N and O being light elements, it was not possible to determine their concentration unambiguously by RBS technique. Therefore, the quantitative identification of elemental impurities present in the USP-dry film was carried out using elastic recoil detection analysis (ERDA) technique and the extracted elemental concentration are plotted in Fig. 5.7c. Referring to Fig. 5.7b, a high concentration of Cl was observed when \( \frac{\text{In}}{\text{S}} = \frac{1}{1} \). The amount of Cl decrease with increase in In/S molar ratio with weak dependence on the substrate temperature. A trace amount of Cl was detected at \( \frac{\text{In}}{\text{S}} = \frac{2}{3} \) for all substrate temperature. The ERDA analysis yielded the concentration of various elemental impurities present in the layer. The traces of Cl, C, N and O elements were detected from the measurements and it was observed that impurity concentration in the layer decrease with increase in molar ratio from 1:1 to 2:2 and that further reduced with rise in substrate temperature from 200°C to 220°C. The described analyses confirmed that in the present case of In/S molar ratio of 2:3 and substrate temperature of 220°C, the layer is contaminated with Cl, O, N and C impurities.
5.3. Solar Cell Characteristics

5.3 Solar Cell with Thermal-In$_2$S$_3$ and USP-In$_2$S$_3$ Buffer Layers

In order to study the influence of indium sulfide buffer layer deposition methods on the PV performance of solar cells, the CIGS solar cells with $\approx$30nm thin indium sulfide buffer layer were developed. Among others, the solar cell with of Thermal-In$_2$S$_3$ buffer layer resulted in the maximum conversion efficiency of 12.6% accompanied by a 9.2% and a 2.8% efficient cells with buffer layer grown by USP-dry and USP-wet methods, respectively. The reference solar cell with CdS buffer layer deposited by CBD technique yielded an efficiency of 14.1%. The Table 5.2 summarizes the PV parameters of the solar cells developed on identical absorber layers obtained from the single deposition run.

<table>
<thead>
<tr>
<th>Buffer</th>
<th>$\eta$ (%)</th>
<th>FF (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA.cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$S$_3$-Thermal</td>
<td>12.6</td>
<td>68.7</td>
<td>626</td>
<td>29.4</td>
</tr>
<tr>
<td>In$_2$S$_3$-USP-dry</td>
<td>9.2</td>
<td>57.8</td>
<td>581</td>
<td>27.5</td>
</tr>
<tr>
<td>In$_2$S$_3$-USP-wet</td>
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<td>42.7</td>
<td>514</td>
<td>12.4</td>
</tr>
<tr>
<td>CdS-ref.</td>
<td>14.1</td>
<td>75.5</td>
<td>648</td>
<td>28.8</td>
</tr>
</tbody>
</table>

Table 5.2: PV parameters of solar cells with In$_2$S$_3$ buffer layers grown by thermal evaporation, USP-dry and USP-wet methods. In$_2$S$_3$ buffered cells were compared with CBD-CdS reference cell.

The respective J-V characteristics and external quantum efficiency curves of the solar cells with In$_2$S$_3$ buffer layer grown by different methods are shown in Fig. 5.8a and Fig. 5.8b, respectively. The quantum efficiency measurements of the solar cell with In$_2$S$_3$ indicated the higher response in high photon energy region (> 2.4 eV) of the solar spectrum than the solar cell with CdS buffer layer. The marked dissimilarities among solar cell performances of devices with In$_2$S$_3$ buffer layer deposited by different techniques can be understood by different growth kinetics governing the layer growth processes leading to formation of layers with varied optical, structural and chemical properties as described in the previous section 5.2.
Chapter 5. Vacuum & Non-vacuum Based In$_2$S$_3$

It is known that the interface between CIGS and In$_2$S$_3$ buffer layer plays an important role in determining the solar cell performance [45,61,73,105–108] which is highly sensitive to In$_2$S$_3$ layer growth conditions (e.g. substrate temperature). Thus, the substrate temperature during buffer layer deposition may significantly affect the USP-In$_2$S$_3$ buffer solar cell characteristics. The inferior performance of solar cell with In$_2$S$_3$ buffer layer deposited by USP-wet technique can be attributed to formation of a non-uniform and inhomogeneous layer with large concentration of randomly distributed microvoids in the buffer layer (Fig. 5.3e). These microvoids acting as shunt paths may be potential cause for deteriorated cell performance. Furthermore, the USP grown buffer layers were found to be contaminated with impurities (Cl, C, N and C) which may act as recombination centers and hence may be responsible for deteriorated solar cell properties. It should also be noticed that poor control over buffer layer thickness during deposition coupled with porous morphology may adversely affect the PV parameters of the USP-wet In$_2$S$_3$/CIGS devices mainly affecting $J_{sc}$. In comparison to USP-wet In$_2$S$_3$ solar cell, the enhanced cell performance of USP-dry In$_2$S$_3$ device can be attributed to the formation of a uniform and dense In$_2$S$_3$ layer with good surface coverage efficiency on underlying rough CIGS absorber layer. On the other hand, thermally grown In$_2$S$_3$ layers uniformly covered the CIGS surface and did not have detrimental impurities that results in the formation of improved CIGS/buffer interface properties and hence higher efficiency cells.
Figure 5.8: $J-V$ characteristics a) and external quantum efficiency b) of solar cells with buffer layer grown by thermal evaporation, USP-dry and USP-wet methods and CBD-CdS reference cell.
5.4 Conclusion

The growth and properties of indium sulfide layers deposited by vacuum based thermal evaporation and solution based non-vacuum USP (-dry/-wet) methods were investigated using various thin film characterization techniques. The atomic force microscopic study revealed the rough morphology of the USP grown layers while the layers grown by thermal evaporation method exhibit a smooth surface morphology. The direct band-to-band optical transition was determined in all the films with optical band gap strongly dependent on their method of preparation. The as-grown amorphous films deposited by thermal evaporation technique crystallized into tetragonal $\beta$-$\text{In}_2\text{S}_3$ after annealing treatment at 200°C. The USP-dry method resulted in the formation of the polycrystalline $\beta$-$\text{In}_2\text{S}_3$ layer whereas, the USP-wet film was amorphous. Consistent with atomic force microscopic study, the scanning electron microscopic investigation revealed the growth of a non-uniform and inhomogeneous layer with existence of large density of randomly distributed microvoids by USP-wet method. The thermally grown layer uniformly covered the CIGS surface while a continuous but rough USP-dry film was observed to form a distinguishable microstructure on the CIGS surface. The presence of Cl, O, C and N was detected in the films grown by USP-dry method. The solar cells with Thermal-$\text{In}_2\text{S}_3$ buffer layer was found to offer better photovoltaic characteristics than cells with USP grown $\text{In}_2\text{S}_3$ layer.
Chapter 6

Flash Evaporated In$_2$S$_3$ Buffer Layer

Recognizing the industrial importance of a low-cost, fast, easily up-scalable, vacuum based and in-line deposition compatible thin film deposition method with high material yield, the flash evaporation technique was employed to fabricate solar cells with In$_2$S$_3$ buffer layers. In$_2$S$_3$ layers were deposited by flash evaporation technique with varying flash rates. An in-depth analysis of layers were performed using various thin film characterization techniques. Based on the properties of the layer investigated in this work, an analytical layer growth model for flash evaporated buffer layer is presented and the solar cell results are discussed.

6.1 Introduction: Flash Evaporation

It is known that the thermal evaporation of In$_2$S$_3$ material results in growth of a non-stoichiometric layer with respect to sulfur content[1] [64]. The compositional deviation from stoichiometric In$_2$S$_3$ in the buffer layer may limit the solar cell

\[\text{see sec. 3.3.1 and sec. 4.1.5}\]
Chapter 6. Flash Evaporated In$_2$S$_3$ Buffer Layer

We have attempted to address the issue of non-stoichiometry in the evaporated In$_2$S$_3$ layer by employing flash evaporation (FE) technique which has potential to form film with stoichiometric composition \[1\]. Additionally, FE is an industrially significant and highly desired technique due to following reasons:

- Fast deposition: deposition time can significantly be reduced in comparison to conventional thermal evaporation technique
- High process yield: amount of material, which largely depends on the desired thickness of layer, to be evaporated can easily be optimized
- Easily up-scalable
- Control over film composition
- In-line compatibility

The interests in flash deposition dates back to about two decades ago. The are some reports on the deposition of CuInSe$_2$ and CuGa$_x$In$_{1-x}$Se$_2$ thin films by using flash evaporation techniques \[112-116\]. However, flash evaporated In$_2$S$_3$ is scarcely studied. Bouabid et al. \[117\] investigated the properties of flash evaporated In$_2$S$_3$ layer, however a detailed analysis of the layer properties are widely lacking in the literature.

