In$_2$S$_3$ alternative buffer layers for Cu(In,Ga)Se$_2$ solar cells deposited by RF magnetron sputtering

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Abstract

A thin semiconducting material of thickness \(\sim 50\) nm known as a buffer layer is the key for obtaining high efficiencies in Cu(In,Ga)Se\(_2\) (CIGSe) thin film solar cells. A thin buffer layer improves the photo-response of a solar cell which significantly enhances the efficiency. Cadmium sulfide (CdS) buffer layer deposited by chemical bath deposition (CBD) is used commercially for large-area high-efficiency CIGSe solar cells. However, toxicity of Cadmium (Cd) and the CBD deposition process makes CdS unsuitable for large-scale production. So-called ‘Cd-free’ or ‘alternative’ buffer layers to CdS, deposited by vacuum-based methods are extensively studied by the photovoltaic (PV) community. Therefore, this thesis primarily explores the potential of In\(_2\)S\(_3\) as a performant buffer layer material when deposited by RF magnetron sputtering.

RF magnetron sputtered In\(_2\)S\(_3\) buffer layers were deposited by two approaches: (i) at “low sputter pressure” using Ar-ion sputtering and (ii) at “higher sputter pressure” using H\(_2\)S/Ar reactive sputtering. The Ar-ion sputtered In\(_2\)S\(_3\) buffer layers reached photovoltaic conversion efficiencies of 13.6% with fill factor (FF) of 53%. However, absorber surface damage and non-uniform buffer layer thickness were the primary limitations impeding cell efficiency. The extent of induced sputter damage and annealing-induced intermixing at the In\(_2\)S\(_3\)/CIGSe heterointerface was estimated using atom probe tomography.

In\(_2\)S\(_3\) buffer layers deposited by H\(_2\)S/Ar reactive sputtering at HSP had lower absorber surface damage. Moreover, crystalline In\(_2\)S\(_3\) thin films with smaller average crystallite size were obtained by reactive sputtering as compared to the amorphous In\(_2\)S\(_3\) thin films by Ar-ion sputtering. This improved optoelectronic performance with lower interfacial recombination and higher photon collection, giving a higher fill factor of 65% and a normalized efficiency of 16.33%.
Elemental intermixing at the In$_2$S$_3$/CIGSe heterointerface for different annealing temperatures was estimated using atom probe tomography. The effect of Cu-self doping of In$_2$S$_3$ from CIGSe, Cu depletion from CIGSe surface and the segregation of Na at In$_2$S$_3$/CIGSe heterointerface suppress the detrimental defect sites at the interface. The passivation of the defect sites results in an effective charge carrier collection, lowered recombination, and thus better cell performance.

With this work, the deposition of In$_2$S$_3$ as a buffer layer material by rf magnetron sputtering is optimized to obtain high-efficiency buffer layer material for CIGSe solar cells. Additionally, a detailed study of the chemistry of buried In$_2$S$_3$/CIGSe heterointerface and its effect (beneficial/detrimental) on electrical properties and cell performance is also presented.
Zusammenfassung


In$_2$S$_3$-Pufferschichten, die durch reaktives H$_2$S/Ar-Sputtern bei HSP abgeschieden wurden, wiesen eine geringere Beschädigung der Absorberoberfläche auf.
Darüber hinaus wurden kristalline In$_2$S$_3$-Dünnfilme mit kleinerer mittlerer Kristallitgröße durch reaktives Sputtern im Vergleich zu den amorphen In$_2$S$_3$-Dünnfilmen durch Ar-Ionen-Sputtern erhalten. Diese verbesserte optoelektronische Leistung mit geringerer Grenzflächenrekombination und höherer Photonensammlung ergibt einen höheren Füllfaktor von 65% und eine normalisierte Effizienz von 16,33%.


Mit dieser Arbeit wird die Abscheidung von In$_2$S$_3$ als Pufferschichtmaterial durch HF-Magnetron-Sputtern optimiert, um hocheffizientes Pufferschichtmaterial für CIGSe-Solarzellen zu erhalten. Darüber hinaus wird auch eine detaillierte Studie der Chemie der vergrabenen In$_2$S$_3$/CIGSe-Heterogrenzfläche und ihrer Wirkung (vorteilhaft/schädlich) auf die elektrischen Eigenschaften und die Zellleistung vorgestellt.
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>APT</td>
<td>Atom probe tomography</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>AZO</td>
<td>Aluminum doped zinc oxide</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>CIGSe</td>
<td>Copper Indium Gallium Diselenide Cu(In,Ga)Se₂ solar cell</td>
</tr>
<tr>
<td>EBIC</td>
<td>electron-beam-induced current</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam lithography</td>
</tr>
<tr>
<td>GIXRD</td>
<td>Grazing incidence x-ray diffraction</td>
</tr>
<tr>
<td>HAADF</td>
<td>high-angle annular dark field</td>
</tr>
<tr>
<td>HSP</td>
<td>High sputter pressure</td>
</tr>
<tr>
<td>I-V</td>
<td>Current - voltage</td>
</tr>
<tr>
<td>J&lt;sub&gt;sc&lt;/sub&gt;</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>LSP</td>
<td>Low sputter pressure</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>RF</td>
<td>Radiofrequency</td>
</tr>
<tr>
<td>SCCM</td>
<td>standard cubic centimeter per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>UV-VIS</td>
<td>Ultraviolet - visible spectroscopy</td>
</tr>
<tr>
<td>V&lt;sub&gt;oc&lt;/sub&gt;</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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A. SPUTTER DEPOSITION PARAMETERS OF Zn BASED BUFFER LAYERS 150
1. Introduction

Energy is the capacity of a system to perform work. Energy is used for heating air and water, transportation, to produce food and products, to illuminate houses and streets, to communicate, use computer and the internet. Energy can be in the form of thermal, chemical, electrical, nuclear, gravitational, or radiant energy. The total amount of energy is always conserved. As human beings, we harvest one of these energies to perform work. However, with growing world population and higher living standards, the demand for energy is constantly increasing. To meet these increasing demands, conventional energy sources like coal and gas are consumed at higher rates than generated. Combustion of fossil fuels generates greenhouse gases like CO₂, which is responsible for global warming and climate change. Therefore, alternative clean energy sources like solar and wind energy are required to meet the needs of society.

Solar energy can be directly harvested to generate energy in the form of electricity that can later be converted into other forms of energy. The mechanism of conversion of solar energy to electricity is known as photovoltaic effect. Photovoltaic (PV) energy conversion devices are known as solar cells. Solar cells are commonly used to power parking meters, streetlights, and as rooftop modules in day-to-day life. Large scale solar power plants can provide clean electricity for a community. Solar power plants are comparatively simple, fast, and low carbon footprint electricity generation technology as opposed to Hydro, Nuclear and Coal/Gas fired power plants.

Key challenge for PV community is to make solar cell production cheaper since conventional crystalline Si solar cells are expensive. One approach to reduce production cost is to use thin film solar cells, which has high efficiency and low material wastage.
Thin film solar cells have active layers of a thickness of a few microns that generate electric current upon illumination. Currently, amorphous Silicon (a-Si), Cu(In,Ga)Se₂ (Copper Indium Gallium di-Selenide/CIGSe), CdTe (Cadmium Telluride) and Perovskite solar cells (PSCs) are a few examples. From these materials, CIGSe is the most important thin film solar cell material due to high efficiency (23.35% [1]), low production cost and long operational lifetime (20+ years [2]). Lightweight and flexibility makes CIGSe solar cells technically advantageous over conventional bulk silicon solar cells. The heterostructure of CIGSe solar cells utilize a so-called ‘buffer layer’ to improve band alignment and interface quality between absorber and front contact.

Chemical-bath deposited (CBD) CdS is currently used as a standard buffer layer in commercial setups due to advantages like high efficiency, good lattice match and stability. However, large-scale use of CBD-CdS as a buffer layer is undesirable since: (a) CdS is classified as a toxic material in European union [3] which can affect future large-scale investments in this technique; (b) wet-chemical based deposition step of CdS is incompatible with an otherwise fully automated dry-vacuum based deposition of CIGSe solar cells; and (c) treatment and safe disposal of Cd-containing massive chemical waste. Additionally, low bandgap of CdS (2.4 – 2.5 eV) results in absorption losses in the energetic blue region of the solar spectrum. This makes CdS unfavorable environmentally and technologically as a buffer layer material. Therefore, an alternative buffer layer material with better optoelectronic properties is needed to replace CdS. However, Cd-free alternative buffer layers for CIGSe solar cells must have the efficiency and reliability of CBD-CdS, which is a great challenge.

Sputtered In₂S₃ buffer layer is a suitable replacement to CBD-CdS. The non-toxic nature and wide bandgap of In₂S₃ is an advantage over CdS buffer layer. Additionally, rf magnetron sputtering process is more relevant for large scale manufacturing setups as compared to wet-chemical bath deposition. Previous works [4, 5] form basis of the current work providing proof of concept for sputter deposited In₂S₃ buffer layers.
However, an extensive study on In$_2$S$_3$ as a buffer layer material and the effect on sputter deposition on the heterointerface has not been conducted before.

The primary aim of this thesis is to deposit rf magnetron sputtered In$_2$S$_3$ buffer layers on CIGSe absorber layers to get high efficiency CIGSe solar cells. Stoichiometry control, conformal deposition and sputter damage of interface are known problems with the sputter deposited In$_2$S$_3$. Sputter-damage creates crystallographic and electrically active defects in the hetero-interface region. These defect states trap (recombine) the photo-generated charge carriers resulting in degraded cell performance. For high efficiency cells interfacial recombination must be minimized by optimizing the sputter deposition conditions.

Therefore, the objective of this thesis is achieved stepwise by: (1) Optimizing the sputter deposition conditions of In$_2$S$_3$ thin films for deposition as buffer layers. (2) Deposition of n-type In$_2$S$_3$ buffer layers on p-type CIGSe solar cells and investigating the effect of sputter damage at the interface on electrical performance of the cell and (3) Controlling the stoichiometry and the sputter deposition conditions to minimize sputter damages to the pn-junction interface.

A very important aspect to achieve the aim of this thesis is to study the chemical intermixing at the In$_2$S$_3$/CIGSe heterointerface and the corresponding electrical performance. Three-dimensional elemental map by atom probe tomography (APT) in combination with electrical performance of the cell is used to understand the effect of chemical intermixing at the interface. This information is used to minimize/eliminate the sputter damages induced on CIGSe surface by In$_2$S$_3$ sputter deposition. The result is high efficiency In$_2$S$_3$ based buffer layers that are uniformly deposited on CIGSe absorbers with high efficiency of 13.84% (16.33% normalized). This is the highest efficiency for sputtered In$_2$S$_3$ buffer layers in literature so far.

This thesis is structured in the following way:
Chapter 2 describes the structure and operation of CIGSe solar cells and summarizes the currently used alternative buffer layers.

Chapter 3 first describes materials and methods used for deposition of In$_2$S$_3$ buffer layers. Second, it describes the characterization techniques used for this work.

Chapter 4 describes the preliminary results obtained with Ar-ion sputter deposition of In$_2$S$_3$ on CIGSe absorbers and analyzes the sputter damage caused, and remedies to improve interface quality.

Chapter 5 uses the optimized sputter parameters and reactive Ar/H$_2$S sputtering to get high quality In$_2$S$_3$/CIGSe heterointerface. Effect of elemental redistribution across the buffer-absorber interface before and after annealing on cell performance is studied using several techniques.

Chapter 6 presents the summary and conclusion of important results from this study and discusses the outlook for further improvisation of current work.
2. Cu(In,Ga)Se$_2$ solar cell

2.1 Cu(In,Ga)Se$_2$ device structure

2.1.1 CIGSe cell configuration

CIGSe solar cells are deposited primarily in two configurations, namely (a) substrate and (b) superstrate. The two configurations have different layers stacked as follows from top to bottom:

Substrate: Ni-Al/ZnO:Al/i-ZnO/buffer/CIGSe/Mo/SLG

Superstrate: SLG/Mo/CIGSe/buffer/i-ZnO/ZnO:Al/Ni-Al

Fig. 2.1.1: Structure of a complete Cu(In,Ga)Se$_2$ solar cell in substrate configuration. For superstrate configuration, the layers are flipped with absorber layer on top and AZO layer deposition at bottom.
For this work, only substrate configuration was used to deposit In$_2$S$_3$ and Zn(O,S) buffer layers using rf magnetron sputtering and chemical bath deposition. In substrate configuration, buffer layers are deposited on top of the absorber layer, which makes study on buffer layers easier compared to superstrate configuration. Since deposition of high-quality absorber layers is a complicated process, these layers were bought from project partners with a high level of expertise with the technique.

### 2.1.2 Substrate and Mo-back contact

Typically, CIGSe absorbers are deposited on a 3 mm soda lime glass (SLG) that provides support and rigidity to the whole device. SLG acts as a source of Na atoms that diffuse to CIGSe absorber and segregate at grain boundaries [6] which is beneficial to the cell efficiency. However, sometimes CIGSe solar cells are deposited on flexible polyimide and steel substrates, which are much lighter and economical as compared to conventional glass substrates.

The SLG is coated with 600 – 800 nm polycrystalline molybdenum using dc-magnetron sputtering. The role of Mo-layer is to block migration of impurities from substrate. This layer is a low resistance back contact for the device. When CIGSe is deposited at high temperatures on the Mo, around 100 nm thin layer of MoSe$_2$ is formed at Mo/CIGSe interface [7]. MoSe$_2$ layer acts as a quasi-ohmic contact to Mo/CIGSe interface, which is otherwise a Schottky rectifier. This layer resists formation of n-type Ga$_2$O$_3$ at the Mo-CIGSe interface, which is highly resistive. Additionally, Mo reflects any transmitted photons which are re-absorbed in CIGSe layer. Ideally, Mo-coated SLG is transferred to the CIGSe deposition chamber in vacuum to prevent the oxidation of Mo. This results in lower conductivity and low fill factor which is detrimental for the device efficiency [8]. The grain size, adhesion, and conductivity of the Mo layer depend on the deposition parameters. An ideal Mo-layer has good adhesion to SLG, high conductivity and large grains which ensures low back contact recombination, high fill factor and larger CIGSe grains [9].
Since these properties are complimentary, a Mo-bilayer is deposited to have a suitable compromise between adhesion, conductivity, and grain size.

### 2.1.3 Cu(In,Ga)Se$_2$ absorber layer

Cu(In,Ga)Se$_2$ is I-III-VI$_2$ semiconductor, which crystallizes in the chalcopyrite structure. The structure corresponds to two stacked zinc blende unit cells with a face-centered tetragonal unit cell, where there is an ordered replacement of Zn atoms by Cu and (In/Ga) atoms. The structure resembles a modified diamond structure where every carbon atom is bound to four carbon atoms in a tetrahedral configuration. Likewise, Se atom is tetrahedrally bonded with two Cu or (In/Ga) atoms, and every metal atom has four Se atoms as the nearest neighbor.

![Unit cell of Cu(In,Ga)Se$_2$ chalcopyrite structure visualized using [10].](image)

CIGSe absorber layer is usually co-deposited by three-stage-process involving controlled fluxes of Cu, In and Ga in the presence of Se atmosphere. The elements are co-evaporated by heating in Knudsen’s effusion cells in high vacuum of the range of $10^{-8}$ mbar. Total deposition time is nearly 60 minutes at a substrate temperature ranging from 350 to 550 °C [11]. In the first stage, In-Ga-Se is deposited directly on Mo layer at around 350 °C giving (In,Ga)$_2$Se$_3$ precursor layer. The substrate
temperature is then raised to 550 °C, followed by influx of Cu and Se. Cu composition at the end of stage 2 is $1.2 < \text{Cu/(In+Ga)} < 1.1$ which makes the Cu(In,Ga)Se$_2$ films Cu-rich. In the third stage or Cu-poor stage, In-Ga-Se is deposited again to get the desired Cu(In,Ga)Se$_2$ composition. The latter two stages are done in a temperature range of 500–550 °C.

Typically, during the growth of Cu(In,Ga)Se$_2$ absorber layers, the second stage ends with an overall Cu-rich stoichiometry of the absorber. This is a key step for absorber growth process which promotes grain growth, recrystallization, and interdiffusion of elements. To achieve Cu-rich stoichiometry, only Cu and Se elemental fluxes are used during growth, which results in formation of a bi-phase system with Cu(In,Ga)Se$_2$ and Cu$_x$Se phases. Cu$_x$Se forms a quasi-solid-liquid type surface layer on stoichiometric Cu(In,Ga)Se$_2$ grains nuclei, allowing In and Ga to diffuse inside promoting grain growth. Thus, the number of grain boundary decreases, and grain size increases. An overall Cu poor stoichiometry is required for high-efficiency CIGSe absorbers. To achieve this, Cu flux is stopped at the end of stage II and In and Ga are evaporated onto the absorber. Se evaporation is kept constant throughout the deposition to avoid formation of Selenium vacancies (V$_{\text{Se}^{2+}}$) donor defects. Low formation energy of Cu vacancies (V$_{\text{Cu}^+}$) is the origin of p-type conductivity of CIGSe.

Ga composition is precisely controlled since bandgap of Cu(In$_{1-x}$Ga$_x$)Se$_2$ ranges from 1.0 eV to 1.67 eV from $x=0$ to $x=1$ [8]. For the absorbers used in this work, Ga/III=0.3 is used, which gives an absorber bandgap nearly 1.15 eV. Traditionally, Ga concentration is kept constant throughout the absorber thickness. But recent studies [13] show that graded Gallium content gives better cell performances mainly due to improvement of open circuit voltage ($V_{\text{OC}}$) and Fill factor (FF), ($V_{\text{OC}}$ and FF defined in section 3.6.2). Ga grading can be achieved by controlling Ga flux rate from effusion cells during CIGSe deposition. In a graded absorber, Ga content is kept higher at the top surface, lower in the intermediate region and gradually increasing towards Mo-back contact. This way, a graded bandgap can be achieved.
by shifting the conduction band position. With a graded absorber bandgap, incident photons are absorbed and collected efficiently in the middle region while penetrating through the absorber thickness. The recombination current is lowered by a higher bandgap at interfaces, increasing the $V_{OC}$. Higher Ga content towards back contact generates a back surface field [14] which acts as an electron reflector, effectively suppressing back-contact recombination with holes. Besides improved $V_{OC}$, higher Ga content at back contact improves adhesion of absorber to Mo. This prevents absorber delamination which improves cell stability and lifetime.

**Role of Na**

CIGSe absorbers were traditionally deposited on high-quality alkali-free substrates. Accidental deposition of CIGSe on SLG gave evidence of the role of Na in high-efficiency CIGSe solar cells [15]. For CIGSe devices that are deposited on SLG, a small amount of Alkali (Na and K) diffuses from SLG to CIGSe grain interiors or grain boundaries. Presence of Na during absorber growth at temperatures exceeding 500 °C led to larger grain size (from 0.3µm to 1µm) [16] and an improved p-type doping behavior [12]. It is still unclear whether Na effect is beneficial due to improved growth conditions or improved p-type behavior of the absorber. Several reports [17-19] suggest that Na modifies the charge carrier concentration by diffusing into the CIGSe grain interiors. The improvement in p-type behavior is also achieved by passivation of donor defects and trap states deep within the band structure [20, 21].

Density-functional theory [22, 23] suggests that enthalpy of formation of copper vacancy ($V_{Cu}$) is low, and In can form antisites defect ($\text{In}_{Cu}^{2+}$) easily which are detrimental to charge conductivity. $\text{In}_{Cu}^{2+}$ creates a barrier for charge carriers (holes) through reduced density of states (DOS) at valance band maximum. Na competes with In to occupy these defects and forms $\text{Na}_{In_{Cu}}$ instead [24]. Suppression of $\text{In}_{Cu}^{2+}$ antisites defects gives an enhanced charge carrier (hole) density leading to an increased $V_{OC}$ and FF.
Na segregation at CIGSe grain boundaries and its effect on the electronic properties of the absorber is not yet fully understood. A few reports [25, 26] suggest that Na segregation at Cu-poor grain boundaries in CIGSe is favorable for movement of photo-generated charge carriers. The diffusion length and lifetime of minority charge carriers in CIGSe absorber is improved which results in lower recombination and higher efficiency. Typically, a small amount of Na (0.1 at.%) doping in Cu(In,Ga)Se\textsubscript{2} absorbers is sufficient to obtain high-efficiency solar cells [15]. To have better control on alkali diffusion from SLG, recently [27] a SiO\textsubscript{2} barrier layer has been inserted between SLG and Mo. This way, Na can be introduced in CIGSe by post-deposition treatment [19]. Alternatively, a thin layer of NaF, Na\textsubscript{2}S or Na\textsubscript{2}Se is deposited on Mo back contact as a source of Na in CIGSe. For alkali-fluoride (KF, RbF) treated CIGSe solar cells [28, 29], the heavier alkali displaces the lighter Na from grain boundaries. Na diffuses to grain interiors occupying Cu vacancies which results in passivation of charged defects [30]. The passivation effect results in reduction of charge defects in the absorber. Contrarily, it has also been reported [31] that the passivation of Na has no effect on the recombination behavior of CIGSe solar cells.

2.1.4 The buffer and window layer stack

A pn-Junction is formed when an n-type layer is deposited on a p-type CIGSe absorber. N-type layer of CIGSe solar cells is typically formed of three layers: the buffer layer, intrinsic ZnO (i-ZnO), and heavily n-doped Al\textsubscript{2}O\textsubscript{3}/ZnO (AZO). These layers are collectively known as window layers.

Selection criteria for buffer layer:

Primary role of the n-type buffer layer is to minimize interfacial recombination of photo-generated electron-hole (e-h) pairs that are generated in space charged region of the absorber. There are several empirical ways to achieve this:
a. Buffer layer bandgap ($E_g$): Bandgap of n-type buffer layer should be sufficiently high, so all incident photons are transmitted to p-type absorber. Higher buffer layer bandgap transmits more photons to absorber layer, generating more e-h pairs, increasing the short circuit current density $J_{SC}$.

b. Lattice match: Buffer layer should have a good match with the lattice plane (112) of CIGSe to minimize interfacial defect (crystallographic and electrically active) states. A large value of lattice mismatch can lead to heavy recombination losses at the pn-Junction interface.

c. Conduction band alignment and Fermi level pinning: Buffer layer bandgap must be tuned to get a favorable conduction band alignment between the CIGSe absorber, buffer, and i-ZnO layer. Fermi level pinning close to the conduction band can generate high enough built-in potential, which may act as a barrier for recombination of holes at junction interface. This can be achieved by heavy doping of the buffer layer.

d. Environmental sustainability: Using Cd-free materials as buffer layer to eliminate Cd-containing compounds for a sustainable environment. The toxicity of Cadmium is a concern and recycling large scale Cd containing waste from solar panels can be a problem during the deposition process, or at the end-of-life of the solar panels.

e. Technological feasibility: Buffer layer deposition should be scalable, ideally, a dry vacuum-based method is preferred.

f. Chemical and thermal stability: Buffer layer must be chemically and thermally inert against elemental diffusivity which can affect cell performance in long run.

g. Conductivity: Buffer layer should have good conductivity to have lower overall series resistance of the cell.

**CdS buffer layer**

Chemically deposited CdS buffer layer with a bandgap of 2.4 eV is so far the best buffer layer material with highest efficiency over 22.6% [32, 33] for CIGSe. One big
advantage of chemically deposited CdS is that CIGSe absorber surface is etched with ammonia during CdS deposition. Second advantage is that there is a pseudo-epitaxial growth between CIGSe (112) and CdS (111) crystal orientation [34]. This gives a high-quality pn-Junction interface with minimal electrically active defect states that act as recombination centers. Apart from good lattice matching, Cd and S atoms favorably alter the surface and bulk chemistry of CIGSe. S atoms passivate the surface defect states, whereas Cd atoms diffuse to CIGSe bulk and aid in defect passivation [35] improving the device performance.

CdS is currently the preferred buffer layer material to produce high-performance large area CIGSe solar cells. However, there are serious environmental concerns on commercial use of CdS buffer layer, so the PV community is trying to replace CdS with alternative buffer layer materials like In$_2$S$_3$, Zn(O,S) and Zn (Mg, O). The topic of alternative buffer layers will be presented in section 2.2.

i-ZnO and AZO window layer

During ’80s and ’90s when CIGSe technology was still evolving, a thick CdS (few µm thick) was deposited as a standalone window layer. However, because of low bandgap and poor transmittances, $V_{OC}$ and FF were low. Some research groups were depositing intrinsic ZnO directly on CIGSe for use as complete devices. Later, these two strategies were combined and a thin CdS buffer was deposited before deposition of an i-ZnO layer.

High-efficiency cells are obtained on annealing cells in temperature range of 180 – 220 °C. Cu diffuses easily into buffer and lowers electrical resistivity of the layer. This may induce a current leakage or shunting of cells, which is highly detrimental for cell performance. To block any shunting leaks, a thin intrinsic layer with high transparency and high resistivity like undoped ZnO is deposited on buffer layer. This layer is referred to as high resistance window layer. The i-ZnO layer limits the electrical losses and acts as a potential barrier between conductive CIGSe grain boundaries and n-type Al-doped ZnO layer (AZO) (to be discussed next).
Suppressed shunting paths improves fill factor, and overall performance of the cell. i-ZnO layer also covers inhomogeneities of the CdS layer and gives a favorable band alignment with wide bandgap AZO layer. Typically, this layer has a resistivity of $>10^5 \Omega/\square$.

