Investigation on the role of Sb doping on grain growth and properties of solution-processed $\text{CuIn}(\text{S},\text{Se})_2$

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2014

Ho, J. C. W. (2014). Investigation on the role of Sb doping on grain growth and properties of solution-processed $\text{CuIn}(\text{S},\text{Se})_2$. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/62509>

<https://doi.org/10.32657/10356/62509>

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A thesis submitted to the Nanyang Technological University

in partial fulfillment of the requirement for the degree of

Doctor of Philosophy

2014

Abstract

Cu(In,Ga)(S,Se)_2 (CIGSSe) has been one of the most promising materials used for photovoltaic application. Solution based synthesis of CuIn(S,Se)_2 (CISSe) cells have achieved 12% efficiency, utilizing toxic hydrazine as the solvent. A shift towards an environmental friendly approach for CIS fabrication is thus necessary. In this thesis, solvothermal syntheses of wurtzite and chalcopyrite CIS nanoparticles are explored. Metastable wurtzite nanoparticles were successfully synthesized at much lower temperature, with a dual amine solvent under excess sulfur environment. Binary Cu_9S_5 and In_2S_3 nanoparticles were also synthesized and spray deposited to make a film. However, nanoparticle deposition resulted in rough and non-uniform film. Hence, aqueous spray pyrolysis of precursor solution was deployed to form CIS film directly on Mo substrate. Oxidation of Mo substrate is avoided by deposition of a precursor layer which acts as a barrier layer isolating Mo surface. The resultant film is dense and uniform but has very fine grains which are detrimental to carrier transport. A hybrid approach using nanoparticles incorporated into precursor solution for spray pyrolysis results in dense and uniform film, with significantly larger grains after selenization. However, the hybrid approach involves complex processing and precise experimental control. Hence, aqueous spray pyrolysis of precursor solution is a better option.

High temperature annealing can enhance grain size of spray pyrolysed CIS film. Annealing under different vapors, namely S, Se and Ar, provides different extent of grain growth. Annealing in Se vapor, selenization, results in the most significant grain growth, due to the abundant formation of liquid Cu_xSe phases which enhances grain growth by liquid phase sintering. Annealing in S vapor is less efficient due to increased difficulty in liquid phase

formation whereas annealing in inert Ar gas does not assist in grain growth. A high or saturated Se flux increases the probability of liquid phase existence, resulting in the most promising grain growth.

Sb doping enhances grain growth during selenization by formation of low melting point Cu_3SbSe_4 compounds. Sb dopant most probably resided along grain boundaries after doping. Cu_3SbSe_4 , which was formed along the grain boundaries during selenization, has a low melting point and exist as liquid phase facilitating atomic diffusion across grain boundaries. The formation of Cu_3SbSe_4 is further justified by selenization of CuSbS_2 film formed by spray pyrolysis using Cu, Sb and S precursors. Cu_3SbSe_4 compounds provide additional liquid phase for effective sintering of the grains. Sufficient doping concentration enhances grain growth significantly by forming large grains of the same magnitude as the film thickness. The extent of grain growth is dependent on diffusion of dopants. Selective Sb doping at top layer of CIS creates a high dopant concentrate gradient, resulting in better grain growth due to increased dopant diffusion. The mechanism of grain growth is similar to liquid phase sintering of CISSe grains by formation of low melting point Cu_3SbSe_4 phases along the grain boundaries.

Optical characterization on Sb doped CISSe film shows a negligible influence on the bandgap as formation of CuSbS_2 is unlikely due to low doping level. Doped devices experienced superior J-V characteristics than undoped devices. An increase in doping level from 0.5 mol% to 1.0 mol% increased device performance further. In addition, selective doping of 1.0 mol% at the top layer proved to enhance device J-V characteristics relative to 0.333 mol% or 1.0mol% evenly doped sample. Cross-sectional TEM images show numerous pores within the film which are detrimental and a result of insufficient liquid phase for sintering. Selected area electron diffraction (SAED) pattern of a particular Sb

doped CISSe grain gives an unknown superstructure, which indicates the presence of ordered defect compounds. Photoluminescence (PL) study conducted at low temperature indicated high potential fluctuation. Power law linear fit shows an excitonic recombination as the main recombination mechanism. High temperature PL intensity quenching fitting shows separation energy of 35 meV. Sb doping enhances carrier lifetimes, according to pump probe measurements. The enhanced lifetimes can be attributed to defect related recombination from less grain boundaries and the higher density of secondary (204)/(220) grain orientations which has lower density of non-radiative recombination centers. Conductive AFM mapping on Sb doped device with best device performance shows similar current map under positive bias and minimal current when the tip bias is negative, illustrating minimal leakage current in the device. Sb doping lowers carrier density, which might reduce probability of recombination, at the expense of lower carrier mobility.

Acknowledgement

First and foremost, I would like to express my gratitude to my supervisor and co-supervisors, Assoc. Prof Alfred Tok and Asst. Prof Lydia Wong for the guidance, encouragement and patience throughout the progress of my research work. The numerous active discussions and valuable suggestions given by both supervisors throughout the progress of my work have benefited and assisted me greatly in my research work.

I would also like to thank Prof Subodh Mhaisalkar for providing lab facilities for me to conduct my research. Furthermore, the numerous discussions during research group meetings have benefited me greatly.

I would like to thank Prof Lam Yeng Ming for the advice and suggestions offered during research group meetings.

I would also like to thank Dr Sudip Batabyal for being a wonderful mentor in my research work. His innovative ideas, helpful suggestions and constant guidance are deeply appreciated.

I would like to thank all the CIGS group members, especially Dr Li Zhenggang and Dr Stevin Pramana for assisting me in characterization.

Special thanks to ERI@N technical staff, Heryani, Karis and Xiaoting for all the technical support in the lab.

Last but not least, I would also like to thank all my colleagues from ERI@N and MSE for all the support and help granted along the way of my research work.

List of Abbreviations

AM1.5	Air mass 1.5
CdS	Cadmium Sulfide
CIGS	Copper Indium Gallium Selenide, Cu(In,Ga)Se ₂
CIGSSe	Copper Indium Gallium Sulfur Selenide, Cu(In,Ga)(S,Se) ₂
CIS	Copper Indium Sulfide, CuInS ₂
CISe	Copper Indium Selenide, CuInSe ₂
DLTS	Deep-Level Transient Spectroscopy
EDA	Ethylenediamine
EDX/EDS	Energy dispersive X-ray/Energy dispersive spectroscopy
E_g	Energy band gap
EPMA	Electron probe microanalysis
EQE	External quantum efficiency
FFT	Fast fourier transform
FTO	Fluorine doped tin oxide
HRTEM	High resolution transmission electron microscopy
ITO	Indium tin oxide
J-V	Current density-Voltage
Np	Nanoparticle
OVC/ODC	Ordered vacancy compound/Ordered defect compound
PCE	Power conversion efficiency
PL	Photoluminescence
SAED	Selected area electron diffraction
SIMS	Secondary ion mass spectroscopy
TCO	Transparent conductive oxide
TEM	Transmission electron microscopy
UV-VIS	Ultra-violet visible spectroscopy
WDS	Wave-dispersive spectroscopy
wz-CIS	Wurzite CuInS ₂
XRD	X-ray diffraction

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Chapter 1

1. Introduction

1.1 Background

Energy consumption throughout the world is rising constantly as huge countries, such as China and India, are developing rapidly, placing an enormous stress on energy production. In the past decades, global warming has resulted in rising sea levels and an increased occurrence in extreme climates had led to countries going green to remove greenhouse gases. Tackling climate change and increasing energy demand have to go hand in hand, which leads to a strong drive towards renewable and clean energy.

Clean energy is defined as the type of energy whereby the energy production does not pollute the atmosphere. Solar, wind, tidal, geothermal and nuclear are examples of clean energy. Nuclear energy is the energy source with the highest output but can be disastrous when a meltdown occurs. The Chernobyl and Fukushima incidents, in 1986 and 2011 respectively, should serve as a reminder on the risks involved in nuclear energy production. Among the other different types of clean energy, solar energy production is rising fast throughout the years. With the sun bearing down on most parts of the Earth daily, efficient tapping of this energy will solve the impending energy crisis. However, the price involved on tapping solar energy is still not competitive. Hence, there is a need for technology advancement to push for higher photovoltaic efficiency. Over the past years, the solar market was dominated by crystalline Si as the absorber material with copper-based

chalcogenide such as CuInGaSe_2 (CIGS) having the strongest potential to overtake Si in the future.

Cu(In,Ga)Se_2 (CIGSe or CIGS) thin film technology for photovoltaic application has been a promising and viable candidate for high efficiency photovoltaic devices. Conventional CIGS and its Chalcopyrites family have achieved power conversion efficiency (PCE) exceeding 20%¹ via high vacuum 3-stage co-evaporation approach. The vacuum approach on CIS/CIGS deposition has been the main focus in the past decades as it has low impurity and provides great flexibility on the processing control such as ease of double grading in CIGS. However, high cost of vacuum setups and significant material wastage keeps the processing cost high, which makes it less competitive in terms of pricing. In addition, the high cost in indium makes material wastage a key concern. This drives research towards low cost non-vacuum approach. The non-vacuum approach such as the solution-based or nanoparticle ink approach have achieved promising efficiencies of 12%²⁻³ but are still lagging behind the vacuum approach. The nanoparticle approach involves the synthesis of the nanoparticles followed by deposition to form a film³⁻⁷. Formation of nanoparticle inks may potentially leave a thick layer of carbon after annealing due to the organic binders used or the capping ligands on the nanoparticles. Spray pyrolysis is a fast and cost effective method to produce thin films. Spray pyrolysis to form CIS/CISe thin films were successfully demonstrated⁸⁻¹¹ but it was conducted on various substrates except on Mo substrate, probably due to the ease of oxidation of Mo at high temperatures in ambient conditions. The use of anhydrous hydrazine brings significant improvement to film qualities, as well as device performance. It has set new record efficiency of 12% on solution processed CuIn(S,Se)_2 (CISSe) thin films. As hydrazine is a strong reducing agent and is capable of dissolving metal sulphides and selenides effectively, film purity is higher. The major drawback is the high toxicity and

volatility of hydrazine, which deters many research groups and industry from working with it.

CIS/CIGS can either adopt a zinc blende¹², chalcopyrite^{5, 13} or wurtzite structures^{12, 14-17}. Chalcopyrite has a similar structure as zinc blende but with an additional ordering involved. Chalcopyrite CIS/CIGS has been widely reported from synthesis to material characterizations but the wurtzite phase CIS/CIGS is a relatively new phase that is metastable at low temperatures. There have been many reports on the synthesis of wurtzite CIS/CIGS¹⁴⁻¹⁸ while the materials properties are still largely unknown. CIS/CIGS thin film has a great potential and advantage over crystalline Si due to its material properties.

CIS/CIGS has a direct bandgap with high optical absorption coefficient of $10^4/\text{cm}$, which requires a thin layer (~ 1 micron) of film to successfully absorb all the light. This gives it a clear advantage over Si which has an indirect bandgap. It has a tunable bandgap by varying S/(S+Se) or Ga/(Ga+In) ratio in the film which allows a bandgap from 1.05eV to 2.50eV. An ideal photovoltaic material is to have the optimum bandgap of 1.1eV with a maximum PCE of 44%, according to Shockley-Queisser limit¹⁹. Hence, there is still much work to be done to get closer to the limit. CIS/CIGS thin film has the ability to be made n-type or p-type by controlling the Cu/(In+Ga) ratio²⁰. A highly Cu-rich film is n-type while a typical stoichiometric or Cu-poor CIS/CIGS is usually p-type. p-type CIS/CIGS is most widely used as semiconductor for photovoltaic applications. On the other hand, n-type CIS/CIGS is rarely used as it contains a high density of binary compounds, from its Cu-rich stoichiometry. These binary compounds are highly conductive, such as Cu_xSe , resulting in device to short circuit, severely impairing photovoltaic performance.