6.1.1 Flash Evaporation Chamber

The flash evaporation of In$_2$S$_3$ source material was carried out in an *in-house* designed vacuum chamber. Figure 6.1 shows the schematic diagram of the vacuum chamber (V) describing its different components (a-j) and their respective functions. The pellets of In$_2$S$_3$ material (a) were loaded in pellet injector (b). The roller (c) attached to pellet injector pushes the pellets towards the pellet guide (d). The pellet in contact with pellet guide is then directed towards the source evaporation crucible (e) kept
6.1. Introduction: Flash Evaporation

at an elevated temperature as measured by a thermocouple (f). This results in sudden generation of an evaporation flux (flash) of source material. On opening the shutter (g), the flux constituents condense on the substrate (h) forming a thin layer of source material. The thickness of the deposited film was monitored by quartz crystal monitor (i). The In$_2$S$_3$ layer of $\approx$50nm thickness was deposited on different substrates at three different flash rates which correspond to three different evaporation crucible temperatures labeled as low ($T_{\text{crucible}} = 950^\circ$C), moderate ($T_{\text{crucible}} = 1050^\circ$C) and high ($T_{\text{crucible}} = 1150^\circ$C) flash rate.

Figure 6.1: Schematic diagram (not to scale) of an “in-house” designed vacuum chamber (V) for flash evaporation of In$_2$S$_3$ buffer layer. Components: a) In$_2$S$_3$ pellet, b) pellet injector, c) roller, d) pellet guide, e) evaporation crucible, f) thermocouple, g) substrate shutter, h) substrate, i) quartz crystal and j) vacuum pump.
6.2 Layer Growth Model

The growth mechanism of the flash evaporated layer can be understood with the help of an analytical model illustrated in Fig. 6.2. Owing to inherent nature of flash evaporation technique, the evaporation flux, consisting of highly energetic adatoms (1) of the source material, arrive at the substrate surface with very high kinetic energy. The high kinetic energy renders high surface mobility to adatoms resulting in enhanced surface diffusion (curved arrow) necessary for the growth of a continuous layer. On encountering a nucleation center, the nuclei grow and form monolayer.

![Schematic 2D illustration of growth model of flash evaporated In$_2$S$_3$ layer: (1) impinging adatoms, (2) atomic displacement (3) reflection, (4) knockout, (5) densification, (6) re-evaporation and lattice damage (dotted circles).](image)

**Figure 6.2:** Schematic 2D illustration of growth model of flash evaporated In$_2$S$_3$ layer: (1) impinging adatoms, (2) atomic displacement (3) reflection, (4) knockout, (5) densification, (6) re-evaporation and lattice damage (dotted circles).

The monolayer subsequently formed is bombarded with a continuous flux of energetic adatoms which may give rise to secondary effects namely, atom displacement (2), reflection (3), knockout (4), lattice damage (dotted circle)$^2$ strain etc. The incessant collision between arriving adatoms and already grown monolayer renders compactness (5) to the layer at the cost of secondary events. During growth, the energy of impinging

---

$^2$Different sizes and shapes of dotted circles in Fig. 6.2 denote different degrees of lattice damage.
adatoms is dissipated to already grown monolayer which may lead to a reverse evaporation of adatoms\(^3\) (6). Hence, layers are expected to grow denser with chemical and structural imperfections that may further increase with rise in flash rate. The growth characteristic of flash evaporated buffer layer deposited on SLG at room temperature was studied by AFM. As a result of thermally induced recrystallization cased by air annealing (10min at 200°C), the granular morphology and continuous growth of \(\text{In}_2\text{S}_3\) layer was observed in AFM study (Fig. 6.3). The pronounced morphological disparity among air-annealed layer may be due to different growth kinetics of the layer formation. The room-mean-square roughness was estimated to be 2-3nm by AFM technique.

6.3 Properties of Flash Evaporated \(\text{In}_2\text{S}_3\) Layers

6.3.1 Optical Properties

Transmission and reflection

The optical transmission and reflection spectra of as-deposited and air-annealed layer grown at three different flash rates were recorded in wavelength region 300-1500nm and are shown in Fig. 6.4. A remarkable difference in reflection and transmission behavior of layer deposited at low flash rate and moderate or high flash rate was observed. It is important to note that the transmission and reflection characteristics of layers varied significantly when flash rate was raised from low to moderate and beyond that no large difference was observed between moderate and high flash deposited layers. Recalling section\(^{[4.1.2]}\) it can be noticed that the layer deposited by conventional thermal evaporation method showed a large difference with one deposited by flash evaporation. The air annealing of the layers resulted in decrease in optical reflection and increase in transmission which

\(^3\)The reader is advised to refer to Ref. \([118]\) for better understanding of thin film growth mechanisms.
Figure 6.3: AFM micrographs of as-deposited and air-annealed In$_2$S$_3$ layers grown on SLG substrate at different flash rates. Low: a) as-deposited and b) air-annealed; Moderate: c) as-deposited and d) air-annealed; High: e) as-deposited and f) air-annealed.

can be correlated to roughening of the surface leading to lower reflection.

**Optical constants**

The layers deposited with varying flash rates were studied by spectroscopic ellipsometry. Following the discussion on multi layer stack model and model dielectric functions employed for spectroscopic ellipsometry analysis of thermally evaporated In$_2$S$_3$ layer described in sec. 4.1.2, a comparative analysis with respect
Figure 6.4: Transmission and reflection spectra of flash evaporated In$_2$S$_3$ layer (as-deposited and air-annealed) grown on SLG substrate at low, moderate and high flash rates.
to suitability of two model dielectric functions, Forouhi-Bloomer (FB) and Tauc-Lorentz (TL) models, was performed on the ellipsometric data acquired from flash evaporated In$_2$S$_3$ layers grown on SLG substrate. Omitting the theoretical considerations of two models in this section, the parameterization of two models for as-deposited and air-annealed flash evaporated In$_2$S$_3$ layer are presented in Tab. 6.1 and 6.2, respectively.

<table>
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<th>Model</th>
<th>Parameters</th>
<th>Layer</th>
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<td>Low</td>
</tr>
<tr>
<td>FB</td>
<td>$A_{FB}$</td>
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<td></td>
<td>$B_{FB}$ (eV)</td>
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<td>$E_{gFB}$ (eV)</td>
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<td>$E_{0TL}$ (eV)</td>
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<td></td>
<td>$C_{TL}$ (eV)</td>
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<tr>
<td></td>
<td>$E_{gTL}$ (eV)</td>
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Table 6.1: Optical parameters of as-deposited In$_2$S$_3$ layers obtained from FB and TL model fitting.

<table>
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<th>Model</th>
<th>Parameters</th>
<th>Layer</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>FB</td>
<td>$A_{FB}$</td>
<td>0.34±0.03</td>
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<td></td>
<td>$B_{FB}$ (eV)</td>
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<td>$C_{FB}$ (eV)$^2$</td>
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<td>$E_{gFB}$ (eV)</td>
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<td>$E_{0TL}$ (eV)</td>
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<td></td>
<td>$E_{gTL}$ (eV)</td>
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</tr>
</tbody>
</table>

Table 6.2: Optical parameters of air-annealed (10min, 200$\degree$C) In$_2$S$_3$ layers obtained from FB and TL model fitting.