Al-doped ZnO layer (AZO) is deposited on i-ZnO layer with a thickness of nearly 250-400 nm. AZO is commonly known as a transparent conductive oxide (TCO) layer. TCO’s have high transmittance in a broad spectral range, good electrical conductivity, and bandgap of nearly 3.9 eV. Conductivity depends on density of free charge carriers and mobility. To have a sufficiently high density of free charge carriers at room temperature, AZO layer is highly n-doped ($\sim 10^{20} \text{ cm}^{-3}$), typically from 1% to 3% wt.% Al$_2$O$_3$ in ZnO. With higher doping levels, a higher number of free electrons can be available. But according to Drude model of electrical conduction [36] with a higher density of free charge carriers, transmittance of the material is reduced, especially at longer wavelengths. Thus, there is typically a trade-off in AZO layer properties between high conductivity and good transmittance. Ideally, AZO layer should have high mobility and low free charge carrier density. Thicker AZO layer will have higher conductivity and low series resistance and high fill factor. But due to lower transmittance, there will be losses in $J_{SC}$. A thinner layer will have high transmittance but may not be sufficiently conductive.

Typically, for AZO layers in CIGSe, Al$_2$O$_3$ dopant concentration under 2 wt.% is used. Heavier doping concentration reduces transmission in longer wavelength region ($>1000 \text{ nm}$) [37] where CIGSe still absorbs (bandgap < 1.24 eV). This results in a loss in quantum efficiency in longer wavelength region and thus reduced cell performance.

### 2.1.5 Ni/Al metal grid

A metallic grid, known as front metal contact, is evaporated on AZO layer to draw current from the cell, as depicted in Fig. 2.1.1. AZO is highly conductive, but
to improve the current collection, a Ni/Al contact is deposited using e-beam deposition. A laser cut shadow mask with an individual cell of size $5 \times 10$ mm (area $0.5 \text{ cm}^2$) is placed on the cell. The shadow mask and the cell are then placed in an e-beam deposition chamber followed by deposition of 10-20 nm Ni and 1.5-1.7 µm Al.

### 2.2 Role of Alternative buffer layers

In chapter 1, we discussed the need for an alternative buffer layer to replace CdS as a buffer layer material because of the technological and environmental concerns associated with CdS. Use of toxic and hazardous heavy metal like Cadmium on an industrial scale is not suitable since Cd-ion containing waste needs to be decontaminated and recycled before releasing. Additionally, chemical bath deposition technique is not industrially friendly for up-scaling. CdS have a relatively low bandgap of 2.4 eV which limits absorption of high energy incident photons with wavelength under 520 nm. This makes the replacement of CdS with an alternative buffer layer material necessary. To replace CdS, there are buffer layer materials which meet the selection criteria discussed in Section 2.1.4. Extensive research on alternative buffer layers like In$_2$S$_3$, Zn(O,S) and (Zn,Mg)O is ongoing. High efficiencies obtained in these studies (Table 2-1) prove that alternative buffer layer materials can indeed replace chemically deposited (CBD) CdS. Dry vacuum-based methods which are commercially used in order of preference are Thermal/e-beam evaporation (PVD), RF magnetron sputtering and atomic layer deposition (ALD). Highest efficiency of 22.8% (in-house measurements) and 22.0% (Fraunhofer ISE certified) [38] has been obtained using CBD-Zn(O,S) based buffer layer on a 0.5 cm$^2$ cell. In$_2$S$_3$ has reached a high efficiency of 17.93% [39] on large 30×30 cm$^2$ module deposited by PVD technique.
Table 2-1: Best performing alternative buffer layer materials for Cu(In,Ga)Se₂ solar cells compared with CBD-CdS.

<table>
<thead>
<tr>
<th>Buffer layer</th>
<th>Dep. Method</th>
<th>Efficiency</th>
<th>Cell area</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>CBD</td>
<td>22.6</td>
<td>0.5 cm²</td>
<td>[40]</td>
</tr>
<tr>
<td>Zn(O,S)</td>
<td>CBD</td>
<td>22.0</td>
<td>0.5 cm²</td>
<td>[41]</td>
</tr>
<tr>
<td>Zn(O,S)/ZnMgO</td>
<td>CBD/ALD</td>
<td>23.3</td>
<td>1 cm²</td>
<td>[1]</td>
</tr>
<tr>
<td>Zn(O,S)</td>
<td>Sputtering</td>
<td>18.3</td>
<td>0.49 cm²</td>
<td>[42]</td>
</tr>
<tr>
<td>Zn(O,S)</td>
<td>ALD</td>
<td>19.8</td>
<td>0.52 cm²</td>
<td>[43]</td>
</tr>
<tr>
<td>(Zn,Mg)O</td>
<td>ALD</td>
<td>18.1</td>
<td>0.5 cm²</td>
<td>[44]</td>
</tr>
<tr>
<td>InₓSᵧ</td>
<td>PVD</td>
<td>18.2</td>
<td>0.5 cm²</td>
<td>[45]</td>
</tr>
<tr>
<td>In₂S₃</td>
<td>Sputtering</td>
<td>13.3</td>
<td>0.5 cm²</td>
<td>[5]</td>
</tr>
<tr>
<td>CdS</td>
<td>CBD</td>
<td>18.7</td>
<td>-</td>
<td>[46]</td>
</tr>
<tr>
<td>Zn(O,S)</td>
<td>CBD</td>
<td>19.6</td>
<td>671 cm²</td>
<td>[47]</td>
</tr>
<tr>
<td>In₂S₃</td>
<td>PVD</td>
<td>17.9</td>
<td>900 cm²</td>
<td>[39]</td>
</tr>
<tr>
<td>In₂S₃</td>
<td>Sputtering</td>
<td>13.84 (16.33*)</td>
<td>0.5 cm²</td>
<td>This work</td>
</tr>
<tr>
<td>Zn(O,S)</td>
<td>CBD</td>
<td>14.05</td>
<td>0.5 cm²</td>
<td>This work#</td>
</tr>
<tr>
<td>ZnS/In₂S₃</td>
<td>Sputtering</td>
<td>12.14</td>
<td>0.5 cm²</td>
<td>This work#</td>
</tr>
</tbody>
</table>

* Normalized with a freshly deposited batch of CIGSe absorber efficiency
# Deposition details presented in Appendix

2.3 The In₂S₃ alternative buffer layer

2.3.1 In₂S₃ crystal structure

In₂S₃ is a III-VI chalcogenide n-type semiconductor that is extensively studied since the crystal structure and optoelectronic properties of this material are tunable. In₂S₃ crystallizes into three allotropic forms: α-In₂S₃, β-In₂S₃ and γ-In₂S₃ [48, 49]. Cubic α-In₂S₃, cubic β-In₂S₃ and tetragonal β-In₂S₃ are commonly reported stable crystalline phases of In₂S₃ synthesized under 600 °C.
Fig. 2.1.3: Phase diagram of In-S system (adapted from [48, 50]). Colored sections of the phase diagram represent phases that are most likely to be formed by the deposition conditions used in this work.

There are several conflicting reports on phase nomenclature of In$_2$S$_3$ [48, 49]. Current work follows the most recent reports [50-53] to describe the structure of In$_2$S$_3$. A common inference derived from these reports indicate that spinel-like tetragonal β-In$_2$S$_3$ is the most stable phase at room temperature. Cubic α-In$_2$S$_3$ is a stoichiometric phase, stable from room temperature up to 400 °C. There is a transition from cubic α-In$_2$S$_3$ to cubic β-In$_2$S$_3$ with marginal loss in Sulphur (S) content. Cubic β-In$_2$S$_3$ is an intermediate phase between cubic α-In$_2$S$_3$ and tetragonal β-In$_2$S$_3$. Hahn and Klinger [49] suggested that the aforementioned structures are much alike, with a difference in ordering of Indium atoms. Lattice constant of cubic α-In$_2$S$_3$ is twice that of cubic β-In$_2$S$_3$ as shown in Table 2-2.
Fig. 2.1.4: Crystal structure of $\alpha$ and $\beta$ modifications of In$_2$S$_3$.

Table 2-2: Crystal structure of various In$_2$S$_3$ phases

<table>
<thead>
<tr>
<th>Properties</th>
<th>$\alpha$-In$_2$S$_3$</th>
<th>$\beta$-In$_2$S$_3$</th>
<th>$\beta$-In$_2$S$_3$</th>
<th>$\gamma$-In$_2$S$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Tetragonal</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Lattice parameter (Å)</td>
<td>a=10.774</td>
<td>a=5.358</td>
<td>a=7.619</td>
<td>a=3.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=32.24</td>
<td>c=9.15</td>
</tr>
<tr>
<td>Space group</td>
<td>227 (Fd\bar{3}m)</td>
<td>216 (F-43m)</td>
<td>141 (I41/amd)</td>
<td>164 (P-3m1)</td>
</tr>
</tbody>
</table>

Crystal structure of $\alpha$ and $\beta$ phases of In$_2$S$_3$ is derived from spinel structure of Al$_2$MgO$_4$ where Al occupies octahedral sites and Mg occupies tetrahedral sites. For In$_2$S$_3$, the Al and Mg atoms are occupied by In, however, a third of tetrahedral sites are vacant [50] as seen from Fig. 2.1.4. This makes In$_2$S$_3$ a quasi-ternary compound with the formula: [In$_{2/3}$\square$_{1/3}$]$_{tet}$[In$_2$]$_{oct}$S$_3$ where ‘tet’ is tetrahedral site, ‘oct’ is
octahedral site and □ represents the unoccupied tetrahedral site [54]. Cubic structure of α-In$_2$S$_3$ is formed by statistical distribution of tetrahedral cationic voids. When these voids line up along the c-axis, a tetragonal β-In$_2$S$_3$ lattice structure is obtained. This is visualized in Fig. 2.1.4 by a grey box, inside the c-axis-oriented α-In$_2$S$_3$ structure which matches the c-axis-oriented β-In$_2$S$_3$ structure when rotated clockwise by 45 degrees. Presence of high density of tetrahedral vacancy sites makes α- and β-structure of In$_2$S$_3$ intrinsically defective.

### 2.3.2 In$_2$S$_3$ thin film buffer layer

In$_2$S$_3$ as a thin film semiconducting material has wide applications because of its photoluminescent and photoconductive properties. This material is extensively studied by PV community for potential applications as a high-performance buffer layer material. The wide bandgap of In$_2$S$_3$ ranges from 2.0 eV [55] to 3.8 eV [56] which varies with changing S/In ratio and/or dopant concentration [57-59]. In$_2$S$_3$ is deposited by various research groups using atomic layer deposition (ALD) [58], ion layer gas atomic reaction (ILGAR) [59], chemical bath deposition (CBD) [60], thermal evaporation (PVD) [39] and RF magnetron sputtering [5, 61, 62]. Record efficiencies for In$_2$S$_3$ for some of these methods have been listed in Table 2-1. As mentioned before, the wide bandgap of In$_2$S$_3$ allows more transmittance in blue wavelength region of the solar spectrum as compared to CdS (bandgap 2.4 eV). Relatively lower absorption losses in high energy blue region led to a higher photocurrent generation. Better optical performance and high efficiency have convinced the PV community that In$_2$S$_3$ is a suitable alternative buffer layer to toxic CdS buffer layer. Industrial establishments (e.g., Avancis GmbH, ZSW, etc.) are already producing In$_2$S$_3$ based CIGSe solar cells to replace the conventional CdS buffer layer.
2.3.3 Structural properties

As mentioned in previous section, the growth technique, deposition conditions, and post-deposition treatments strongly influence the crystalline properties of In$_2$S$_3$. El-Nahass et al. [63], observed that the crystalline parameters of In$_2$S$_3$ were independent of the film thickness, however, the crystallite size was found to increase linearly with annealing time and temperature up to 300 °C.

Sputter deposited In$_2$S$_3$ follows a columnar grain growth where the growth direction is perpendicular to the CIGSe surface. Fig. 2.1.5 shows the columnar grain structure of In$_2$S$_3$ buffer layer deposited on CIGSe. A 500 nm thick In$_2$S$_3$ buffer layer was deposited to visualize the grain structure.

![Columnar grains of In$_2$S$_3$](image)

*Fig. 2.1.5: STEM image of the thin lamella of CIGSe/In$_2$S$_3$/AZO with 500 nm thick In$_2$S$_3$ buffer layers deposited by RF magnetron sputtering.*

Columnar grain structure is a common feature for PVD based deposition techniques where the columnar grains extend through the thickness of the deposited films. For chemically deposited In$_2$S$_3$ [64] the grains are only a few nanometers in size. Fig. 2.1.6 shows the XRD stick patterns of the In$_2$S$_3$ structure compared with CIGSe. As discussed in section 2.3.1, the cubic α-In$_2$S$_3$ and tetragonal β-In$_2$S$_3$ have a similar structure and thus the XRD spectra stack up with matching 2θ values. Ideally, for high-quality interface, the strongest crystallographic orientation of the two layers should have minimal difference in their interplanar spacing (i.e., low lattice
mismatch). For n-type In$_2$S$_3$, a heterointerface with p-type CIGSe is formed with cubic $\alpha$- and tetragonal $\beta$- In$_2$S$_3$ phases with a lattice mismatch of 1.93% (Fig. 2.1.6).

![X-ray diffraction stick patterns](image)

**Fig. 2.1.6: X-ray diffraction stick patterns of different structures of In$_2$S$_3$ (red) stacked with CIGSe XRD stick pattern (blue).**

Lattice adjustments can be made by substitution (doping) of host atoms with smaller or larger ionic radii than In in the crystalline lattice of In$_2$S$_3$ [65-68]. Since the interplanar spacing of the primary crystallographic orientation of In$_2$S$_3$ ($d=3.24$, (hkl)=(311), $2\theta=27.5^\circ$) is lower than CIGSe ($d=3.31$, (hkl)=(112), $2\theta=26.9^\circ$), a larger host atom is necessary to adjust the lattice mismatch. For example, Na with a larger cationic radius than In is abundant in CIGSe grain boundaries and can easily diffuse to the In$_2$S$_3$ layer (discussed in chapter 5).

### 2.3.4 Optoelectronic properties

The optical properties of In$_2$S$_3$ like bandgap ($E_g$), photoconductivity ($\sigma$), absorption ($\%A$), transmittance ($\%T$), refractive index ($n$), absorption coefficient
(a) and extinction coefficient (k) strongly depend on the crystalline structure, composition and doping of In$_2$S$_3$.

There has been a wide discrepancy regarding the bandgap nature of In$_2$S$_3$ in the literature [69-71] that report direct or indirect band-to-band transition. Rehwald et al. [72] first reported this nature where a direct transition (E$_1$) at 2.03 eV, a higher transition (E$_2$) at 2.45 eV and a weak indirect transition (E$_0$) at 1.1 eV was reported. Direct bandgap of In$_2$S$_3$ varies from 2.0 eV to 3.8 eV [56, 60, 64, 73, 74]. Highest bandgap (3.8 eV) for thermally evaporated In$_2$S$_3$ after annealing treatment at 500 °C was reported by Zhong et al. [56]. However, for use as buffer layer material, the empirical upper limit for In$_2$S$_3$ based devices is 275 °C after which the cell parameters degrade substantially [35]. For In$_2$S$_3$ deposited by ALD [58, 75], an amorphous layer with bandgap 3.3 eV was reported, which dropped to 2.25 eV upon annealing at 200 °C.

A thorough study was done by Kim et al. [76] for tetragonal β-In$_2$S$_3$ where the S content in the film was varied for In$_2$S$_x$ from (x=2–4) to get bandgap from 2.0 eV to 3.9 eV. To summarize, for PVD-based stoichiometric In$_2$S$_3$ thin films with a polycrystalline nature with film thickness between 50-100 nm, an average direct bandgap of nearly 2.7±0.2 eV is obtained.

Apart from S content, the bandgap of In$_2$S$_3$ buffer layer deposited on CIGSe is influenced by the diffusion of Na and Cu atoms during deposition or upon annealing treatment. The variation of In$_2$S$_3$ bandgap with respect to Na and Cu content in the films is presented in Fig. 2.1.7.
Addition of Cu atoms to In$_2$S$_3$ crystalline matrix narrows the bandgap, whereas Na atoms widen the bandgap. The substitution of Cu and Na atoms affect the band structure depending on Pauling scale of electronegativity values. Electronegativity ($\chi_r$) is the tendency of an atom to attract a shared pair of electrons. Copper has higher electronegativity ($\chi_r=1.9$) than Indium ($\chi_r=1.8$). When Cu is introduced in the In$_2$S$_3$ structure, it attracts electrons resulting in reduction of charge carrier concentration. This results in filling of the states blocking any thermal or optical excitation. Na with $\chi_r=0.9$ is less electronegative (read electropositive) as compared to In and will donate electrons resulting in an overall increase in charge carrier concentration. This can explain the change in bandgap according to the Moss-Burstein effect [79] of band filling.

### 2.3.5 Defects in In$_2$S$_3$

The primary function of solar cell is to generate current in the form of electrons and holes. Electrons and holes reaching the external circuit without recombination contribute to the current generated by the solar cell. Charged defect states act as electron/hole traps which suppresses current collection by defect
recombination. Therefore, the efficiency of a solar cell is largely affected by these defect levels in the bandgap.

The structure of In$_2$S$_3$ is highly defective (as discussed in section 2.3.1) giving rise to intrinsic crystallographic defects in the material. These defects contribute to the n-type conductivity of In$_2$S$_3$. The native defects in In$_2$S$_3$ include indium vacancy (V$_\text{In}$), Sulphur vacancy (V$_\text{S}$), interstitial Indium (In$_\text{i}$), interstitial Sulphur (S$_\text{i}$), Sulphur antisites (S$_\text{In}$) and Indium antisites (In$_\text{S}$). Pai et al. [80] have stated that a lower In concentration than stoichiometry (<40 at.%) will result in large number of Indium vacancies (V$_\text{In}$) in In$_2$S$_3$. Sulphur vacancies (V$_\text{S}$) can exist for all In:S concentrations. In a recent study, Ghorbani et al. [81] showed that n-type conductivity of the material originates from donor-type defects In$_\text{S}$, In$_\text{i}$ and V$_\text{S}$. Intrinsic acceptor-type defects S$_\text{In}$ and V$_\text{In}$ are deep defects formed far from the valance band edge and do not contribute to hole formation in In$_2$S$_3$. The nature and density of defects depend mainly on the growth conditions (In-rich or S-rich). For In-rich conditions, the formation energies of V$_\text{S}$ > In$_\text{i}$ > In$_\text{S}$ > V$_\text{In}$ > S$_\text{In}$; whereas for S-rich conditions, S$_\text{In}$ > V$_\text{In}$ > V$_\text{S}$ > In$_\text{i}$ > In$_\text{S}$.

The presence of tetrahedral vacancy sites (V$_\text{In}$) makes the structure of α- and β- In$_2$S$_3$ defective. For In$_2$S$_3$ deposited on CIGSe as a buffer layer, the most commonly diffusing ions in In$_2$S$_3$ are Na$^{2+}$ and Cu$^{2+}$. With a negative formation energy of -0.06 eV [82], Na$_\text{In}$ can be easily formed in In$_2$S$_3$. Additionally, Cu can diffuse from CIGSe to In$_2$S$_3$ by electromigration in an electric field [83]. With low formation energy of 0.85 eV, Cu$_\text{In}$ can be formed upon annealing. Na and Cu when substituting In sublattice form deep acceptor levels. Na$_\text{In}$ lies at +0.40 eV and +1.49 eV above the valance band maximum (VBM), whereas Cu$_\text{In}$ is at +2.01 eV and +1.97 eV above VBM. Na$_\text{S}$ creates a deep and shallow donor level below conduction band maximum (CBM) at -1.25 eV and -0.05 eV. Cu$_\text{S}$ has a double donor-acceptor-type transition level below CBM at -0.19 eV [82].
2.3.6 In$_2$S$_3$ as a buffer layer on CIGSe solar cells

D. Hariskos et al. [60] in 1996 first reported a newly developed novel Cd-free CBD process for the deposition of In-S based buffer layer with chemical formula In$_x$(OH,S)$_y$. An efficiency of 14.9% was achieved for Cu(In,Ga)Se$_2$ solar cells with 630 mV $V_{OC}$, 32.4 mA/cm$^2$ $J_{SC}$ and FF of 73%. This study invoked significant interest in the PV community to explore the In-S based buffer layers for CIGSe solar cells using different deposition techniques. In$_x$(OH,S)$_y$ was then chemically deposited by several groups [84-86] with an aim to better understand the buffer layer properties and improve the efficiency.

N. Barreau did extensive work on In$_2$S$_3$ buffer layers [54, 57, 67, 68, 77, 87] deposited mainly using Thermal evaporation (PVD). These studies revealed details about the crystalline structure, stoichiometry, doping levels, and film quality of In$_2$S$_3$ for deposition as buffer layers. One of the significant findings was the improvement in cell parameters and external quantum efficiency when Na-enriched CIGSe absorber surface was used [16]. N. Barreau in most of their works has studied the effect of Cu and Na atoms diffusing in In$_2$S$_3$ buffer layer from CIGSe absorber. Besides the work by N. Barreau, thermally evaporated In$_2$S$_3$ buffer layers developed by Avancis GmbH have reached a high efficiency of 17.9% for large 30×30 cm$^2$ modules [39].

Atomic layer deposition (ALD) In$_2$S$_3$ buffer layers were deposited by Yousfi et al. [88] for the first time in the year 2000. This was one of the first successful studies of Cd-free dry deposition techniques for In$_2$S$_3$ buffer layers in CIGSe solar cells. Device efficiency of 13.5% was measured without anti-reflection coating. Naghavi et al. [89] reported high efficiency of 16.4% using 30 nm thick ALD deposited In$_2$S$_3$. The higher bandgap of 2.8 eV gave an improved collection efficiency in the blue region as compared to Cds. The key parameters in obtaining high efficiencies were found to be deposition temperature of 220 °C and a film thickness of 30 nm. High $V_{OC}$ and FF values (665 mV and 78% respectively) gave evidence of a high-quality
interface formation between In$_2$S$_3$ and CIGSe. Spiering et al. [90] used Atomic layer chemical vapor deposition (ALCVD) to deposit In$_2$S$_3$ on large area 30×30 cm$^2$ CIGSe modules with an efficiency of 13%.

In$_2$S$_3$ buffer layers were deposited using Ion layer gas atomic reaction (ILGAR) layers by Allsop et al. [59] with an efficiency of 13.1%. The process was improvised by deposition of ZnS-nanodots containing In$_2$S$_3$ [91]. This prevented the diffusion of Cu in In$_2$S$_3$ and pinned the Fermi level at the conduction band giving an enhancement in efficiency up to 15.7%.

The following table summarizes the cell parameters for In$_2$S$_3$ buffer layers deposited by different techniques on CIGSe or CuInSe$_2$ (CIS) absorber layers.

Table 2-3: Comparison of cell parameters of In$_2$S$_3$ buffer layers deposited on CIGSe solar cells

<table>
<thead>
<tr>
<th>Deposition technique</th>
<th>Efficiency</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF</th>
<th>Cell area (cm$^2$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBD</td>
<td>15.7%</td>
<td>37.4</td>
<td>574</td>
<td>68</td>
<td>0.5</td>
<td>[60]</td>
</tr>
<tr>
<td>ILGAR</td>
<td>16.1%</td>
<td>35.5</td>
<td>631</td>
<td>72</td>
<td>0.48</td>
<td>[92]</td>
</tr>
<tr>
<td>ALD</td>
<td>16.4% (18.2*)</td>
<td>31.5</td>
<td>665</td>
<td>78</td>
<td>0.5</td>
<td>[93]</td>
</tr>
<tr>
<td>Sputtering</td>
<td>12.2</td>
<td>27.6</td>
<td>620</td>
<td>71</td>
<td>0.5</td>
<td>[5]</td>
</tr>
<tr>
<td>Sputtering</td>
<td>11.0</td>
<td>26</td>
<td>615</td>
<td>65</td>
<td>0.5</td>
<td>[4]</td>
</tr>
</tbody>
</table>

CBD-Chemical bath deposition; ILGAR-Ion layer gas reaction; ALD-Atomic layer deposition; * with anti-reflective MgF$_2$ coating

Sputtered In$_2$S$_3$ buffer layers in CIGSe solar cells

Thermally evaporated (PVD) In$_2$S$_3$-based buffer layers have reached a high efficiency of 17.9% for 30×30 cm$^2$ module [39]. But scaling up these modules to large area commercial solar panels (area >1 m$^2$) is difficult since the PVD technique is expensive with high material wastage. It has issues like film homogeneity, poor stoichiometry, and adhesion. This makes sputter deposition of buffer layers more suited for large-scale industrial production. Unfortunately, only limited work has
been done to explore the possibility of obtaining high-efficiency In$_2$S$_3$ buffer layers by using RF magnetron sputtering.

So far only two authors, Abou-Ras et al. [4] and Hariskos et al. [5], have reported sputter deposition of In$_2$S$_3$ buffer layers directly on CIGSe. Siol et al. [94] deposited In$_2$S$_3$ using reactive sputtering but on Cu$_2$ZnSnS$_4$ (CZTS) absorbers, whereas Ho et al. [95] deposited In$_x$(O,S)$_y$ buffer layers by RF magnetron sputtering.

Abou-Ras et al. [4] sputtered In$_x$S$_y$ buffer layers on CIGSe absorbers at room temperature, 230 °C and 340 °C using Ar-ion sputtering. For 230 °C samples, 11% efficiency was measured, which dropped to 1.9% for 340 °C samples. Cu and Ga were found to diffuse from CIGSe to In$_x$S$_y$, whereas In diffused into the CIGSe absorber. At annealing temperatures above 250 °C, CuIn$_5$S$_8$ is formed that enhances recombination at the pn-junction being detrimental for cell performance. A Cu depleted, In enriched layer at 230 °C at the In$_x$S$_y$/CIGSe interface was found to improve the band alignment by downward band bending.