1.2 Motivation

Solution-based CIGSSe via hydrazine approach is able to achieve improved device performance with PCE of 15.2% through antimony, Sb, doping²¹. However, the use of highly toxic hydrazine is an environmental and safety concern. There is a strong need for development of an environmentally friendly and safe process for solution-based fabrication of CIS/CIGS thin film.

A close comparison of the average grain size of CIS/CIGS thin film fabricated by vacuum approach and non-vacuum approach shows an obvious grain size difference between these two approaches. CIS/CIGS thin film with a small average grain size would have more grain boundary areas, which are potential recombination centers²²⁻²³, limiting photovoltaic performance. A wide range of grain boundaries study was conducted, showing that the presence of certain defects at the grain boundary could be beneficial to the grain boundaries²³⁻²⁸. However, reduction of grain boundary areas would still be the key focus to enhance electrical properties of the absorber layer to achieve better device performance.

There are numerous ways of improving grain growth. The simplest and most direct way would be increasing annealing temperature or duration. However, this would lead to a thicker MoS₂ or MoSe₂ layer which affects absorber film adhesion and increases the series resistance of the full device. Studies on the grain growth mechanism of Si have shown interesting doping effects²⁹⁻³⁰. With appropriate dopant choice, significant grain enhancement could be achieved. The key breakthrough in grain enhancement of CIGS was achieved by Sb doping³¹. Sb doping resulted in significant grain growth and improvement of device IV characteristics. Grain enhancement effects achieved through Sb doping are also shown in CIGS³²⁻³⁴ or CZTS³⁵ thin films fabricated from different approaches with a contrasting method of dopant introduction. Although the results achieved were generally

similar, the mechanism on grain enhancement and the effect of doping on electrical properties is still unclear. A better understanding on dopant effect and grain growth mechanism allows the possibility of developing a dopant selection rule for grain growth in chalcopyrite CIS/CIGS or other materials. Optimization on properties CIS/CIGS thin film would also be made possible with better knowledge of doping on material properties.

1.3 Objectives and Scope

This thesis aims to understand the effect of elemental doping on grain growth of solution-processed CISSe absorber layer to reduce grain boundary recombination and achieve higher device performance. As there are many different stoichiometric variations of CISSe, the target stoichiometry is $\text{Cu}_{0.85}\text{In}(\text{S},\text{Se})_2$. The S/(S+Se) ratio will not be fixed as it is dependent on annealing environment and parameters. An environmentally friendly and facile fabrication of CISSe thin film will be developed first before introduction of dopants. Antimony, Sb, will be the only elemental dopant used. The effect of annealing vapors on the grain growth of doped and undoped CISSe thin films will be investigated. Most importantly, the effects of Sb doping amount and doping position on the grain growth of CISSe will also be investigated. A detailed mechanism of grain growth for Sb doped CISSe will be proposed to explain the role of Sb on grain growth. A comprehensive characterizations of Sb doped CISSe will be performed to investigate the effect of Sb doping on the electrical and optical properties of CISSe film. Characterization techniques used includes: scanning electron microscope (SEM), electron probe microanalysis (EPMA), secondary ion mass spectroscopy (SIMS), X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), Raman spectroscopy, conducting atomic force microscopy (C-AFM), Hall Effect measurement, pump probe and photoluminescence measurement (PL). CISSe thin films made into complete devices are characterized by J-V measurement and

external quantum efficiency (EQE) measurements. The bandgap of CISSe varies with S/(S+Se) ratio and is determined by UV-vis spectrometer or derived from EQE measurement.

In summary, the key objectives are:

- Development of an environmentally friendly approach for solution-processed CISSe film.
- Investigate the effect of annealing vapors on the grain growth of CIS/CISSe film.
- Investigate the effect of Sb doping on grain growth of CISSe film and determine the mechanism of grain growth.
- Investigate the effect of Sb doping on electrical and optical properties of CISSe film.

1.4 Organization of the Thesis

The flow of the thesis is organized as follows:

Chapter 1 Introduction provides the research background, motivation of work and the objectives and scope.

Chapter 2 Literature Review gives a range of literature studies to provide greater understanding and knowledge about past research work conducted. This includes photovoltaic principles, doping and grain growth studies performed on copper chalcogenide and other semiconductors.

Chapter 3 Experimental Procedure gives an overall summary of all the experimental information which includes synthesis process, annealing process and material characterization.

Chapter 4 Synthesis and Growth of $\text{CuIn}(\text{S},\text{Se})_2$ This chapter focuses on different methods employed to fabricate CISSe thin film. This includes CIS nanoparticle synthesis via solvothermal process, binary nanoparticles deposition and annealing, spray pyrolysis from precursor solution and hybrid of nanoparticles with precursor solution spray pyrolysis.

Chapter 5 Grain Growth of $\text{CuIn}(\text{S},\text{Se})_2$ from Precursor Solution. This part of the thesis aims to study grain growth on spray pyrolysed CIS thin film under different annealing environments, which includes Ar, S and Se vapors. In addition, the effect of Se flux on the grain growth of CISSe is discussed.

Chapter 6 Sb doping on $\text{CuIn}(\text{S},\text{Se})_2$. This chapter focuses on the effects of Sb on the grain growth of CISSe during annealing. A range of doping level was introduced with different observed grain growth effects. The Sb dopant is doped evenly throughout the film and selectively doped at specific layer to investigate the effect of concentration gradient on grain growth. A mechanism of grain growth is proposed to explain the role of Sb on grain growth.

Chapter 7 Understanding the effect of Sb doping on optoelectronic properties of $\text{CuIn}(\text{S},\text{Se})_2$. This chapter focus on the characterization of Sb doped CISSe to understand the optical and electrical properties of CISSe with and without doping. The effect of doping level and doping concentration gradient on device performance is discussed. Key electrical properties such as defect nature and carrier properties are discussed.

Chapter 8 Conclusion and Future Work gives a summary of the overall research work with the scientific contributions highlighted. It also provides some suggestions on future directions to continue on current work.

Chapter 2

2. Literature Review

2.1 Basic working principle of a chalcopyrite CIGS thin film solar cell

In most cases, CIGS is the p-type absorber and CdS is commonly used as the n-type buffer layer. At the CdS and CIGS interface, a p-n junction is formed. Electrons and holes diffuse along a concentration gradient to achieve equilibrium at the interface forming the p-n junction. As the n-type CdS layer has excess electrons and p-type CIGS has excess holes, the electrons and holes diffuse across the interface, leaving behind a positive donor at the n-side and a negative acceptor at the p-side, forming a depletion region or space charge region (Figure 2.1). In this region, the resulting positive charge at the n-side and negative charge at the p-side will result in an electric field. Conversion of light to electricity in a solar cell occurs at the p-n junction. In the case of chalcopyrite CIGS thin film solar cell, the individual layers which form the device has been illustrated (Figure 2.2). Sunlight is made up of packets of energy, called photons. As light is shone onto the device, the photons can be reflected, absorbed or transmitted upon reaching each individual layers in the device, depending on the bandgap of the material. Most of the photons will be absorbed by the CIGS absorber layer. As photons are absorbed, an electron-hole pair will be formed. The electron will be attracted by the electric field to the n-side and holes will be attracted by the p-side. Electrons will be collected by the transparent conducting oxide layer (TCO), aluminum-doped zinc oxide (AZO) or tin-doped indium oxide (ITO), which are commonly used materials for TCO, and holes will be collected by the Mo back contact.

Figure 2.1 Illustration of p-n junction indicating space charge region.

Figure 2.2 Illustration of a CIGS device structure.

2.2 Fabrication of CISSe/CIGS absorber layer

2.2.1 Vacuum-based approach

CISSe/CIGS fabrication can be achieved via two main approaches, namely vacuum-based and non-vacuum based approach. The vacuum-based approach is the pioneer method in CIS³⁶ and CIGS device fabrication. It involves the use of equipment which operates at high vacuum to deposit the absorber layer and had successfully achieved efficiency of 20% for CIGS devices via 3 stage co-evaporation³⁷⁻³⁸. Co-evaporation is a widely used technique due to easy control of film purity and greater ease of bandgap engineering from a multiple-stage co-evaporation process (Figure 2.3). It also allows stoichiometric variation at different

stages, such as initial deposition of Cu rich film to form larger grain size. Sputtering from single source target without selenization has also been shown to be a viable way to fabricate CIGS devices with much room for optimization³⁹. However, there are also research groups which conduct selenization after sputtering of singular and binary compound layers to form CIGS⁴⁰. Although the typical substrate used for CIGS solar cells via vacuum approach are Mo-coated soda-lime glass, there are other groups which focus on alternative substrates such as steel or polyimide⁴¹⁻⁴⁴. The use of flexible substrates has been successful and has achieved efficiency of 18.7% for thin film CIGS solar cell with polyimide as the flexible substrate⁴⁵. The vacuum-based approach has been successful for achieving high efficiency chalcopyrite solar cells, specifically CIGS and CISSe. The main advantage would be high stoichiometry control and low impurity introduction which tend to produce good quality absorber films. However, high cost of processing, mainly due to equipment cost, has deterred general research focus on non-vacuum based approach.

2.2.2 Non-vacuum based approach

There are many non-vacuum based synthesis approaches for CIGS solar cells and the three main categories are namely, particulate, electrochemical and precursor solution. The particulate approach focuses on the use of nanoparticles of CIS/CIGS dissolved or mixed homogeneously in selected solvent to form ink for printable photovoltaic or deposition of nanoparticles on substrates via spray pyrolysis^{5, 13, 46}. They are promising routes to achieve low cost solar cells but there is still much research to improve efficiency. The electrochemical approach relies on electro-deposition to deposit thin film CIGS, achieving efficiency of around 10%⁴⁷⁻⁴⁸. The precursor solution approach works by dissolving individual precursors in solvent to achieve a homogeneous solution before deposition via spray pyrolysis or spin coating on a preheated substrate. The state-of-the-art solution-based

approach on CIS/CIGS/CISSe device fabrication is proposed by Mitzi et al. who chose anhydrous hydrazine as the solvent and a record efficiency of 10.3%⁴⁹⁻⁵⁰ and 12%² for CIGS and CISSe devices were achieved respectively. The use of hydrazine granted several advantages, mainly impurity reduction and ability to dissolve selenium and selenides (In_2Se_3 , Ga_2Se_3 , Se) well to form homogenous solutions. However, due to its acute toxicity and environmental concerns arising from its toxicity, it is best to avoid the use of hydrazine. An alternative solvent would be water to dissolve water soluble precursors such as chlorides (InCl_3 , GaCl_3 , CuCl_2) and use of sulfur ($\text{CS}(\text{NH}_2)_2$) to replace selenium (Se) to fabricate CIS devices instead^{11, 51}.

Generally, CIS devices tend to yield lower efficiencies due to difficulties in controlling sulfur during deposition. Higher diffusion of metals and impurity species, even at low temperatures, slow down the development of this material⁵². However, this can be overcome by selenization of CIS to form CISSe which has achieved efficiency of around 5% from drop casting of CIS nanoparticles⁵³. The ratio of sulfur to Se will determine the bandgap as CIS and CISE have the bandgaps of approximately 1.50 eV and 1.05 eV. Selenization is a process whereby the chalcopyrite thin film will undergo thermal annealing in the presence of Se_2 or H_2Se vapor. The process has been performed widely on different chalcopyrite precursor thin films for reduction of oxides, densification and grain growth⁵⁴⁻⁵⁷. The use of Se_2 vapor is preferred as compared to H_2Se as the latter is a highly toxic gas which would pose a risk to user and the environment⁵⁸.

Figure 2.3 Illustration of a CIGS co-evaporation process.