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$^4$The reader is advised to refer to sec. 4.1.2 for a description (within the scope of thesis) of spectroscopy ellipsometry analysis.
As discussed in the sec. 4.1.2, TL model was employed to extract the meaningful and reliable optical constants of flash evaporated \( \text{In}_2\text{S}_3 \) layer. The dispersion curves of refractive index and extinction coefficient for layers deposited at different flash rates are shown in Fig. 6.5a and 6.5b for as-deposited and air-annealed layers, respectively.

As evident from Fig. 6.5a, in case of as-deposited layers, an increase in refractive index with rise in flash rate was observed which indicated the densification and presence of different structural arrangements, inherent to growth mechanism described in section 6.2. Fig. 6.5a and Fig. 6.5b also suggested that the optical constants of the layer depend on the flash rate. A decrease in flash rate dependent refractive index accompanied by a blue shift in extinction coefficient was determined in air-annealed layers as shown in Fig. 6.5b. Interestingly, the similar values of band gap energy (2.5-2.55 eV) were calculated for layers deposited at three different flash rates (inset in Fig. 6.5b). The band gap increased to 2.8 eV, 2.73 eV and 2.61 eV after air annealing treatment of layers grown at low, moderate and high flash rate, respectively.

The XPS measurements revealed the presence oxygen impurity in \( \text{In}_2\text{S}_3 \) layer. In addition, a trace amount of Na impurity was also detected in layer grown at high flash rate which further increased after air annealing treatment. The concentration of oxygen impurity in the layer was found to be proportional to flash rate which further increased after air annealing treatment. The oxygen incorporation in \( \text{In}_2\text{S}_3 \) as \( \text{In}_2\text{S}_3-3x\text{O}_{3x} \) has been identified to cause lattice compression giving rise to band gap widening until \( x < 0.15 \) phase separation takes place into secondary phase of \( \text{In}_2\text{O}_3 \) [34,71,119]. In addition, Na incorporation in \( \text{In}_2\text{S}_3 \) also induces band gap widening and it tends to occupy tetragonal vacant In \( (V_{\text{In}}) \) sites [108,120,121]. Interestingly, contrary to anticipated increase in band gap with amount of oxygen inclusion (proportional to flash rate), the band gap showed weak dependence and inverse relationship with flash rate for as-deposited and air-annealed layers, respectively.

The band gap of thin film semiconductor may strongly be affected by the imperfections such as grain size, grain boundaries,
Figure 6.5: Optical constants of (a) as-deposited and (b) air-annealed In$_2$S$_3$ layers grown at different flash rates.
6.3. Properties of Flash-In$_2$S$_3$ Layers

orientation, nonstoichiometry, defect level, localized charges, strain and crystallinity present in the film. Quantum mechanical considerations suggest the generation of localized mid-band gap states due to structural and thermal disorder present in the film [122,123], consequently decreasing the band gap.

The photoluminescence (PL) characterization of In$_2$S$_3$ layers indicated the existence of intermediate defect states generated due to chemical disorder present in the layer [124]. An experimental evidence of existence of intermediate defect states related to point defects of In (In$_i$) interstitial and occupancy of sulfur vacancy by oxygen (O$_{Vs}$) was obtained from room temperature PL measurements (shown in Fig. 6.10) of Flash-In$_2$S$_3$ layers. Therefore, the existence of localized defect states in the band gap can be visualized as a consequence of growth of structurally (sec. 6.3.3) and chemically (sec. 6.3.2) disordered layer deposited by flash evaporation technique (layer growth model in Subsec. III.A). These defect states in the layer may negate the effect of oxygen and Na incorporation into In$_2$S$_3$ matrix on band gap widening. Hence, two opposite effects of band gap

- widening due to oxygen and Na impurities inclusion and,
- lowering due to presence of intermediate defect states (structural and chemical disorder)

compete resulting in similar values of band gap for as-deposited layers (inset of Fig. 6.5b).

The AFM morphological study of the layer (Fig. 6.3) revealed the grain growth and recrystallization in the layer after air annealing treatment. The thermally driven structural rearrangements in the layer may result in lowering in disorder in the layer and thus, increasing the band gap energy (inset of 6.5b) as a consequence of annihilation of intermediate defect states. In addition to blue shift in extinction coefficient (increment in band gap) after air annealing, it also decreased indicating weaker photon absorption by electron transition due to thermally assisted annihilation of intermediate defect states.
Chapter 6. Flash Evaporated In$_2$S$_3$ Buffer Layer

The XPS analysis, described in sec. 6.3.2, confirmed a significant increase in oxygen concentration (from relative 2.5 at% to 17.8 at%) in the layer as a result of air annealing. The layer grown at low flash rate (less structurally defective) showed the largest increase in band gap compared to layers grown at moderate and high flash rate which possess higher defect density and hence, have lesser effect of oxygen inclusion on band gap widening caused by air annealing. Moreover, the structural modifications owing to air annealing may favor the relaxation process in highly disordered layer causing decrease in layer destiny which is evident from decrease in refractive index after air annealing treatment (Fig. 6.5b). It should be pointed out that in case of layers grown at moderate and high flash rate, the air annealing temperature of 200°C is not high enough to annihilate the same order of defects as it does in case of layer deposited at low flash rate. Therefore, higher annealing temperature is needed for layers grown at moderate and high flash rate to obtain same increment in the band gap as observed in layer deposited at low flash rate. Hence, the optical constants and band gap considerations support the proposed layer growth model in sec. 6.2.

6.3.2 Chemical Properties

RBS investigation

The RBS measurements were performed to determine the chemical composition of layers grown at three different flash rates. Contrary to expected stoichiometric growth of the deposit by flash evaporation technique, a substantial shift in chemical composition from stoichiometric In$_2$S$_3$ was measured. Figure 6.6 shows the RBS spectra of layers with inset showing the layer density and relative concentration (atomic fraction) of elements (In and S) detected in the layers. As indicated in the figure, the layers were found to be sulphur deficient with overall chemical composition given by In$_2$S$_x$, where 2.47<$x<$2.8. It should be emphasized that compositional shift broadened ($x$ decreased) with rise in flash rate indicating, higher the flash rate, higher is sulfur-loss in the layer.
6.3. Properties of Flash-In\textsubscript{2}S\textsubscript{3} Layers

Miller et al. reported the dissociation of In\textsubscript{2}S\textsubscript{3}(s) in In\textsubscript{2}S(g) and S\textsubscript{2}(g) constituents and identified the occurrence of congruent dissociation in slightly sulfur-poor indium sulfide material \[^{82,83}\]. Moreover, high flash evaporation temperature (>950°C) and large difference in the partial pressure of dissociated constituents \([p(\text{In}_2\text{S})\approx 10^3\cdot p(\text{S}_2)]\) may assist the growth of a non-stoichiometric layer as a consequence of incongruent dissociation of In\textsubscript{2}S\textsubscript{3} \[^{83,84,113}\]. This suggests that the flash evaporation of In\textsubscript{2}S\textsubscript{3} with present evaporation parameters (pallet composition and evaporation crucible temperature) may favor incongruent dissociation of In\textsubscript{2}S\textsubscript{3} material causing a significant deviation from stoichiometric In\textsubscript{2}S\textsubscript{3} composition in the layer. Additionally, the re-evaporation of sulfur from layer may further lead to formation of non-stoichiometric layer. This suggests that the degree of incongruent dissociation enhances with increase in flash rate (evaporation temperature). Therefore, the layers grown at moderate (In\textsubscript{2}S\textsubscript{2.55}) and high (In\textsubscript{2}S\textsubscript{2.47}) flash rate are more sulfur-deficient than one grown at low flash rate (In\textsubscript{2}S\textsubscript{2.8}). The chemical composition investigation also led to an important conclusion that a control over layer composition was attainable with higher flash rates \(T_{\text{crucible}} > 1050^\circ\text{C}\) depo-
Chapter 6. Flash Evaporated In$_2$S$_3$ Buffer Layer

Moreover, it should also be noticed from RBS spectra that the layer deposited with low flash rate was thicker than one deposited with higher flash rates due to reflection and/or re-evaporation events illustrated in Fig. 6.2. The layer density deduced from RBS measurements showed a strong dependence on the flash rate (inset of Fig. 6.6). The increase in layer density with rise in flash rate was observed. Notably, a small decrease in density in the layer deposited at high flash rate, compared to layer grown at moderate flash rate, was observed. This may be attributed to inhomogeneity in packing density of the adatoms in layer grown at high flash rate. A relative 7% decrease in film density was observed after air annealing, this indicated the occurrence of thermally driven restructuring or relaxation processes in the layers. Hence, the layer density considerations are in agreement with variation in refractive index before and after air annealing discussed in the previous subsection.