Hariskos et al. [5] deposited In$_x$S$_y$ buffer layers from a stoichiometric In$_2$S$_3$ target using Ar-ion sputtering at a fast deposition rate of 20 nm/min. The layer thickness was between 30–80 nm at a deposition temperature from 25 °C to 400 °C. In-S stoichiometry ratio of 1:1 was obtained for In$_2$S$_3$, with a relatively low bandgap of 1.9 eV. With increasing deposition temperature, stoichiometric In$_2$S$_3$ was deposited with an increased bandgap of 2.2 eV. For small aperture area of 0.5 cm$^2$, an efficiency of 13.3% was measured, with $V_{OC}$ of 637 mV and FF of 72.3%.

Ho et al. [95] deposited In$_x$(O,S)$_y$ buffer layers on CIGSe absorber layers using a 1:1.25 stoichiometry In-S target with reactive O during sputtering. Bandgap of 2.2–2.4 eV was obtained for these buffer layers which gave an efficiency of 11.04% with a low $V_{OC}$ of 553 mV and FF 68%. Changing the sputter deposition pressure modified the band alignment possibly by a change in the composition of the films. The cliff in the electronic band structure was reduced from -0.25 eV to a flat band
of +0.07 eV. This creates a favorable path for the electrons to flow out of the absorber suppressing the interfacial recombination.

From the above reports, sputtered In$_2$S$_3$ can prove to be a cost-efficient, reproducible, and high efficiency buffer layer for CIGSe solar cells. However, because of limited studies, sputtered In$_2$S$_3$ buffer layers, has none or limited application and usage commercially. With module efficiency value close to CdS/CIGSe solar cells (see Table 2-1), In$_2$S$_3$ is one of the best alternative buffer layer materials to CdS.

Ideal properties of sputtered In$_2$S$_3$ buffer layers

Selection criteria for ideal buffer layers are already discussed in section 2.1.4. However, for sputtered In$_2$S$_3$ buffer layers, a few inferences have been made from literature survey to get good optoelectronic performance. The most important property is that the sputter deposition should induce minimal sputter damage to the absorber layer to avoid charged defects at the heterointerface. Second, a crystalline buffer layer with sputtering will lower the interfacial recombination. Last, the grain size of the buffer layer should be kept smaller to ensure higher optical transmittance to the absorber layer.
3. Materials and Methods

3.1 Device Fabrication

3.1.1 Sputtering process

Sputtering is a process where atoms are ejected from a source material by the bombardment of energetic particles or ions. The source material is called the target, and it is placed in a vacuum chamber along with the substrate. The ejected atoms from the target condense onto the substrate and form a thin film.

![RF magnetron sputter tool with cross section of a cathode.](image)

**Fig. 3.1.1:** RF magnetron sputter tool with cross section of a cathode.
3.1.2 RF Magnetron sputtering

Radio frequency (RF) magnetron sputtering is an environmentally friendly thin film deposition technology that is used to deposit wide range of semiconducting materials. In this work, RF magnetron sputtering is used to deposit In$_2$S$_3$, ZnO, ZnO:Al and ZnS thin films.

The RF magnetron sputter deposition apparatus and the cross section of a sputter cathode is presented in Fig. 3.1.1. This process takes place in a vacuum chamber with high base pressure ($< 10^{-6}$ mBar) and a low Argon (Ar) pressure ($\sim 10^{-3}$ mBar) during the deposition process. Sputter target is mounted on a cathode with a set of strong permanent magnets to confine free electrons near the target surface. The cathode is constantly water cooled to avoid overheating and system failure. Substrate is placed on a substrate holder that is usually positively biased with reference to the cathode.

A high frequency RF power supply (13.56 MHz) is applied between the target cathode and the substrate. The applied electric field between anode and cathode ionizes the Ar atoms ($\text{Ar} \rightarrow \text{Ar}^+ + e^-$). The Ar$^+$ ions are accelerated to the negative cathode, striking with kinetic energy of a few KeV dislodging or ‘sputtering’ the target material. The dislodged atoms condense on a substrate to form a thin film. In magnetron sputtering, the secondary electrons created by ionization of Ar atoms move in cycloidal trajectories along the magnetic lines of force from the permanent magnets. This enhances the ionization rate and thus the deposition rate.

RF sputter deposition is particularly used for non-conducting dielectric or ceramic targets (most semiconducting materials) where the charge build-up at target surface is prevented by high frequency RF potential. This results in an alternative bombardment of the positively charged sputter gas ions and negatively charged electrons. In RF sputtering, the target surface is self-biased negatively since the electron mobility is several orders of magnitude higher than ion mobility. This way,
a high enough negative charge is ensured maximizing the possibility of sputter gas ions striking the target cathode.

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**Fig. 3.1.2:** (a) Front view of the Sputter tool used in this work and (b) inside view of the sputter deposition chamber.

**Reactive magneton sputtering**

Reactive sputtering is the process where a reactive gas (usually O\(_2\) or N\(_2\)) is introduced in the sputter chamber along with Ar. The O and N react at the target surface giving the corresponding oxides and nitrides of the target material. The reactive gas atom can also be used for doping or to alter the stoichiometry of the films. In this work, reactive H\(_2\)S is introduced to improve the S concentration in the films and to deposit Sulphur containing ZnO films (Zn(O,S)).

**Description of sputter tool used for this work**

The sputter tool used in this work is shown in Fig. 3.1.2 (a). The tool has a load-lock chamber with a robotic arm to transfer samples from atmospheric pressure to the sputter chamber that remains under high vacuum. The load-lock (volume 30 liters) have base pressure \(\sim1\times10^{-7}\) mBar and the sputter chamber (volume 80 liters) have base pressure \(\sim7\times10^{-8}\) mBar. Both the chambers are individually pumped by a turbo molecular pump (TMP) backed by a dry scroll pump. There are three sputter cathodes manufactured by Thin film consulting, Grafenberg (Germany) with target
diameter 100 mm in a confocal orientation. The total surface area of sputter target is 78.5 cm², which is used to convert input sputter power from (W) to power density (W/cm²). Sputter targets are powered by (1) 600 W RF (2) 300 W RF and (3) 2000 W DC power supplies that can be switched from one cathode to the other. Sputter power (w) used in this work ranged from 25W to 250W. Substrate stage rotation speed (r) can be varied from 2 to 30 RPM, whereas the substrate-to-target distance (d) can be varied from 20 to 80 mm. Inlet gases (Ar, O₂, N₂ and H₂S) are precisely controlled by a mass flow controller. Sputter deposition process can be performed within a pressure range of 1×10⁻³ mBar to 7×10⁻² mBar to get stable sputter pressures (p). The substrate heater has a temperature limit of 850 °C, however the substrate temperature (T) is much lower ~400 °C (measured by a non-contact infrared laser pyrometer). A temperature-controlled water chiller cools the cathodes, TMP’s, walls of the sputter chamber and the substrate heater casing.

3.2 Substrate preparation

3.2.1 CIGSe absorber

CIGSe absorber layer used in this work were procured from Zentrum fur Sonnenenergie- und Wasserstoff-Forschung Baden-Wurttemberg (ZSW), Stuttgart, Germany. The CIGSe absorbers (2.0 – 2.2 µm thick) were grown in a multi-stage inline co-evaporation process on Mo coated soda lime glass substrate at 600°C [11]. Mo layer with a thickness of 0.55 µm was deposited on the soda lime glass substrate using dc magnetron sputtering [96]. Overall Ga concentration Ga/III in the absorber is ≈ 0.3 with a higher Ga grading at the CIGSe/Mo interface. Fig. 3.2 shows the GIXRD patterns of CIGSe absorber layers. The diffraction peaks match with the tetragonal structure of Cu(In,Ga)Se₂ (JCPDS #00-035-1102). The cell parameters are a=5.736 Å and c=11.448 Å with space group I-42d.
Fig. 3.2.1: XRD spectra of CIGSe absorber layer used in this work.

The absorbers were transported from ZSW in a sealed protective boxed under vacuum. The CIGSe absorbers were stored in vacuum and used for several months. However with time, the absorber surface degradation takes place [97]. To partially revert the surface modification caused by air exposure and ageing process, the absorber surface was rinsed with De-ionized (DI) water and treated with NH$_4$OH and KCN solutions.

**DI water rinsing:** For freshly deposited CIGSe absorber layers, surface contamination like dust and In- and Ga-oxides formed on the CIGSe. This type of surface contamination can be removed by rinsing with DI water and drying with low-pressure Nitrogen.

**NH$_4$OH etching:** The absorbers were dipped in 10% NH$_4$OH solution for 3 minutes and rinsed with DI water. NH$_4$OH etching removes the Se- and Cu- based oxides that are formed after prolonged storage of CIGSe absorbers up to 12 months.

**KCN etching:** CIGSe absorbers stored in vacuum for over 12 months were etched with 0.15M KCN solution for 3 minutes. NH$_4$OH etching could not etch the absorber surface from unwanted oxides and selenides formation for samples stored for 1 year or more. KCN etching is commonly used for chalcopyrite absorbers remove unwanted Cu-Se based phases formed on the absorber surface. KCN etches the oxides and selenide layers on CIGSe that are not etched by NH$_4$OH. The absorbers
are rinsed with DI water to remove any residual KCN, dried with nitrogen and transferred to the load-lock chamber for buffer layer deposition.

3.2.2 Quartz and Silicon substrate

To analyze the deposited samples with x-ray diffraction spectroscopy, UV-Visible spectroscopy, Raman spectroscopy and Scanning electron microscopy, quartz and silicon substrates were used. The quartz and silicon substrates were dipped in DI water and ultrasonicated for 3 minutes to remove water soluble contaminants. Organic contaminants were removed by ultrasonication in analytical-grade Acetone for 3 minutes. Finally, the substrates were ultrasonicated in iso-propyl alcohol for 5 minutes to remove any residual acetone. Residual alcohol was removed by heating the substrate on a hot plate at 150 °C for 20 minutes before transferring to the sputter chamber for deposition.

3.3 RF magnetron sputtering of buffer layers

Thin film buffer layers for this work were deposited with the conventional top-down approach. In$_2$S$_3$ ceramic sputter target with 100 mm diameter and 4 mm thickness, bonded to 8 mm thick Cu back plate is used. The base pressure of the sputter chamber and load-lock chamber was better than $7 \times 10^{-8}$ mBar at an ambient temperature of 22–25 °C. The samples once inserted in the load lock chamber were transferred to the sputter chamber when the pressure in the load lock chamber reached pressure $< 5 \times 10^{-7}$ mBar. Ar with purity 99.9999% (grade 6N) was used as the sputter gas. The Ar flow in the sputter chamber was kept constant whereas the sputter-pressure or working-pressure was controlled downstream using a butterfly valve. A pre-sputtering or target conditioning was done for 120s at 100W for all target materials prior to the actual sputter deposition process while keeping the substrate shutter closed.
Sputtered films used in this thesis are deposited at room temperature (RT) without deliberate substrate heating. Post deposition annealing was preferred over in-situ heating, to ensure better control over annealing temperature. Precise control of substrate temperature (±5 °C) and short annealing times (10-15 minutes) are difficult with the existing sputter tool due to technological limitations. To get reliable and reproducible results for this work, heat treatment was performed ex-situ on precision hot plate from Lab Tech SRL, Italy in 2017.

3.3.1 \( \text{In}_2\text{S}_3 \) buffer layer deposition

\( \text{In}_2\text{S}_3 \) thin films were deposited directly from a 3N grade purity stoichiometric \( \text{In}_2\text{S}_3 \) ceramic target from RHP Technologies GmbH, Siebersdorf, Austria. The \( \text{In}_2\text{S}_3 \) thin films investigated in this work were deposited by two approaches using RF magnetron sputtering technique:

A. Sputtering with Ar-ion OR Non-reactive RF magnetron sputtering

B. Sputtering with \( \text{H}_2\text{S}/\text{Ar} \) OR Reactive RF magnetron sputtering

3.3.1.1 Ar-ion Sputtering

Non-reactive RF magnetron sputtering was used in the preliminary experiments for the deposition of \( \text{In}_2\text{S}_3 \) thin films.

The sputter pressure \((p)\) used for deposition of \( \text{In}_2\text{S}_3 \) films was \( 3 \times 10^{-3} \) mBar with an Ar flow rate of 80 SCCM. Downstream pressure control was done using a butterfly valve. The target-substrate distance \((d)\) was kept constant at 50 mm and the substrate carrier was rotated \((r)\) at a speed of 20 RPM. Sputter deposition process lasted for 15 minutes at a sputter power \((w)\) of 50W giving a sputter rate of 1.83 Å/s. Average film thickness of 55±5 nm was obtained with these parameters. These sputter deposition conditions were adapted from a previous work by Hariskos et al. [5].
The GIXRD spectra and UV-Visible transmission spectra of Ar-ion sputtered In$_2$S$_3$ buffer layer is presented in Fig. 3.2.1 (a) and (b) respectively. The as-deposited (RT) films show an amorphous nature and do not crystallize after an annealing treatment at 210 °C for 15 minutes. The small diffraction peak obtained in the spectra matches the JCPDS reference file #00-036-0643 for tetragonal InS with space group I4/mmm and unit cell parameters a=3.823 Å and c=10.868 Å. The UV-Visible spectra show a small improvement in transmittance behavior after annealing treatment. The S/In ratio of 1.38±0.05 obtained by EDS for the as deposited (RT) samples and 1.22±0.05 after annealing. The S content in the film was much lower than 1.5 (stoichiometric In$_2$S$_3$).

Fig. 3.3.1: (a) GIXRD spectra and (b) UV-Visible transmission spectra of Ar-ion sputtered In$_2$S$_3$ buffer layers at room temperature (black) and annealed at 210 °C (red) for 15 minutes. The S/In ratio measured by EDS for room temperature (25 °C) and 210 °C samples shown on a secondary axis in (b).

These preliminary results were used to deposit In$_2$S$_3$ buffer layers on CIGSe solar cells (see chapter 4). However, it was observed that the CIGSe absorber suffered significant surface damage due to the sputter deposition. Sputter damaged absorber surface is highly detrimental for cell performance and must be avoided or minimized. Sputter damage can be minimized by using (1) higher sputter deposition pressure, (2) large target to substrate distance and (3) lower sputter power. With higher sputter pressure and large target-substrate separation, the sputtered atoms undergo
multiple collisions with gas molecules. This lowers the kinetic energy of impinging energetic sputter atoms, minimizing the absorber surface.

This strategy was used to deposit In$_2$S$_3$ buffer layers for CIGSe solar cells with minimal sputter damage. The problem of low S content in the films was solved by using additional S source during film growth. This topic is discussed in the next section.

3.3.1.2 H$_2$S/Ar Sputtering

Ar-ion sputtered In$_2$S$_3$ films had inherently low Sulphur (S) content due to the high vapor pressure of S (1 mBar at 175 °C). A lower S containing In$_2$S$_3$ thin films have inferior optoelectronic properties as compared to stoichiometric In$_2$S$_3$ (discussed in chapter 5). To overcome this, reactively sputtered In$_2$S$_3$ films were deposited with an additional S source (H$_2$S) to obtain higher S concentration in the films. H$_2$S gas with concentration of 0.25% (purity grade 2.5N) was introduced as a reactive gas in the chamber along with Ar.

Influence of sputter power (w):

The underlying mechanism of reduced sputter damage of the heterointerface with respect to sputter parameters are discussed in chapter 5. To minimize sputter damage, high sputter pressure and large target-to-substrate distance were necessary to lower the kinetic energy of impinging energetic sputter atoms. The highest stable pressure achieved by the sputter tool is $6 \times 10^{-2}$ mBar with a maximum target-to-substrate separation equal to 80 mm. Keeping these two parameters constant, In$_2$S$_3$ films were deposited at sputter powers 40W, 60W, 80W and 100W with reactive H$_2$S gas (H$_2$S/Ar - 0.25% H$_2$S with 99.75% Ar) under room temperature deposition conditions (Fig. 3.3.2). For comparison, Ar-ion sputtered In$_2$S$_3$ films were deposited using the same sputter deposition conditions.
Fig. 3.3.2: GIXRD spectra of (a) H$_2$S/Ar sputtered and (b) Ar-ion sputtered In$_2$S$_3$ thin films and UV-Visible transmission spectra of (b) H$_2$S/Ar sputtered and (d) Ar-ion sputtered In$_2$S$_3$ thin films deposited at different sputter powers. Ar-ion sputtered samples are completely amorphous whereas reactive H$_2$S/Ar sample deposited at 40 W is crystalline at room temperature (RT). The overall transmittance of H$_2$S/Ar sputtered In$_2$S$_3$ is blue-shifted for all sputter powers.

Crystalline In$_2$S$_3$ films were deposited with reactive H$_2$S/Ar sputtering at 40W sputter power (see Fig. 3.3.2 (a)), 6×10$^{-2}$ mBar sputter pressure, 80 mm target-to-substrate distance and 5 RPM substrate rotation speed. In$_2$S$_3$ films deposited at higher sputter powers of 60W, 80W and 100W were fully or partly amorphous. Similar sputter deposition conditions were used for Ar-ion sputtered In$_2$S$_3$ ((see Fig. 3.3.2 (b,d)) for comparison, which were found to be amorphous for all sputter powers.

**Influence of sputter pressure (p)**

The effect of sputter pressure (p) on the film structure and transparency was studied. The sputter deposition pressure was applied between 3×10$^{-3}$ mBar and 6×10$^{-2}$ mBar as shown in Fig. 3.3.3(a). Other sputter parameters (w=40W, r=5 RPM, d=80 mm) were adopted from the previous sub-section that gave crystalline In$_2$S$_3$
thin films. After measuring/calibrating the film growth rate for each sputter pressure, deposition time was adjusted to get constant film thickness of 170 nm. The thickness was empirically chosen to get sufficient counts in the XRD spectra. In$_2$S$_3$ thin films are then deposited at different sputter pressures under room temperature (RT) conditions without in-situ heating. Annealing or heat treatment (HT) was performed on these samples at 225 °C for 15 minutes. The XRD spectrum (Fig. 3.3.3 (a,c)) shows that the RT films were either amorphous or only partly crystalline (dotted line) and the HT films were crystallized (solid lines).

**Fig. 3.3.3**: GIXRD spectra of (a) H$_2$S/Ar sputtered and (b) Ar-ion sputtered In$_2$S$_3$ thin films and UV-Visible transmission spectra of (b) H$_2$S/Ar sputtered and (d) Ar-ion sputtered In$_2$S$_3$ thin films deposited with different sputter pressures at room temperature (dotted line) and after annealing at 225 °C for 15 minutes (solid line). The peak widths (FWHM) of XRD spectra are inversely proportional to the crystallite size.
For H$_2$S/Ar reactive sputtering, the In$_2$S$_3$ thin films (dotted line, RT) are deposited in a partly crystalline form at room temperature. The diffraction peak intensities of these films improve at higher sputter deposition pressure indicating improvement in crystallinity. This is however not the case with Ar-ion sputtered In$_2$S$_3$ under similar deposition conditions (Fig. 3.3.3 (c)). They show completely amorphous character at room temperature for all sputter pressures.

Upon annealing, the crystalline character improves for both H$_2$S/Ar and Ar-ion sputtered In$_2$S$_3$ films. H$_2$S/Ar sputtered and Ar-ion sputtered samples deposited at sputter pressure $3 \times 10^{-3}$ mBar (lowest pressure) shows show similar GIXRD spectra upon annealing. There is however a notable difference in the widths (FWHM) of peaks in the respective spectrum. This observation is discussed in section 3.3.1.3. The spectra for these two samples match the cubic structure of In$_2$S$_3$ with lattice parameter 10.82 Å (JCPDS reference file #051-1159). For the samples deposited at highest pressure of $6 \times 10^{-2}$ mBar post annealing, the GIXRD spectra also matches the cubic structure of In$_2$S$_3$ (JCPDS #03-065-0459), but with different cell parameters ($a=10.77$ Å, space group Fd-3m). The samples deposited at intermediate pressures are a mixture of the aforementioned cubic structure of In$_2$S$_3$. These observations are valid for both H$_2$S/Ar sputtered and Ar-ion sputtered In$_2$S$_3$ post annealing.

The transmission spectra of H$_2$S/Ar and Ar-ion sputtered In$_2$S$_3$ are presented in Fig. 3.3.3 (b) and (d) respectively. It has been observed that the overall transmission spectra for all samples undergoes a blue-shift upon annealing. Samples deposited at low pressure of $3 \times 10^{-3}$ mBar have better transmission in the short (blue and UV) wavelength region. With increasing sputter pressure, the transmission is better in the visible region. The samples deposited with H$_2$S/Ar reactive sputtering have better average optical transmittance than Ar-ion sputtered In$_2$S$_3$. 

Influence of target-substrate distance (d)

The effects of target-substrate distance (d) on In$_2$S$_3$ film properties were studied. With an increasing d the kinetic energy of sputter atoms arriving on the substrate surface is decreased while undergoing multiple collisions with gas atoms in the sputter chamber. With lower d values, the energy and flux of atoms arriving at the substrate is higher. This locally heats up the substrate surface facilitating grain growth, giving larger crystallite size. Changing the target-to-substrate distance mainly affects crystallite size and growth rate of the films [98]. For this work, ideally, larger value of d is preferred so that there is minimal sputter damage to the soft CIGSe absorber layer while depositing In$_2$S$_3$ buffer layer.

![Graph showing the influence of target-substrate distance on H$_2$S/Ar reactive sputtering properties](image)

Fig. 3.3.4: GIXRD (a) and UV-Visible transmission spectra (b) of H$_2$S/Ar sputtered In$_2$S$_3$ thin films deposited at different target-substrate distance: at room temperature (dotted line) and after annealing at 225 °C for 15 minutes (solid line).
Crystalline nature of H$_2$S/Ar deposited In$_2$S$_3$ thin films before and after annealing for 40 mm, 60 mm and 80 mm was similar. The diffraction peaks obtained for these samples matches the cubic structure of In$_2$S$_3$ (JCPDS #03-065-0459) with cell parameters $a=10.77$ Å and space group Fd-3m. Sample deposited at 20 mm was amorphous in the as-deposited state. Upon annealing, it crystallized, and the primary diffraction peak partly matched the (101) reflection of InS (JCPDS # 036-0643).

The UV-visible transmission spectra of H$_2$S/Ar samples deposited at different $d$ is presented in Fig. 3.3.4 (b). Highest transmission is obtained for samples deposited at $d=20$ mm. With increasing sample thickness, the overall transmission decreases in the blue and red/infrared religions and increases in the visible region.

### 3.3.1.3 Effect of reactive sputtering on film growth and crystallization

The crystalline nature of In$_2$S$_3$ films by Ar-ion sputtering and H$_2$S/Ar sputtering were different in the as-deposited state. Polycrystalline In$_2$S$_3$ films are deposited with H$_2$S/Ar sputtering at room temperature, whereas amorphous In$_2$S$_3$ films are deposited at room temperature with Ar-ion sputtering. This difference had a major influence on the crystallite size that was obtained after heat treatment.

The crystallite size of Ar-ion deposited amorphous In$_2$S$_3$ films after annealing was $25\pm2.8$ nm. In comparison, the average crystallite size of $9.3\pm1.5$ nm for H$_2$S/Ar deposited In$_2$S$_3$ films was much smaller. This is evident from broader XRD peaks (FWHM) of H$_2$S/Ar deposited In$_2$S$_3$ films after annealing, as compared to the Ar-ion deposited In$_2$S$_3$ films after annealing.

The larger crystallite size depends on the initial deposition state of the material according to Kamins [99]. For a material that is initially deposited in an amorphous state, annealing will result in larger and smoother grains than the ones that are initially polycrystalline. With a denser nuclei concentration for polycrystalline material, the grain growth is constrained. Whereas for amorphous material, there are no such constrains and grains grow much larger upon annealing.
Thus, depositing In$_2$S$_3$ films with H$_2$S/Ar sputtering at room temperature gave polycrystalline In$_2$S$_3$ thin films in the as-deposited state. After annealing at 225 °C for 15 minutes, the average crystallite size was around 10 nm.

### 3.3 Deposition of ZnO, ZnO:Al (AZO) and Ni/Al layers

Window layers in CIGSe solar cells (ZnO and AZO) are critical for solar cell performance since they form a combination of a low-resistance and high-resistance layers. The intrinsic i-ZnO forms a high resistance layer (resistance of the order of MΩ/□) whereas ZnO:Al forms a low resistance layer (< 1 Ω/□).

i-ZnO forms a high resistivity high optical transmittance shunting screen, preventing parasitic pathways from front contact to back contact. This significantly increases the shunting resistance of the cell giving an improved cell performance. ZnO layer also prevents the diffusion of Al from AZO layer to absorber layer.

ZnO:Al (AZO) on the other hand forms a low resistivity high optical transmittance conductive layer (known as transparent conductive oxide - TCO). This allows maximum electrical conductivity with minimal absorption losses.

Ni/Al (Nickel/Aluminum) electrical grid deposited by e-beam evaporation works as external contacts to draw current out of the cell. Formation of a rectifying metal oxide layer between AZO and Al is avoided by the 10 nm thick Ni layer. The shadow created by Ni/Al layer is 10% of the total 0.5 cm$^2$ CIGSe cell area that needs to be subtracted while calculating the efficiency. Additionally, during Ni/Al e-beam deposition, the mask must be placed in good contact with CIGSe to avoid formation of diffused borders of the metal grid.