2.3 Device physics of CIGS chalcopyrite semiconductor

2.3.1 Defects and stability of defects

Chalcopyrite CIGS has many advantages over other thin film material for solar cell application due to the presence of defects which are termed beneficial. Zhang et al. conducted detailed studies on the defect physics of CIGS chalcopyrite semiconductor⁵⁹ which provides a deeper understanding on the stability of CIGS for photovoltaic applications.

Firstly, CIGS device is observed to be capable of tolerating larger deviation from ideal stoichiometry of Cu/In/Se ratio of 1:1:2 due to the existence of various ordered defect compounds (ODC) with various Cu/In/Se ratios, such as CuIn_5Se_8 , CuIn_3Se_5 and $\text{Cu}_3\text{In}_5\text{Se}_9$, which are not observed in II-IV semiconductors. Secondly, CIGS has the ability to be doped via native defects. The introduction of these defects is not done extrinsically but rather through changing the stoichiometry of Cu content and annealing atmosphere during the synthesis stage. It is commonly understood that p-type CIGS can be fabricated under maximum Se pressure during annealing of a Cu poor sample and the reverse for n-type CIGS. Lastly, the structural defects that were formed are electrically benign which make

polycrystalline CISE as good as its single crystalline counterpart. The three phenomena are finally attributed to the formation of $(2V_{Cu} + In_{Cu})$ which is very stable and easy to form, requiring an optimal chemical potential of -1.46 eV. Furthermore, charging to form $(2V_{Cu}^- + In_{Cu}^{2+})$ instead of $(2V_{Cu} + In_{Cu})$ lowers the minimum formation energy further to -5.57 eV/pair, which explains the existence of the ordered defect compounds as listed previously. $(2V_{Cu}^- + In_{Cu}^{2+})$ does not contain deep gap levels and is electrically neutral due to electronic passivation of the deep level, In_{Cu}^{2+} , by $2V_{Cu}^-$. As Cu vacancies have low formation energy and shallow defect level above the valence band maximum, CISE can be self-doped to p-type by lowering Cu content in film.

2.3.2 Device efficiency calculation and factors affecting device efficiency

The determination of device efficiency or power conversion efficiency, η , can be calculated from Equation (1)⁶⁰.

$$\eta = \frac{J_{sc} V_{oc} FF}{P_s} \dots\dots\dots (1)$$

The quantities are: J_{sc} , short circuit current density; V_{oc} , open circuit voltage; FF , fill factor and P_s incident light power density. J_{sc} , V_{oc} and FF are important characteristic of a solar cell. In general, solar cells with higher V_{oc} will generally result in a lower J_{sc} measured as both the J_{sc} and V_{oc} are highly dependent on the material used, particularly the band gap of the semiconductor. The band gap of CIS is around 1.50 eV and CISE is 1.05 eV. Hence, CISSe bandgap would be in between 1.05-1.50 eV, depending on the sulfur/selenium ratio. This applies to CIGS ($CuIn_{1-x}Ga_xSe_2$) whereby CISE has a band gap of 1.05 eV and CGSe has a band gap of 1.70 eV. The maximum theoretical efficiency of a single junction solar cell is given by the Shockley-Queisser limit (Figure 2.4)¹⁹. The optimum bandgap is given as ~1.10eV with a maximum theoretical efficiency of 44%. In CIGS device, the V_{oc} is highly

dependent on the interface properties of the p-n junction, i.e. the interface between CdS and CIGS. A good and uniform coverage of n-type CdS on the p-type CIGS will yield a good V_{oc} . Hence, chemical bath deposition of CdS is most commonly used for highly efficient devices with high V_{oc} , as it is easy to use, offers good coverage capability and forms a strong n-type layer in CIGS⁶¹⁻⁶². J_{sc} reflects on the amount of light induced carriers collected, hence its value depends on the light absorption efficiency and the extent of recombination or carrier traps within the device. FF is generally limited by the quality of all the individual layers that form the complete device and the interface between the layers.

Figure 2.4 The Shockley-Queisser limit illustrating maximum theoretical efficiency of a single p-n junction solar cell¹.

2.4 Grain boundary and grain size

2.4.1 Grain boundary physics and Na incorporation effects

Single crystalline material, such as Si, usually results in better photovoltaic performance but the opposite is true for the case of CIGS chalcopyrite semiconductor. There is an existence of

¹ Reproduced with permission from Shockley, W.; Queisser, H. J., Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. J. Appl. Phys. 1961, 32, 510-519. Copyright 2014, AIP Publishing LLC. <http://dx.doi.org/10.1063/1.1736034>

a hole barrier in the grain boundaries (GB) of polycrystalline CISE²⁵. The hole barrier along GB is attributed to presence of Cu vacancy based reconstruction. Extrinsic doping by neutral impurities, such as Na, result in formation of polar (112) surfaces. Monovalent Na, lacks *d* orbitals hence Na_{Cu}^0 defects will be electrically inactive and create a hole barrier due to lack of *p-d* repulsion. As impurities tend to segregate along GB, the grain interior (GI) would eventually be much purer. The hole barriers deprive holes from entering GB which contains impurities, whereby chemical traps are present and hence prevent recombination. This could be a potential reason for polycrystalline CISE device performing better than its single crystalline counterpart as the grain interior is highly pure. The hole barrier arises from the reconstruction of surfaces which resulted in Cu-vacancy, reducing p-d repulsion. The use of Atomic Force Microscopy (AFM) and Scanning Kelvin Probe Microscopy (SKPM) on the surface of CIGS was conducted to confirm the presence of hole barrier as a built-in potential is detected along the GB²⁸. The use of AFM is to prove that the signal from SKPM is not resultant from topological effects. Results concluded that a higher surface potential (~150 mV) or smaller work function is present at the GB as compared to the grain surface (Figure 2.5)²⁸. However, the study does not reflect similar behavior of the grains that are buried from the surface as SKPM is a surface measurement technique. In addition, the SKPM also confirmed the segregation of Na around the GB by comparing the measurement before and after rinsing the sample surface with highly pure water to dissolve Na. The segregation behavior of Na along GB further confirms the passivation effect of GB by Na which has been shown to improve efficiencies⁶³⁻⁶⁴. The beneficial effects of Na incorporation has been studied which shows that Na has an effect on the growth kinetics, resulting in structurally and electronically modified absorber material⁶⁵⁻⁶⁶. The built-in potential drops drastically when Ga content in CIGS film is increased to 38% from 28% and the efficiency of the

resultant device changes⁶⁷. Hence, it can be concluded that the built-in potential affects the efficiency of device significantly.

Figure 2.5 (a) AFM and (b) the corresponding SKPM images of CIGS films after cleaning in high purity water; (c) shows a line profile along the arrows in (b) together with a potential line profile taken before the water-cleaning for comparison.²

2.4.2 Grain size analysis for device application

The grains of evaporated chalcopyrite thin films, such as CIGS, are usually very large and these devices have achieved high efficiencies of 18-20%^{37-38, 68}. Although CIGS has a high absorption coefficient⁶⁹, high efficiency devices would generally have the absorber thickness up to around 1.5-2.0 μm in order to optimize light absorption. Lower thickness translates to lower light absorption and hence affects device performance⁷⁰. In addition, the grain size of the absorber layer should be large and preferably in the range of the film thickness after final annealing or selenization of the absorber film (Figure 2.6a, b)³⁷ for high efficiency devices. Smaller grains would mean a larger amount of GB, which are potential recombination centers. Furthermore, the presence of hole barriers (discussed in Section 2.4) in GB might

² Reproduced with permission from Jiang, C. S.; Noufi, R.; AbuShama, J. A.; Ramanathan, K.; Moutinho, H. R.; Pankow, J.; Al-Jassim, M. M., Local built-in potential on grain boundary of $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin films. *Appl. Phys. Lett.* **2004**, 84, 3477-3479. Copyright 2014, AIP Publishing LLC. <http://dx.doi.org/10.1063/1.1737796>

possibly resist hole transport to the Mo layer due to existence of GB²⁵. On the other hand, the grain size of solution processed CIGS⁵⁰ or CISSe² are relatively smaller which is close to 1.0 μm (Figure 2.6c, d⁵⁰). The short circuit current, J_{sc} , for evaporated CIGS, solution-based CIGS and solution-based CISSe are 35.5 mA/cm^2 , 25.7 mA/cm^2 and 29.8 mA/cm^2 respectively. A lower J_{sc} of solution-based CIGS device (Figure 2.6d) as compared to the solution-based CISSe (Figure 2.6c) could also be attributed to the lower absorber thickness of 1.0 μm as compared to 2.0 μm but record efficiency of evaporated film have grains at least as large as the thickness of the film.

Figure 2.6 (a) SEM cross-section and (b) plan view for co-evaporated CIGS device with 19.9% efficiency³; SEM cross section for solution deposited (c) CISSe⁴ and (d) CIGS⁵ with 12.2% and 10.3% efficiency respectively.

³ Repins, I.; Contreras, M. A.; Egaas, B.; DeHart, C.; Scharf, J.; Perkins, C. L.; To, B.; Noufi, R., 19.9%-efficient ZnO/CdS/CuInGaSe₂ solar cell with 81.2% fill factor. Prog. Photovoltaics Res. Appl. 2008, 16, 235-239. Copyright © 2014 Repins, I. <http://onlinelibrary.wiley.com/doi/10.1002/pip.822/abstract>

⁴ Reprinted (adapted) with permission from Liu, W.; Mitzi, D. B.; Yuan, M.; Kellock, A. J.; Chey, S. J.; Gunawan, O., 12% Efficiency CuIn(Se,S)₂ Photovoltaic Device Prepared Using a Hydrazine Solution Process. Chem. Mater. 2010, 22, 1010-1014. Copyright 2014 American Chemical Society.

⁵ Mitzi, D. B.; Yuan, M.; Liu, W.; Kellock, A. J.; Chey, S. J.; Deline, V. R.; Schrott, A. G., A High-Efficiency Solution-Deposited Thin Film Photovoltaic Device. Adv. Mater. 2008, 20, 3657-3662. Copyright © 2014 Mitzi, D. B. <http://onlinelibrary.wiley.com/doi/10.1002/adma.200800555/abstract>

2.5 Annealing and grain growth

2.5.1 Theoretical aspect of grain growth

Grain growth occurs when the average grain size of a fully crystallized or recrystallized film increases. This is normally done by annealing treatment which provides sufficient energy, in the form of heat, for grain boundary motion. Normal or abnormal/secondary grain growth refers to a process whereby the grains follow a monomodal growth and bimodal growth rate respectively⁷¹. Secondary grain growth can form grain sizes which exceeds the film thickness⁷². The driving force for such growth in the initial stage is normally surface energy anisotropy. Stress and strain in the sample film, which can be a driving force for growth, can affect the growth rate and the final size of grain⁷³⁻⁷⁴. Other than surface energy and strain energy minimization, the other driving force would be interfacial energy minimization. A model is built by Thompson et al. to study secondary growth rates and results indicate that the growth rates increase with increasing grain boundary energy, surface energy anisotropy, grain boundary mobility and temperature⁷². The film thickness is also found to affect growth rates whereby thinner film promotes growth but the final grain size would be generally smaller as the size is limited by overall film thickness for normal grain growth.

2.5.2 Grain growth on CIGS and other Chalcopyrites

A final annealing process is normally carried out after deposition of the CIGS or other chalcopyrites to instill grain growth. It is unclear if the grains follow a normal or abnormal growth. However, a temperature of at least 550°C is needed to obtain sufficient atomic diffusion for significant grain growth in vacuum annealing⁷⁵. The final grain size is also highly dependent on the percentage of Cu inside the film. A higher Cu content tends to

promote grain growth and this could be attributed to the higher diffusivity of Cu atoms. There is a preferred growth of (112) oriented grains at the expense of other orientations energetically. The deposition of Cu₂Se layer was found to have a positive impact on grain growth via sputtering of Cu₄₀In₆₀ target and Cu₅₀Ga₅₀ target, followed by selenization in Se vapor⁷⁶. This observation is due to the introduction of Cu atoms from the Cu₂Se layer, which is highly diffusive, hence promoting grain growth. This further confirms that Cu rich films will facilitate grain growth due to lowering of activation energy⁷⁵.