XPS analysis

The layers were further examined by XPS technique. The oxygen and sodium impurity concentration derived from XPS measurements on layers grown at low and high flash rates are plotted in Fig. 6.7. The as-deposited layers were found to be contaminated with oxygen impurity. The impurity concentration increased with increase in flash rate followed by a further increment after air annealing treatment. Notably, a trace amount of Na impurity in as-deposited high flash rate layer was also detected which further increased with subsequent air annealing step. These observations implied a larger defect density in the layer grown at high flash than that existing in low flash rate layer. It is well documented that the cationic impurity such as Cu$^+$ and Na$^+$ can not only fill vacant tetrahedral In sites (V$_{In}$) but also substitute In atom in In$_2$S$_3$ matrix [108][109]. Under the influence of a net concentration gradient, arising from large defect density in buffer layer, across buffer/SLG system, Na may diffuse from SLG substrate into buffer layer even at room temperature. Consequently, Na may not only fill vacant In sites but also it can replace In in In$_2$S$_3$ matrix. In addition, higher oxygen content in high flash rate as-deposited layer than layer
grown at low flash rate suggested that the layer grown at high flash rate possesses larger concentration of chemically active defects than in layer grown at low flash rate. The XPS results are coherent with RBS analysis emphasizing that high flash rate leads to higher degree of chemical disorder in the layer and as a result the layer grown at high flash rate is likely to be more contaminated than one grown at low flash rate.

![Graph showing concentration of oxygen and sodium impurities deduced from XPS measurements on as-deposited and air-annealed In$_2$S$_3$ layer grown at low and high flash rates.]

**Figure 6.7:** Concentration of oxygen and sodium impurities deduced from XPS measurements on as-deposited and air-annealed In$_2$S$_3$ layer grown at low and high flash rates.

### 6.3.3 Structural Investigation

**XRD study**

As described in the previous sections [6.3.1](#), change in refractive index of as-deposited and air-annealed films suggests structural changes occurring as a result of flash evaporation. To further examine this, GA-XRD investigations were performed on as-deposited and air-annealed layers. Figure [6.8](#) presents the GA-XRD pattern of In$_2$S$_3$ layers deposited at different flash rates. The as-deposited layers were detected to be amorphous regardless the flash rate. The layer deposited at low flash rate was
found to be (partially) crystallized in $\beta$-$\text{In}_2\text{S}_3$ phase after air annealing treatment. Interestingly, in case of layers deposited at moderate and high flash rate, no structural changes after air annealing of the layers were detected. The absence of crystalline character after air annealing in layers grown at moderate and high flash rate is consistent with results emphasized in sec. 6.3.1 that moderate and high flash rate deposition conditions induce higher degree of structural disorder in the layers and annealing temperature of 200°C is inadequate to give rise to structural modifications to an extent as in layer grown at low flash rate. The GA-XRD analyses indicated that as-deposited layer grown with moderate and high flash rate were amorphous (higher structural disorder). However, it is important to point out that the Raman investigation discussed in the following section confirmed the presence of crystalline arrangement which is more reliable as there are high chances of X-rays reaching the glass substrate passing through a very thin $\approx$50nm $\text{In}_2\text{S}_3$ layer.

**Figure 6.8:** GA-XRD of as-deposited and air-annealed $\text{In}_2\text{S}_3$ layers deposited at different flash rates ($\omega_{\text{grazing}} = 3^\circ$).

**Raman spectroscopy**

The GA-XRD suffers from low lateral and depth resolution due to relatively large volume of specimen is probed by x-rays. Thus,
one needs to be careful while making conclusions solely based on GA-XRD characterization. On the other hand, the Raman spectroscopy is capable of extracting materials information from the scale up to a few lattice spacing resulting in very high spatial resolution.

The layers grown at three different flash rates were examined by Raman scattering technique. The Raman signals corresponding to $\beta$-In$_2$S$_3$ phase was detected in as-deposited (Fig. 6.9a) and air-annealed layers (Fig. 6.9b). Notably, the peak shift in as-deposited layer grown at three different flash rates was observed, which can be attributed to lattice perturbation caused by oxygen or/and sodium inclusion in crystalline $\beta$-In$_2$S$_3$ matrix. Furthermore, the peak broadening with rise in flash rate further suggested the lowering of crystalline arrangement (increase in structural imperfection) in the moderate and high flash rate layers. The air annealing of the layers resulted in enhanced crystalline character of the layers as evident from Fig. 6.9b.

Photoluminescence study

The room temperature PL spectra of flash-evaporated layers was obtained. A distinct PL signal at $\approx$680nm was present in all the layers grown at three different flash rates. Figure 6.10 shows the PL spectra of layer grown at high flash rate (see page 95 for a detailed discussion.

SEM investigation

In$_2$S$_3$ layers were deposited on CIGS/Mo/SLG substrate at three different flash rates. Figure 6.11 shows the scanning electron micrographs of the In$_2$S$_3$ layer deposited at low flash rate on CIGS surface. Although In$_2$S$_3$ layers conformally covered the rough CIGS surface, infrequent discontinuity at big CIGS grain edges was also distinguishable in cross-section SEM (inset Fig. 6.11) study indicating poor adhesion between CIGS and In$_2$S$_3$ layers. In order to improve the growth characteristics (adhesion) of buffer layer with CIGS layer, the buffer deposition step was
Figure 6.9: Raman spectra of In$_2$S$_3$ (a) as-deposited and (b) air-annealed layers grown at three different flash rate.
6.3. Properties of Flash-In$_2$S$_3$ Layers

![Room temperature photoluminescence spectrum of In$_2$S$_3$ layer grown at high flash rate.](image)

**Figure 6.10:** Room temperature photoluminescence spectrum of In$_2$S$_3$ layer grown at high flash rate.

followed by an *ex-situ* low temperature air annealing treatment at 100°C for 20min prior to window layer deposition.

![SEM plan-view and cross-section micrographs of In$_2$S$_3$/CIGS layer stack.](image)

**Figure 6.11:** SEM plan-view and cross-section micrographs of In$_2$S$_3$/CIGS layer stack.
6.4 Solar Cell Performance

The solar cells buffered with In$_2$S$_3$ layer deposited at three different flash rates were characterized by measuring their J-V characteristics. The PV parameters of Flash-In$_2$S$_3$ and CdS reference devices are plotted in Fig. 6.12.

![Figure 6.12: PV parameters of 'best' CdS reference and Flash-In$_2$S$_3$ buffered solar cells before and after air annealing for 20min at 200°C.](image)

The cells with In$_2$S$_3$ buffer layers yielded low efficiency compared to CdS reference cell primarily due to substantial loss in $J_{sc}$ and FF. The poor performance of In$_2$S$_3$ devices can be understood by presence of conduction band offset (cliff) at In$_2$S$_3$/CIGS heterointerface as suggested by Jacob et al. \[75\] (see. Fig. 1.4).

The low temperature j-V measurement was performed to identify the dominant recombination path in the device with buffer layer grown at high flash rate. The activation energy of 0.99 eV of the dominant recombination process, lower than
the band gap (1.14 eV) of absorber, revealed the buffer/absorber heterointerface as the dominant recombination path in the device with In$_2$S$_3$ buffer layer. This finding indicated the existence of conduction band offset at buffer/CIGS heterointerface in Flash-In$_2$S$_3$ device. Moreover, insufficient degree of surface inversion can further result in loss of cell performance \cite{70}. The higher efficiency of the cell, due to high $V_{oc}$ and FF, with low flash rate In$_2$S$_3$ buffer layer can be attributed to the superior quality of junction formed between CIGS absorber and chemically (near stoichiometry) and structurally (partially crystallized) less disordered In$_2$S$_3$ layer (sections 6.3.2 and 6.3.3) leading to reduced interface recombination losses. Notably, except device with buffer grown at moderate flash rate, the open circuit voltages of other devices were found to be close to $V_{oc}$ of CdS device.