Thus, ZnO, AZO and Ni/Al together play an important role in achieving good cell efficiencies. Inferior optical transmittance of ZnO and AZO can adversely affect the formation of charge-carriers in the space charged region. Low electrical
conductivity of AZO and Ni/Al layers can cause considerable losses in the collection of charge carriers. The next section presents the deposition conditions used in the deposition of these three layers. The deposition parameters of ZnO, AZO and Ni/Al were kept constant for the optimization of In$_2$S$_3$ buffer layers and deposition of CdS reference layers.

### 3.4.1 ZnO deposition

Intrinsic ZnO or i-ZnO was deposited at a pressure of $3 \times 10^{-3}$ mBar with an Ar flow rate of 80 SCCM. The target-substrate distance was kept constant at 50 mm and the substrate carrier was rotated at a speed of 20 RPM. i-ZnO was sputtered for 15 minutes with sputter power of 200W giving a film thickness of 120±10 nm. The sputter parameters used here were adapted from literature [100], and from successful depositions by project partners on the CIGSe absorber layers used in this work.

![Fig. 3.4.1: Transmission spectra of intrinsic-ZnO layer.](image)

The UV-Visible transmission spectra (Fig. 3.4.1) show an average transmittance of 89.9% between 400 to 800 nm with onset from 275 nm. High transmittance of window layer ensures that most of the incident solar flux is transmitted to the absorber layer while blocking any shunt paths. This layer is also known as high resistance window. Resistivity of this layer should be as high as possible (typically $> 10^5$ Ω/□) [101]. The resistivity of 120 nm thick ZnO layer was greater than 1 M
Ω/□ as measured by Van-der-Pauw method (accurate measurement of high resistivity films is not possible due to limitation of the existing setup). The deposition parameters mentioned previously for ZnO gave high transparency, good surface coverage and high resistivity. Since the study and optimization of i-ZnO is out of scope of this thesis, known deposition parameters are used for this work without further optimization.

### 3.4.2 AZO deposition

ZnO:Al or AZO thin films were deposited from a 2 wt.% Al₂O₃ from a 4.5N grade purity ceramic targets from FHR Anlagenbau GmbH, Ottendorf-Okrilla, Germany. The deposition was done at a pressure of 5×10⁻³ mBar with an Ar flow rate of 100 SCCM. The target-substrate distance was kept constant at 50 mm and the substrate carrier was rotated at a speed of 20 RPM. 400±20 nm thick AZO layer was deposited after sputtering for 15 minutes with sputter power of 250W. A low resistivity of 2.89E⁻⁵ Ω-m is measured for this layer, as calculated by Van-der-pauw method. The resistivity of AZO at different power and pressure values is shown in Fig. 3.4.2 (a). The low resistivity AZO layer with thickness 400±20 nm has 82.5% average transmittance between 400 to 800 nm (Fig. 4.3.2 (b)).

![Graph showing resistivity and transmission spectra of AZO layer](image)

**Fig. 3.4.2:** (a) Resistivity of AZO layers at different sputter powers (black) and at different sputter pressures (red), the lowest resistivity value is marked with red arrow, (b) transmission spectra of AZO layer with the lowest resistivity.
Further optimization of ZnO and AZO is necessary to reach higher fill factors and improve cell efficiency since optical losses in these two layers can significantly affect cell performances. Ideally, thinner ZnO and AZO layers with higher optical transmittance, complete and uniform surface coverage, and low resistivity (for AZO) must be deposited. However, further optimization of ZnO and AZO layers is out of scope of this thesis.

### 3.4.3 Ni/Al E-beam deposition with a shadow mask

For drawing current out of the cell, metallic grid patterns were evaporated on top of the CIGSe solar cell. The metallic grid was deposited by placing a shadow mask with patterns in an e-beam deposition tool at Interface Chemistry and Surface Engineering Department, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf. The shadow masks had micron-sized patterns fabricated using precision laser cutting on steel by RJ Lasertechnik GmbH at Übach-Palenberg in Germany.

![E-beam deposition of Ni/Al metal grids on CIGSe solar cells](image)
The substrates (25 × 25 mm) were placed on a shadow mask and placed in a UHV e-beam deposition chamber for deposition as shown in the Fig. below. 10 nm Ni and 1.5 µm Al is deposited on AZO layers as metal grids using elemental Ni and Al pellets with 5N grade purity. The thickness and deposition rate were monitored using a quartz crystal microbalance whereas the substrates were rotated at 30 RPM for homogenous deposition of the layer. The emission current for Ni was maintained at 100mA at 6 kV with a deposition rate of 0.1 Å/s. For Al, the emission current was varied between 350 mA and 400 mA for a deposition rate of 10 Å/s.

3.4.4 Mechanical scribing

Mechanical scribing was done on the 25 × 25 mm CIGSe sample to isolate the 8 cells for measurement of different electrical properties. The reason for isolating large area cells is to minimize the current losses from non-performant areas of the cell that may have structuring and deposition defects/inhomogeneities. This ensures that high-performance areas are measured with minimal performance losses.

![Mechanical scribing of complete CIGSe solar cells.](image)

Aluminum (500 nm) was sputter deposited on the rear side of the substrate by DC sputter deposition using the same sputter tool. This was done to ensure better electrical contact while performing efficiency (IV) and quantum efficiency (EQE) measurements.
3.5 Summary of the experimental process

With this work, a methodology was developed for the fabrication of functioning solar cells on CIGSe absorbers that required deposition of several semiconducting layers, with a newly commissioned sputter deposition tool.

First, appropriate sputter conditions were used for In$_2$S$_3$ deposited with Ar-ion sputtering as buffer layer on CIGSe absorbers. Simultaneously, the deposition conditions and layer properties of i-ZnO and AZO window layers were optimized which are necessary to get working CIGSe solar cells. Using several characterization techniques, the shortcomings of the In$_2$S$_3$ layer were identified (discussed in chapter 4) namely absorber surface damage and low S concentration in films.

After obtaining preliminary results with In$_2$S$_3$ buffer layers in CIGSe solar cells, the sputter deposition parameters for In$_2$S$_3$ were further optimized. The aim was to minimize the absorber surface damage. This was achieved by systematically optimizing the sputter power, pressure, and target-to-substrate distance. Additionally, H$_2$S/Ar reactive sputtering was used to improve the S content and obtain crystalline In$_2$S$_3$ films at room temperature. CIGSe cells deposited with reactively sputtered In$_2$S$_3$ gave better cell performance as compared to Ar-ion sputtered In$_2$S$_3$ (Chapter 5).

The work with window layer optimization needs further development since better optical and electrical performances can be achieved as compared to the current values. By optimizing the deposition conditions of i-ZnO, higher optical transmittance and complete coverage of this layer on CIGSe is possible. Additionally, the transparency of AZO can be further enhanced without compromising the electrical conductivity by further optimizing the sputter parameters. This will significantly improve the $J_{SC}$ and $FF$ of the cell leading to improved efficiency. However, window layer optimization is out of the scope of this thesis.
Since several layers are deposited for functioning solar cells, the following flowchart simplifies the processing steps and the characterization methods used:

---

**Fig. 3.5.1:** Flowchart showing the deposition steps of the fabrication process used in this work for CIGSe solar cells.

1. **Cu(In,Ga)Se$_2$ absorber**
   - Chemical etch with KCN / NH$_4$OH (3-8 minutes) + DI water rinse, dry with N$_2$ gas → step:2

2. **Buffer layer deposition**
   - Magnetron Sputtering of In$_2$S$_3$ and Zn(O,S)

3. **In$_2$S$_3$ deposition**
   - Ar-ion sputtering

4. **ZnO deposition**
   - Magnetron Sputtering
     - *Al-doped ZnO (AZO) deposition*

5. **Ni/Al electrical contact grids**
   - E-beam evaporation

6. **Mechanical scribing**
   - + Indium contact pads soldering

7. **Al deposition (back side)**
   - Magnetron Sputtering

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1. ZSW Stuttgart
2-4. Aurion sputter tool (MPIE/RWTH)
5. PVD Cluster (MPIE)
6. Custom designed mechanical scriber
7. Aurion sputter tool (MPIE/RWTH)
Analytical Methods

3.6 Electrical characterization

3.6.1 Van-der-Pauw (VdP)

The electrical resistance of AZO thin films was determined by Van-der-Pauw (VdP) method [102]. This method is commonly used for measuring the sheet resistance (R□) of a square shaped sample using a 4-point connection. The home-made measurement apparatus for VdP is shown in Fig. 3.6.1 with four-point probe connections attached to a Keithley 2400 Source meter.

![Van-der-Pauw measurement setup](image)

*Fig. 3.6.1: Van-der-Pauw measurement setup for sheet resistance measurement.*

The specific resistivity (ρ) is given by the following formula:

\[ \rho = R \square d \]  \hspace{1cm} (3.1)

where \( R \square \) is the sheet resistance and \( d \) is the film thickness. Current is swept across two adjacent ends of the sample (AB) and the corresponding voltage is measured on the other two (CD) giving a Current vs Voltage plot (IV-Curve). Sheet resistance is measured from the slope of the IV curve. To improve the measurement precision by reciprocity and to cancel any offset voltages, eight IV measurements are taken in total as shown in the Fig. 3.6.2 below.
The average vertical and horizontal resistances are calculated and using Newton Raphson numerical method, the following equation is solved to get the $R_{\parallel}$ values:

$$e^{-\pi R_{\text{vertical}}/R_{\parallel}} + e^{-\pi R_{\text{horizontal}}/R_{\parallel}} = 1$$  \hspace{1cm} (3.2)

For symmetric samples, the vertical and horizontal values are averaged, and the above equation simplifies to:

$$R_{\parallel} = \frac{\pi R}{\ln (2)}$$  \hspace{1cm} (3.3)

Where $R$ is the averaged value of all the measured resistances in horizontal and vertical measurement configuration. Substituting the $R_{\parallel}$ value from equation 3.6.3 to Eq. 3.6.1 along with the film thickness, the resistivity (in $\Omega/\square$) of the film is obtained.

### 3.6.2 Current-Voltage characteristics of solar cell

#### 3.6.2.1 Solar radiation:

The intensity of solar radiation in vacuum (or space) outside the earth’s atmosphere is called the solar constant is equal to 1,367 W/m$^2$. Since the solar radiation is not affected in vacuum, the solar spectrum in space is termed as Air
Mass 0. Upon entering the earth’s atmosphere, the solar radiation is largely reflected and attenuated by the earth’s atmosphere, water vapor, etc. Solar radiation is also absorbed by different gases like Oxygen, Ozone, Carbon dioxide, Argon, and Nitrogen present in the atmosphere. Additionally, the attenuation depends on the distance travelled by radiation travels through the atmosphere before reaching the earth’s surface. At the equator, this distance is minimum, and maximum at the poles. Details of the air mass and solar spectrum are presented with the following figure:

Fig. 3.6.3: (a) Air mass (A.M.) 0, 1.0, 1.5 and 2.0 representing the proportion of atmosphere light must pass through before striking earth and (b) spectral distribution of sun for A.M. 0 and A.M. 1.5 solar spectrum.
3.6.2.2 Current generation in solar cells:

A photovoltaic cell is typically a p-n junction diode with n-type and p-type semiconductors forming a heterojunction. Due to junction formation, electrons and holes inter-diffuse across the junction to create an equilibrium state creating a so-called charge-neutral region/space charged region/depletion region at the junction. The Fermi level of the p-type material is close to the valance band, and for the n-type material, it is close to the conduction band. When a pn-junction is formed, the Fermi level equalizes creating band bending at the junction. On either side of the depletion region, there are free charge carriers that give the depletion region a built-in electric field as shown in the figure below.

Fig. 3.6.4: Electron-hole pair (current) generation process in the typical solar cell showing diffusion and drift of charge carriers in the neutral and depletion region respectively [103].

With irradiation of photons, the incident energy is absorbed in different regions of the cell depending on the wavelength (energy) creating electron-hole pairs. The built-in electric field in the depletion region drives the photo-generated charge carriers in opposite directions. For “substrate” configuration, the electrons move towards the n-type region to the front contact whereas the holes move towards the p-type region to the back contact (Fig. 3.6.4). The diode ideality factor $A (A=1-2)$ indicates the perfectness of the solar cell which is affected by charged defects and
impurities. For $A=1$ (i.e., ideal condition), the transport of charge carriers is dominated by the diffusion process, giving $L_e$ and $L_p > W$.

### 3.6.2.3 The Single Diode model:

The electronic transport in CIGSe thin film solar cells is described using the single diode model [104] where $J$ is the photogenerated current density, $J_0$ is the saturation current density. The ideal diode is shown in a grey box in Fig. 3.6.5, where the series resistance $R_S$ is zero and the parallel (shunting) resistance $R_{sh}$ is infinite. For non-ideal behavior, $J_{sh}$ is the shunt current leakage density, $R_S$ is the series resistance, $R_{sh}$ is the shunt resistance.

For a solar cell operated in dark, the current-voltage response showing a rectifying behavior and can be described with the following equation:

$$j(V) = j_0 \left( e^{\frac{qV}{k_B T}} - 1 \right)$$  \hspace{1cm} (3.4)

where $j(V)$ is the current density, $j_0$ is the saturation current density, $q$ is the electronic charge, $V$ is the bias voltage, $A$ is the diode ideality factor, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature.

![Fig. 3.6.5: Equivalent circuit of the ideal diode model showing photogenerated current density $J_p$, Diode current density $J_0$, Series and parallel resistances $R_{sh}$ and $R_S$ respectively and voltage $V$.](image)

For non-ideal conditions with parasitic resistances in the cell, the following equation is valid:
\begin{equation}
    j(V) = J_0(V) + J_{sh}(V) - J_p \tag{3.5}
\end{equation}

Here, \( j(V) \) is the current density, \( J_0 \) is the diode current density, \( J_{sh} \) is the shunt current leakage density and \( J_p \) is the photo-generated current density.

\begin{equation}
    J_0(V) = j_0 \left( e^{\frac{q(V-R_s j(V))}{A k_B T}} - 1 \right) \tag{3.6}
\end{equation}

\begin{equation}
    J_{sh}(V) = \frac{V - R_s j(V)}{R_{sh}} \tag{3.7}
\end{equation}

Thus, from equation 3.5, we have:

\begin{equation}
    j(V) = j_0 \left( e^{\frac{q(V-R_s j(V))}{A k_B T}} - 1 \right) + \frac{V - R_s j(V)}{R_{sh}} - J_p \tag{3.8}
\end{equation}

[105]

3.6.2.4 Solar cell parameters:

The photovoltaic performance of the solar cell is measured collectively by the open-circuit voltage \((V_{OC})\), short-circuit current \((I_{sc})\), fill factor \((FF)\), efficiency \((\eta)\), series resistance \((R_s)\) and shunting resistance \((R_{sh})\).

3.6.2.5 Open-circuit voltage

Open-circuit voltage \((V_{OC})\) is defined as the maximum voltage generated by a solar cell in open circuit condition i.e., current cannot flow through the cell (similar to an infinite load connected in the circuit). When electrons and holes accumulate near the front contact and back contact respectively, a so-called “photo-voltage” is generated in the device due to the electric field. Under illumination conditions, the \(V_{OC}\) is difference between the quasi-fermi levels for the electron and holes on the n- and p- sides respectively as shown in Fig. 3.6.6. Therefore, higher the bandgap difference between P-type absorber and N-type buffer, higher is the \(V_{OC}\). The open circuit voltage of the device as derived from equation 3.8 can be written as:
\[ V_{OC} = \frac{A k_B T}{q} \ln \left( \frac{J_p}{J_0} + 1 \right) \approx \frac{A k_B T}{q} \ln \left( \frac{J_p}{J_0} \right) \quad (3.9) \]

Material properties and cell structuring influences the saturation current density \( J_0 \). Therefore, the recombination losses in the space charged region and at the hetero-interface limits the \( V_{OC} \).

![Diagram of solar cell junctions](image)

*Fig. 3.6.6: (a,b) Fermi-level adjustment upon junction formation and (c) difference in quasi-Fermi levels under illumination resulting in open circuit voltage.*

### 3.6.2.6 Short circuit current

Current passing through the cell in short-circuit conditions (i.e., when front and back contacts are connected externally) with no series resistance is the short circuit current \( (I_{sc}) \) of a solar cell. Short circuit current is due to the generation and collection of photo-generated charge carriers in the solar cell. An ideal solar cell will have zero series resistance and thus the short circuit current will be equal to photo-generated current. Therefore, short circuit current is the maximum current that can be drawn out of a solar cell. Short circuit current density \( J_{SC} \) is the current generated per unit area of the solar cell.

\[ J_{sc} = J_0 \left( e^{\frac{qV_{OC}}{A k_B T}} - 1 \right) - J_p \quad (3.10) \]
and

\[ J_{sc} = qAG(L_n + L_p) \]  

(3.11)

\( G \) is the rate of generation, \( L_n \) and \( L_p \) are the diffusion lengths of electrons and holes, respectively. Under short-circuit conditions, \( V_{OC} = 0 \) and for ideal diode, \( A=1 \). This gives:

\[ J_{sc} = J_p = qG(L_n + L_p) \]  

(3.12)

Fig. 3.6.7: Current-voltage characteristics of CIGSe solar cell.

3.6.2.7 Fill Factor

Fill factor (FF) is ideally the “squareness” of the IV curve measured under illumination. Fill factor can be calculated by taking the ratio between the maximum power \( P_{max} \) (\( P_{max} = I_{max} \times V_{max} \)) and product of \( V_{OC} \) and \( I_{sc} \).

\[ FF = \frac{I_{max}V_{max}}{I_{sc}V_{OC}} \times 100\% \]  

(3.13)

Therefore,

\[ P_{max} = I_{sc} \times V_{OC} \times FF \]  

(3.14)

3.6.2.8 Efficiency

The conversion efficiency (\( \eta \)) of a solar cell is the ratio between the incident power to the maximum generated power of the solar cell. The efficiency is typically
calculated under standard test conditions where the light source has A.M. 1.5 spectrum (as mentioned previously in this section) with an irradiance of 1000 W/m².

\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{I_{\text{sc}} \times V_{\text{OC}} \times \text{FF}}{P_{\text{in}}} \]  

(3.15)

An example of FF and efficiency calculation is given in Fig. 3.6.7.

3.6.2.9 Series (R_s) and shunting (R_{sh}) resistances

Series resistance originates mainly at the interfaces between semiconducting material of the solar cell and external metallic contacts that are non-ohmic in nature. Contacts are formed. Series resistance can arise from bulk resistance of semiconducting layers and the resistivity of front and back contacts. However, the contribution of TCO layer (AZO) is significantly high as compared to other layers. Optimizing AZO deposition conditions to obtain high optical transmittance with low electrical resistivity significantly improves series resistance of the cell (See section 2.1.4 and 3.4.2 for more details). With increasing series resistance, rectifying behavior of IV-curve is enhanced. This is evident from negative slope of the IV curve i.e., from \( V_{\text{OC}} \) to “knee” of the IV-curve (Fig. 3.6.7) approaching zero. This adversely affects the fill factor of the cell, lowering the maximum power drawn out of the device and thus decreases the cell efficiency. The slope of this feature can be calculated to estimate series resistance \( R_s \) of the device.

Shunt resistance or parallel resistance originates from alternative current paths that allow the passage (or leakage) of current through pinholes and grain boundaries. These imperfections are mainly due to manufacturing defects rather than poor solar cell design. Shunting resistance reduces the current flowing through the solar cell, suppressing the efficiency. Ideally, a cell should have infinite shunting resistance but for real devices, the shunting resistance is of the order of \( 1K \Omega \square \). A high shunting resistance cell will have a near-flat feature of the IV-curve starting from short circuit condition (i.e., \( V=0 \)) (See Fig. 3.6.7). As the shunting resistance decreases, the negative slope of this feature will increase. Similar to the effect of series resistance
on the cell, low shunting resistance will degrade the cell performance by a reduction in fill factor.

For real cells with the presence of series and shunting resistances, the following equation is valid:

\[
\text{j}(V) = j_0 \left( e^{\frac{q(V - R_s j(V))}{A k_B T}} - 1 \right) + \frac{V - R_s j(V)}{R_{sh}} - J_p \tag{3.8}
\]

For an ideal cell with zero series resistance and infinite shunting resistance, the IV curve will resemble a perfect square (or rectangle) with fill factor close to unity.

3.6.2.10 Solar simulator

The above electrical characterizations were performed on an Oriel Sol3A Class AAA solar simulator with a 450 W Xenon lamp with spectral uniformity ≥ 98% output and output power of 100mW/cm². Solar spectrum emitted by the solar simulator matches the standard ASTM G173 – 03(2012) [106] that is most commonly referred to as AM-1.5G spectrum. The measurements were taken at ∼ 25 °C in forward bias mode with a current sweep from 0.0–0.71 V.

3.6.3 External quantum efficiency

The external quantum efficiency (EQE) of a solar cell is defined as the ratio of the total charge carriers collected to the number of incident photons at a given wavelength. The EQE is experimentally measured whereas the internal quantum efficiency (IQE) can be derived by measuring the reflectivity of the sample.

\[
\text{EQE}(\lambda) = \frac{j(\lambda)}{q \Phi_0(\lambda)} = (1 - R_{\lambda}) \text{IQE}(\lambda) \tag{3.16}
\]

\(\Phi_0\) is the photon flux in photons (m²s⁻¹), \(j(\lambda)\) is the current density of the device as a function of incident photon wavelength, \(R_{\lambda}\) is the reflectivity and \(q\) is the elementary charge. When EQE is measured under zero bias voltage, the short circuit current density \(J_{SC}\) of the device can be calculated from the solar spectrum:
\[ J_{sc} = q \int_0^\infty \text{EQE}(\lambda)\Phi_0(\lambda) d\lambda \quad (3.17) \]

Fig. 3.6.8: External quantum efficiency of representative CIGSe solar cell showing collection losses due to optical, structural, and material defects and imperfections (adapted from [107-109]).

For an ideal cell with 100% collection efficiency, every incident photon will create an electron-hole pair, that contributes one carrier to the photocurrent. However, in real solar cells, there are always collection losses (recombination) that take place when the photo-generated charge carriers drift and diffuse through different layers of the solar cell. Since photon absorption in solar cell depends on the corresponding energy (see Fig. 3.6.4) the location of the loss mechanism can be determined using quantum efficiency curves. Fig. 3.6.8 presents the breakdown of the collection losses in different regions of the CIGSe solar cell [107, 108].

Short wavelength and high energy photons are absorbed by the AZO layer (Fig. 3.6.8) (1). These absorbed photons may generate electron-hole pair, but they are not collected due to low diffusion length. This is valid for photons absorbed in the ZnO layer (2) as well. Photons with energy between 300 and 500 nm are absorbed by the
buffer layer (3). If the space charge region (SCR) extends to the buffer layer, then the charge carriers may be collected. Most of the charge carriers generated by photons absorbed in the CIGSe SCR are collected (4), however, the others may be lost to recombination at interfaces, defects, and grain boundaries. Incident photons with energy lower than absorber bandgap are below the threshold for current generation. They are reflected/absorbed by Mo back contact or lost as heat (5). Incident photons are reflected from the surface of AZO/ZnO/Buffer/CIGSe (6,7); and due to Ni/Al metal grid on the device, there are direct losses to the incident photon flux due to shadowing (8). The shadowing losses are directly proportional to the total area of the metal grid deposited on the cell.

External quantum efficiency measurements were performed on IQE-Scan manufactured by PV-tools, Waldburg, Germany. The spectral response was acquired with spot illumination of size 1 \times 3 \text{ mm}^2 from 300 to 1200 nm wavelength range at 25 °C.

## 3.7 Optical and structural characterization

### 3.7.1 Ultraviolet-Visible spectroscopy

The optical transmission of thin film samples was measured by ultraviolet-visible (UV-Vis) spectroscopy \[110\] using a Perkin-Elmer Lambda 25 UV-visible spectrometer in the wavelength range from 300 to 1200 nm with a resolution of 0.5 nm and a scan speed of 240 nm/min. The measurements were performed at I.Physikalisches Institut IA, RWTH Aachen in Germany.

### 3.7.2 Grazing incidence x-ray diffraction

Structural characteristics (crystalline or amorphous) nature of thin film samples were determined using grazing incidence x-ray diffraction (GIXRD) measurements \[111\]. The experiments were performed with a PANalytical X’Pert Pro setup by
Philips using Cu-Kα radiation ($\lambda = 1.5405$ Å) at a grazing incidence of 0.7 ° from $2\theta=10–80$ °. The measurements were performed at I.Physikalisches Institut IA, RWTH Aachen in Germany.

### 3.8 Electron microscopy-based methods

#### 3.8.1 Scanning electron microscopy and Focused ion beam lithography

Scanning electron microscopy (SEM) technique [112] in combination with Focused ion beam lithography (FIB) is an important tool in this work. SEM/FIB is used for preparing needle and thin wedge-shaped specimens for analysis with atom probe tomography (APT), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). SEM-based methods like EDS (Energy dispersive x-ray spectroscopy) and EBIC (Electron beam-induced current) were used for compositional analysis and electrical properties, respectively. FEI Helios Nanolab 600, 600i and 650i DualBeam SEM/FIB were used for this work to prepare APT and TEM/STEM specimens, and to perform EBIC and EDS measurements. The microscopes were used collectively at Microstructure Physics and Alloy Design Department at Max-Planck-Institut für Eisenforschung GmbH in Düsseldorf and I.Physikalisches Institut IA, RWTH Aachen in Germany.