2.6 Elemental doping on grain growth

2.6.1 Sb doping in chalcopyrite CIGS/CIS

Generally, doping or addition of impurities in metals will decrease grain boundary mobility and increase the activation energy, Q , for grain growth⁷². Hence, impurities would normally inhibit grain growth. It has been experimentally concluded that chlorine and oxygen decreases grain growth rate⁷⁷. This is also true for chalcopyrite as oxygen, carbon and chlorine impurities are to be avoided for high efficiency solar cell⁵⁰. However, the doping of antimony, Sb, in CIGS film has been found to promote grain growth (Figure 2.7) during the annealing stage³¹. The fill factor (FF), short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) increased for the sample with Sb doping (V_{oc} : 0.55→0.57V, J_{sc} : 27.7→30.3mA/cm², FF: 67.6→71.2% and η : 10.3→12.2%). There is no observable change in the optical band gap probably due to the small amount of doping (0-0.5 mol% Sb). Secondary ion mass spectrometry (SIMS) analysis indicated migration and segregation of the Sb to the back interface (Mo-CIGS interface). Analysis suggests that the majority of Sb did not take part in any reaction with bulk CIGS but through an indirect mechanism to increase grain size which is also observed in Sb doped CdSe thin films⁷⁸. The detailed mechanism remains to be investigated.

The grain growth effect is also observed for Sb doped (1.2 mol% Sb) CIGS annealed at much lower temperature of 360°C and 400°C⁷⁹. At lower temperature, grain growth is observed but the average grain size is much lower at approximately 200 nm. In addition, at 400°C, grain growth is significant enough for the grain size to go up to 1.0 µm, yielding efficiency of 10.5%. This efficiency and grain size is comparable to device annealed at 525°C in an earlier report⁵⁰. Hence, there is still room for further enhancement in device performance. With a Ga grading and high temperature treatment of 540°C, record power conversion efficiency of 15.2% for CIGSSe has been successfully achieved²¹. This brings forward a major boost for solution processed CIGS as they had achieved comparable efficiency with commercialized Si solar cells. XRD analysis of Sb doped samples reveals a stronger orientation of [220]/[204] grains at the expense of [112] grains (Figure 2.8)^{31, 79}. This stronger orientation is believed to result in more homogenous optoelectronic properties and a lower density of non-radiative recombination centers in the film⁸⁰. A high density of non-radiative recombination centers is detrimental to photovoltaic device but promoting secondary grain orientation remains a challenge. In addition, most of the solution-based processed CIS/CIGS absorber layer resulted in preferred growth orientation in [112] direction²⁻⁴, possibly due to its lowest energy for thin film growth. With either Sb doping or changing preferred orientation of Mo, the growth orientation of CIGS/CIS could be varied.

Figure 2.7 Cross-sectional SEM of the CIGS film ($\text{Ga} = 0.3$) with (a) no Sb doping, (b) 0.25 mol% Sb doped, and (c) 0.5 mol% Sb doped.⁶

Figure 2.8 Evolution in full width at half maximum and preferential orientation for (112) and (220)/(204) reflections upon Sb addition in CIGS film ($\text{Ga} = 0.3$) (intensity axis is normalized separately for the left and right panels).⁷

There have been other reports on Sb doping in CIGS. Sb doping has also been tried on vacuum based fabrication of CIGS. Sb was introduced on single target sputtering of CIGS by coating a thin layer of Sb_2S_3 layer onto CIGS layer via chemical bath deposition³². The Sb dopant was shown to enhance grain growth (Figure 2.9)³², which is a similar trend observed in other doping studies. However, there is no device or electrical characterization to provide greater insights into possible change in film properties. The deposition of 10-50

⁶ Reprinted (adapted) with permission from Yuan, M.; Mitzi, D. B.; Liu, W.; Kellock, A. J.; Chey, S. J.; Deline, V. R., Optimization of CIGS-Based PV Device through Antimony Doping. Chem. Mater. 2009, 22, 285-287. Copyright 2014 American Chemical Society.

⁷ Reprinted (adapted) with permission from Yuan, M.; Mitzi, D. B.; Liu, W.; Kellock, A. J.; Chey, S. J.; Deline, V. R., Optimization of CIGS-Based PV Device through Antimony Doping. Chem. Mater. 2009, 22, 285-287. Copyright 2014 American Chemical Society.

nm thick Sb layer sandwiched between Mo layer and CIGS absorber layer was shown to improve grain growth and device J-V characteristics³⁴. The CIGS absorber layer was deposited by a 3 stage molecular beam epitaxy system at high temperatures up to 550°C. However, grain enhancement effect was not observed when an alkali barrier of SiO_x layer was deposited on the soda-lime glass substrate. This indicated that the grain enhancement was brought by the presence of both Sb dopants and elemental Na which diffuses from the soda-lime glass substrate. Sb doping in the absence of alkali barrier results in better V_{oc} with optimal doping level of 10 nm of Sb layer while the J_{sc} improves consistently with increased doping. The presence of alkali barrier SiO_x layer resulted in better J_{sc} and FF while V_{oc} remains largely unchanged as doping level increases. Similar segregation behavior of Sb at the back contact was observed but it might be due to slow diffusion of Sb into CIGS as Sb layer was originally deposited at the back contact.

Figure 2.9 Cross-sectional SEM images of Mo/CIGS after annealing at (a) 400°C (b) 450°C and (c) 550°C and Mo/CIGS/Sb₂S₃ after annealing at (d) 400°C, (e) 450°C and (f) 550°C.⁸

⁸ Reprinted (adapted) with permission from Zhang, S.; Wu, L.; Yue, R.; Yan, Z.; Zhan, H.; Xiang, Y., Effects of Sb-doping on the grain growth of Cu(In, Ga)Se₂ thin films fabricated by means of single-target sputtering. Thin Solid Films 2013, 527, 137-140. Copyright 2014, with permission from Elsevier.

The use of CuSbSe_2 as a form of sintering flux for CISE at low temperature was shown⁸¹. The liquid phase facilitates rapid elemental transfer during grain growth process, promoting in grain growth via liquid phase sintering. With a good wettability accompanied by low melting point, CuSbSe_2 has successfully promoted grain growth of CISE at 500°C with improved electrical conductivities from 8 to 15 S/cm as doping level increases from 0 to 1% doping. XPS analysis indicated slight Cu_3SbSe_4 presence in the Sb doped CISE film. However, it remains unclear if Cu_3SbSe_4 is responsible for enhancing grain growth as Cu_3SbSe_4 is supposed to have a lower melting point⁸².

An investigation on the effect of Sb on CIGS formation via Cu-Se intermediate phases yielded interesting results³³. Solvothermal synthesis of Cu-Se nanoparticles in presence of Sb resulted in the formation of Cu_3SbSe_3 , which decomposes at 507.1°C . Further characterization shows that the Cu_3SbSe_3 phase might possibly be a mobile phase below the decomposition temperature. Hence, Cu_3SbSe_3 phase was concluded to be the responsible species for promoting CIGS thin film formation.

2.6.2 Doping effects on other semiconductor

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has a kesterite structure and can be a cheaper alternative to CIGS by replacing In and Ga with more abundant Zn and Sn. Sb doping has been shown to improve grain growth and render a crack free and homogenous CZTS after annealing treatment in Se atmosphere³⁵. Sb is introduced via ligand exchange to remove organic ligands and was found to be removed after annealing at temperatures above 500°C . This was surprising as most of studies on Sb doped CIS/CIGS showed Sb segregation towards the back contact^{31, 34}. The absence of Sb was verified by composition analysis of the nanoparticles film before and after annealing with EDX, ICP and XPS. It was believed that Sb forms low melting point compounds which promotes diffusion controlled crystallization.

The effect of doping on semiconductor was also conducted on other semiconductors, such as silicon. Doping of Si with P is common but there was significant grain growth observed when Si is heavily doped with P³⁰. Doping level in excess of $4 \times 10^{20} \text{ cm}^{-3}$ is found to enhance grain growth. The driving force of the primary recrystallization is found to be interface energy with activation energies of primary and secondary grain growth at 2.4 and 1.0 eV. Another separate study on p-type doping and n-type doping of Si shows negligible effect for p-type dopant (Boron, B)²⁹. The study shows similar significant grain growth for P doped Si but little grain growth enhancement when Arsenic, As, is introduced instead. Analysis of As doped samples shows clusters formation which is believed to prevent GB migration. The enhancement effect is attributed to the increase in vacancy concentration. The significant enhancement from heavily P-doped Si is attributed to the change in GB diffusion activation energy during segregation of P atoms in Si, which result in the huge change in grain growth activation energy.

Chapter 3

3. Experimental Details

3.1 Wurtzite and Chalcopyrite CuInS₂ nanoparticles

3.1.1 Materials

Copper (II) Chloride Dihydrate (CuCl₂·2H₂O), indium (III) chloride tetrahydrate (InCl₃·4H₂O, 97%), thiourea (SC(NH₂)₂) and ethylenediamine (NH₂CH₂CH₂NH₂) were purchased from Sigma Aldrich. They were used as received, without any further purification.

3.1.2 Synthesis of CuInS₂ Nanoparticles

A solvothermal synthesis method was employed by dissolving CuCl₂·2H₂O (1.1 mmol), InCl₃·4H₂O (1 mmol) with thiourea (5 mmol) in ethylenediamine (4 ml) to form a brownish complex in a Teflon-lined hydrothermal bomb. The resultant complex was diluted with additional 4ml ethanol. Propionic acid (0.25 ml) was added into the complex to make the pH acidic and form a deep blue complex. The hydrothermal bomb was heated to 150°C in an oven (Mettler Paraffin oven UNE PA) for 12 h. After heat treatment, the solvothermal bomb was cooled to room temperature and the resultant nanoparticles were extracted to a centrifugal tube together with the solvent. The nanoparticles were obtained by centrifuging the nanoparticles solution with Kubota 4000 at 6000 rpm for 5 min. Finally, the nanoparticles were washed with ethanol for at least 3 times to remove the complex.

The same experimental procedure was repeated at different heating temperature (120°C and 180°C) and heating time (18 h and 24 h), to study the effect of temperature and time on the

wz-CIS formation.

3.1.3 Characterization

Nanoparticles synthesized at 150°C for 12 h in the presence of acid were dispersed in ethanol and drop casted on carbon tape to observe under field emission scanning electron microscope (FESEM), JEOL JSM-7600F, with an energy dispersive X-ray (EDX) spectrometer attachment. The same batch of samples was dispersed in ethanol before dropping on lacey carbon coated nickel transmission electron microscope (TEM) grid for TEM analysis using JEOL JEM-2100F at 200 keV. The crystal structure of the drop cast film was characterized by XRD, recorded by Bruker D8 Advance Diffractometer. The samples were prepared by dispersing the nanoparticles in ethanol before deposited on a microscopic glass slide via drop casting and left to dry in air. Chalcopyrite CuInS₂ and wz-CIS nanoparticles were drop cast on quartz glass slide and used for UV-Vis measurement using Shimadzu UV-3600 Spectrophotometer. Similarly, both types of nanoparticles were drop cast on normal glass slide for Raman measurements at room temperature using a micro-Raman spectrometer (Horiba-JY T64000) in the backscattering configuration excited with a solid state laser of 785 nm at an output power of 100 μ W, measured with a hand-held power meter at the sample surface. The as synthesized wz-CIS nanoparticles were deposited via drop cast technique on microscopic glass to form a film with contacts enhanced with silver paste for Hall effect measurement via Accent HL5500 Hall System.