The substitution of sulphur by oxygen in In$_2$S$_3$ causes decrease in electron affinity which leads to reduction in conduction band offset consequently, increasing $V_{oc}$ and FF \cite{74}. In the present case of flash evaporated In$_2$S$_3$ buffer layer, an increase in oxygen content with increase in flash rate was determined by XPS investigation. This explains the increase in $V_{oc}$ and FF with rise in flash rate from moderate to high. The combined effect of reduction in conduction band offset due to presence of oxygen and CIGS surface type-inversion induced by Cu depletion from CIGS surface explains the increase in FF and $J_{sc}$ due to air annealing of the complete device.

The EQE characterization of the devices with buffer layer deposited at three different flash rates yielded the wavelength dependent short-circuit current profile of the cells as shown in Fig. 6.13. It can be inferred from the EQE of the devices, the buffer layer grown with different flash rates had different band gap and showed entirely different junction characteristics leading to a pronounced variation in collection efficiencies over the entire range of irradiant spectrum.

An insight into IQE of In$_2$S$_3$ device indicated the occurrence of type-inversion at CIGS surface as consequence of air annealing. Figure 6.14 shows the IQE of the device with In$_2$S$_3$ buffer layer grown at high flash rate and compares with CdS reference device. Owing to larger band gap of In$_2$S$_3$ layer than CdS,
the enhanced carrier generation in blue region was observed in In$_2$S$_3$ device. Moreover, the air annealing of the In$_2$S$_3$ buffered device resulted in decrease in collection efficiency in blue region followed by a remarkable improvement in longer wavelength region (480-1100 nm). The thermally induced elemental interdiffusion across In$_2$S$_3$/CIGS heterointerface has been reported in literature [45,61]. The experimental observations are in agreement with the formation of Cu depleted CIGS surface due to Cu diffusion from CIGS to In$_2$S$_3$ junction partner [73,105].

The element Cu can readily diffuse from CIGS into In$_2$S$_3$ buffer layer altering its optical properties and the junction characteristics due to formation of graded interface with CIGS layer. The inclusion of Cu in In$_2$S$_3$ buffer layer lowers the band gap of the layer mainly affecting the valance band maximum position and thus the conduction band offset remains unaffected [73,125,126]. Therefore, a decrease in carrier collection in blue region accompanied by a large enhancement for photons $\lambda>480$ nm can be understood by thermally assisted Cu diffusion from
CIGS to In$_2$S$_3$ layer which has twofold effects,

1. lowering of band gap as a consequence of incorporation of Cu in structurally defective In$_2$S$_3$ matrix which is favored by the presence of vacant tetrahedral In sites (V$_{In}$) and chemical defects originated from growth mechanism and,

2. the Cu depletion from CIGS surface tends to form n-type (type-inversion) ordered vacancy compound resulting in inversion of the CIGS surface into n-type.

Hence, Fermi level shifts towards conduction band at the CIGS surface. Above discussion suggests that the diffusion of Cu from CIGS to In$_2$S$_3$ gives rise to enhanced collection efficiency in photon energy region below band gap of buffer layer which results in significant gain in current as shown in Fig. 6.12 and inset of Fig. 6.14.

The out-diffusion of oxygen from $i$-ZnO to In$_2$S$_3$ even at room temperature deposition condition has been reported by Spiering et al. [61]. In the present case of flash evaporated In$_2$S$_3$, the layers are inherently contaminated with oxygen impurity with chemical disorder proportional to flash rate. This implies that in addition to oxygen inclusion from growth process, its incorporation into In$_2$S$_3$ defect structure is further favored by the presence of $i$-ZnO layer. Interestingly, the XPS analysis also revealed that the solubility limit of oxygen in In$_2$S$_3$ resulting from air annealing is nearly same in the layer and hence is independent of flash rate (Fig. 6.7). This important finding can further be extended asserting that irrespective of different flash rates, the air annealing of Flash-In$_2$S$_3$ buffered devices may cause same degree of reduction in conduction band offset at the In$_2$S$_3$/CIGS hetrointerface. This explains the similar values of FF and $V_{oc}$ obtained after air annealing of the device (Fig. 6.13). Hence, two concomitant effects,

1. Cu diffusion from CIGS to In$_2$S$_3$ and,

2. oxygen incorporation during layer growth as well as from $i$-ZnO to In$_2$S$_3$ and,
are responsible for enhanced cell performance after air annealing of the complete device.

It should be noted that as a consequence of air annealing of the device, the gain in photocurrent collection in long wavelength region (480<\lambda<1190 \text{ nm}) is larger than the loss in blue region (\lambda<480 \text{ nm}). Moreover, the carrier collection length of air-annealed In$_2$S$_3$ device in long wavelength region is similar to that of CdS device. This implies that performance of In$_2$S$_3$ buffered device is strongly governed by degree of surface type-inversion in CIGS layer required minimizing the recombination losses occurring at the buffer/absorber interface.

![Figure 6.14: Internal quantum efficiency of CdS reference and high flash rate In$_2$S$_3$ buffered solar cells.](image)

Pursuing above discussion of carrier collection profile of the solar cell, the numerical calculations to quantify the gain (or loss) in $J_{sc}$ further confirmed the significant improvement in electronic quality of junction after air annealing treatment. However, contribution from altered optical absorption (or reflection) from device originating from change in refractive indices of layers due to air annealing was found to be comparatively small.
The total $J_{sc}$ in the wavelength region $\lambda_a$ and $\lambda_b$ is defined as,

$$J_{sc} = \int_{\lambda_a}^{\lambda_b} q \cdot \Phi(\lambda).EQE(\lambda)d\lambda \quad (6.1)$$

where, $\Phi(\lambda)$ is incident photon flux density corresponding to standard AM1.5 spectrum and $q$ is elementary charge. The change in $J_{sc}$ ($\Delta J_{sc}^{1-2}$) as a consequence of air annealing can be decoupled into optical ($\Delta J_{sc}^{opt}$), electronic ($\Delta J_{sc}^{elec}$) and other ($\Delta J_{sc}^{oth}$) components. The optical component, $\Delta J_{sc}^{opt}$, accounts for the change is optical absorption (or reflection) of the device caused by air annealing and can be expressed as,

$$\Delta J_{sc}^{opt} = \int_{\lambda_{ZnO}}^{\lambda_{CIGS}} q \cdot \Phi(\lambda).[A_{opt}^2(\lambda) - A_{opt}^1(\lambda)]d\lambda \quad (6.2)$$

where, superscripts '1' and '2' notify as-deposited and air-annealed devices, respectively. $A_{opt}(\lambda) (=1-R(\lambda))$ is spectral absorption and $R(\lambda)$ spectral reflection of the device. The integral limits $\lambda_{CIGS} (= \frac{hc}{E_g^{CIGS}})$ and $\lambda_{ZnO} (= \frac{hc}{E_g^{ZnO}})$, where, h is plank’s constant, c the speed of light and $E_g^{ZnO}$ and $E_g^{CIGS}$ are the band gap energies of ZnO and CIGS layers, respectively, define the usable photon energy region by the solar cell. Since, IQE accounts for collection of charge carriers generated due to absorption of the photons, the eq. 6.3 denotes the electronic component of change in $J_{sc}$,

$$\Delta J_{sc}^{elec} = \int_{\lambda_{ZnO}}^{\lambda_{CIGS}} q \cdot \Phi(\lambda).[IQE^2(\lambda) - IQE^1(\lambda)]d\lambda \quad (6.3)$$

From above mathematical analysis, the optical and electric components of $\Delta J_{sc}^{1-2}$ were calculated to be -0.48 mA.cm$^{-2}$ and 4.1 mA.cm$^{-2}$, respectively. The negative sign of optical component, $\Delta J_{sc}^{opt}$, termed as ‘optical loss’ indicated the current loss under the effect of air annealing of the solar cell. On the other hand, the air annealing of the device led to a significant increase in the short circuit current referred as ‘electronic
Chapter 6. Flash Evaporated $\text{In}_2\text{S}_3$ Buffer Layer

Gain’, $\Delta J_{\text{sc}}^{\text{elc}}$. An absolute increase in short circuit current of $\approx 7 \text{ mA.cm}^{-2}$ was measured from $j-V$ measurement of the same device. This suggests that $\approx 56\%$ of the $\Delta J_{\text{sc}}^{1-2}$ is originated from electronic component of $J_{\text{sc}}$ indicating a significant improvement in the electronic quality of the junction and hence increasing the carrier collection in the device.