#### 3.8.2 Electron beam induced current

Electron beam induced current (EBIC) is an experimental technique analogous to IV-characterization of a solar cell. EBIC uses electron beam excitation in SEM to generate electron-hole pairs in the semiconducting layer in a small volume. The location and intensity of collected charge carrier is recorded by the system, generating a current profile in form of an image. With EBIC, an accurate map of the width of the space charged region, the electrical activity of grain and grain
boundary, recombination and defects can be studied for solar cells. Details about this technique can be found in reference [113]. The EBIC measurements were performed on Gatan DigiScan in FEI Helios Nanolab 650 SEM at I.Physikalisches Institut IA, RWTH Aachen in Germany.

3.8.3 Transmission electron microscopy

Transmission electron microscopy (TEM) technique enables the observation of nanoscale features of the multilayered structure of CIGSe solar cells. JEOL JEM-2200FS operated at 200 kV was used for imaging the buffer-absorber heterointerface in TEM and SAED modes. Samples for TEM (wedge-shaped lamella) were prepared by the standard lift-out method [114] using Focused-ion-beam (FIB) milling. The experiments were carried out at the Structure and Nano-/Micromechanics of Materials Department at Max-Planck-Institut für Eisenforschung GmbH in Düsseldorf, Germany.

3.9 Compositional analysis

3.9.1 Energy dispersive x-ray spectroscopy

Energy dispersive x-ray spectroscopy (EDS) is a chemical microanalysis technique [112] used with scanning electron microscopy, for elemental analysis of materials. For this work, EDS was used to estimate the composition of In and S in In$_2$S$_3$ thin films at SEM acceleration voltage of 20kV and electron beam current of 0.2 nA. The measurements were carried out using Oxford Instruments X-Max 80 mm$^2$ EDS detector on FEI Helios Nanolab 650 SEM at I.Physikalisches Institut IA, RWTH Aachen in Germany.
3.9.2 X-ray photoelectron spectroscopy

Surface elemental composition and chemical state analysis of thin film samples were performed using x-ray photoelectron spectroscopy (XPS). The XPS investigations were performed on a PHI Quantera II Scanning XPS Microprobe with a monochromatic Al Kα source (1486.6 eV) at pass energy of 23.5 eV. These experiments were performed at the Interface Chemistry and Surface Engineering Department, Max-Planck-Institut für Eisenforschung GmbH in Düsseldorf, Germany.

3.9.3 Atom probe tomography

Atom probe tomography (APT) or Local-electrode-atom-probe (LEAP) is a material characterization technique for determining chemical compositions of nanostructures in three-dimensions with sub-nanoscale spatial resolution. It is a combination of (1) field-ion microscopy (FIM) where one sees atoms in direct space and (2) time-of-flight (TOF) mass spectrometer that gives the chemical identity of the atom. This technique enables the study of dopant distribution in 3D with a detection sensitivity of nearly 1 ppm. The interfacial roughness, segregation at defects and interfaces, diffusion kinetics, lateral distribution of elements at the nanoscale, phase transformation, etc. can also be analyzed.
Fig. 3.9.1: Schematic of local electrode atom probe (LEAP) with microchannel plate and a position sensitive detector. Surface atoms are field evaporated from the apex of a needle-shaped specimen by a high electric field (and laser pulse) between local electrode and specimen. Atoms on the tip ionize and fly towards the detectors (MCP and PSD) recording the x and y position and time of flight (chemical identity).

The APT technique is based on the principle of field ionization and field evaporation of surface atoms in the presence of a high electric field [115]. Field evaporation is a phenomenon where under an external field, the ionic state of an atom becomes more stable than the neutral state at a specific distance from the surface (Fig. 3.6.2). Thus, APT is a destructive method where atoms are ionized and successively removed from a needle-shaped specimen with radius \( \sim 50-100 \text{ nm} \). The process takes place under ultra-high vacuum (< 1x10^{-10} mBar) with specimen cooled at cryogenic temperatures (\( \sim 20-60 \text{ K} \)) reducing the atomistic vibrations. Due to the special shape of the specimen, high local electric field in excess of 10 V/nm is present at the apex of the tip. The sample is kept at a constant voltage fraction whereas the local electrode is pulsed with a high frequency voltage of the order of \( \sim 160-250 \text{ MHz} \) and pulse energy \( 2-5 \text{ pJ} \).
hundreds of kHz. For non-conducting or semiconducting samples, a UV-laser pulse with energy $\sim 5$ pJ and pulse rate $\sim 100$-300 kHz is given.

![Fig. 3.9.2: Plot of the potential energy vs distance of atom from surface illustrating mechanism of field evaporation.](image)

In voltage mode, when the applied high-frequency electric pulse is enough to break the bond of surface atoms, ionization of the atom takes place. In laser mode, short laser pulses to the atom undergo thermally induced field evaporation and ionizes. Assuming a spherical tip apex, the electric field can be given by [115]:

$$F = \frac{V}{k_f R} \quad (3.18)$$

Here, $V$ is the applied voltage, $R$ is the radius of curvature and $k_f$ is the field correction/reduction factor. There is a reduction of the electric field by tip geometry and so the field correction factor value is $3 < k_f < 8$ calculated for W sample [116]. Ideally, the tip radius must be smaller than 50 nm for facilitating high local electric field.

Thus, the APT technique records the x and y coordinates for each atom using the position sensitive detector, the time of flight (m/z ratio) from the microchannel plate and sequence of evaporation to generate an (x, y, z, m/z). This data is recorded for several millions of atoms which are reconstructed in the form a three-dimensional elemental map representing the analyzed volume. The 3D reconstruction thus
obtained is an apex-truncated cone with a hemispherical cap. Since the specimen is needle-shaped, the radius of the cone increases with respect to the length of the sample.

The detection efficiency of APT depends on the open area of the apertures on a microchannel plate (MCP) ranging from 37% to nearly 80% for modern LEAP systems [117]. So the remaining atoms that are ejected either fly away or hit the inter-channel regions of the MCP [118].

**Fig. 3.9.3:** Needle shaped sample preparation procedure for APT starting from (a) milling out trenches from 3 sides to form a lamella. (b) micromanipulator insertion, platinum welding and lamella lift-off. (c,d) mounting the lamella on Si-post on a commercially purchased Si-post array coupon. (e) cutting a small sample out of the lamella onto the Si-post. (f) platinum welding on both sides of the sample. (g) rough annular milling at high FIB beam current up to an apex radius 500 nm. (h) fine annular milling at low FIB beam current up to apex radius 100 nm. (i) Low kV milling to remove amorphous layer – final tip for APT measurement.
APT sample preparation procedure

Needle-shaped samples with radius ≤ 50 nm were prepared by FEI DualBeam SEM/FIB with the region of interest within the first 100 nm from the apex of the tip using the method described in [119]. The step-by-step lift-out procedure is as follows:

1. ROI identification and protective Platinum layer deposition: The region of interest (ROI) is defined and ideally a protective Pt layer (∼ 200 nm) is deposited using e-beam deposition with stage tilted at 52 °. Ideally, the lamella is 25 × 2.5 × 2.5 μm (l × w × h).

2. Cutting trenches on 3 sides: The SEM stage is tilted to 22 ° and trenches are cut on three sides at a high beam current of ∼ 2.5 nA at 30 kV. The longer side of the trench is l + 2 μm long and 2w wide with respect to the lamella. The stage is rotated by 180 ° and the process is repeated. (Fig. 3.9.3 (a))

3. Micromanipulator insertion and Pt deposition: Stage is tilted at 0 ° and the micromanipulator is inserted. A gentle contact between the micromanipulator and free end of the cantilever is made. Pt deposition is done at the point of contact followed by making the wedge free from the bulk sample by milling a trench on the 4th side. (Fig. 3.9.3 (b))

4. Lamella lift-off and mount: The lamella is carefully lifted off from the bulk of the sample and moved to the Si/Mo post for mounting. The bottom of the lamella is gently placed on the Si-post and welded with Pt. A FIB cut between the manipulator needle and lamella makes the sample free-standing on the Si-post. (Fig. 3.9.3 (c,d,e))

5. Pt deposition: The sample is rotated by 180 ° and Pt is deposited at bottom of the sample. This stabilizes the sample and secures from thermal and electrical shock failures. Sample from the top is trimmed to 1.5 × 2.5 μm (Fig. 3.9.3 (f)).

6. Annular milling: Stage is tilted at 52 ° and rough annular milling is performed at 16 kV, 0.13 nA FIB beam current. The apex radius at the end of this stage...
is \sim 500 \text{ nm}. This is followed by fine annular milling where the FIB beam current is lowered to \sim 28 \text{ pA} and the inner radius of circular milling pattern is as low as 100 \text{ nm} (Fig. 3.9.3 (g,h)). The annular milling process is carefully monitored by SEM to avoid any accidental loss or damage of the specimen.

7. Low-kV milling: High KE Ga\textsuperscript{+} ions from the FIB induce surface amorphization of the sample. To remove the amorphous surface layer, low-kV surface cleaning is performed for 100 \text{ nm} sample length from the apex to improve the quality of results obtained by APT. (Fig. 3.9.3 (i))

The APT samples prepared by FIB/SEM are transferred immediately to the load-lock chamber of LEAP to avoid sample contamination due to ambient conditions.

APT measurements were performed on CAMECA LEAP 4000X Si at RWTH Aachen (Germany) with a straight flight path of 90 mm. The probing was conducted in laser mode by applying UV-laser (355 nm) operated at a frequency of 250 kHz and pulse energy of 5 pJ and 12 ps pulse length. The sample was cooled to 40 K.
4. CIGSe solar cells with RF sputtered In$_2$S$_3$ buffer layers

In this chapter, the interdependence of interfacial properties and photovoltaic performance of the sputter deposited In$_2$S$_3$ buffer layers in CIGSe solar cells is investigated. Ar-ion sputtered In$_2$S$_3$ buffer layers with different thickness were deposited on a quartz substrate. In$_2$S$_3$ buffer layer with good optical transmittance in the energetic blue region (<450 nm) is then deposited on CIGSe absorbers to form In$_2$S$_3$/CIGSe heterointerface. Deposition of window layers and metallic contacts completes the cell. The cell is then annealed, and electrical measurements are performed using EQE and IV characterizations. In$_2$S$_3$/CIGSe heterointerface of the best performing cells is then analyzed further. The cross-section of In$_2$S$_3$/CIGSe heterointerface is visualized using techniques like STEM in the HAADF mode and HR-TEM. Finally, to understand the relationship between interfacial elemental redistribution and the cell performance upon annealing, the optoelectric properties described above will be correlated with the APT results. The effect of sputter power on the interface is studied with APT as well. EBIC is used to study the effect of annealing on the electrical properties of the solar cells.

In$_2$S$_3$ buffer layer was sputtered at 50W power, 3×10$^{-3}$ mbar working pressure, 50 mm target to substrate distance, 15 RPM substrate rotation speed with deposition time of 5 minutes. The sputter deposition was done with Ar-ion sputtering without introducing any reactive gases. The as-deposited samples at room temperature will be mentioned as In$_2$S$_3$-RT. Samples annealed at 210 °C for 15 minutes will be mentioned as In$_2$S$_3$–HT throughout this chapter.
4.1 Photovoltaic performance of complete CIGSe solar cells with In$_2$S$_3$ buffer layers

4.1.1 UV-Visible transmission spectra

Transmission spectra of In$_2$S$_3$ buffer layers were measured from 300 to 900 nm for In$_2$S$_3$ buffer layers. The layer thickness determined by FIB cross-section was found to be 25nm, 55nm, 85nm, and 110nm for sputter deposition time of 150s, 300s, 450s, and 600s, respectively. For transmittance measurements, the In$_2$S$_3$ films were deposited on quartz substrates to ensure transparency in the near-UV region. The samples were then annealed at 210 °C for 15 minutes. From Fig. 4.1.1 (a) we can see that thinner buffer layers have higher transparency in the near-UV or blue wavelength region. With increasing thickness, the buffer layers transmit more light in the visible region. In$_2$S$_3$ with 25 nm film thickness showed relatively high transmission of 38% at 400 nm transmission wavelength. However, at 700 nm, the thicker film of 110 nm shows a near-absolute transmission.

The absorption coefficient $\alpha$ of the deposited films can be measured by Lambert-Beer’s law using the following equation:

$$\alpha = -\frac{1}{d} \ln \left[ \frac{T}{(1-R)^2} \right]$$

(4.1)

where $d$ is film thickness, $T$ is transmittance, and $R$ is reflectance[79]. The transmittance and reflectance of the film are measured by UV-Visible spectrometer. The absorption coefficient $\alpha$ can be used in the Tauc relation below to obtain the value of bandgap $E_g$:

$$\alpha E = A (h\nu - E_g)^m$$

(4.2)

here $\nu$ is photon energy, $E_g$ is bandgap, $A$ and $m$ are constants. The value of $m$ is either $\frac{1}{2}$ or 2 denoting direct or indirect nature of band-to-band transition in the semiconductor. The semiconducting nature of β-In$_2$S$_3$, whether it has direct [77] or
indirect [58] type of bandgap is a matter of debate. Here, \( m = \frac{1}{2} \) has been used since these samples showed a good fit with direct bandgap values. The plot of \( (ahv)^2 \) vs \( E \) is presented in Fig. 4.1.1 (b). Bandgap values for 25 – 110 nm thick films is between 3.3 to 3.4 eV, which is close to a similar investigation on sputter deposited In\(_2\)S\(_3\) films by S. Karthikeyan et al. [53]. It should, however, be noted that the bandgap values of these films will be different when deposited on a CIGSe absorber surface.

![Graph showing transmission spectra and (ahv)² vs E plot of In\(_2\)S\(_3\) buffer layers deposited on quartz substrates with different film thickness after annealing at 210 °C for 15 minutes.](image)

**Fig. 4.1.1:** (a) Transmission spectra and (b) \( (ahv)^2 \) vs \( E \) plot of In\(_2\)S\(_3\) buffer layers deposited on quartz substrates with different film thickness after annealing at 210 °C for 15 minutes. The overall transmittance and thus, the bandgap changes with increasing thickness.

### 4.1.2 Absorber surface preparation for buffer layer deposition

After obtaining preliminary results on optoelectronic properties of In\(_2\)S\(_3\) buffer layers deposited on quartz, the next step was to proceed with deposition In\(_2\)S\(_3\) buffer layers on CIGSe absorbers. Before the deposition, the surface of the absorber was rinsed with de-ionized water and etched with a 10% aqueous solution containing 28% (v/v) NH\(_3\) in H\(_2\)O (NH\(_4\)OH) for 3 minutes. The etching process removed any excess Na impurities or In- and Ga-based oxides from absorber surface [97]. This ensured a similar absorber surface chemistry for improved reproducibility. The substrates were then dried with N\(_2\) and placed in the load lock chamber of the sputter deposition tool for degassing.
4.1.3 I-V characteristics of In$_2$S$_3$/CIGSe solar cells

In$_2$S$_3$ buffer layers were deposited on NH$_4$OH etched CIGSe absorbers with different thickness. From literature, the thickness for high-efficiency In$_2$S$_3$ buffer layers was typically between 40-70 nm [5, 92, 120]. Hence to understand the dependence of thickness on cell parameters for this study, In$_2$S$_3$ buffer layer with different thicknesses (25 nm, 55 nm, 85 nm, and 110 nm) were deposited on CIGSe absorbers. To complete the cells, 100 nm intrinsic ZnO (i-ZnO) and 400 nm of 2% Al$_2$O$_3$ doped ZnO (AZO) were deposited on the In$_2$S$_3$ buffer layer. Front metal contacts such as 10 nm Nickel and 1.5 µm Aluminum were e-beam evaporated using a shadow mask to make contact-patterns on the solar cell. The multilayer stack had the following configuration: Ni/Al/AZO/i-ZnO/In$_2$S$_3$/CIGSe/Mo deposited on a 3 mm thick soda-lime glass. Finally, the completed cells were annealed in air for 15 minutes at 210 °C. These completed cells were then tested for their IV and EQE characteristics.

![Graphs showing cell parameters](image)

Fig. 4.1.2: Cell parameters of CIGSe solar cells with respect to In$_2$S$_3$ buffer layer thickness after annealing in air at 210 °C for 15 minutes. Highest cell parameters ($J_{SC}$, $V_{OC}$, FF, and Efficiency) were measured for 55 nm thick buffer layer.
The photovoltaic parameters of complete CIGSe solar cells with respect to In$_2$S$_3$ buffer layer thickness are presented in Fig. 4.1.2. The IV measurements were performed under the AM1.0 test conditions with 100mW/cm$^2$ illumination at 25 °C. Since these were preliminary results for this study on functioning CIGSe solar cells with In$_2$S$_3$ buffer layers, only post-annealing results are presented here. The averaged cell parameters: $J_{SC}$, $V_{OC}$, fill factor (FF) and efficiency ($\eta$) of four best-performing cells for different buffer layer thickness are shown here. An efficiency of 11.71% was measured for a cell with 55 nm thick In$_2$S$_3$ buffer layer. For this thickness, the $J_{SC}$, $V_{OC}$, FF, and efficiency was higher than the samples with 25 nm, 85 nm, and 110 nm buffer layer thickness.

![Fig. 4.1.3: External quantum efficiency (EQE) curves of CIGSe solar cells with respect to In$_2$S$_3$ buffer layer thickness normalized at 700 nm. The inset plot shows the EQE curves before normalization.](image)

Fig. 4.1.3 shows the External quantum efficiency (EQE) curves for In$_2$S$_3$/CIGSe solar cells with different buffer layer thicknesses. The spectra have been normalized [121] at 700 nm for better visualization of the effect of buffer layer thickness on collection efficiency. The thinner 25 nm buffer layer has the highest collection in the blue region between 350-500 nm. Blue region collection decreases as the buffer layer thickness increases from 25 nm to 110 nm. With increasing buffer thickness, more
photons are absorbed by the buffer layer due to lower transmittance as seen from Fig. 4.1.1 (a). The photons absorbed by buffer layer generate minority charge carriers. However, due to low mobility, they are not collected and thus wasted. So ideally, the buffer layer must transmit most of the incident photons to the absorber layer. Therefore, thinner buffer layers are preferred to improve light transmittance in the bulk of the absorber layer.

The results of the electrical characterizations described above, proves that for complete CIGSe solar cells, In$_2$S$_3$ buffer layers with 55 nm thickness have the best cell parameters. However, the EQE results show that the thinner 25 nm buffer layer has better blue-wavelength response from 400 – 600 nm. The discrepancy between these two results can be explained by the rough CIGSe topography (surface root-mean-squared roughness of ~100 nm). Deposition of thinner buffer layer (25 nm) will have inferior surface coverage and increased possibility of formation of pin holes or discontinuity on the CIGSe absorber. Hence, for improved surface coverage of In$_2$S$_3$ on CIGSe absorbers, 55 nm thick layers were deposited and investigated further in this work.

The CIGSe absorbers used for this work were stored in vacuum, but due to the aging effect, surface oxides are formed. Therefore, longer NH$_4$OH etching time of 5 minutes was used to ensure removal of unwanted impurities from the absorber surface. Applying these processing modifications to deposition conditions significantly improved the cell parameters. Additionally, cell parameters before and after annealing were studied and compared with CdS-reference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>η (%)</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS – Reference</td>
<td>16.1</td>
<td>673</td>
<td>31.95</td>
<td>75%</td>
</tr>
<tr>
<td>In$_2$S$_3$-RT</td>
<td>0.9</td>
<td>143</td>
<td>20.71</td>
<td>36%</td>
</tr>
<tr>
<td>In$_2$S$_3$-HT</td>
<td>13.6</td>
<td>688</td>
<td>32.52</td>
<td>53%</td>
</tr>
</tbody>
</table>
The I–V characteristics of the cells with improved deposition conditions for 55 nm thick In$_2$S$_3$ buffer layer is presented in Table 4-1. In$_2$S$_3$-RT sample has poor open circuit voltage ($V_{OC}$) of 193 mV and a low fill factor (FF) of 36%. After annealing at 210 °C for 15 minutes, a significant improvement in efficiency from 0.9% to 13.6% and $V_{OC}$ improvement from 193 mV to 688 mV was observed for the In$_2$S$_3$-HT sample. $V_{OC}$ obtained for sputtered In$_2$S$_3$ was higher than CdS reference due to the higher bandgap of In$_2$S$_3$. The diode ideality factor calculated from the ln(J) – V curve was found to be as high as 6.62, which is due to the low shunting resistance of 71.02 Ω cm$^2$ recorded for the best performing cell with efficiency 13.6%.

The external quantum efficiency curves presented in Fig. 4.1.4 for In$_2$S$_3$/CIGSe solar cells show significant improvement in collection efficiency from room temperature to annealed cell. Onset of quantum efficiency for room temperature (In$_2$S$_3$-RT) sample is from 450 nm, indicating higher recombination at In$_2$S$_3$/CIGSe interface. This is likely due to an inferior quality of interface and formation of recombination centers due to sputter deposition. High recombination can occur due to cliff type conduction band offset formation at the In$_2$S$_3$/CIGSe heterointerface.

Fig. 4.1.4: The measured external quantum efficiency (EQE) curves of In$_2$S$_3$/CIGSe solar cells before (In$_2$S$_3$-RT) and after (In$_2$S$_3$-HT) annealing.
This is evident from the low \( V_{OC} \), FF and \( J_{SC} \) values as seen from Table 4-1. When the cell is annealed at 210 °C for 15 minutes, there is a significant improvement in the overall collection efficiency. This indicates that the defect-states acting as recombination centers at the In\(_2\)S\(_3\)/CIGSe interface are passivated.

### 4.2 In\(_2\)S\(_3\)/CIGSe heterointerface formation

A heterointerface is formed when n-type In\(_2\)S\(_3\) buffer layer is sputter deposited on p-type CIGSe absorber layer. It has been frequently reported [124-126] that the In\(_2\)S\(_3\)/CIGSe interface quality (uniform coverage, low defect density) dominates the cell performance. This makes study of the heterointerface formed by deposition of sputtered In\(_2\)S\(_3\) on CIGSe crucial for this work.

#### 4.2.1 In\(_2\)S\(_3\)/CIGSe cross-sectional analysis

The layer properties of sputter deposited In\(_2\)S\(_3\) on CIGSe were studied by STEM-HAADF, HR-TEM and SAED. A thin lamella of around 50 nm thickness was milled-out from the In\(_2\)S\(_3\)/CIGSe cell by using a dual beam focused ion-beam/Scanning electron microscopy (FIB/SEM). Fig. 4.2.1 presents the AZO/i-ZnO/In\(_2\)S\(_3\)/CIGSe stack for the In\(_2\)S\(_3\)-HT sample imaged by STEM in HAADF mode. The film thickness was found to vary between \( \sim 30 \) nm to \( \sim 110 \) nm due to rough CIGSe surface with the same deposition parameters mentioned in the previous section 4.1. Layer thickness measured on a thin lamella extracted from CIGSe multilayer is more accurate than the thickness estimation from a FIB cross section on plane-quartz substrate in section 4.1. When the buffer layer is deposited on CIGSe, the layer thickness varies due to shadowing effect of the rough absorber. The surface area of valleys or steps is more per unit area, than a flat top surface. So, the buffer layer deposited in valleys and steps is thinner than at peaks and flat-top surfaces. Fig. 4.2.1 illustrates the effect of non-uniform buffer layer thickness due to shadowing.
The flat-top surface has a thicker deposition of In$_2$S$_3$ buffer layer than the inclined surface of the CIGSe absorber.

Fig. 4.2.1: (a,b) STEM HAADF image of the cross-section of an In$_2$S$_3$-Ar sample showing the multilayer structure of In$_2$S$_3$/CIGSe cell with different magnifications. Due to rough CIGSe topography, the buffer layer deposition is thicker on peaks or flat-tops whereas thinner in valleys and steps.

The crystallinity of the sputter deposited In$_2$S$_3$ buffer layer was investigated by high-resolution TEM (HRTEM). Fig. 4.2.2 shows the HRTEM image of the i-ZnO/In$_2$S$_3$/CIGSe stack. The HRTEM studies reveals that the In$_2$S$_3$ layer was amorphous after deposition that crystallized (with an approximate crystallite size of around 10 nm as seen in Fig. 4.2.2 b) after annealing. Moreover, the selected area electron diffraction (SAED) pattern in Fig. 4.2.2 c shows a mixture of spot and ring patterns, indicating that the In$_2$S$_3$ buffer layer was not fully crystallized after annealing at 210 ºC for 15 min. The presence of secondary phases such as Cu$_2$Se and Ga$_2$O$_3$ or In$_2$O$_3$ or the presence of ordered defects compounds (ODC) was not detected at the CIGSe surface as suggested by Cojocaru-Mirédin et al. [91]. and Abou-Ras et al.[127].
Fig. 4.2.2: HRTEM image of In$_2$S$_3$-HT sample showing (a) the i-ZnO/In$_2$S$_3$/CIGSe stack (b) nanocrystalline structure of In$_2$S$_3$ and i-ZnO layers and (c) SAED pattern of the buffer layer, the CIGSe/In$_2$S$_3$ interface is marked as a dotted line.