3.2 Spray pyrolysis of CuInS₂ from precursor solution

3.2.1 Materials

Copper (II) Chloride Dihydrate (CuCl₂·2H₂O, 99.99%), Indium (III) Chloride (anhydrous, InCl₃, 99.999%) and thiourea (SC(NH₂)₂) were purchased from Sigma Aldrich.

3.2.2 Spray Pyrolysis of CuInS₂

Precursor solutions were prepared by extracting required volume from their individual stock solutions (0.1M CuCl₂, 0.1M InCl₃ and 1.0M thiourea) to achieve the required Cu/In ratio.

In a 2 solution spray, the first solution was Cu-rich and the second solution was Cu-poor.

The Cu rich layer helps in the formation of Cu_xS intermediate phase which is able to assist grain growth during selenization. The purpose of the Cu-poor precursor solution was targeted to lower final average Cu/In ratio of as deposited CIS film to be in the range of 0.75-0.9. Spray pyrolysis of single precursor solution with a Cu/In ratio similar to the average of the two precursor solutions yield similar result. Excess sulfur was added to the precursor solution to prevent the formation of a white precipitate, believed to be Cu-thiourea complex. The dispersion containing the white precipitates is viscous and difficult to spray.

N₂ was selected as the carrier gas to deposit precursor solution on heated substrate (Figure 3.1). A low initial substrate temperature of 120°C was chosen to cover the substrate surface with an amorphous precursor layer to prevent the oxidation of Molybdenum. The temperature was ramped up concurrently as the spray process is ongoing (Cu-rich precursor solution followed by Cu-poor precursor solution or a Single precursor solution ratio) with the final temperature set at 300-350°C. The spraying rate can lowered for better film thickness uniformity. Once the spray deposition was completed, the substrates were left to cool down naturally in ambient condition. Similar spray pyrolysis process was also conducted on Mo substrate with the substrate being preheated to 300-350°C prior to the start

of spray pyrolysis of precursor solutions. Thicker films can also be deposited with more precursor solutions prepared until the required thickness is met. Normally, deposited thickness was in range of 600-1100 nm.

3.2.3 Characterization

The as deposited CIS films are characterized by FESEM (JEOL JSM-7600F) and XRD (Bruker D8 Advance). Cross-sectional images are obtained by cleaving the sample and observe under FESEM. Stoichiometry was characterized by EDS detector attached to the FESEM. The accelerating voltage used was 20 keV. Structure, crystallinity and grain orientation are studied with XRD. Raman spectral was collected on Renishaw inVia Raman system with 532 nm excitation wavelength at an output power reduced to 1.0mW.

Figure 3.1 Schematic diagram of spray pyrolysis process.

3.3 Binary In_2S_3 and Cu_9S_5 nanoparticles and Nanoparticle Precursor Spray Pyrolysis

3.3.1 Materials

Copper (II) Chloride Hydrate ($\text{CuCl}_2 \cdot n\text{H}_2\text{O}$, $n \approx 2$, 99.999%) and Indium (III) Chloride (anhydrous, InCl_3 , 99.99%) were purchased from Alfa Aesar. Sodium Sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, $\geq 98.0\%$) was purchased from Sigma Aldrich.

3.3.2 Nanoparticle synthesis

Cu_9S_5 nanoparticles were synthesized by mixing Na_2S and CuCl_2 in the molar ratio of 2:1 in deionised water at room temperature. Similarly, In_2S_3 nanoparticles were synthesized by mixing Na_2S and InCl_3 in the ratio of 5:2 in deionised water at room temperature. The resultant mixture was centrifuged and washed with deionised water before drying in vacuum.

3.3.3 Nanoparticle precursor spray pyrolysis

Nanoparticles are deposited on Mo substrate by spray pyrolysis similar to the precursor solution spray pyrolysis (section 3.2.2). The nanoparticles were dispersed in precursor water/ethanol and sonicated for 10min before spray pyrolysis. After the deposition, precursor solution was sprayed above the nanoparticle layer to fill the pores and adjust the overall Cu/In stoichiometry to the desired ratio of 0.75-0.85 (Figure 3.2)⁸³. Prior to the final precursor solution deposition, a rough stoichiometric check on the film was conducted by EDS to determine the Cu/In ratio to be sprayed.

Figure 3.2 Schematic diagram to illustrate the two precursor film design: (a) Precursor solution approach and (b) Mixed nanoparticles/precursor solution approach containing CuS nanoparticle and In_2S_3 nanoparticles⁹.

3.4 Selenization and Device Fabrication

3.4.1 Materials

Selenium pellets (Se, 99.99%), Cadmium Acetate Hydrate ($(\text{CH}_3\text{CO}_2)_2\text{Cd} \cdot x\text{H}_2\text{O}$, $\geq 99.99\%$), Ammonium Hydroxide solution (NH_4OH , 28-30% NH_3 basis), Ammonium Acetate ($\text{CH}_3\text{CO}_2\text{NH}_4$, $\geq 99.99\%$) and thiourea ($\text{SC}(\text{NH}_2)_2$) were purchased from Sigma Aldrich.

3.4.2 Selenization

The sprayed CIS films (nanoparticle incorporated, Sb doped etc.) were annealed in Se vapor, selenization, at different temperature ranging from 400°C to 500°C to form CISSe film. Selenization was conducted using an in-house quartz tube furnace as shown in Figure 3.3. The inner quartz tube was used to hold the samples with a small outlet to allow gas flow. The quartz tube was vacuumed and refilled with Ar at least 3 times to ensure no oxygen remains in the tube before heating process. Se vapor was generated from the evaporation of

⁹ Reprinted (adapted) with permission from Cai, Y.; Ho, J. C. W.; Batabyal, S. K.; Liu, W.; Sun, Y.; Mhaisalkar, S. G.; Wong, L. H., Nanoparticle-Induced Grain Growth of Carbon-Free Solution-Processed $\text{CuIn}(\text{S},\text{Se})_2$ Solar Cell with 6% Efficiency. ACS Appl. Mater. Interfaces 2013, 5, 1533-1537. Copyright 2014 American Chemical Society.

Se pellets with different total mass (10-30 mg) to control the flux. Selenization was carried out for a range of duration from 10 min to 1 h. After selenization, the tube was left to cool naturally. Before removal of sample, the selenization tube was vacuumed and refilled with Ar at least once to remove any residual Se vapor. Samples are removed when the tube had cooled to below 100°C.

3.4.3 Device Fabrication

After selenization, a thin CdS buffer layer (~50 nm) was deposited immediately by chemical bath deposition. The chemical bath was prepared by dissolving cadmium acetate, ammonium acetate and thiourea in DI water. The temperature of bath was maintained at 80-85°C and the pH of the bath solution was adjusted by ammonium hydroxide to approximately 9.0-9.1. After CdS deposition, i-ZnO (80-100 nm) and Al:ZnO (TCO layer, 350 nm) were sputtered on top of CdS followed by thermal evaporation of Al/Ni electrode on top of the TCO layer. The TCO layer used was aluminum doped zinc oxide and deposited via DC sputtering with an applied power of 200 W. After thermal evaporation of Al/Ni electrode, the cells were isolated by mechanical scribing with a cell area of 0.10-0.12 cm².

3.4.4 Characterization

Cross-section images of the cleaved samples were obtained by FESEM (JEOL JSM-7600F) and stoichiometry of the film by the EDS. The crystallinity and phase of the samples were characterized by X-Ray Diffraction XRD. The current density–voltage (J-V) characteristics of the CuIn(S,Se)₂ devices were measured in ambient conditions under AM 1.5G illumination (100 mW/cm²) using a Keithley SMU 2400 sourcemeter. The light intensity was calibrated by using an NREL calibrated silicon photodiode.

Figure 3.3 Schematic diagram on the selenization setup.

3.5 Other Characterizations

Photoluminescence (PL) study: Micro-PL measurements were conducted using continuous wave diode laser at excitation wavelength of 532nm. With a 20X objective lens (Nikon CFI60 Lu Plan Epi ELWD), the laser beam was focused to a spot size $< 10 \mu\text{m}$ in diameter, so that regions can be selectively excited. For temperature-dependent PL, the samples were placed in a cryostat with temperature ranging from 6-300K. All PL signals were collected by an InGaAs array detector (Princeton Instruments OMA V) attached to a monochromator (Princeton Instruments Acton Series SP2300) equipped with a 150g/mm grating blazed at 500 nm (Princeton Instrument). Liquid nitrogen is used to cool the stage whereby the sample is located to 78K.

Electron probe micro-analysis (EPMA) measurement: Wave dispersive spectroscopy (WDS) is conducted using the JXA-8530F field emission gun electron probe X-ray micro-analyzer (FEG-EPMA). Multiple point analyses were carried out with a $5 \mu\text{m}$ defocused beam at a beam current of 20 nA and an accelerating voltage from 8-15 kV, depending on film thickness. Calibration is done with natural and man-made standards used for EPMA. Peak and background counting times were adjusted to 40 seconds for all elements.

Conducting atomic force microscopy (C-AFM) measurements: Conductive AFM is performed with an ORCA holder on Asylum Instrument (MFP-3D with ARC2 controller). The current mapping is conducted on random positions of the sample with a scan area of $1\mu\text{m}$ by $1\mu\text{m}$. The positive or negative voltage bias was varied 150mV to 500mV. Imaging analysis was done using the software ARgyle Light.

Transient Pump-Probe Spectroscopy: The femtosecond laser pulses (100 fs, 1 kHz) were produced by a mode-locked Ti: Sapphire laser seeded Ti: Sapphire regenerative amplifier pumped OPA (Spectra physics, Mai Tai-Spitfire Ace-TOPAS Prime). Direct and SHG 800 nm (400 nm) wavelengths were used as pumps; and beam from OPA used as probe. Differential probe signals were collected using photodiode and lock-in amplifier, with respect to pump delay. In this experiment, the pump and probe pulses were orthogonally polarized with the incident angle between both the beams less than three degrees. The ratio of energy between the pump and the probe pulses were less than 5 %.

Transient photocurrent measurements: Transient photocurrent studies were conducted using mode-locked Ti: Sapphire laser seeded Ti: Sapphire regenerative amplifier pumped OPA (Spectra physics, Mai Tai-Spitfire Ace-TOPAS Prime). laser pulses were tuned from 300 nm- 1200nm wavelengths (100-fs duration, and 1000-Hz repetition rate), which were exposed onto the photoconductor devices with a circular spot diameter of ~ 5 mm. Optical neutral density filters were employed to control the laser pulse energy. A laser power meter was used to measure the average power of the laser pulses. The laser pulse temporal profiles and transient photocurrents were monitored with the 50-ohm-terminated, 400-MHz–bandwidth digital oscilloscope.

Secondary Ion Mass Spectroscopy (SIMS) measurements: The concentration depth profile of individual elements including Sb dopants in the compound CISSe were studied by SIMS using a Cs^+ as the primary ion with sputter energy of 3keV. Sputtering current was fixed at 14nA to ensure a constant sputtering rate. The selected sputter area is approximately 200 μm by 200 μm . Depth profile measurements are conducted at random positions of sample to ensure consistency in the concentration depth profile obtained. The measurements were taken till the concentration of Mo had saturated indicating that the analysis had hit the bulk of the Mo substrate.

Hall Effect measurements on Sb doped CISSe thin film: Carrier density, mobility and other film properties were obtained by Hall Effect measurement with H-50 Hall measurement controller from MMR's Variable Temperature Hall System (VTHS). Samples are kept in sample chamber connected to vacuum pump. Multiple measurements are done at room temperature with different magnetic field strength ranging from 2000 to 10000 Gauss. Au contacts are thermally evaporation onto samples to improve on contact.