6.5 Conclusion

$\text{In}_2\text{S}_3$ layers were deposited by flash evaporation technique with varying flash rates. The optical constants of layers based on Tauc-Lorentz model dielectric function were extracted from spectroscopic ellipsometry measurements. X-ray photoelectron spectroscopic investigation revealed the presence of oxygen impurity in as-deposited and air annealed layers with traces of Na inclusion in the layer grown at high flash rate. With rise in degree of crystalline order after air annealing treatment, the existence of crystalline arrangement in as-deposited layer was confirmed by Raman spectroscopic analysis. Rutherford backscattering measurements revealed the growth of chemically disordered layers at all flash rates. An analytical layer growth model has been proposed supporting the results obtained by various layer characterization techniques.

The solar cells were prepared with flash evaporated $\text{In}_2\text{S}_3$ buffer layers and their performances were compared with CdS reference cell. A significant gain in short circuit current was obtained after air annealing of the complete device at $200^\circ\text{C}$ for 20min. A maximum conversion efficiency of 12.6% was attained by a cell consisting of $\text{In}_2\text{S}_3$ buffer layer evaporated at high flash rate. The oxygen inclusion in $\text{In}_2\text{S}_3$ layer and CIGS surface type-inversion was analytically found to be primarily responsible for determining the solar cell performance. The improvement in device performance after air annealing treatment is explained by thermally enhanced Cu and oxygen diffusion from CIGS and $i$-$\text{ZnO}$ to $\text{In}_2\text{S}_3$ layer, respectively.
Chapter 7

Flexible Solar Cells with Thermally Evaporated \( \text{In}_2\text{S}_3 \) Buffer Layer

Thermally evaporated \( \text{In}_2\text{S}_3 \) buffered flexible solar cells on polyimide substrate were fabricated. The efforts were primarily focused on the improvement on the solar cell efficiency to an appreciable value. The flexible solar cell buffered with chemical bath deposited CdS layer served as reference cell offering a direct comparison on the solar cell properties of the cells with two different buffer layers. The impact of air-annealing of the complete cell and CIGS surface modification caused by introduction of an additional intermediate step of chemical treatment prior to \( \text{In}_2\text{S}_3 \) buffer deposition on the solar cell performance was analyzed.
7.1 Growth of CIGS Layer on Mo Coated Polyimide Substrate

It has been experimentally verified that the supply of Na into CIGS is essential for achieving high solar cell performance \cite{127,128}. It is believed that occupancy of Cu vacancies ($V_{Cu}$) present in CIGS by Na tends to reduces the defect states generated by In occupying vacant Cu site ($In_{Cu}$). This results in increase in p-type character of CIGS absorber. In case of conventional CIGS solar cells developed on glass substrate, the substrate acts as source of Na supply to CIGS layers. Whereas, Na free substrate needs to have an external source of Na available for CIGS layer. In the present experimental study, we started with Mo coated 12.5 $\mu$m thick polyimide substrate followed by deposition of CIGS layer at substrate temperature at 450°C using our baseline 3-stage process described in sec. \ref{sec:2.2.3} and Ref. \cite{81} and the supply of Na to CIGS was ensured by applying a post-deposition treatment (PDT) of NaF precursor compound \cite{127}. The $In_2S_3$ buffer layers of 50 nm thickness were then deposited followed by the deposition of a window bilayer of ZnO:Al/ZnO by rf-sputtering. The solar cells were completed by depositing Ni/Al metal contact grid. No anti-reflection coating was applied to any of the cells.

7.2 $In_2S_3$ Deposition on CIGS/Mo/PI Substrate

The growth of thermally evaporated $In_2S_3$ buffer layer on CIGS surface was studied by SEM technique. Figure \ref{fig:7.1} presents the SEM plan-view and cross-section micrographs of $In_2S_3$ deposited on CIGS layer. The inset in Fig. \ref{fig:7.1} shows the as-received CIGS absorber layer indicating a small microstructural contrast before and after $In_2S_3$ deposition. Notably, the presence of an intermediate layer between $In_2S_3$ buffer and CIGS absorber was observed. The EDX analysis revealed the presence of Na on the surface of bare of CIGS which originate from post-
7.2. \( \text{In}_2\text{S}_3 \) Deposition on CIGS/Mo/PI Substrate

deposition treatment with NaF precursor after CIGS growth resulting in formation of an intermediate layer of Na-compounds. However, a thorough study is needed to characterize the CIGS surface and effects of surface treatments.

Figure 7.1: SEM micrographs of \( \text{In}_2\text{S}_3/\text{CIGS/Mo/PI} \) stack with inset showing the bare CIGS surface grown on Mo/PI substrate: (a) plan-view and (b) cross-section
7.3 Solar Cell Performance

Without giving immediate attention to a detailed material analysis of detected intermediate layer of Na related compounds, our research initially focused on the development of solar cells and their performance enhancements with application of engineered processing steps. In order to achieve the target, the work was primarily focused on the solar cell performance enhancement by introducing an intermediate chemical etching step prior to In$_2$S$_3$ buffer layer deposition.

7.3.1 CIGS Surface Treatment

In order to fabricate flexible solar cell on PI substrate, In$_2$S$_3$ buffer of $\approx 30$nm was evaporated on as-received (NaF post-deposition treated) CIGS absorber. The cell performance was studied by measuring J-V characteristic of the device. The SEM investigation (Fig. 7.1b) revealed the existence of an intermediate layer between CIGS and In$_2$S$_3$ buffer. The influence of presence of intermediate layer on the solar cell properties was studied by inserting a chemical based surface treatment to CIGS layer prior to thermal evaporation of buffer layer. Table 7.1 describes the PV parameters of the solar cells with "No" CIGS surface treatment (as-received CIGS), "Water" treated CIGS and "Ammonia" etched CIGS. The as-deposited cell yielded the maximum efficiency of 4.5% which further improved to 8.2% after air annealing of the cell at 200°C for 10min. The etching of CIGS surface by NH$_3$ solution is known to remove Na from the surface making it Na-free surface and to realize that the CIGS was immersed in a NH$_4$OH solution. However, considering the undesired complete removal of Na from CIGS surface a water cleaning step was chosen to ensure that at least some amount of Na remains at the surface of CIGS absorber layer. Additionally, from point of view of industrial production of large area solar cells and modules, the water cleaning treatment can be preferred to NH$_3$ solution etching treatment. The following solutions were used for etching or cleaing CIGS surface.
7.3. Solar Cell Performance

- Water: 200ml of deionized water.
- Ammonia: 25ml of NH$_4$OH (20% vol.) mixed in 200ml of deionized water.

The etching of CIGS surface was carried out by immersing the CIGS/Mo/PI substrate for 15min in etching solution already kept at 70°C.