4.2.2 Effect of annealing on the In$_2$S$_3$/CIGSe heterointerface

Fig. 4.2.3: 3D elemental map of In$_2$S$_3$/CIGSe interface for (a) In$_2$S$_3$-RT and (b) In$_2$S$_3$-HT samples showing the redistribution of Cu (blue), In (pink), Ga (orange), Se (red) and S (yellow). (c) and (d) show the proximity histograms of the In$_2$S$_3$/CIGSe hetero-interface. There is redistribution of all elements post heat treatment. The Cu concentration has significantly flattened after annealing. This makes CIGSe surface Cu-deficient, with S and In diffusing into the CIGSe surface.
Fig. 4.2.3 (a,b) shows the three-dimensional elemental distribution at the Cu(In,Ga)Se$_2$/In$_2$S$_3$ interface for In$_2$S$_3$-RT and In$_2$S$_3$-HT samples, whereas Fig. 4.2.3 (c,d) shows the respective proximity histogram (or proxigram; for more information see ref. [128]). These proxigrams are divided into three regions: (I) Cu-depleted CIGSe surface (so-called CIGSe surface reconstruction [129]), (II) interfacial intermixing region and (III) heat-induced intermixing region.

Region I of the In$_2$S$_3$-RT sample was artificially modified by the high energy In atoms (In is heavier than Cu, Ga, and Se) inducing a sputter damaged region with a size larger than 3 nm (see Fig. 4.2.3 c). In region I, the Cu-depletion was accompanied by an In-enrichment, showing thus an In-Cu anticorrelation [130]. After annealing (see Fig. 4.2.3 d), the region I of In$_2$S$_3$-HT sample showed an even stronger depletion in Cu and enrichment in In. In contrast, APT experiments performed on a chemically deposited In$_2$S$_3$ buffer layer [91] showed a Cu-depleted CIGSe surface of around 3 nm but no change in In concentration.

Region II in Fig. 4.2.3 c was assigned to the *interfacial intermixing* between In$_2$S$_3$ and CIGSe. It is believed that the sputter-induced intermixing zone, in this case, is maximum-2.5 nm. It should be noted here that the 2 nm width of the intermixed region measured from the proxigram is the improved value obtained after applying very gentle deposition conditions. Interface intermixing of similar magnitude (1-2 nm) has been previously observed for chemically deposited CdS or In$_2$S$_3$ buffers [91, 131]. This suggests that the sputter damages were considerably reduced when depositing In$_2$S$_3$ buffers with the previously mentioned sputter parameters. In this work, after annealing (see Fig. 4.2.3 d), the width of the intermixed region became wider by around 3.5 nm. This is mainly due to the heat-induced intermixing or diffusion of mainly Cu towards the In$_2$S$_3$ layer and In, S towards the CIGSe layer. Especially for Cu, a continuous diffusion profile starting from CIGSe and continuing inside In$_2$S$_3$ in region III is observed as shown in Fig. 4.2.3 d. Region III in Fig. 4.2.3 d is thus entirely assigned to the heat-induced intermixing between In$_2$S$_3$ and CIGSe.
However, such a heat-induced intermixed region is also observed for the non-annealed sample, i.e., for In$_2$S$_3$-RT sample. Sputter deposition process generates heat is locally by the bombardment of energetic sputtered atoms. The maximum temperature measured directly on the CIGSe absorber using a point contact thermocouple during sputtering was 75 °C, however, the actual temperature on the surface can be much higher. This promotes elements to slightly diffuse during the sputter deposition process, explaining thus the existence of a small region III of ~1 nm thick for the In$_2$S$_3$-RT sample. Only Cu was diffusing in this region, indicating high mobility of Cu atoms as discussed before.

Table 4-2: The measured concentration of In (Indium), S (Sulphur), Cu (Copper), Ga (Gallium), Se (Selenium), H (Hydrogen) and O (Oxygen) for In$_2$S$_3$ and CIGSe layers within the first 50 nanometers from the interface before and after annealing. A significant drop in S concentration is seen after annealing due to low S vapor pressure, change in In$_2$S$_3$ crystallinity, and elemental redistribution across the interface.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Sample</th>
<th>In</th>
<th>S</th>
<th>Cu</th>
<th>Ga</th>
<th>Se</th>
<th>H</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$S$_3$</td>
<td>In$_2$S$_3$-RT</td>
<td>38.06</td>
<td>56.35</td>
<td>2.65</td>
<td>0.01</td>
<td>1.83</td>
<td>0.65</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>In$_2$S$_3$-HT</td>
<td>±0.16%</td>
<td>±0.01%</td>
<td>±0.04%</td>
<td>±0.00%</td>
<td>±0.02%</td>
<td>±0.01%</td>
<td>±0.01%</td>
</tr>
<tr>
<td>CIGSe</td>
<td>In$_2$S$_3$-RT</td>
<td>49.60</td>
<td>47.12</td>
<td>1.67</td>
<td>–</td>
<td>1.60</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>In$_2$S$_3$-HT</td>
<td>±0.14%</td>
<td>±0.02%</td>
<td>±0.04%</td>
<td>–</td>
<td>±0.02%</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>CIGSe-RT</td>
<td>20.34</td>
<td>9.64</td>
<td>50.36</td>
<td>0.92</td>
<td>0.35</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>CIGSe-HT</td>
<td>±0.07%</td>
<td>±0.06%</td>
<td>±0.05%</td>
<td>±0.03%</td>
<td>±0.01%</td>
<td>±0.01%</td>
<td>±0.01%</td>
</tr>
</tbody>
</table>

An estimation of the S concentrations by the proxigram is not precise due to the peak overlaps ($^{65}$S$_2^+$ with $^{65}$Cu$^+$ and $^{97}$S$_3^+$ with $^{97}$CuS$^+$) observed in the mass-to-charge spectrum. To overcome this limitation, the mass spectra of the In$_2$S$_3$ layer and the CIGSe layer in the proximity of the junction were evaluated separately and precise elemental concentrations were obtained by decomposing the convoluted peaks by ratio of their isotopic abundance. The obtained values for both layers, before and after annealing are shown in Table 4-2. S concentration dropped from
56.35 at.% to 47.12 at.% after annealing, which can be attributed to the high vapor pressure of S. This led to a significant change in the In$_2$S$_3$ stoichiometric ratio in the layer.

### 4.2.3 Cu-diffusion at the In$_2$S$_3$/CIGSe interface with respect to annealing time:

![Cu proximity histogram at the interface](image)

**Fig. 4.2.4:** Cu proximity histogram at the interface for: In$_2$S$_3$-RT sample before annealing (blue), after 15 minutes annealing at 210 °C (In$_2$S$_3$-HT sample) (red) and 60 min annealing (black). These concentration profiles reveal how Cu diffusion into the In$_2$S$_3$ layer depletes Cu from the CIGSe surface on prolonging the annealing time at 210°C.

Our experiments confirm Cu diffusion from the CIGSe into the In$_2$S$_3$ buffer layer at temperatures above 210 °C, depleting Cu from the CIGSe surface. Fig. 4.2.4 compares the proximity histogram of Cu for the as-deposited In$_2$S$_3$-RT sample, for 15 minutes heat treated In$_2$S$_3$-HT sample and for 60 minutes heat treated In$_2$S$_3$/CIGSe sample. For In$_2$S$_3$-RT, the Cu drop is abrupt at the interface. However, after annealing, there is a significant depletion of Cu on the CIGSe side making the surface region overall Cu-poor. This change in Cu composition significantly modifies the local doping at the interface region. On annealing the In$_2$S$_3$-HT sample additionally for 45 minutes (60 minutes in total) at 210 °C, stronger Cu diffusion into the In$_2$S$_3$ layer (making the CIGSe surface even more Cu-deficient) is observed.
4.2.4 Alkali segregation near the In$_2$S$_3$/CIGSe interface

Alkali segregation (Na and K) at CIGSe grain boundary has previously been reported [132, 133]. However, there are not many reports for Na [134] and K segregation at the buffer/absorber interface. In this work, Na segregation has been found at a depth of 10-40 nm from the In$_2$S$_3$/CIGSe interface for In$_2$S$_3$-HT samples. This kind of layer formation resembles buried homojunction formation near the p-n junction interface. There have been previous reports on the existence of buried homojunction formation in CI(G)S based solar cells [135, 136]. It was formed by diffusion of Cd from the CdS buffer layer. Cd with cationic radius 0.97 Å acts as a substitutional donor on Cu (ionic radius 0.96 Å) sites [137]. This inverts the p-type CIGSe region to n-type Cd-doped region creating thus a homojunction. Formation of homojunction enhances the cell performance, but in this case instead of Cd substitution, Na segregation is seen. Na segregation/passivation behind the p-n junction interface is not yet reported. It can, however, be stated that when Na passivates Cu vacancies of In$_{Cu}$ antisites, it suppresses the defect state recombination and results in improved cell performance. Nearly 0.3 at.% Na is found to be segregated from a distance of 10-40 nm from the CIGSe/In$_2$S$_3$ p-n junction interface for samples annealed at 210 °C (Fig. 4.2.5). Besides Na, a small amount of K (0.1 at%) is also found in this region. As mentioned earlier, the implications of such segregation are not clear.
Fig. 4.2.5: (a,d) 3D elemental map of $\text{In}_2\text{S}_3$/CIGSe with (b,e) Na and K segregation behind $\text{In}_2\text{S}_3$/CIGSe interface and (c,f) the proximity histogram of Na and K distributed from 10 nm to 40 nm behind the interface.

4.2.5 $\text{In}_2\text{S}_3$/CIGSe Space-charged region (SCR) analysis

Electron beam induced current (EBIC) analysis was used to investigate the charge carrier activity in the device before and after annealing. Fig. 6(a-d) shows the SEM image and the corresponding EBIC map for $\text{In}_2\text{S}_3$-RT and $\text{In}_2\text{S}_3$-HT
samples. Here bright contrast represents increased minority charge carrier (here electrons) collection or the current collection and vice versa. The space charge region (SCR) emerges brightest due to the maximum separation of charge carriers occurring in this region. It is noted here that the space charge region is around 500 nm deep into CIGSe extending from the buffer layer. Moreover, the J-EBIC (junction-EBIC) image shows that most of the grains in the CIGSe bulk are active and contribute to the EBIC current, which was consistent over several cross sections studied for this device. This indicates that the buffer and window layers are uniformly deposited on the absorber. Fig. 6e shows the EBIC/Ebeam line profile from the regions marked in the EBIC images. The position 0 where the EBIC current peaks are located represents the position of the electrical junction coinciding with the physical junction present at the buffer-absorber interface. It is evident from Fig. 6e that the overall EBIC current has significantly increased after annealing.

Fig. 4.2.6: (a-d) SEM images and the corresponding EBIC maps of AZO/i-ZnO/In_{2}S_{3}/CIGSe/Mo stack before and after annealing at 210 °C. (e) EBIC/Ebeam depth profiles for the respective samples from the marked regions in the EBIC maps. The dotted line in (e) represents the position of the p-n junction. The depth profiles show the improved current collection at the p-n junction for the sample annealed at 210°C for 15 minutes.
4.3 Discussions

4.3.1 Effect of annealing on optical and electrical properties

Before annealing, the cells showed low \( V_{OC} \) values implying a defective p-n junction. This is attributed to the fact that the CIGSe surface is damaged by the highly energetic In and S atoms during \( \text{In}_2\text{S}_3 \) deposition, creating a high density of interfacial defects. Using SRIM calculations [138], the average kinetic energy of In and S atoms was calculated based on the penetration depths given by APT data of 4 nm and 1.5 nm, respectively. The calculated values for the averaged kinetic energy are \(~0.7\) keV and \(0.2\) keV, respectively. Moreover, EBIC experiments showed that current collection before annealing is considerably lower. This is explained by the presence of a high number of radiative and SRH recombination active defects at the CIGSe surface that can adversely affect the cell efficiency.

After annealing, the significant increase in \( V_{OC} \) and cell efficiency confirms an improvement of p-n junction quality. The latter can be explained by (i) the passivation of interfacial defects, (ii) improved crystallinity of \( \text{In}_2\text{S}_3 \) buffer, and (iii) diffusion of Cu across the interface. However, it is believed that the \( V_{OC} \) and hence efficiency values can be by further improved by completely crystallizing the \( \text{In}_2\text{S}_3 \) layer. The presence of a small fraction of amorphous \( \text{In}_2\text{S}_3 \) indicates that the \( \text{In}_2\text{S}_3/\text{CIGSe} \) interface may still contain recombination active centers. The low fill factor value of 53\%, low shunting resistance of \(71.02 \ \Omega \cdot \text{cm}^2\), high ideality factor of 6.62 and a nonlinear \( \ln(J) - V \) behavior indicates that there is still room for improvement of the device quality.

The \( J_{SC} \) values vary only little after annealing as seen in Table 4-1. Based on Ref. [139] the \( J_{SC} \) is directly proportional to the diffusion length of minority carriers, i.e. electrons (\( l_e \)) or holes (\( l_h \)) for \( \text{In}_2\text{S}_3 \), from the equation:

\[
J_{SC} = eG(l_e + w + l_h) \tag{3}
\]
where \( G \) is generation rate and \( w \) is width of the depletion region. The fact that \( J_{SC} \) did not changed upon annealing (no modification of \( l_e \) or \( l_h \)). This means that no deep defects have been introduced in CIGSe and \( \text{In}_2\text{S}_3 \) bulk during sputtering, i.e., recombination is negligible in the CIGSe or \( \text{In}_2\text{S}_3 \) bulk. This observation proves that \( V_{OC} \) is the most affected parameter by sputtering of the \( \text{In}_2\text{S}_3 \) buffer layer, i.e., sputtering drastically increases the recombination phenomenon at the interface region.

The EBIC results show the formation of a uniform continuous pn junction across the CIGSe layer which is crucial for solar cell operation. Enhanced J-EBIC spectrum intensity after annealing indicates better charge carrier separation at the p-n junction, i.e., the \( \text{In}_2\text{S}_3/\text{CIGSe} \) interface (Fig. 6a-d). This results in better collection of charge carriers resulting in an overall increase in efficiency of the device. Hence, EBIC results agree well with the increased efficiency observed for annealed samples. Additionally, narrowing of the peak at the pn-junction indicates improvement in the junction quality, crystallinity of \( \text{In}_2\text{S}_3 \), and passivation of interfacial defects.

4.3.2 Effect of annealing on composition and the heterointerface

The APT results support the optoelectronic properties, i.e., the enhanced Cu-depletion behavior at the CIGSe surface after annealing positively impacts the cell efficiency. It is suggested that the Cu vacancies (\( V_{\text{Cu}} \)) are occupied by In antisites (\( \text{In}_{\text{Cu}}^{2+} \)) in this region. The latter one’s act as donor defects leading to a downward band bending and, hence, Fermi level pinning at the interface close to the conduction band. This effect improves the total charge carrier concentration in CIGSe and, hence, the \( V_{OC} \) value.

Moreover, the interfacial intermixing region (II) in Fig. 4 had completely changed after annealing. A partial passivation/substitution of Se by S has been observed. The selenium vacancies (\( V_{\text{Se}} \)) in CIGSe are donor-like defects that promote
n-type conductivity in CIGSe that are detrimental to the cell efficiency, are replaced by Sulphur (S). S also passivates these vacancies and dangling bonds near the CIGSe surface [140] thus sulphurizing the absorber surface. This results in an enhanced bandgap of CIGSe, improving the band alignment with In$_2$S$_3$ resulting in a higher charge carrier concentration at the pn junction [141]. A similar process happens when Cu vacancies are passivated by S at the CIGSe surface. This inter-diffusion and surface passivation on annealing largely suppresses the interfacial defects. Bär et al. [142] studied the intermixing at the In$_2$S$_3$/CIGSe interface and found that a pronounced inter-diffusion at the In$_2$S$_3$/CIGSe interface improves the band alignment. This lowers the e-h recombination and enhances the photosensitivity of the device. Thus, the combined process of Fermi-level pinning in the region I and sulphurization/defect passivation of region II significantly increases the absorber bandgap locally. It minimizes the undesired interfacial recombination by suppressing the electrical charge defects [142]. This may be a plausible reason for the substantial improvement in $V_{OC}$ observed after annealing.

![Graph](image)

**Fig. 4.2.7:** First nearest neighbor distribution (1NN) for Cu atoms in In$_2$S$_3$. The randomized data peak overlaps with the peak for obtained data implying that there is no Cu-cluster formation in In$_2$S$_3$.

As mentioned earlier, Cu diffusion into the In$_2$S$_3$ layer is observed before applying any annealing treatment i.e., during sputter deposition at room
temperature. To identify clustering of Cu for the as-deposited samples, maximum separation method [143] was used. First nearest neighbor distance (1NN) was calculated in the region close to the interface. The obtained data distribution (Fig. 4.2.7) overlapped with the randomized reference data suggesting that there is no cluster formation for Cu in In$_2$S$_3$.

The heat-induced intermixing region (III) is formed by the diffusion of Cu across the junction interface before and after annealing. From Fig. 4.2.4, it can be observed that after annealing, a significant amount of Cu has diffused into the In$_2$S$_3$ layer making the interface region overall Cu-deficient. This trend continues by further annealing the sample for 60 minutes.

Cu diffusion in In$_2$S$_3$ bulk might have a significant effect on the solar cell performance. Pronounced Cu diffusion into the In$_2$S$_3$ bulk is detrimental due to the formation of complex Cu-In-S based ternary alloys [87]. Cu-In-S phase has a lower bandgap and lower transmission than In$_2$S$_3$, blocking the blue energy region of the solar spectrum. Cu-In-S phases can form when the Cu-concentration in In$_2$S$_3$ reaches an upper solubility limit of 10% [144, 145]. In this study, the maximum Cu-concentration found in In$_2$S$_3$ for the highest cell efficiency of 13.6% was 4.0 at.%. Although not concise, the Cu-content in the In$_2$S$_3$ layer obtained in this study seems to be a good compromise between In$_2$S$_3$ defect passivation and avoiding the formation of Cu-In-S phases in the In$_2$S$_3$ buffer layer. Thus, lower amount of Cu in In$_2$S$_3$ is beneficial for improved cell performance. It improves the In$_2$S$_3$ crystallinity by passivating the In vacancies. Additionally, Cu-diffusion from CIGSe to In$_2$S$_3$ makes the CIGSe surface Cu-deficient without forming Cu-In-S phases.

It has been inferred from several studies [146, 147] that Cu diffusion in In$_2$S$_3$ layers above 200 °C improves the In$_2$S$_3$ crystallinity. In this study, it is observed that annealing the sample at 210 °C for 15 minutes only partially crystallizes the amorphous In$_2$S$_3$. However, even with a partly crystalline In$_2$S$_3$ buffer layer, a high-efficiency CIGSe device was deposited.
4.3.3 Influence of rough CIGSe surface topography

Interestingly, a higher Cu concentration of 2.65±0.04 at.% was detected by APT in In$_2$S$_3$ for the non-annealed In$_2$S$_3$-RT than for the annealed In$_2$S$_3$-HT sample which was 1.67±0.04 at.%. This is not unusual since out of the several samples analyzed by APT after annealing, the copper concentration found in the In$_2$S$_3$ ranged from 1.5 at.% to up to 4 at.%. Non-consistency in Cu concentration is related to the interface geometry which depends on CIGSe topography. As evident from the HAADF images, the CIGSe topography has unevenly distributed valleys and peaks. In$_2$S$_3$ is comparatively thinner in the valleys as compared to the peaks because of the shadowing effect during sputter deposition. Thus, In$_2$S$_3$ deposited in the valleys will have a higher concentration of copper in its vicinity as compared to In$_2$S$_3$ deposited at the peaks. On the other hand, the volume fraction of In$_2$S$_3$ is lower in valleys as the thickness of this layer is less. This means that the amount of Cu in In$_2$S$_3$ may vary depending on the local surface geometry of CIGSe (Fig. 7). This not only changes the crystallinity of In$_2$S$_3$ but also the local electron concentration of In$_2$S$_3$.

![Fig. 4.2.8: Variation of local Cu concentration with respect to In$_2$S$_3$ buffer layer thickness. Thinner buffer layer deposited in the valleys has much higher Cu content in its proximity than the thicker In$_2$S$_3$ deposited at the peaks. This results in non-uniform Cu-diffusion in the buffer layer.](image)

The presence and the localization of Na for the current set of samples studied is debatable. Usually, the presence of Na at the CIGSe surface has been previously
reported [148, 149]. Trace amount (20 PPM) of Na is present in the CIGSe bulk and much larger concentration (> 500 PPM) is present at the CIGSe grain boundaries. However, buried layer of Na in the CIGSe absorber has not reported yet. Na passivation suppresses the defect states, improving the charge carrier diffusion length, but the effect buried Na layer in CIGSe needs further investigation. Additionally, present study agrees with [148] that relates Na presence at interface to Na-rich grain boundary vicinity, rather than annealing treatment.
5. Reactive H$_2$S sputtering of In$_2$S$_3$ buffer layers on CIGSe solar cells

The photovoltaic performance and interfacial properties of Ar-ion sputtered In$_2$S$_3$ buffer layers in CIGSe solar cells were discussed. The In$_2$S$_3$ buffer layers were deposited at relatively low sputter pressure of 3×10$^{-3}$ mBar (considering the lower limit of the tool at 1×10$^{-3}$ mBar). However, significant sputter damage of the CIGSe absorber surface was observed. These sputter damages were partly recovered by annealing. In this chapter, an alternative approach is discussed, where sputter deposition conditions are improvised to reduce sputter damages to the absorber layer and deposit crystalline buffer layer at room temperature. The modified parameters from the previously used conditions are: (a) Increasing the sputter deposition pressure and (b) Reactive magnetron sputtering of In$_2$S$_3$ with H$_2$S. The details are as follows:

**Increasing the sputter deposition pressure:**

Sputter damages are caused when atoms are ejected from the target with high kinetic energy (KE) onto a substrate. Deposition occurring with high energy is essential for obtaining dense and crystalline films. However, for multilayered films, high KE atoms are undesirable since sputter damage of the interfaces can negatively affect the device properties. To avoid this, the sputtering pressure was increased to
lower the KE of sputter atoms by inducing collisions. This effectively lowered the mean free path of the atoms ($\lambda$) between collisions. This relationship is given by:

$$\lambda = \frac{k_B T}{\sqrt{2\pi d^2 p}}$$  

(3)

where $k_B$ is Boltzmann constant, $T$ is the gas molecule temperature, and $d$ is the molecular diameter and $p$ is the sputtering pressure. Thus, the mean free path decreases as the sputter pressure increases. With lower mean free path, the scattering of sputtered atoms before reaching substrate increases and the KE decreases, thus lowering the sputter damage of the interface.

**Reactive magnetron sputtering of In$_2$S$_3$ with H$_2$S**

Due to high vapor pressure of S (1 mBar at 175 °C), the S content in the film decreases when the annealing temperature exceeds 200 °C. To address this issue, reactive magnetron sputtering of In$_2$S$_3$ buffer layers was performed using a mixture of Ar and H$_2$S gases. This gave higher S content of nearly 65% (see figure 5.1.5) in the as-deposited films. With higher S content, the crystallinity and optical transmittance in the energetic blue wavelength region was higher.

The above-mentioned strategies are used in this chapter to sputter deposit In$_2$S$_3$ buffer layers at higher working pressures of $6 \times 10^{-2}$ mBar at a fixed sputter power of 40W. The sputter gases used were either pure Ar or a mixture of Ar and H$_2$S. In the previous chapter, the target to substrate distance was 50 mm. However, to increase the mean free path, this distance was increased to 80 mm which is maximum available height for this setup. Modified sputter deposition parameters sharply decreased the deposition rate from the previous value of 1.83 Å/s to 0.22 Å/s. The positive impact of lower sputter damages on cell performance will be discussed in the following section.

Structural and compositional properties were studied using XRD, XPS, and APT, whereas the electrical properties of complete cells were measured by J-V and
EQE. The electrical performance and film quality of reactively sputtered In$_2$S$_3$ buffer layers on CIGSe absorbers were at-par to that of chemically deposited buffer layers.

5.1 Optical, structural, and compositional properties of reactively sputtered In$_2$S$_3$ buffer layers

5.1.1 Enhanced optical transmittance in the blue wavelength region

Transmission spectra of In$_2$S$_3$ buffer layers with modified sputter parameters in the range from 250-1100 nm are shown in Fig. 5.1.1. The In$_2$S$_3$ buffer layer was deposited on quartz substrates for this experiment. Except for sputter pressure and type of sputter gas, other deposition parameters were kept constant. Sputter power 40W, target to substrate distance of 80 mm, substrate rotation speed of 5 RPM and layer thickness of 80 nm were used.

![Transmission spectra](image)

*Fig. 5.1.1: Transmission spectra of In$_2$S$_3$ buffer layers deposited with Ar-ion sputtering at $3\times10^{-3}$ mBar (◇), Ar-ion sputtering at $6\times10^{-2}$ mBar (○) and reactive H$_2$S/Ar sputtering at $6\times10^{-2}$ mBar (□).*
There is a clear improvement in the layer transparency in the blue region when the sputter pressure is increased from $3 \times 10^{-3}$ mBar to $6 \times 10^{-2}$ mBar for non-reactive Ar-ion sputtering. When reactive H$_2$S gas is introduced with Ar, the blue and near-UV region transmission is significantly improved. This is clear evidence that transparency of In$_2$S$_3$ buffer layer improved at higher sputter pressures and with a reactive H$_2$S gas sputtering.