Chapter 4

4. Synthesis and Growth of $\text{CuIn}(\text{S,Se})_2$

4.1 Introduction

The high cost and material wastage incurred in conventional vacuum approach employed in CIGS/CISSe processing provide a great motivation for research to focus on cheaper solution-based alternatives. The common solution based techniques, such as nanoparticle or nano-ink approaches, have produced acceptable device performances^{4, 13, 84-88}. However, solution-based approaches usually have higher residual impurities (e.g. C, O and Cl) which affect the electrical properties^{46, 89}. Furthermore, the use of organic solvents would result in thick carbon residue layers⁹⁰ or carbon impurities within the absorber film⁹¹⁻⁹³. These carbon impurities were traced to the solvent or other binder materials. Carbon containing devices^{90-91, 93} typically produces inferior IV-characteristics (lower open-circuit voltage (V_{oc}) and fill factor (FF)) with a higher series resistance (R_s) relative to the carbon-free hydrazine approach^{2, 21, 50}. However, the use of highly toxic and volatile hydrazine as a solvent should be avoided as it is not environmentally friendly. Another approach is to synthesize CIGS chalcopyrite nanoparticles before processing it to form the absorber film^{5, 13, 84}. The use of pure CIGS nanoparticles or its nanocrystals inks for film formation provides better uniformity in stoichiometry of the resultant film and lower impurities, with device efficiency as high as 12%⁸⁸. Nanoparticles are usually coated with ligands during synthesis. However, they must be removed as these ligands form highly resistive layer. These ligands can be removed by additional Ar annealing and the resultant film could be selenized to produce decent power conversion efficiency (PCE) of 7.1%⁶. However, ligandless fabrication of

nanoparticles would be preferred as an additional processing step (ligand removal) can be avoided from the overall fabrication procedures. CuInS_2 (CIS) has two main phases namely wurtzite and chalcopyrite phase. In this chapter, the synthesis of both phases will be explored.

4.2 Synthesis and Characterization of Metastable Wurtzite CuInS_2

Numerous synthesis methods of Copper Indium Sulfide / Copper Indium Selenide ($\text{CuInS}_2/\text{CuInSe}_2$) nanoparticles⁹⁴⁻⁹⁷ have focused on the more thermodynamically stable chalcopyrite phase (i.e. roquesite) with lower emphasis on the hexagonal closed-packed wurtzite phase^{16, 94} which is metastable at low temperature. Wurtzite- CuInS_2 (wz-CIS) is only stable between 1045°C and 1090°C in the bulk phase, with a random sharing of common lattice sites for the Cu and In ions¹⁶. Among the different synthesis routes for wz-CIS^{12, 14-17, 95, 98-99}, a large proportion include capping ligands for better shape and size control. However, the presence of capping ligands may potentially limit the electrical properties of the material. Furthermore, the removal of ligands can introduce porosity in the film. A direct and simple solvothermal synthesis method was performed at 150°C. With ethylenediamine as the solvent, the formation of metastable wz-CIS or its more stable chalcopyrite phase can be successfully tuned by varying the amount of sulfur precursor used.

Although there have been few reports on the synthesis of wz-CIS, details on the electrical and optical properties still remain unclear. Synthesis and characterization of wz-CIS aims to have a better understanding on the electrical and optical properties to explore the feasibility of wz-CIS for device application. As the wurtzite phase is metastable, the thermal stability of the material has to be studied before using it for device fabrication. This chapter aims to explore an environmentally friendly and facile synthesis of CIS absorber layer for further studies on film properties and additional doping studies. The use of a dual amine solvent

successfully lowered the synthesis temperature of wz-CIS. Electrical properties of wz-CIS are comparable to the widely studied chalcopyrite phase and wz-CIS was found to convert to chalcopyrite phase when heated at elevated temperature.

4.2.1 Materials Characterization

4.2.1.1 Structural Characterization

Simulated powder diffraction patterns of both wurtzite and chalcopyrite CIS are shown respectively (Figure 4.1a-b). The more stable chalcopyrite phase has a tetragonal crystal system while the metastable wurtzite phase belongs to a hexagonal closed packed crystal system. As-synthesized wz-CIS were drop casted on a glass substrate for XRD measurements under room temperature in ambient conditions. The XRD pattern indicated that the metastable wz-CIS (space group of $P6_3mc$) was formed (Figure 4.1c). Numerous wurtzite and chalcopyrite peak positions overlap which makes the determination of yield of respective phases difficult. Quantification on the yield of wurtzite and its chalcopyrite phase were done by Rietveld refinement¹⁵⁻¹⁶, which proves wurtzite as the major phase (88%) with the remaining being chalcopyrite phase.

Figure 4.1 Simulated powder XRD peaks of (a) wz-CIS with unit cell model and parameters (inset), (b) Chalcopyrite CuInS_2 with unit cell model and parameters (inset) and (c) Rietveld refinement of XRD patterns of sample synthesized at 150°C for 12 h.

Capping ligands were commonly utilised in earlier reported synthesis of wz-CIS to achieve a better morphology and size control with oleylamine as the solvent^{3-4, 7, 9}. Our synthesis methodology focused on avoiding the use of surfactants and explored ethylenediamine as the main solvent due to its dual -NH_2 functional groups. As there is a high chance that the kinetic influence on the formation of metastable wz-CIS over its chalcopyrite phase could be attributed to the amine coordination to the metal cations as suggested by Norako et al.⁷, the use of dual amine group may be more effective in promoting the formation of wz-CIS at a lower temperature. The presence of a dual amine functional group would affect the reaction kinetics and possibly favour the formation of metastable wurtzite phase at lower temperatures. The low boiling point (118°C) of ethylenediamine could then be used for low temperature solvothermal reaction. Indeed, ethylenediamine has lower down the minimum temperature on the synthesis of wz-CIS to 150°C .

Reaction temperature and time on wurtzite growth

Temperature and time effects on wurtzite phase formation were analysed. The lowest reaction temperature limited by the boiling point of ethylenediamine was 120°C . Synthesis of wz-CIS was performed and characterized by XRD. In addition to the characteristic CuInS_2 peaks observed in the sample prepared at 150°C , other noticeable impurities peaks which cannot be identified successfully were also observed. Intermediate states of the complex formed with the solvent could possibly have contributed to the unidentified peaks. The complex peaks were not observed when the reaction was performed in presence of propionic acid, which resulted characteristic peaks of wurtzite and chalcopyrite phase CuInS_2 . The use of propionic acid is believed to promote the formation of a more stable complex between Cu and ethylenediamine which aids in the solution of Cu salt in ethylenediamine solvent. The acid assisted stabilization of the complex formed between the

solvent and precursors was also observed by Bao et al.⁵ although a different acid, oleic acid (OA), was introduced to decelerate the growth of CIS. The complex colour after reaction changes with the addition of acid. Complexation (or catalytic action) of acid with the precursors resulted in higher proportion of wurtzite phase being formed at temperatures $<180^{\circ}\text{C}$ over the 12 h reaction. However, the absence of acid would result in greater wurtzite concentration as the reaction duration was prolonged. This showed that the time predominates over the presence of acid for long reaction times. Longer reaction duration will generally favour the formation of the thermodynamically stable chalcopyrite phase as compared to wurtzite phase. The wurtzite nanoflakes could be formed with the reaction duration reduced to 3 h (Figure 4.2).

Figure 4.2 XRD pattern of CIS nanoparticles synthesized with different durations of a) 12 h, b) 6 h and c) 3 h.

Sulfur concentration on wurtzite growth

The influence of sulfur concentration on wurtzite phase formation was studied by varying the sulfur over indium ratio. A decrease in wurtzite formation was observed when the ratio of indium to sulfur was reduced from 1:5 to 1:2 (Figure 4.3). Some of the peaks that are characteristic of wurtzite phase would not be detected for the chalcopyrite rich samples as their signals are too weak and usually overshadowed by the background counts. Reaction temperature is kept at 150°C. This proves that sulfur concentration plays a key role in the formation of wurtzite, as observed previously by Bao et al.⁵ Excess sulfur promotes the formation of CuS or Cu₂S intermediate phases at low temperatures which further react with In³⁺ to form wurtzite CIS at higher temperatures. Kruszynska et al. has demonstrated formation of biphasic CuS-CuInS₂ as intermediate phases before transformation to pure wz-CIS⁴. Hence, the keys factors in wurtzite formation are amine groups and an excess sulfur precursor concentration in the reaction.

Figure 4.3 Rietveld Refinement of sample synthesized at different sulfur ratio a) In : S = 1 : 2 and b) In : S = 1 : 5.

4.2.1.2 Morphological Studies

As-synthesized nanoparticles were drop casted on carbon tape for morphological characterization under FESEM and TEM. Spheres (diameter $\approx 1\text{-}1.5\ \mu\text{m}$) formed by the agglomeration of smaller individual nanoflakes could be observed from FESEM (Figure 4.4a inset). From TEM images, the size of individual nano-flakes size range from 20 nm to 80 nm with some up to hundreds of nanometers (Figure 4.4a). There was no requirement for the nanoparticles to have a narrow size distribution as they would be used for thin film deposition involving post thermal annealing to improve the density and promote grain growth in the wz-CIS absorber film.

Figure 4.4 TEM images of wz-CIS nanoflakes stacking randomly (inset shows the FESEM image) (a), selected area diffraction (SAED) pattern on a single wurtzite nanoflake (b), and chalcopyrite nanoflakes (c).

High resolution TEM (HRTEM) image of the as synthesized wurtzite nanoflakes was shown in Figure 4.4b with selected area electron diffraction (SAED) pattern taken along zone axis of [001] as the inset. The diffraction pattern matches that of wz-CIS. The wz-CIS share the same orientation as the zone axis but with a slight rotation, indicated by smeared (elliptical) spots. Majority of past reports were on polycrystalline wz-CIS⁷ or wz-CuInSe₂^{4,6} whereas

nanocrystalline wz-CIS synthesis, preferentially oriented along [001], were not common. The pronounced orientation agrees well with the analysis of the XRD pattern by Rietveld refinement of the synthesized nanocrystals. The HRTEM image of the tetragonal chalcopyrite phase is shown in Figure 4.4c with the fast fourier transform (FFT) pattern (inset) aligned along [111] zone axis. In comparison with wurtzite, the chalcopyrite has more random crystallite orientation.

4.2.1.3 Stoichiometry of wz-CIS

Random positions of the sample were selected for EDX analysis at accelerating voltage of 20 kV. Analysis results confirmed the purity of the nanoflakes, due to absence of elemental impurities based on the detection limits of EDX detector. A vast majority of the nanoflakes are copper rich ($\text{Cu}_{1.1}\text{InS}_2$) which matches the nominal compositional ratio of the precursors at Cu:In:S = 1.1 : 1 : 5. The error range of EDX measurement is within 5%, calibrated with standard sample. Other techniques such as Rutherford Back Scattering Spectroscopy (RBS), X-Ray Fluorescence Spectroscopy (XRF) or Inductively Coupled Mass Spectrometry (ICPMS) may be used for more accurate determination of stoichiometry.

4.2.1.4 Optical absorption and bandgap

The wurtzite nanoflakes were dispersed in ethanol to study the optical absorption behavior by UV-Vis spectroscopy. The nanoflakes start to absorb at approximately 1400 nm and peak at 400 nm whereas the absorption curve of chalcopyrite nanoflakes is more gradual from 1500 nm to 300 nm (Fig. 4.5 inset). With a strong absorption along the visible light wavelength, wurtzite phase CIS could be a potential candidate for photovoltaic applications. Past reports on wurtzite nanoparticles indicated the absorption would begin approximately at 1000 nm¹⁸ or at an even lower wavelength of 850 nm¹³, which is far below our reported

values. A possible explanation would be due to the presence or variation in specific capping ligands that were introduced during synthesis which influenced the optical absorption properties.

Figure 4.5 UV-Vis absorption spectra and plot of $(\alpha h\nu)^2$ against energy, $h\nu$, of wurtzite CIS (blue line) and chalcopyrite CIS (red line).