![Figure 7.2: The best and average PV parameters of In$_2$S$_3$ buffered solar cells with and without CIGS chemical cleaning and etching treatments. Figure also shows the PV parameters of CdS reference device. The points are connected for the sake of clarity of data.](image)

Figure 7.2 shows the PV parameters of the solar cells developed on as-received, deionized water cleaned and ammonia etched CIGS absorber layers. Apparent from Fig. 7.2, although a positive effect on CIGS chemical treatment is beneficial to achieve superior cell performance, no significant difference between cells corresponding to Water cleaned and NH$_3$ solution
Table 7.1: PV performance of the “best cells” developed on: as-received, water treated and ammonia etched CIGS absorber layers. The complete device was annealed in air at 200°C for 20min

<table>
<thead>
<tr>
<th>CIGS surface treatment</th>
<th>Cell</th>
<th>$\eta$ (%)</th>
<th>FF (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA.cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>as-dep.</td>
<td>4.5</td>
<td>39.1</td>
<td>447</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>air-annld.</td>
<td>8.2</td>
<td>45.7</td>
<td>590</td>
<td>30.3</td>
</tr>
<tr>
<td>Water</td>
<td>as-dep.</td>
<td>6.6</td>
<td>51.9</td>
<td>391</td>
<td>32.3</td>
</tr>
<tr>
<td></td>
<td>air-annld.</td>
<td>9.5</td>
<td>58.9</td>
<td>536</td>
<td>29.9</td>
</tr>
<tr>
<td>Ammonia</td>
<td>as-dep.</td>
<td>5.4</td>
<td>46.5</td>
<td>364</td>
<td>31.7</td>
</tr>
<tr>
<td></td>
<td>air-annld.</td>
<td>10.1</td>
<td>59.6</td>
<td>530</td>
<td>31.8</td>
</tr>
<tr>
<td>CdS-ref.</td>
<td></td>
<td>11.4</td>
<td>68.7</td>
<td>594</td>
<td>27.7</td>
</tr>
</tbody>
</table>

etched CIGS was observed. This indicated that CIGS surface cleaning with water brings about the same positive effects as ammonia etching step does. An insight into PV parameters of the solar cell indicated that the improvement in solar cell performance after CIGS surface etching was mainly due to a significant gain in short-circuit current. A ubiquitous positive effect of air annealing of the complete device on the solar cell performance was observed in case of flexible solar cell with thermally evaporated In$_2$S$_3$ buffer layer. As a results of CIGS surface treatment and air annealing, a high performance cell with conversion efficiency of 10.1% was realized.

7.4 Conclusion

The solar cells developed on as-received CIGS absorber layer exhibited very poor solar cell performance. The SEM study revealed the existence of a residual layer between CIGS and In$_2$S$_3$ buffer layer which was speculated to originate from post-deposition treatment of NaF precursor sequenced at the end of CIGS growth. The presence of an intermediate layer of Na compounds was found to have key role in determining the solar cell performance. A set of experiments on the study of PV perfor-
mance of solar cells consisting of CIGS: as-received, deionized water cleaned and ammonia etched, indicated the beneficial impact of CIGS surface treatment prior to In$_2$S$_3$ deposition. The CIGS surface treatment is believed to remove excess Na that is harmful for solar cell performance. A 10.1% efficient cell with In$_2$S$_3$ buffer with respect to 11.4% CdS reference cell was realized. However, a large extent of irreproducibility and inconsistency in PV performance of the solar cells was observed and more experimental investigation is required to understand the effects of various processing sequences on the solar cell performance.
Chapter 8

Conclusion and Outlook

In$_2$S$_3$ is among the forerunners of buffer layers that have potential to replace chemically deposited CdS buffer layer in CIGS solar cell technology. One of the most important characteristics of In$_2$S$_3$ buffer layer is that its properties can be tailored with the choice of its method of deposition and doping concentration. Efficiency close to that delivered by CdS buffer device has been achieved by ALD-In$_2$S$_3$/CIGS solar cell. However, in view of large area deposition and in-line deposition compatibility, PVD method has an edge over other thin film deposition techniques. The present work is devoted to vacuum based deposition of In$_2$S$_3$ buffer layer for the development of CIGS solar cell on glass and flexible substrate. Use of thermally evaporated In$_2$S$_3$ buffer layer as a substitute to chemically grown CdS buffer layer in CIGS solar cell technology is highly desired.

As a first step towards the realization of PVD-In$_2$S$_3$ buffered solar cells, the initial research was focused on the material characterization of In$_2$S$_3$ source powder used for depositing buffer layer in a vacuum chamber. A comparative study of the In$_2$S$_3$ source materials (Powder-A and Powder-B) with respect to their chemical and microstructural stability over an extended period of evaporation was performed. A significant amount of sulfur loss and microstructural inhomogeneity in the Powder-B was observed. The direct influence of differed evaporation behavior
of two source materials on the chemical composition of the deposited indium sulfide buffer layer was analyzed with the help of RBS measurements. The effect of evaporation behavior of two different In$_2$S$_3$ source materials on the solar cell performance was further studied. The superior performance of solar cell with buffer layer evaporated from Powder-B than one related to Powder-A was attributed to sulfurization of CIGS surface by Powder-B leading to higher FF and $V_{oc}$. Based on the solar cell performances, the Powder-B was selected for further study. However, more experimental study is needed to study the evaporation characteristics of two source powders and their direct impact on the buffer layer properties and the solar cell performance.

After making a choice over In$_2$S$_3$ source powders, the research was focused on the characterization of thermally evaporated In$_2$S$_3$ buffer layer. The study led to a detailed analysis of growth and properties of buffer layer. The thermal evaporation resulted in a uniform and continuous layer morphology with conformal coverage of rough CIGS layer. The optical constants of the layers were determined by Ellipsometry technique. The suitability of Forouhi-Bloomer and Tauc-Lorentz model dielectric functions has been tested on the spectroscopic ellipsometry data acquired from thermally evaporated buffer layer. The use of Tauc-Lorentz model dielectric function led to precise determination of the optical constants of In$_2$S$_3$. The as-deposited layer were detected to be amorphous and crystallized into tetragonal $\beta$-In$_2$S$_3$ phase after annealing in air at 200°C. The minor increase in band gap of the layer after air annealing at 200°C was determined. The layer was found to be sulfur deficient with overall chemical composition of In$_2$S$_{2.8}$. The effect of in-situ post-deposition annealing treatment after buffer deposition was studied and explained with the help of thermally assisted elemental interdiffusion across buffer/CIGS interface. As a result of extensive efforts of process optimization related to buffer layer deposition step, we successfully developed a 14.1% efficient cell on glass substrate.

The research was further extended to compare the properties of thermally evaporated buffer with layer grown by a non-
vacuum ultrasonic spray pyrolysis technique. The experimental study encompassed the layer growth by two modifications of USP technique namely, USP-dry and USP-wet. The USP-dry technique resulted in growth of continuous layer with granular morphology. Whereas, the USP-wet layer exhibited the formation of randomly distributed microvoids with needle-like porous microstructure of the layer. The XRD and Raman spectroscopy examination confirmed the presence of tetragonal $\beta$-In$_2$S$_3$ phase in as-deposited USP-dry layer. However, the USP-wet layer was found to be amorphous in nature. The chemical composition and presence of impurity in USP-dry layer was determined by RBS and ERDA measurements. The layer was found to be contaminated with C, Cl, N and O impurities with their concentration strongly dependent on precursor concentration and substrate temperature. Using identical CIGS absorber, the solar cells with In$_2$S$_3$ buffer layer deposited by thermal evaporation, USP-dry and USP-wet yielded conversion efficiency of 12.6%, 9.2% and 2.8%, respectively.

Our previous experimental study indicated that the thermal evaporation of In$_2$S$_3$ buffer layer is associated with loss of sulfur from the source materials resulting in growth of a non-stoichiometric layer. The problem of chemical disorder in the evaporated buffer layer was addressed by exploiting flash evaporation technique. The layers with varying flash rates were grown and their optical, structural, chemical, microstructural and growth properties were investigated in detail. The optical constants extracted using Tauc-Lorentz model were found to depend on flash rate indicating the different degree of structural disorder existing in the layer. The layers were found to be highly off-stoichiometric from In$_2$S$_3$ composition with chemical disorder increasing with rise in flash rate. Nevertheless, a control over layer composition was achievable at higher flash rate corresponding to crucible temperature $> 1050^\circ$C. With a trace amount of Na in the layer grown at high flash rate, the layers were found to be contaminated with oxygen impurity at all flash rates. The Raman spectroscopic investigation of the Flash-In$_2$S$_3$ indicated the presence of crystalline arrangements corresponding to $\beta$-In$_2$S$_3$ phase. An in-depth analysis of flash evaporated layer lead us to an important conclusion that "higher
The flash rate higher is the degree of chemical and structure disorder in the layer”. Based on the results obtained a layer growth model was proposed.