5.1.2 In$_2$S$_3$ buffer layers: deposition conditions

The deposition conditions described in section 3.3 for reactively sputtered In$_2$S$_3$ are used here for the deposition of crystalline $\beta$-In$_2$S$_3$ buffer layers. In$_2$S$_3$ buffer layers were deposited using reactive H$_2$S sputtering on plain-quartz and CIGSe/Mo/SLG glass substrates (where SLG stands for “soda lime glass”) in a single step using rf magnetron sputtering. The sputter parameters are shown in Table 5-1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputter target</td>
<td>In$_2$S$_3$ - 4.5N</td>
</tr>
<tr>
<td>Sputter power</td>
<td>40W</td>
</tr>
<tr>
<td>Working pressure</td>
<td>$6 \times 10^{-2}$ mbar</td>
</tr>
<tr>
<td>Base pressure</td>
<td>$7 \times 10^{-8}$ mbar</td>
</tr>
<tr>
<td>Target-to-substrate distance</td>
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</tr>
<tr>
<td>Sputter direction</td>
<td>Top-down</td>
</tr>
<tr>
<td>Reactive gas</td>
<td>H$_2$S – 2.5N</td>
</tr>
<tr>
<td>Ar/H$_2$S (SCCM)</td>
<td>99.75/0.25 (SCCM)</td>
</tr>
<tr>
<td>Deposition time</td>
<td>3600s</td>
</tr>
<tr>
<td>Buffer thickness</td>
<td>80 nm</td>
</tr>
</tbody>
</table>

Prior to In$_2$S$_3$ deposition, CIGSe absorbers were etched in 0.15 M KCN [97] for 3 minutes, rinsed in DI water and dried with nitrogen gas. CIGSe absorbers were transferred immediately to the load lock chamber to avoid oxidation/contamination of the cleaned CIGSe surface. These samples were kept for drying in the load lock chamber for nearly 30 minutes before transferring to the sputter chamber for In$_2$S$_3$ deposition. The sputtered $\beta$-In$_2$S$_3$ thin films deposited on quartz substrates for XRD measurements will be mentioned hereby as ‘In$_2$S$_3$/Quartz’. Additionally, $\beta$-In$_2$S$_3$
deposited on CIGSe absorbers for XRD, XPS, and APT measurements will be referred to as ‘\textit{In}_2\textit{S}_3/\textit{CIGSe}’. The CBD-CdS reference cell was deposited at ZSW on a CIGSe absorber taken from the same deposition batch.

To obtain working cells, intrinsic ZnO and ZnO:Al were deposited with the same sputter setup using the secondary and tertiary cathodes of the sputter unit. i-ZnO was sputtered at $3 \times 10^{-3}$ mbar sputter pressure and at 200W sputter power while ZnO:Al (AZO) was sputtered at $5 \times 10^{-3}$ mbar sputter pressure and at 250W sputter power. Metal contacts of Ni/Al with a thickness of $\sim 10\text{nm}/1.5\mu\text{m}$ respectively were deposited by e-beam evaporation using a shadow mask. The Ni-Al/AZO/i-ZnO/In$_2$S$_3$/CIGSe complete cells (to be referred to as “\textit{In}_2\textit{S}_3/\textit{CIGSe-cells}” or “\textit{cells}” hereafter in this work) were then subjected to different annealing conditions. Annealing conditions used were 175 °C, 225 °C and 275 °C in air for 15 minutes. In$_2$S$_3$/quartz, In$_2$S$_3$/CIGSe, and In$_2$S$_3$/CIGSe-cells were annealed simultaneously under the same conditions mentioned above.
5.1.3 Structural properties of In$_2$S$_3$ buffer layers on CIGSe absorbers

Grazing incidence x-ray diffraction (GIXRD) measurement was used to study the crystallinity of the deposited thin films. Fig. 5.1.2 presents the GIXRD patterns.
of In$_2$S$_3$ thin films on (a) quartz substrate (In$_2$S$_3$/Quartz) and (b) CIGSe absorber layers (In$_2$S$_3$/CIGSe) using H$_2$S as a reactive gas measured at a grazing incidence of 0.7°. For better comparison, both In$_2$S$_3$/Quartz and In$_2$S$_3$/CIGSe were simultaneously annealed at 175 °C, 225 °C and 275 °C for 15 min. GIXRD spectra of room temperature and annealed In$_2$S$_3$/Quartz samples can be indexed to the cubic structure of In$_2$S$_3$ [150, 151] (JCPDS #065-0459), \(a=10.774\ \text{Å}\) with space group Fd-3m. The most intense peak was observed at a \(2\theta\) value of 27.5° with (311) as the preferred orientation. Polycrystalline In$_2$S$_3$ was obtained with diffraction peaks indexed for (111), (220), (311), (222), (400), (422), (511), (440), (531) and (620) orientation. Average crystallite size measured from Debye-Scherer formula increased from 12.8 nm for the as-deposited state at room temperature to 16.8 nm after annealing at 275 °C for 15 min. The lattice strain \(\varepsilon\) for the strongest reflection at a \(2\theta\) value of 27.5° (311) decreased from 11.2\(\times\)\(10^{-3}\) to 9.6\(\times\)\(10^{-3}\) indicating improvement in crystallinity with annealing temperature [150]. An additional peak at a \(2\theta\) value of \(\sim 25°\) emerges for the In$_2$S$_3$/quartz sample annealed at 175 °C which does not match with the In$_2$S$_3$ phase. The intensity of this peak increases with annealing temperature up to 275 °C, suggesting formation of a secondary In-S based phase. Cubic and tetragonal \(\beta\)-In$_2$S$_3$ have a similar structure and thus the XRD spectra stack up with matching \(2\theta\) values. A presence of a diffraction peak at a \(2\theta\) value of 17.4° in tetragonal \(\beta\)-In$_2$S$_3$ is the primary difference from cubic \(\beta\)-In$_2$S$_3$ structure as seen in Fig. 5.1.2 (a). The absence of this peak indicates that In$_2$S$_3$ has crystallized in the cubic form for the deposition parameters used here. No recrystallization/secondary phase formation was observed for pristine In$_2$S$_3$ films on quartz.

For the In$_2$S$_3$/CIGSe sample, characteristic CIGSe reflection for (101), (112), (220) and (312) planes were obtained with tetragonal CIGSe corresponding to JCPDS #035-1102. The peaks belonging to the In$_2$S$_3$ buffer layer on CIGSe were similar to the ones obtained for the In$_2$S$_3$/quartz samples with a cubic In$_2$S$_3$ structure formation. For In$_2$S$_3$ deposited on quartz (Fig. 5.1.2 (a)), a diffraction peak appears
at a 2θ value of 25° on annealing at 225 °C or higher. This can be attributed to the formation of secondary In-S based phases at higher temperatures. However, for In₂S₃ deposited on CIGSe (Fig. 5.1.2 (b)), no such secondary phase formation is detected up to 275 °C. The crystalline character of In₂S₃/CIGSe samples annealed at 175 °C and 225 °C is similar, but there is a significant change in the elemental distribution at the heterointerface, to be discussed in detail in section 5.2.2.

![GIXRD spectra comparison](image)

**Fig. 5.1.3:** Comparison of GIXRD spectra for In₂S₃/CIGSe at room temperature (RT) (black), annealed at 175 °C (red), 225 °C (blue), and 275 °C (green) respectively. The relative peak intensity between In₂S₃ (311) and CIGSe (112) is increasing with the temperature of annealing up to 225 °C suggesting improvement In₂S₃ crystallinity. At 275 °C, there is a clear shift in the In₂S₃ (311) diffraction peak corresponding to CuIn₅S₈. The CIGSe (112) peak position in the spectra remains unchanged after annealing.

At an annealing temperature of 275 °C, a small shift of all the peaks belonging to the In₂S₃ buffer layer to a higher 2θ value is observed. The shifted peaks correspond to CuIn₅S₈ (JCPDS #01-072-0956), similar to the results obtained for thermally evaporated CuIn₅S₈ thin films by Khedmi et al. [24]. To understand this effect better, the highest intensity diffraction peaks belonging to In₂S₃ buffer layer and CIGSe absorber are presented separately. Fig. 5.1.3 shows the (112) CIGSe orientation at a 2θ value of 27.0°; and the (311) In₂S₃ orientation at a 2θ value of
27.6°. The shift in the (311) In$_2$S$_3$ diffraction peak position is apparent, but there is no shift in the (112) CIGSe position. Additionally, there is a visible change in the relative peak intensity between CIGSe and In$_2$S$_3$ upon heat treatment, indicating improvement in In$_2$S$_3$ crystallinity.

Contrary to the non-reactive sputter deposited In$_2$S$_3$ buffer layers in the previous chapter, here crystalline In$_2$S$_3$ layers are obtained by reactive H$_2$S/Ar sputtering at room temperature. Room temperature deposition of tetragonal In$_2$S$_3$ has been previously reported [25]. However, this is the first report of cubic In$_2$S$_3$ structure deposited at room temperature. Considering small film thickness of around 80 nm for In$_2$S$_3$/Quartz and In$_2$S$_3$/CIGSe, crystalline form of In$_2$S$_3$ films were deposited irrespective of the substrate used. Moreover, this study indicates that the optimized deposition conditions mentioned in Table 5-1 were sufficient to obtain crystalline In$_2$S$_3$ at room temperature.

If we compare the XRD relative peak intensities of (112) CIGSe with (311) In$_2$S$_3$ reflections at $\theta$ value of 27° and 27.5°, the intensity of (311) In$_2$S$_3$ increases when the samples are annealed from 175 °C to 225 °C. This indicates that the crystallinity of In$_2$S$_3$ buffer layer is improved upon annealing by Cu diffusion that can occupy the vacant tetrahedral sites in the In$_2$S$_3$ structure [26]. It has also been speculated that crystalline In$_2$S$_3$ may accommodate less Cu than In$_2$S$_3$ with lower crystallinity due to the lower density of grain boundaries [26]. At 275 °C, Cu-diffusion from the CIGSe absorber induces structural changes in In$_2$S$_3$ which is evident from the shift of the (311) diffraction peak of the buffer layer. As mentioned above, the shifted XRD peak positions corresponding to the CuIn$_5$S$_8$ secondary phases formed at 275 °C. This kind of phase formation has been reported for In$_2$S$_3$/CIGSe based solar cells by Abou-Ras et al. [13]. Stoichiometric CuIn$_5$S$_8$ phases can form if the Cu concentration in In$_2$S$_3$ is around 7 at.%, that is likely to be achieved at higher annealing temperatures.
5.1.4 Enhanced optical transmittance upon annealing

Fig. 5.1.4: Comparison of optical transmittance spectra for In$_2$S$_3$/quartz at room temperature (black), annealed at 175 °C (red), 225 °C (blue), and 275 °C (green) respectively.

Optical transmittance of the film in the blue wavelength region has increased upon annealing from RT to 275 °C. The improvement is however small but there is a clear trend of enhanced optical transmittance as seen from the inset in Fig. 5.1.4. XRD measurements (Fig. 5.1.2 (a)) reveal that the crystallinity of In$_2$S$_3$ improves upon annealing. There is however no significant change in the grain size upon annealing, nor the thickness. According to Burstein-moss effect [152], there may be an enhancement in the number of charge carriers in the material after annealing, leading to higher bandgap and thus higher optical transmittance.

5.1.5 Surface analysis of In$_2$S$_3$ buffer layer deposited on CIGSe

5.1.5.1 EDS analysis

The chemical composition of In$_2$S$_3$/Quartz samples was estimated by EDS analysis for room temperature (25 °C) and annealed samples at 175 °C, 225 °C, and
275 °C. The stoichiometric ratio S/In for In$_2$S$_3$ is 1.5. However, due to the additional S source in the form of reactive H$_2$S gas, the S/In ratio for the as-deposited sample at 25 °C is high (1.64). Annealing the films at different temperatures (Fig. 5.1.5) results in a decrease in the S content. This experiment was not performed on In$_2$S$_3$/CIGSe samples since the interaction volume of the electron beam is 1-2 μm in depth. Thus, a large contribution will come from In present in CIGSe giving an inaccurate estimation of S/In ratio for In$_2$S$_3$.

![Graph showing S/In ratio vs. annealing temperature](image)

Fig. 5.1.5: EDS analysis of In$_2$S$_3$/quartz samples at room temperature (25 °C) and annealed at 175 °C, 225 °C and 275 °C. Additional H$_2$S source during sputtering gives higher S/In ratio than stoichiometric In$_2$S$_3$.

### 5.1.5.2 XPS analysis

The chemical composition of In$_2$S$_3$/CIGSe was estimated by measuring the XPS spectra on the surface of an 80 nm thick In$_2$S$_3$ deposited on CIGSe. This study was performed to understand the Cu diffusion behavior with increasing annealing temperature. Fig. 5.1.6 (a) presents high resolution XPS spectra of Cu 2p region (Cu 2p$_{3/2}$ at 932.6 eV and Cu 2p$_{1/2}$ at 952.4 eV). For as-deposited sample and annealed sample at 175 °C, a weak Cu 2p$_{3/2}$ signal is obtained around 932.6 eV. This reveals that either In$_2$S$_3$ does not completely cover the CIGSe layer; or that Cu has diffused into the In$_2$S$_3$ layer already at room temperature. The In$_2$S$_3$ coverage on CIGSe was checked by milling out a thin (50 nm) lamella from different locations.
The deposition of In\textsubscript{2}S\textsubscript{3} buffer layer on CIGSe is uniform with no discontinuities. This indicates that Cu diffusion in In\textsubscript{2}S\textsubscript{3} takes place at room temperature itself. For the In\textsubscript{2}S\textsubscript{3}/CIGSe samples annealed at 225 °C and 275 °C, a strong Cu 2p signal is detected at 932.6 eV and 952.4 eV [153], indicating the presence of Cu\textsuperscript{+} state as commonly observed in CIGSe [26]. Fig. 5.1.6 (b) and (c) present the In 3d region (In 3d\textsubscript{5/2} at 444.6 eV and In 3d\textsubscript{3/2} at 452.2 eV) and the S 2p region (convoluted peaks for S 2p\textsubscript{3/2} and S 2p\textsubscript{1/2} at 161.5 eV and 162.6 eV), respectively. The approximate positions of the fitted peaks for the two core level spectra for S are shown in dotted and dashed lines (in Fig 5.1.6 (c)) for reference. The binding energies have been calibrated taking C 1s at 284.8 eV as reference. For higher annealing temperatures, the core level binding energy for In and S gradually shift to a higher value. Fig. 5.1.6 (b) and (c) are plotted with an offset for clarity.

Fig. 5.1.6: (a) Cu 2p (b) In 3d and (c) S 2p core level XPS spectra for In\textsubscript{2}S\textsubscript{3}/CIGSe sample at room temperature and after annealing at 175°C, 225°C, and 275°C. A weak Cu signal is detected at the surface of the 80 nm thick In\textsubscript{2}S\textsubscript{3} layer deposited on CIGSe at RT and for the In\textsubscript{2}S\textsubscript{3}/CIGSe sample annealed at 175 °C, whereas a strong Cu signal was observed for the In\textsubscript{2}S\textsubscript{3}/CIGSe sample annealed at 225 °C and 275°C. Spectra shown in (b) and (c)
highlight the shifts in In and S peak positions, i.e. shifts to higher binding energy due to change in chemical environment by Cu doping.

The weak Cu 2p signal detected at the In$_2$S$_3$ surface suggests that a small amount of Cu diffuses from CIGSe to In$_2$S$_3$ even during sputter deposition. At 175 °C, the Cu signal is still weak indicating that the activation energy for Cu diffusion is not high enough at this temperature. Upon annealing the samples at 225 °C and 275 °C, Cu rapidly diffuses through the 80 nm thick buffer layer to the In$_2$S$_3$ surface as Cu$^{2+}$. The appearance of a weak satellite peak around 945 eV can indicate Cu-In-S phase transition as seen from the GIXRD spectra for the same sample. A similar observation was made by Hauschild et al. [154] where Cu-In-S based phases were observed for In$_2$S$_3$/CIGSe based solar cells.

The presence of Cu as a dopant in the In$_2$S$_3$ layer results in a gradual shift of binding energies of In 3d and S 2p peaks to higher energy levels. Cu doping in In$_2$S$_3$ changes its chemical environment. Cu$^+$ has higher electronegativity than In$^{3+}$ on the Pauling scale ($\chi_r$). Thus, when Cu$^+$ occupies the tetrahedral vacancy sites in the In$_2$S$_3$ structure, it bonds with In and S attracting an electron pair that was previously unshared. With a shared electron pair, the core level electron exhibits higher binding energy due to enhanced Coulombic interaction with the ion core. This makes it more difficult to ionize a core level electron resulting in an increase in the binding energy [155] and thus the shift.

Cu diffusion in In$_2$S$_3$ improves the series resistance of the cell by injecting charge carriers in an otherwise intrinsic and highly resistive In$_2$S$_3$ [156] buffer layer. This reduces the overall resistance of the cell resulting in better cell parameters. Additionally, Strohm et al. [126] have shown that for cells with In$_2$S$_3$ buffer, the ZnO/In$_2$S$_3$ interface impedes cell performance. To passivate these sputter-induced defects states, Cu diffusing in In$_2$S$_3$ must reach the In$_2$S$_3$/ZnO interface to lower the series resistance of the cell to draw higher short-circuit currents. This condition is
met only for the cell annealed at 225 °C as reported from In$_2$S$_3$ surface analysis by XPS.

5.2 In$_2$S$_3$/CIGSe interface: Effect of elemental redistribution on photovoltaic performance

5.2.1 Elemental redistribution as a function of annealing temperature

Fig. 5.2.1 presents the proximity histogram or proxigram [157] obtained from APT measurements at the In$_2$S$_3$/CIGSe interface for all four samples. These proxigrams reveal the interdiffusion behavior of different elements in the vicinity of the interface for different annealing temperatures. The crossover of S and Se in the concentration profile can be assumed as the median (zero-point) of the heterointerface. We consider the interface thickness equal to the width of Ga concentration slope from nearly 0 at.% in the In$_2$S$_3$ buffer to around 8 at.% at the CIGSe surface. This region is known as the interfacial intermixing region (marked by two dashed lines). Reactive In$_2$S$_3$ sputtering at room temperature leads to a sharp interface with a thickness of around 3 nm, consistent with interfacial thicknesses obtained by chemical bath [158] and ILGAR [91] deposited buffer layers. Moreover, the abrupt transition between In$_2$S$_3$ buffer layer and CIGSe absorber suggests that there was no or only minimal sputter damage to CIGSe during buffer layer deposition. The sputter deposition rates were intentionally kept low at 0.22 Å/s to minimize sputter damage on CIGSe surface.

5.2.2 Cu re-distribution across the In$_2$S$_3$/CIGSe interface

Cu diffuses into In$_2$S$_3$ during reactive sputtering at room temperature because of the high mobility of Cu [159] observed even at low temperatures [83]. During
reactive sputtering, the temperature on the sample surface is much higher than 25 °C, due to high energy sputtered atoms on the absorber surface.

At 175 °C, the interface layer widens (Fig. 5.2.1 (b)) to around 4 nm due to the low amount of Cu diffusion from the CIGSe surface to the In$_2$S$_3$ buffer layer. The latter observation agrees with the XPS measurement shown in Fig. 5.1.6 (a). At 175 °C, the CIGSe surface has a small change from the as-deposited state. This is evident from In and Cu concentrations in CIGSe layer, which are constant after 5 nm from interface in (b) as compared to 3 nm in (a).

**Fig. 5.2.1:** Proximity histogram of the In$_2$S$_3$/CIGSe hetero-interface at (a) room temperature and (b, c, d) after annealing at 175 °C, 225 °C, and 275 °C, respectively. Cu, In, Ga, Se, S, and Na linear profiles are represented here in blue, magenta, orange, red, yellow, and green. The interface region (the region between the two dashed lines) gradually broadens with annealing temperature. Second Y-Axis towards right of all plots represents Na atomic concentration for the respective samples. Cu depletion from CIGSe surface and Na
segregation at In$_2$S$_3$/CIGSe interface begin at 225 °C. This behavior seems to be intensified when the sample is annealed at 275 °C.

At 225 °C, a significant elemental re-distribution is observed (see Fig. 5.2.1 (c)), broadening the interface up to 8 nm. Best cell efficiencies are obtained upon annealing at this temperature (discussed in the next section). Accelerated Cu-diffusion from the CIGSe surface to the In$_2$S$_3$ buffer layer takes place at this temperature as already observed from the XPS measurement. This effect depletes the CIGSe surface of Cu. Simultaneously, In diffuses from In$_2$S$_3$ into CIGSe up to 25 nm from the interface. Cu depletion and In enrichment at CIGSe surface can occur due to In-Cu anticorrelation [130], where one depleted species is complimented by enrichment of the other. Annealing treatment at 225 °C has modified the CIGSe surface up to 25 nm from the interface where the In atomic concentration is at least 4 at.% higher than that of Cu. The concentration of Ga and Se at 225 °C is nearly constant as compared to sample at 175 °C. A correlation between Se and S concentration profiles is observed indicating that V$_{Se}$ is occupied by S at the CIGSe interface. However, unlike the pronounced In diffusion in CIGSe at elevated temperatures, S diffusion in CIGSe was limited only to the first few nanometers.

For the sample annealed at 275 °C (Fig. 4 (d)), there is a significant structural reconstruction on either side of the interface. The interfacial thickness is around 10 nm, four times higher to the as-deposited state. In CIGSe layer, concentration of Cu, In, Ga and Se was 7 at.%, 28 at.%, 8 at.% and 56 at.%, respectively. Stoichiometrically, this matches the composition of Cu deficient Cu(In,Ga)$_5$Se$_8$ phase which is known as ordered defect/vacancy compound (ODC/OVC) [160]. The thickness of this layer measured from the interface is around 50 nm, whereas the Cu depletion depth is nearly 80 nm as clearly can be seen from Fig. 5.2.2.
Fig. 5.2.2: (a) 3D elemental map of In$_2$S$_3$/CIGSe sample annealed at 275 °C for 15 minutes. The region between dashed and dotted line represents the Cu-deficient phase Cu(In,Ga)$_5$Se$_8$ formation which is evident from the proximity histogram in (b).

### 5.2.3 Na segregation at the In$_2$S$_3$/CIGSe interface

For room temperature and 175 °C heat-treated samples, Na segregation is not observed. However, for the samples heat-treated at 225 °C, a clear Na segregation is found at the In$_2$S$_3$/CIGSe interface. From Fig. 5.2.1 (c) we can see that Na segregation peaks at the center of the interfacial intermixing region with 0.15 at.% Na. The concentration drops from 0.15 at.% to 0 at.% in the CIGSe layer. Na segregation follows the concentration profile of S and terminates where the S concentration drops nearly to 0 at.%. On the In$_2$S$_3$ side (left side), a low amount of Na diffuses deeper into the buffer layer likely due to the presence of tetrahedral vacancies in the In$_2$S$_3$ structure [87]. At 275 °C, Na segregation is more pronounced (see Fig. 5.2.1(d)) as compared to 225 °C. Nearly 0.4 at.% Na is segregated near the interface, which gradually drops inside In$_2$S$_3$ buffer layer. The excess concentration
of Na atoms present at the In$_2$S$_3$/CIGSe interface, known as the Gibbsian interfacial excess ($\Gamma$) was calculated as per the method described in Ref. [161]. For room temperature and 175 °C, no interfacial excess atoms were found, however at 225 °C, calculated $\Gamma_{\text{Na}}$ was 0.5 at/nm$^2$, increasing to 1.5 at/nm$^2$ at 275 °C.

Another beneficial effect of Na segregation at the interface can be related to improvement in the lattice mismatch between CIGSe and In$_2$S$_3$. When Cu and Na diffuse and segregate near the In$_2$S$_3$/CIGSe interface, a solid solution of Na$_x$Cu$_{1-x}$In$_5$S$_8$ is likely to form [87]. From the XRD results in section 5.1.3, the two primary XRD reflections for In$_2$S$_3$ (311) and CIGSe (112) have an interplanar spacing of 3.248 Å and 3.312 Å, respectively. The lattice mismatch between the two is 1.93%. With the introduction of Na$^+$ in the crystalline lattice, the lattice mismatch is lower, since Na$^+(1.13$ Å) has a higher cationic radius than In$^{3+}(0.76)$ in a four-fold coordinated site as per Shannon [162]. With a minimal lattice mismatch, interfacial recombination can be substantially suppressed, and a high-quality crystalline interface can be achieved. This improves the short-circuit current density and FF that gives better cell performance.