As CIS is a direct bandgap semiconductor, the optical absorption, α , obeys the following equation around the bandgap.

$$\alpha h\nu \propto \frac{\sqrt{(h\nu - E_g)}}{h\nu} \quad \dots\dots\dots (2)$$

Where: α is the absorption coefficient

ν is the light frequency

h is the Planck's constant

E_g is the band gap energy

By plotting $(\alpha h\nu)^2$ against $(h\nu)$ and extrapolating the straight line to $(\alpha h\nu)^2 = 0$ axis would provide an estimate on the bandgap, E_g , of CIS. The band gap of both phases of CIS determined from the extrapolation of the curves (Figure 4.5) was found to be 1.59 eV. This is slightly above the widely reported bulk chalcopyrite CuInS_2 of 1.50-1.55 eV¹⁹. The higher energy of the band gap may be attributed to quantum confinement effect of nanoflakes or errors in extrapolation. Quantum confinement is highly possible as the nanoflakes are formed by aggregate of much smaller nanoparticles that are less than 20 nm in size (Figure 4.4a). The estimated extrapolation error is 15% for chalcopyrite rich plot and 5% for wurtzite rich plot. There is a higher extrapolation error for chalcopyrite rich sample as absorption is relatively weaker.

4.2.1.5 Phase Purity analysis by Raman Spectroscopy

The chalcopyrite and wurtzite CIS were characterized by Raman spectroscopy as shown in Figure 4.6. The excitation laser energy (1.58 eV) is nearly in resonant with the materials with a band gap of ~1.59 eV. Raman signals for both structures were strong and sharp with reasonable intensity indicating that the nanoflakes are of good crystallinity. The Raman spectra were fitted with multi-Lorentzians function to obtain individual peak position, while the photoluminescence (PL) lineshape was chosen to be a Gaussian function. The main A_1 mode at 290 cm^{-1} that is usually dominant in chalcopyrite rich CIS, which coincides with many other reports²⁰⁻²², was prominent but has a lower intensity than the $E(L)/B_2(L)$ modes at 345 cm^{-1} . Other peaks detected could be traced to $E(L)/B_2(L)$ modes at 259 cm^{-1} , Cu-Au ordered phase at 303 cm^{-1} and photoluminescence (PL) at 324 cm^{-1} . PL peak arises from the

interaction of laser and sample. The Cu-Au ordered phase is a metastable phase which was mainly observed in Cu poor films²³ but is present in our overall Cu rich CIS nanoflakes possibly due to stoichiometric variations of Cu-rich and Cu-poor phases within the sample.

According to the Raman selection rule, $E(L)$ and $B_2(L)$ modes are forbidden modes but their appearances in our experimental measurements indicate a breakdown of the Raman selection rule²⁴ which was previously reported²⁵, due to resonant Raman effect. The Raman spectra of wurtzite phase CIS was similar to chalcopyrite phase but with a slight shift of 1-2 cm^{-1} for all the individual peak positions. There were no Raman vibration peaks corresponding to known binary phases (i.e., CuS, In_2S_3 , etc) which confirmed the purity of the nanoflakes. The slight shift in peak positions could be attributed to stoichiometric variation in Cu/In and/or changes in the chemical environment of the atoms of different crystal structures.

Figure 4.6 Raman spectra for chalcopyrite CIS (red, top) and wz-CIS (blue, bottom).

4.2.1.6 Electrical properties of wz-CIS

The widely understood chalcopyrite CuInS_2 can be either p-type or n-type depending on the amount of sulfur and the vapour pressure during the annealing stage¹⁹. However, limited electrical properties study of wz-CIS synthesized under low temperature ($<250^\circ\text{C}$) have been conducted. In terms of application, measurement of annealed samples would be more beneficial but the percentage of wurtzite/chalcopyrite phase changes upon annealing even at low temperature (300°). A high temperature of $>550^\circ\text{C}$ is needed for grain growth and film densification. Attempt to improve on the thermal stability of wurtzite CIS was not successful.

Table 4-1 Electrical parameters of wurtzite CIS from Hall Effect measurements and chalcopyrite from literature.

Sample	Sheet resistivity ($\Omega/\square$)	Mobility (cm^2/Vs)	Sheet Carrier conc. ($/\text{cm}^3$)
1	2.00E+05	0.454	6.89E+13
2	1.48E+05	0.448	9.39E+13
Average	1.74E+05	0.451	8.14E+13
Literature	2.0E+05	0.8	1.6 E+18
chalcopyrite²⁶			

Hall Effect measurements on wurtzite nanoflakes confirm it as a p-type semiconductor. The measured values are tabulated in Table 4-1. Measurements were taken at random points of two different samples with the average values for sheet resistivity (ρ) as $\sim 2 \times 10^5 \Omega/\text{sq}$, Hall coefficient $\sim 10 \text{ m}^2/\text{C}$, mobility of $\sim 0.5 \text{ cm}^2/\text{V-s}$ and sheet carrier concentration of $\sim 7 \times 10^{13}/\text{cm}^2$. As there are limited reports on wz-CIS, the measured average values are benchmarked with the widely understood chalcopyrite phase. The measured wurtzite sheet

resistivity is near the typical values of $\sim 2 \times 10^5 \Omega/\text{sq}$ for chalcopyrite CIS. The mobility measured is comparable to $\sim 1 \text{ cm}^2/\text{V-s}$ for polycrystalline CIS²⁶ but lower than single crystalline CIS ($\sim 10 \text{ cm}^2/\text{V-s}$)¹⁹. This is expected as the nanoflakes film were measured directly without any post annealing treatment for grain growth hence higher recombination was experienced along the grain boundaries. Furthermore, the wurtzite CIS film was porous with higher resistivity as the drop casting deposition technique would result in a rougher film surface which would influence electrical measurements.

4.2.2 Thermal stability of wurtzite nanoflakes

The use of nanoparticles for chalcopyrite devices has been demonstrated with acceptable efficiencies³⁻⁴. However, an additional heat treatment stage for densification of grains is required. As wurtzite is a metastable phase, its thermal stability would determine the final phase structure. As the main peak of chalcopyrite phase overlaps with one of the peaks from wurtzite phase at $2\theta = 27.8^\circ$, an increase in chalcopyrite phase will result in higher peak intensity. Heat treatment at 400°C under Ar or Se environment resulted in conversion of wurtzite to the more stable chalcopyrite phase (Fig. 4.7). Hence, the thermal stability of wurtzite nanoflakes is independent on the heat treatment environment. The higher temperature resulted in much greater phase conversion but no total conversion to chalcopyrite phase at 480°C was observed. A shift or appearance of peak shoulder at lower 2θ angle due to an increase in d-spacing caused the replacement of S by the larger Se atom during heat treatment under Se atmosphere. This substitution was more significant at higher temperature of 480°C , due to a larger Se vapour pressure. There was no observable improvement on the crystallinity or the crystallite size of the wz-CIS after heat treatment. Grain growth and densification of nanoparticles is more challenging which requires higher temperature closer to the recrystallization temperature whereby liquid phase exist to

facilitate grain growth via liquid phase sintering. As the nanoparticle approach in device fabrication typically involves heat treatment under S or Se atmosphere above 500°C, the thermal stability of wurtzite nanoflakes has to be improved for its use in photovoltaic applications.

Figure 4.7 XRD pattern of a) pristine sample, b) sample annealed at 400°C for 10min, c) sample selenized at 400°C for 10min and d) sample selenized at 480°C for 10min.

4.3 Spray pyrolysis of CuInS_2 from precursor solution

4.3.1 Gradual heating and spray process to prevent Mo oxidation

High temperature spray pyrolysis on Mo substrate in ambient condition will encounter substrate oxidation which resulted in poor film quality. Spray pyrolysis of CIS/CISE had been done on glass substrates or other conductive substrates which are more stable in

ambient (FTO, ITO etc.). Mo has a low oxidation temperature following equation [3]. Formation of a barrier layer around Mo can effectively isolate Mo from oxygen in ambient environment. A thin layer of MoS₂ film or CIS precursor itself can be a potential candidate as the barrier layer. Sulfurization of CIS films would form a thin MoS₂ film while low temperature deposition of precursor solution will react to form crystalline CIS film at elevated temperature. Chemical equations on formation of MoS₂ or CIS film are shown in equations [4-5] and [6] respectively¹⁰⁰. A reduction of Cu²⁺ ions to Cu⁺ by thiourea was observed when the aqueous precursor solutions are mixed. Thiourea also serves as a sulfur source for the formation of CIS. The reaction product, cyanamide (H₂NCN), would react with water or oxygen during the pyrolysis process and is then subsequently removed as volatile compounds¹⁰¹.

Glancing Angle X-Ray Diffraction (GAXRD) with incidence angle of 1.0° was used to characterize the film at the initial, intermediate and final phase of spray process (Figure 4.8). The initial phase of spray refers to the first 5 min of spray pyrolysis at 120-150°C (Initial phase). XRD pattern reveals Mo (JCPDS card no. 42-1120) as the only crystalline phase observed as the low deposition temperature of 120-150°C is insufficient to initiate reaction between precursor solutions. The precursor layer was compact (<100nm), consisting of precursor materials which covered the substrate surface completely, serving as an effective

barrier layer protecting Mo surface from oxygen in the ambient. Intermediate phase of spray refers to the spray after 10 min at slightly higher temperature of 200-250°C. At this phase, low intensity CIS peak (JCPDS No- 85-1575) was observed. At this intermediate temperature, precursors would react to form polycrystalline CIS film but with a high degree of structural disorder. At the current phase, the CIS film would be much thicker (>100nm) which effectively blocks oxygen from the Mo surface. However, the wide FWHM (full width half maximum) and low intensity peaks indicate poor crystallinity with small crystallite size (Scherrer's equation¹⁰³). The end phase refers to the end of the whole spray process which includes the main part of the spray deposited at 300-350°C. Significant increase in peak intensity indicating better crystallization was observed. In order to learn the importance of substrate heating, spray pyrolysis of precursor solution directly onto the substrate preheated to 300-350°C prior to spraying was conducted and analyzed (purple pattern in Figure 4.8). Both XRD spectrums show a shoulder peak at $2\theta=26.5^\circ$ at the end phase (gradually heated substrate and preheated substrate), indicating presence of $\beta\text{-In}_2\text{S}_3$ phase. This was expected as the overall film is Cu deficient (Cu/In=0.85) and a similar spectrum was observed in spray deposited CIS on glass substrate with Cu/In ratio of 1.0 and 0.8^{10, 89, 104}. Other possible binary compounds that might have existed, such as Cu_xS , was not detected in the CIS film. MoO_2 formation can be successfully prevented by carefully controlled heating and spraying as the MoO_2 peak at $2\theta=36.9^\circ$ (JCPDS card no. 32-0671) was not observed unlike direct CIS deposition on preheated Mo. A higher atomic percentage of oxygen was detected in CIS film deposited on preheated Mo (control sample) (14 ± 1 at%) as compared to the gradually heated Mo substrate (6 ± 1 at%). It should be noted that part of the oxygen originates from the glass substrate.

The cross-section SEM images of the films deposited on preheated Mo (control sample) and gradually heated Mo are shown in Figure 4.9, illustrating a small average grain size of 15 nm. The small grain sizes would be a major drawback for high efficiency devices due to higher probability of recombination along these grain boundaries unless they are well-passivated. Hence, further processing such as selenization or modification to current processing conditions have to be modified to achieve larger grains. Cross-sectional image of control sample shows a thinner film with poorer uniformity. This could be caused by MoO_2 formation which would reduce the wettability of water on the oxidized MoO_2 surface. Furthermore, a larger number of pores were observed (circled in Figure 4.9a) which are formed closer to the CIS/Mo interface. It is possible that the porosity and uniformity issues were due to the large decrease in volume when MoO_2 was reduced to Mo or MoS_2 . Similarly, these issues were not present in the gradual heating and spray process. Hence, gradual heating and spray pyrolysis produce a denser and more uniform film which is ideal for photovoltaic device application.