The solar cells were developed with Flash-In$_2$S$_3$ buffer layers grown at different flash rates and compared with CdS reference cell. A positive effect of air annealing of the complete device at 200°C was measured in the flash-In$_2$S$_3$ devices. The combined effect of CIGS surface type-inversion governed by thermally induced Cu diffusion from CIGS to its junction partner In$_2$S$_3$ and oxygen incorporation into chemically and structurally defective In$_2$S$_3$ buffer layer from $i$-ZnO was found to be prime reason for enhancement in the PV properties of the high rate flash-In$_2$S$_3$ device. The temperature dependent J-V measurements suggested the interface recombination being the dominant recombination mechanism in high rate flash-In$_2$S$_3$ device. A maximum conversion efficiency of 12.6% efficient was realized after air annealing of the complete cell. The experimental verification of the elemental interdiffusion across $i$-ZnO/buffer and buffer/CIGS is required in support of the results discussed above.

With an aim to transfer the know-how acquired from experiments on SLG substrate, the solar cells with In$_2$S$_3$ buffer layer were developed on the polyimide substrate. The initial attempts were primarily focused on the solar cell performance enhancement. The presence of an intermediate layer between CIGS and In$_2$S$_3$ buffer layer was observed in cross-section SEM investigation. We believe that the intermediate layer may originate from NaF post-deposition treatment to CIGS absorber layer. However, a detailed study is needed to further investigate the CIGS surface properties influenced by PDT step. The intermediate layer was found to have critical role in achieving high efficiency solar cells. The experimental evidence of adverse effect of intermediate layer was determined by introducing a CIGS surface treatment step prior to buffer layer deposition. The CIGS surface cleaning in deionized water and chemical etching by NH$_3$ solution resulted in a significant gain in $J_{sc}$. The air annealing of the complete cell at 200°C for 20min further improved the PV properties of the solar cell. We report a 10.1% efficient solar cell with thermally evaporated buffer In$_2$S$_3$ layer developed on
flexible polyimide substrate\footnote{65} which, to the best of our knowledge, is the best efficiency reported to date by any group on this kind of solar cell. It should be emphasised that further analysis and characterization of CIGS surface and optimization of buffer deposition parameters accordingly, are needed to gain a clear understanding of process governing the device performance.
Acknowledgment

I am highly grateful to Prof. Dr. Danilo Pescia for accepting me as a doctoral candidate under his supervision.
I am highly grateful to Prof. Dr. Ayaodhya Nath Tiwari for allowing me to perform my doctoral research work under his supervisor and guidance. Due to Prof. Tiwari’s incessant inspiration, I have had ample of opportunities to hone my research skills. His constant inflow of encouragement to my work enabled me to meet the set goals.
I express my sincere gratitude to Dr. Friedrich Kessler for being external co-examiner to my doctoral work and giving valuable inputs and recommendations. I would like to thank Dr. Hans Zogg for his ready support and guidance in academic and administrative affairs.
My sincere words of thanks to Dr. Marc Kaelin who has been my mentor for first year of research work. Thank you very much Marc for explaining me the operations of various machines and helping me adapt to new environment and guiding me at various stages.
I thankfully acknowledge the help of those who directly and indirectly contributed to this work.
I would like to thank Dr. Martin Arnold for his nice company during lunch at Migros restaurant, helping me understand some of the aspects of the Swiss culture and giving useful career oriented tips. Thanks to David Brêmaud for fruitful discussions and giving CIGS absorbers and Dr. Dominik Rudmann for explaining BAK-2. Thanks to my colleague Adrian Chiria for giving N number of absorbers, discussions, very funny and cool
jokes, letting me steal his chocolates several times and for endless support he offered, Dr. Dominik Güttler for RBS measurements, providing CIGS samples, helping me learn \LaTeX and for giving useful tips and for being wonderful colleague sitting left to me, Julian Perrenoud for his significant contribution to Flash Evaporation chamber and help in all possible ways, Stephan Bücheler for numerous kinds of support, Sigi for providing most reliable information and helping me understand German and sometimes French too. Ferdinand Felder for IT support at Technopark and of course the movie sessions, Jachen for helping me reinstall machines at EMPA, Oliver Meier and Ruedi Flück for making sample holders and other stuff. Mohammad Rahim for sharing light jokes and giving valuable tips about ETHZ's administrative matters, Mattias Fill for AFM measurements, Alexender Uhl for being nice colleague and offering me some cool candies, Dr. Yaroslav Romanyuk for his valuable inputs at group presentations and administrative support, Fabian Pianezzi for electronic characterization of solar cells. Thanks to Patric Blösch for IT support at EMPA and helping during machine installation, Dr. Shiro Nishiwaki for fruitful discussions and help during machine installation at EMPA. Chantal Hänni for her ready support with various administrative matters, Caro lin Fella for small chit-chats, Lukas Kranz for cool talks. I would also like to acknowledge following people for their help and contribution: Kaia Ernits, Maxim Ganchev, Dr. Osvaldo Moreira, Dario Corica, Christopher Hibberd, Debjit Datta and people at EMPA and ETH Zurich Workshops. I am highly thankful to Swiss National Science Foundation for providing me financial assistance.

In the end, I would like to dedicate this thesis to my parents and my wife Kanu Verma whose endless support throughout this work helped me reach this height in my career.
## Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AM1.5</td>
<td>Air mass 1.5</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>CIGS</td>
<td>Cu(In,Ga)Se$_2$</td>
</tr>
<tr>
<td>CO</td>
<td>Classical-Oscillator</td>
</tr>
<tr>
<td>dc</td>
<td>Direct current</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
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<tr>
<td>FB</td>
<td>Forouhi-Bloomer</td>
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<tr>
<td>FE</td>
<td>Flash evaporation</td>
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<tr>
<td>IQE</td>
<td>Internal quantum efficiency</td>
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<tr>
<td>$j$-$V$</td>
<td>Current density-voltage</td>
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<tr>
<td>PDT</td>
<td>Post-deposition treatment</td>
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<tr>
<td>PI</td>
<td>Polyimide</td>
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<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford back scattering</td>
</tr>
<tr>
<td>rf</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>SLG</td>
<td>Soda-lime-glass</td>
</tr>
<tr>
<td>TE</td>
<td>Thermal evaporation</td>
</tr>
<tr>
<td>TL</td>
<td>Tauc-Lorentz</td>
</tr>
<tr>
<td>USP</td>
<td>Ultrasonic spray pyrolysis</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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Abbreviations and Symbols

$T_{\text{annl.}}$  
Annealing temperature

$J_{\text{sc}}$  
Short circuit current

$V_{\text{oc}}$  
Open circuit voltage

FF  
Fill factor

$\eta$  
Efficiency

$\phi^p$  
Barrier height for holes

$\phi^n_b$  
Barrier height for electrons

$E_c$  
Conduction band

$E_v$  
Valance band

$E_f$  
Fermi level

$E_g$  
Band gap

$\alpha$  
Absorption coefficient

$E$  
photon energy

$T$  
Optical transmission

$R$  
Optical reflection

$A_{\text{opt}}$  
Optical absorption

$n$  
Refractive index

$k$  
Extinction coefficient

$\chi$  
Mean square error

$M$  
Number of experimental data points

$P$  
Number of model parameters

$I_s(\lambda)$ and $I_c(\lambda)$  
Ellipsometric raw data

$\delta(t)$  
Phase shift

$I_0(\lambda)$  
angle

$A_n$, $B_n$ and $C_n$  
Fitting parameters

$\epsilon_\infty$  
High frequency dielectric constant

$\epsilon$  
Complex dielectric function

$A$  
Amplitude

$E_0$  
Peak transition energy

$C$  
Broadening

$p$  
Principle value of integration

$E_{gFB}$  
Band gap derived from Forouhi-Bloomer model

$E_{gTL}$  
Band gap derived from Tauc-Lorentz model

$q$  
Elementary charge

$\Phi(\lambda)$  
Incident photon flux density

$\lambda$  
Wavelength
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