![Fig. 5.2.3: Cu-depletion depth from the surface of CIGSe at different annealing temperatures estimated from APT measurements.](image-url)

Fig. 5.2.3: Cu-depletion depth from the surface of CIGSe at different annealing temperatures estimated from APT measurements.
Table 5-2: Composition of In$_2$S$_3$ buffer layer measured near the In$_2$S$_3$/CIGSe interface at different annealing treatments.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Run #</th>
<th>Sulphur(S)</th>
<th>Indium(In)</th>
<th>Copper(Cu)</th>
<th>Sodium(Na)</th>
<th>Selenium (Se)</th>
<th>Gallium(Ga)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>1</td>
<td>60.27±0.00%</td>
<td>39.13±0.08%</td>
<td>0.49±0.01%</td>
<td>0.00±0.00%</td>
<td>0.08±0.00%</td>
<td>0.02±0.00%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>59.50±0.00%</td>
<td>38.99±0.05%</td>
<td>1.41±0.01%</td>
<td>0.00±0.00%</td>
<td>0.09±0.00%</td>
<td>0.01±0.00%</td>
</tr>
<tr>
<td>175 °C</td>
<td>1</td>
<td>60.87±0.04%</td>
<td>36.93±0.06%</td>
<td>2.04±0.02%</td>
<td>0.00±0.00%</td>
<td>0.16±0.01%</td>
<td>0.01±0.00%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>59.30±0.05%</td>
<td>37.42±0.06%</td>
<td>3.14±0.02%</td>
<td>0.12±0.01%</td>
<td>0.00±0.00%</td>
<td>0.01±0.00%</td>
</tr>
<tr>
<td>225 °C</td>
<td>1</td>
<td>59.22±0.00%</td>
<td>38.65±0.04%</td>
<td>1.15±0.01%</td>
<td>0.12±0.00%</td>
<td>0.84±0.00%</td>
<td>0.02±0.00%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>59.64±0.04%</td>
<td>37.90±0.08%</td>
<td>2.21±0.02%</td>
<td>0.05±0.00%</td>
<td>0.13±0.01%</td>
<td>0.06±0.01%</td>
</tr>
<tr>
<td>275 °C</td>
<td>1</td>
<td>58.30±0.04%</td>
<td>36.17±0.07%</td>
<td>3.62±0.03%</td>
<td>0.35±0.01%</td>
<td>1.30±0.01%</td>
<td>0.25±0.01%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>56.54±0.21%</td>
<td>34.41±0.26%</td>
<td>6.60±0.16%</td>
<td>0.90±0.06%</td>
<td>0.61±0.04%</td>
<td>0.94±0.06%</td>
</tr>
</tbody>
</table>

Table 5-2 shows the atomic concentration of In$_2$S$_3$ buffer layer within the first 40 nm from the interface. This was measured by extracting a volume of 20 × 20 × 40 nm$^3$ (region of interest) from the 3D elemental map of the respective samples. For all the samples, In$_2$S$_3$ stoichiometric concentration S/In is over 1.5, that agrees well with EDS analysis. The EDS analysis was performed on In$_2$S$_3$/quartz samples to avoid any In signal from Cu(In,Ga)Se$_2$ absorber. Cu content in In$_2$S$_3$ buffer gradually increases as Cu diffusion from CIGSe surface is higher at elevated temperatures. The atomic concentration of Na is negligible up to 175 °C, but increases sharply on annealing at 225 °C and further at 275 °C. Na is mainly found to segregate at the In$_2$S$_3$/CIGSe interface for the sample annealed at 225 °C. It should be noted that the amount of Na diffusion in buffer or segregated at the In$_2$S$_3$/CIGSe interface may strongly vary from one region to another (for details please see Ref. [148]).
5.3 Photovoltaic performance as a function of annealing temperature

5.3.1 J-V characteristics

![J-V and EQE characteristics](image)

Fig. 5.3.1: (a) J-V and (b) External quantum efficiency (EQE) characteristics of reactively sputtered In$_2$S$_3$/CIGSe-cell with area 0.5 cm$^2$ annealed at 175 °C, 225 °C and 275 °C compared with the CdS-Reference cell. In$_2$S$_3$/CIGSe-cells annealed at 225 °C has the highest $V_{OC}$, $J_{SC}$, FF and EQE gain in the overall spectral region.

The dependence of J-V characteristics on the annealing temperature of In$_2$S$_3$/CIGSe-cells is presented in Table 5-3 and Fig. 5.3.1 (a). Overall cell performance is highest at an annealing temperature of 225 °C in terms of a maximum efficiency of 13.84%, which is the highest efficiency available in literature so far for sputtered In$_2$S$_3$. There is a substantial increase in $J_{SC}$ from 25.24 mA/cm$^2$ to 32.33 mA/cm$^2$ when the annealing temperature increases from 175 °C to 225 °C. Additionally, the buffer layer deposition on the CIGSe absorber was uniform since an average efficiency of 13.21% was achieved for 8 individual cells of 0.5 cm$^2$ each.

When compared with the CBD CdS-reference, the open-circuit voltage Voc for the In$_2$S$_3$/CIGSe annealed at 225 °C cell is higher. The short-circuit current density $J_{SC}$ is only slightly lower. However, lower FF of In$_2$S$_3$/CIGSe leads to inherently lower efficiency as compared to CdS-reference. Annealing the cell at higher
temperatures (here 275 °C) further deteriorates the J-V characteristics (mainly Voc and FF).

Table 5-3: Comparison of cell parameters between the CdS Reference cell and the In$_2$S$_3$/CIGSe-cells heat-treated at 175 °C, 225 °C and 275 °C for 15 minutes each. Best values are found for the In$_2$S$_3$/CIGSe-cell heat-treated at 225 °C. A significant drop in Voc is registered after annealing the In$_2$S$_3$/CIGSe-cell at 275 °C.

<table>
<thead>
<tr>
<th>Cell</th>
<th>η (%)</th>
<th>Voc (mV)</th>
<th>Jsc (mA/cm$^2$)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS Reference</td>
<td>14.83</td>
<td>630</td>
<td>32.61</td>
<td>72</td>
</tr>
<tr>
<td>175 °C</td>
<td>9.33</td>
<td>628</td>
<td>25.24</td>
<td>59</td>
</tr>
<tr>
<td>225 °C</td>
<td>13.84 (16.33$^*$)</td>
<td>660</td>
<td>32.33</td>
<td>65</td>
</tr>
<tr>
<td>275 °C</td>
<td>10.11</td>
<td>588</td>
<td>32.21</td>
<td>58</td>
</tr>
</tbody>
</table>

* Normalized with a freshly deposited batch of CIGSe absorber efficiency

Table 5-4. Solar cell parameters corresponding to the diffusion current ($J_{01}$) and recombination current ($J_{02}$), ideality factor ($n_2$), shunt ($R_{SH}$) and series ($R_S$) resistances extracted from the two-diode model [163] fitting of the J-V curves.

<table>
<thead>
<tr>
<th>Cell</th>
<th>$J_{01}$ (mA/cm$^2$)</th>
<th>$J_{02}$ (mA/cm$^2$)</th>
<th>$n_2$</th>
<th>$R_{SH}$ (Ω cm$^2$)</th>
<th>$R_S$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Under</td>
<td>175 °C</td>
<td>1.30×10$^{-14}$</td>
<td>1.62×10$^{-05}$</td>
<td>3.37</td>
<td>460</td>
</tr>
<tr>
<td></td>
<td>225 °C</td>
<td>5.20×10$^{-15}$</td>
<td>7.30×10$^{-07}$</td>
<td>2.43</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>275 °C</td>
<td>3.81×10$^{-14}$</td>
<td>1.05×10$^{-05}$</td>
<td>2.93</td>
<td>263</td>
</tr>
<tr>
<td>Dark</td>
<td>175 °C</td>
<td>2.91×10$^{-14}$</td>
<td>2.47×10$^{-06}$</td>
<td>2.68</td>
<td>6844</td>
</tr>
<tr>
<td></td>
<td>225 °C</td>
<td>1.51×10$^{-13}$</td>
<td>1.85×10$^{-07}$</td>
<td>2.3</td>
<td>10409</td>
</tr>
<tr>
<td></td>
<td>275 °C</td>
<td>1.24×10$^{-22}$</td>
<td>2.76×10$^{-07}$</td>
<td>2.04</td>
<td>13851</td>
</tr>
</tbody>
</table>

5.3.2 Quantum efficiency measurements

The EQE measurement (Fig. 5.2.4 (b)) of the In$_2$S$_3$/CIGSe-cells shows an improved response in the blue wavelength region as compared to the CdS reference cell. This implies that because of the higher bandgap than CdS, the In$_2$S$_3$ buffer layer performs better in the short wavelength region. Highest spectral response is exhibited for the In$_2$S$_3$/CIGSe-cell annealed at 225 °C. Curiously, for the sample annealed at 275 °C, a small gain in quantum efficiency in the blue region is observed.
This gain is however combined with greater losses in the red region, deteriorating the overall cell performance.

### 5.3.3 Inferences from the results obtained on In$_2$S$_3$ buffer layers by reactive magnetron sputtering

Best cell performance and spectral responses for In$_2$S$_3$/CIGSe-cells were obtained for cells annealed at 225 °C. The 3-D concentration profile along the interface obtained from APT proxigram reveals the plausible conditions that were met to obtain better cell performance which could be:

a) Cu-depleted CIGSe surface, and  
b) Na segregation at the In$_2$S$_3$/CIGSe surface.

Additionally, XRD and XPS studies has revealed that:

c) the crystallinity of In$_2$S$_3$ has improved at this temperature without any phase transition and  
d) Cu diffusion lowers the sheet resistance of In$_2$S$_3$.

Points (a) and (b) above will be discussed in the next section.

For the cells annealed at 275 °C, the higher Na content in the buffer layer can be a possible reason for the small blue shift in quantum efficiency. APT investigations reveal that > 0.1 at.% Na segregation can extend over 40 nm into the In$_2$S$_3$ buffer layer at 275 °C. Lafond et al. [78] and N. Barreau [164] have shown that Na doping in Cu-In-S based materials can enhance the bandgap allowing better light transmission in the blue region. On the other hand, loss in quantum efficiency in the red region may be due to excessive negative charge accumulation in the ODC layer formed near the interface [165]. Besides, the bandgap of the ODC layer is 1.32 eV [166] or 939 nm which is the region where the quantum efficiency loss is observed. Strong diffusion of sodium into In$_2$S$_3$ for the sample annealed at 275 °C leads to a loss of Na in the CIGSe layer, explaining the loss in $V_{oc}$ and FF for this sample.


5.4 Discussions

Pure In$_2$S$_3$ is highly resistive (order of MΩ cm$^2$) and needs dopants to lower resistance. This improves the total charge carrier concentration resulting in higher current generation. In this thesis, self-doping of Cu in In$_2$S$_3$ from CIGSe was achieved by annealing the cells at 225 °C for 15 minutes to get better cell performance. With such annealing treatment, a Cu depleted CIGSe surface with a thickness of (22 ± 4) nm is formed as seen in Fig. 5.2.1 (c) and Fig. 5.2.3. Cu depleted from the CIGSe surface diffuses to the buffer layer due to the abundance of tetrahedral vacancy sites [73] in the In$_2$S$_3$ crystal structure. Fig. 5.2.1 (c) shows distinct Na segregation peaking at 0.15 at.% in the middle of the heterointerface resulting in improved interface quality. The role of the aforementioned elemental redistribution in the enhancement of cell performance are explained as follows:

5.4.1 Cu-depleted CIGSe surface layer

A Cu deficient layer is formed unintentionally at the CIGSe surface during the deposition process [167, 168]. A Cu-deficient layer aids in improving the band alignment by shifting the valance band maximum downwards [169] at the CIGSe surface creating a valance band offset (VBO). This effectively suppresses the interfacial recombination rate [124, 125] by repelling holes from the VBO created due to the Cu deficient layer [170]. This thesis gives direct evidence of the formation of a Cu-depleted layer [168, 171] at 225 °C on the CIGSe surface and its beneficial effect on In$_2$S$_3$/CIGSe-cell performance (see table 3). For In$_2$S$_3$/CIGSe-cells, a lower Cu content (Cu-deficiency) at the absorber surface is desired for better efficiencies [61, 142]. APT proxigram analysis suggests that an annealing temperature of around 225 °C for 15 minutes is required to initiate Cu-depletion at the CIGSe surface. Abou-Ras et al. [62] speculated that a Cu-depleted and In-enriched absorber surface improves the band alignment between In$_2$S$_3$ and CIGSe. Additionally, S passivation widens the bandgap of CIGSe surface thus reducing the recombination rate at the
interface and improving cell performance. Thus, a combined effect of Cu-depletion and S doping at the CIGSe surface not only improves the band alignment with the buffer but also passivates the CIGSe-surface defect states. $J_{02}$ value for the sample annealed at 225 °C is the lowest as compared to other annealing temperatures. This implies that the recombination at the CIGSe surface is lower due to the defect passivation at the CIGSe surface in the SCR region. Excessive Cu depletion at the CIGSe surface at a higher annealing temperature of 275 °C proves to be detrimental to cell efficiency. Clear evidence of the formation of Cu(In,Ga)$_5$Se$_8$ phase at the CIGSe surface due to excessive out-diffusion of Cu has been shown by APT studies.

5.4.2 Cu diffusion in In$_2$S$_3$ buffer layer

XPS results (Fig. 5.1.6 (a)) have confirmed that Cu diffusion from the CIGSe into the In$_2$S$_3$ buffer layer is accelerated when the sample is annealed at 225 °C. The APT proxigrams (Fig. 5.2.1) show a strongly changed Cu concentration profile when annealed at 225 °C as compared to room temperature samples. Results have shown a significant increase of diffusion of Cu from 0.02 atoms/nm$^3$ at room temperature to 0.283 atoms/nm$^3$ at 225 °C in the In$_2$S$_3$ buffer layer. There are several reports [81, 142, 172] suggesting that Cu diffusion in In$_2$S$_3$ results in an improved $V_{oc}$ and cell performance. Significant enhancement of $V_{oc}$ (32 mV) and FF (6%) is obtained after annealing from 175 °C to 225 °C giving an efficiency of 13.84% (14.83% with a CdS reference). The improved cell performance at 225 °C can be attributed to Cu diffusion in In$_2$S$_3$ or Cu-depletion of the CIGSe surface is not clear. However, Cu diffusion certainly lowers the series resistance of the buffer layer improving the overall current collection of the cell.

The drop in $V_{oc}$ and FF for the sample annealed at 275°C could be caused by the formation of the Cu(In,Ga)$_5$Se$_8$ phase and high copper content in the In$_2$S$_3$ layer. It is known that Cu in In$_2$S$_3$ layer forms Cu-In-S phase with a lower, deteriorating the device performance.
5.4.3 Na segregation at In$_2$S$_3$/CIGSe interface

Na segregation at the heterointerface plays an important role in the passivation of interfacial defect states. Due to the high mobility of Cu [159], Cu vacancies ($V_{Cu}$) with low formation energy [173, 174] can be formed near the interface in the presence of a local electric field [83]. Cu vacancies can also be formed by the impinging sputter atoms during buffer layer deposition or during annealing treatment. $V_{Cu}$ at the interface is usually occupied by In and Ga forming $In_{Cu}$ and $Ga_{Cu}$, which are shallow donors [175]. These antisites defects act as active recombination centers at the In$_2$S$_3$/CIGSe interface that degrades the cell performance. However, the In$_2$S$_3$/CIGSe interface must be of high quality to obtain good efficiencies [124, 125, 176]. The formation of antisites defects is suppressed by Na segregation at the interface, forming $Na_{InCu}$ or $Na_{GaCu}$ instead of $In_{Cu}$ or $Ga_{Cu}$ [12, 177]. Thus, Na passivating the defects at the interface minimizes the interfacial recombination.

![3D elemental map of In$_2$S$_3$/CIGSe interface for (a,b) 225 °C and (c,d) 275 °C. The elements are color-coded as Cu (blue) In (magenta), Ga (orange), Se (red), S (yellow) and Na (green). (b) and (d) show the segregation of Na at In$_2$S$_3$/CIGSe interface.](image)

These results indicate that Na segregation at the interface has a bigger role in obtaining higher device efficiencies as compared to Cu diffusion. Previous studies [67, 178] have shown that Na plays an important role in high efficiency In$_2$S$_3$ buffered
CIGSe solar cells. However, in this thesis, direct evidence of Na-segregation at \( \text{In}_2\text{S}_3/\text{CIGSe} \) interface and its impact on the cell performance is proved.
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6. Conclusions and outlook

This thesis is focused on the development of Cd-free alternative vacuum-based material to be used as a buffer layer in Cu(In,Ga)Se$_2$ (CIGSe) solar cells. In$_2$S$_3$ was primarily investigated as a buffer layer material owing to its excellent and tunable optoelectronic properties. Buffer layers were deposited using Ar-ion and H$_2$S/Ar reactive sputtering on a plain quartz substrate and CIGSe absorber layers and analyzed using UV-visible spectroscopy, GIXRD, IV, EQE, EBIC, XPS, TEM and APT. These techniques were used in conjunction to understand the effect of sputter deposition parameters and annealing conditions on the In$_2$S$_3$/CIGSe heterojunction.

The starting point of this work was the optimization of In$_2$S$_3$ buffer layers. This thesis confirms that reactively sputtered In$_2$S$_3$ buffer layers deposited at room temperature are structurally and optically superior to the amorphous Ar-ion sputtered In$_2$S$_3$ buffer layers. H$_2$S/Ar sputtered In$_2$S$_3$ crystallized at 40W sputter power and 6×10$^{-2}$ mBar sputter pressure. Amorphous In$_2$S$_3$ films were deposited at higher sputter powers of 60W, 80W and 100W with H$_2$S/Ar sputtering. However, the Ar-ion sputtered In$_2$S$_3$, films typically gave deposited in an amorphous state at room temperature for all sputtering powers.

Ar-ion sputtered In$_2$S$_3$ buffer layers deposited at low sputter pressure (LSP) of 3×10$^{-3}$ mBar and 50W sputter power showed good optical transmittance at 55 nm thickness. Complete CIGSe solar cells with 55 nm thickness showed best cell parameters and higher cell efficiencies as compared to other buffer layers thicknesses. Thinner 25 nm buffer layer with showed better quantum efficiencies owing to higher blue-region transmittance. For 55 nm In$_2$S$_3$ buffer layer thickness, highest cell efficiencies of 13.6%, fill factor of 53%, Voc of 688 mV and $J_{SC}$ of 32.52 mA/cm$^2$ were obtained upon annealing at 210 °C. GIXRD and TEM studies of these
samples reveal that the films did not completely crystallize at this annealing temperature.

APT proxigram revealed that the interface intermixing region for the sputtered In$_2$S$_3$ buffer layer was $\sim$ 2 nm, similar to the chemically deposited CdS buffer layers. Significant sputter damage to the CIGSe absorber layer up to 5 nm from the interface was observed by 3-dimensional concentration profile measured by APT. Upon annealing, the sputter damage is recovered, which is indicated by improved efficiency from 0.9% to 13.6%.

Cu diffused in range from 1 at.% to 4 at.% in In$_2$S$_3$ at room temperature which can be attributed to high mobility of Cu. The concentration of Cu in In$_2$S$_3$ varies depending upon CIGSe surface topography and thus the Cu-proximity volume. Additionally, S doping of CIGSe surface passivates the Selenium vacancies (V$_{Se}$) which suppress n-type conductivity in CIGSe.

EBIC measurements showed that the space-charged region for In$_2$S$_3$/CIGSe is wide and most of the grains are actively contributing to charge carrier generation. The peak position of the EBIC/Ebeam current for annealed sample overlaps with the In$_2$S$_3$/CIGSe heterointerface indicating that physical and the electrical p-n junction coincide for this material.

H$_2$S/Ar reactively sputtered In$_2$S$_3$ buffer layers gave significantly higher optical transmittance as compared to Ar-ion sputtered In$_2$S$_3$ buffer layers deposited under similar conditions and film thickness. At annealing temperature of 225 °C for 15 minutes, reactively sputtered In$_2$S$_3$ crystallizes with much smaller crystallite size of $\sim$ 9 nm as compared to $\sim$ 25 nm and higher for Ar-ion sputtered In$_2$S$_3$.

Higher sputter pressure (HSP) and slower sputter rate significantly lowered the kinetic energy of impinging sputter atoms resulting in no or minimal sputter damage to CIGSe surface. Interface quality and efficiency achieved this way were comparable with chemically deposited CdS layer which was the primary objective of this thesis.
Sputter damage at the absorber’ surface for HSP In$_2$S$_3$/CIGSe (~2 nm) is much lower than LSP In$_2$S$_3$/CIGSe (~5 nm), as estimated from the APT analyses. Cell efficiencies of 13.84% (16.33% normalized), fill factor of 65%, Voc of 660 mV and $J_{SC}$ of 32.33 mA/cm$^2$ are obtained for reactively sputtered In$_2$S$_3$ buffer layers with CIGSe solar cells.

Elemental redistribution at the interface with different annealing treatments and the respective cell parameters reveal that a Cu depletion of the CIGSe surface is a prerequisite for achieving high efficiencies. Contrarily, the formation of Cu-poor Cu(In,Ga)$_5$Se$_8$ phase at higher annealing temperatures is detrimental for cell performance.

XPS studies show accelerated Cu$^+$ doping of the In$_2$S$_3$ buffer from CIGSe at 225 °C. This lowered the series resistance of In$_2$S$_3$ by Cu self-doping from CIGSe. Carefully chosen annealing conditions prevented the formation of unwanted Cu-In-S based phases which are opto-electronically inferior to In$_2$S$_3$. Cu depletion on CIGSe surface up to a few nanometers improved the cell performance.

At 225 °C, Na segregates at the In$_2$S$_3$/CIGSe heterojunction, actively suppressing the formation of charged In$_{Cu}$ or Ga$_{Cu}$ antisites defects and lowering the recombination in the space charged region (SCR). This is evident from the lower diffusion current $J_{01}$ and recombination current $J_{02}$ for this annealing temperature. Lower $J_{01}$ indicates reduced recombination outside SCR, and lower $J_{02}$ indicates reduced Shockley-Read-Hall (SRH) recombination in the SCR. Also, multi-level recombination is changed to recombination via one defect with a decrease in ideality factor $n_2$.

The In$_2$S$_3$ buffer layer deposition process developed in this work was very successful experimentally and analytically. Using p-type CIGSe absorbers as starting material and using a systematic approach for optimization of n-type In$_2$S$_3$ buffer layer, the efficiency of CIGSe solar cells was improved gradually from 0% to 16.3%. The promising results obtained in this work can be instrumental for further
improvement of efficiency with Cd-free, sputter deposited In$_2$S$_3$/CIGSe based solar cells. With an aim to carry forward the experimental and analytical findings of In$_2$S$_3$/CIGSe solar cells in this thesis, future work to further enhance the efficiency is suggested as follows:

1. Further optimization of ZnO and AZO layers (thickness vs optical transmittance/resistivity) to improve the overall transmittance of incident photons to the space charge region. Additionally, optimizing the deposition parameters to minimize cracks in the window layers (improved FF, $V_{OC}$, and efficiency).

2. Optimization of e-beam deposition parameters and improved mask design for Ni/Al metal contacts to improve the conductivity and minimize shadowing area of the grid.

3. Optimization of In$_2$S$_3$ buffer layer thickness to improve spectral response in the blue-wavelength region with a uniform CIGSe layer coverage.

4. Understanding the relation of the crystallite size of In$_2$S$_3$ buffer layers with respect to optical transmittance.

5. Doping of In$_2$S$_3$ to enhance the bandgap of In$_2$S$_3$ and minimize Cu-diffusion in the buffer layer.

6. Drive level capacitance profiling to correlate the change in defect density with respect to the I-V measurement and concentration profiles obtained from atom probe tomography.
List of publications


Sputtering as a viable route for In$_2$S$_3$ buffer layer deposition in high efficiency Cu(In,Ga)Se$_2$ solar cells; P Soni, M Raghuwanshi, R Wuerz, B Berghoff, J Knoch, D Raabe, O Cojocaru-Mirédin; Energy Science & Engineering 7, 478- 487 (2019)

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Interface engineering and nanoscale characterization of Zn (S, O) alternative buffer layer for CIGS thin film solar cells; P Soni, O Cojocaru-Mirédin, D Raabe; 2015 IEEE 42nd Photovoltaic Specialist Conference (PVSC) 1, 1-5 (2015)
Appendix

A. Sputter deposition parameters of Zn based buffer layers

Materials such as Zn(O,S) and ZnS/In$_2$S$_3$ are important alternative buffer layers yielding high efficiencies. These layers were deposited using RF magnetron sputtering as a sub-project in this work. Zn(O,S) was deposited by two approaches:

1. Co-sputtering of ZnS and ZnO targets and
2. Reactive sputtering of ZnO target with H$_2$S/Ar

Mixed buffer layers of ZnS/In$_2$S$_3$ were sputtered using sequential sputtering of ZnS and In$_2$S$_3$ targets. The experimental details of sputter deposition of these buffer layers are as follows:

A.1 Co-sputtering of Zn(O,S) buffer layers

ZnO and ZnS targets were fired-up simultaneously to get a mixture of ZnS/ZnO thin films as buffer layers. ZnO/ZnS co-sputtering was done at a sputter pressure of 3×10$^{-3}$ mBar with an Ar flow rate of 80 SCCM. The Target-substrate distance was kept constant at 50 mm and the substrate carrier was rotated at a speed of 20 RPM. Sputter deposition process lasted for 5 minutes at a sputter power of 25W for ZnS and 75W for ZnO.

A.2 Reactive sputtering of Zn(O,S) buffer layers

ZnO was reactively sputtered with H$_2$S/Ar to deposit Zn(O,S) buffer layers. The reactive sputter deposition was done at a pressure of 6×10$^{-2}$ mBar. Ar as sputter gas was introduced with 0.25% concentration of H$_2$S/Ar as reactive gas in the chamber.
The Target-substrate distance was kept constant at 80 mm and the substrate carrier was rotated at a speed of 5 RPM. Sputter deposition process lasted for 30 minutes at a sputter power of 0.5 W.

A.3 Deposition of ZnS/In$_2$S$_3$ mixed buffer layers

Mixed buffer layers with ZnS/In$_2$S$_3$ were deposited using sequential sputtering of ZnS and In$_2$S$_3$ targets. The sputtering was done at a pressure of $3 \times 10^{-3}$ mBar with an Ar flow rate of 80 SCCM. The Target-substrate distance was kept constant at 50 mm and the substrate carrier was rotated at a speed of 20 RPM. First, ZnS target was ignited from 0 to 45 seconds at 50W. From 30 seconds to 300 seconds, the In$_2$S$_3$ target was ignited at 50W (with an overlapping co-sputter time of 15 seconds between ZnS and In$_2$S$_3$ targets).
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