Spray pyrolysis of aqueous precursor solution is a direct and simple approach which is environmentally friendly as deionized water is the only solvent used. The only main drawback is the small grain size which requires additional grain growth processes.

Figure 4.8 XRD patterns of the sprayed CIS films at different phase of deposition.

Figure 4.9 Cross-sectional SEM images of spray deposited CIS film deposited on (a) preheated Mo and (b) gradually heated Mo.

4.4 Binary In_2S_3 and Cu_9S_5 nanoparticles

The synthesis of binary compounds followed by further processing to form single phase CISSe ternary compound is a viable approach. Both In_2S_3 and Cu_9S_5 nanoparticles could be

synthesized in a facile manner by mixing precursors under room temperature. The resultant nanoparticles were dispersed in solvent and spray deposited to form a film. The use of Cu_9S_5 nanoparticles is hypothesized to promote a localized region with Cu-rich stoichiometry which will assist in grain growth. These Cu-rich regions are expected to react with Se during selenization to form Cu_2Se or CuSe containing some level of liquid phase during selenization temperature to achieve secondary grain growth by liquid phase sintering. This approach aims to mimic the state-of-the-art 3-stage co-evaporation technique for high performance CIGS solar cells³⁷⁻³⁸. However, the nanoparticles film was highly porous without the use of binder. Hence, a hybrid system of nanoparticles and precursor solution has to be explored.

4.4.1 Materials Characterization

The as-synthesized binary nanoparticles were observed under FESEM individually. The SEM images showed that the Cu_9S_5 and In_2S_3 nanoparticles agglomerated together (Figure 4.10 a & b respectively) possibly due to absence of capping ligands. The particle size is very fine which coincides with the broad peak base from the XRD pattern (Figure 4.10c). Due to their small size, these nanoparticles can disperse in water or organic solvent easily before being spray deposited onto the Mo substrate. The film stoichiometry was controlled within Cu/In ratio of 0.75-0.85 by weighing individual components before mixing and dispersing the two binary nanoparticles evenly in deionised water. However, it is still a challenge to achieve a stoichiometry with a narrow range between different batches of prepared films. The cross-sectional SEM image of the spray deposited film from nanoparticle precursor shows a highly porous and rough film (Fig. 4.10d). A highly porous film requires an additional densification process or a much higher temperature for grain growth. The use of organic solvents, additives or binding agents along with the nanoparticles could promote a

denser and more uniform film but this tends to leave a carbon impurity layer in the chalcopyrite films after selenization^{7, 56, 87}. Hence, there is a need to explore hybrid systems to achieve a better film quality.

Figure 4.10 SEM images on as synthesized a) Cu₉S₅ nanoparticles agglomerate, b) In₂S₃ nanoparticles agglomerates, c) XRD pattern of Cu₉S₅ (red) and In₂S₃ (blue) nanoparticles and d) cross-sectional SEM image of a spray deposited nanoparticle film.

4.5 Binary In₂S₃ and Cu₉S₅ nanoparticles with CIS precursor solution

As spray deposition of binary In₂S₃ and Cu₉S₅ nanoparticles encountered porosity and uniformity issues, the addition of precursor solution consisting CuCl₂, InCl₃ and thiourea dissolved in deionized water was introduced to fill the pores forming fine CIS grains. The Mo substrate temperature was increased for the reaction of the precursor materials forming

CIS. The precursor solution will react to form CIS film simultaneously while the binary nanoparticles were deposited and eventually embedded in the precursor film. The advantage of using the precursor solution was the ability to seep through pores easily to form a final dense layer retaining the advantage of using binary nanoparticles. The final Cu/In film stoichiometry could be kept within the target ratio of 0.75-0.85 as additional precursor solutions could be spray pyrolysed on top of the existing CIS film to adjust the Cu/In ratio. The resultant film was selenized at high temperature resulting in significant grain growth forming CuIn(S,Se)_2 (CISSe).

4.5.1 Materials Characterization

The selenized film was characterized by X-ray diffraction experiments. The film formed with the introduction of binary nanoparticles along with the precursor will be noted as np-precursor film. The XRD patterns of both films (np-precursor and precursor only) are shown in Figure 9a. The diffraction peaks of both films without selenization match well with chalcopyrite CuInS_2 (JCPDS No- 85-1575). There was no trace of metal oxide and binary In_2S_3 and Cu_9S_5 nanoparticles. Although the binary nanoparticles were not detected by XRD, it is possible that only part of the binary nanoparticles has reacted during the spray process to form CIS with a higher crystallinity. The In_2S_3 and Cu_9S_5 nanoparticles have to be in close proximity for the reaction to take place as the spray temperature of 300-350°C was too low for diffusion of Cu from the Cu rich regions to the In rich region. The highly crystalline CIS formed from the reaction of binary In_2S_3 and Cu_9S_5 nanoparticles could possibly overwhelm the peaks of the individual nanoparticles.

4.5.2 Selenization of In_2S_3 and Cu_9S_5 nanoparticles with CIS precursor solution for grain growth

As the spray deposition temperature of 300-350°C was low to induce complete crystallization or reaction of the binary nanoparticles, high temperature selenization above 450°C is necessary. After high temperature selenization at 480-500°C for 10 minutes, the diffraction peaks of both films match well with CISSe (JCPDS no. 36-1311) (Figure 4.11b) with a left shift in peak positions, observed due to the substitution of S with larger Se atoms, which resulted in increase in the lattice parameters. Rietveld refinement on the diffraction peaks was performed to estimate the S/S+Se ratio of the selenized CISSe films and found to be approximately 0.29-0.41 (Table 4-2). The higher intensity and narrow peak base of (112) peak of both films indicate improved crystallinity and larger crystallite size (Scherrer equation¹⁰³) after selenization (Figure 4.11b). There is a preferred grain growth along the (112) plane at the expense of (204)/(220) oriented grains which was observed by Contreras et al.⁸⁰.

Figure 4.11 XRD pattern of the sprayed film from the precursor solution and the nanoparticle incorporated precursor solution a) before selenization and b) after selenization.

Table 4-2 Rietveld refinement results of nanoparticle incorporated and pure CuInS₂ films before and after selenization.

Sample	Lattice Parameter		Atomic %	
	a (Å)	c (Å)	S (%)	Se (%)
Precursor only	5.518	11.254	100	0
Np-precursor	5.495	11.103	100	0
Np-precursor –after selenization	5.695	11.501	29	71
Precursor only – after selenization	5.664	11.448	41	59

The morphology and grain growth of both films were characterized by FESEM. The cross-sectional images of both films from precursor and np-precursor are shown in Figure 4.12. The np-precursor film is uniform and dense due to the additional precursor solution showing a similar uniformity to that of the pure precursor film. There is no significant difference in terms of grain size between the np-precursor spray and precursory spray with the former having a higher surface roughness which was most likely due to the size of the embedded binary nanoparticles.

Figure 4.12 Cross-sectional FESEM images of spray deposited absorber layer from precursor solution before (a), and after selenization (b), and from ns-precursor solution before (c), and after selenization (d).

Selenization resulted in considerable grain growth of both precursor film and np-precursor film (Figure 4.12 b & d). The level of grain growth for np-precursor film was more significant than that without additional nanoparticles after selenization. The addition of the binary nanoparticles resulted in final grain size that is more than 5 times larger (600-700nm) than that of precursor film (100nm). The grain enhancement was most possibly due to the presence of localized Cu-rich nanoparticles which act as nucleation sites for grain growth. Nanoparticles introduction aims to promote the formation of Cu-rich regions mimicking the vacuum based 3 stage co-evaporation approach in the fabrication of high efficiency solar devices³⁷⁻³⁸. It is proposed that the Cu-rich and In-rich regions, formed around the Cu_9S_5 and In_2S_3 nanoparticles, act as nucleation sites for grain growth. During selenization, the two regions would diffuse and react together in the presence of Se at high temperature to form large grain CISSe. In addition, the Cu rich regions would react with Se vapor to form Cu_xSe

which melt and assist in the liquid phase sintering of the CISSe film. The In_2S_3 nanoparticles together with the precursor solution spray are crucial in the prevention of the formation of CuSe or Cu_2Se phases which are highly conducting and detrimental to device performance. Hence, KCN etching of the selenized CISSe film, commonly used to etch CuSe and Cu_2Se phases, can be avoided which is an additional environmental advantage. The use of precursor solution with nanoparticles would avoid the use of organic solvent or binders which would result in a substantial level of carbon within the chalcopyrite films^{7, 56, 87}.

4.6 Conclusion

The metastable wurtzite CIS nanoflakes were synthesized at low temperature by a solvothermal approach with ethylenediamine as solvent in presence of excess sulfur in precursor. The wurtzite phase nanoflakes have optical properties and electrical properties similar to the more stable chalcopyrite CIS. The limited electrical and optical characterizations did not reveal any advantage of wz-CIS relative to chalcopyrite phase. Further characterization on wz-CIS is required to understand any advantage of wz-CIS, if any. In addition, the low temperature stability limits its use in photovoltaic applications as the wurtzite phase would convert to chalcopyrite phase at temperature as low as 400°C. Typical device fabrication requires an annealing step to remove ligands and promote grain densification. Wz-CIS would not be able to pass the annealing stage due to its low temperature stability. Hence, wz-CIS is unable to be used for device application before improving its thermal stability. Spray pyrolysis of precursor solution is a simple approach to form dense CIS film. It can also be spray pyrolysed on Mo substrate without oxidation by a multi-stage spray pyrolysis process. The formation of a dense precursor film at low deposition temperature can act as a barrier layer preventing oxidation at higher temperature.

Cu_9S_5 and In_2S_3 binary nanoparticles were synthesized under room temperature and spray deposited on Mo substrate to form a film with a localized region of Cu-rich phases to assist in grain growth. High porosity and poor deposition uniformity with a rough surface resulted in the addition of precursor solution to form a hybrid spray of both nanoparticles and pyrolysis of precursor solution to form CIS film. This approach has greater flexibility and better stoichiometric control with the benefit of using nanoparticles to create Cu rich phases for grain growth enhancement. However, the process might be time intensive as there is usually a need to spray another layer with precursor solution to adjust the final stoichiometry. Among the different approaches explored, spray pyrolysis of precursor solution would be the simplest and most direct way of absorber layer formation. The ideal temperature for spray pyrolysis of CIS precursors would be at 300-350°C. However, as Mo substrate degrades upon oxidation, a multi-phase spray is required. The small grain size could be overcome easily by high temperature selenization. In conclusion, the nanoparticle synthesis methodology of wurtzite or chalcopyrite CIS for device application is more complex than precursor solution spray pyrolysis as resultant film thickness uniformity and densification remains a major challenge during device application. In the following chapters, grain growth studies would be conducted on spray pyrolysed CIS thin film to investigate effect of annealing temperature and environment on grain growth. Sb dopants would eventually be incorporated into CIS thin film to enhance grain growth.

Chapter 5

5. Grain Growth of $\text{CuIn}(\text{S,Se})_2$ from Precursor Solution

5.1 Introduction

Solution-processed $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ film has a disadvantage of having small fine grains with a high density of grain boundary relative to vacuum based approach. Neutral or uncharged grain boundaries are believed to be potential recombination centers, especially along the space-charged region²²⁻²³. Grain boundaries that are columnar would have a minor impact on the collection efficiency within the space-charged region but grain boundaries parallel to junction are highly detrimental. However, a depletion of Cu along grain boundaries or positively charged grain boundaries exists along grain boundaries which repel holes and lowers recombination probability in high performance devices^{25, 28, 67, 105-106}. Intrinsic CISE grain boundaries contain deep gap states acting as non-radiative recombination centers but defect segregation can clean the gap states, resulting in it being electrically benign^{24, 107}. Although numerous studies on grain boundaries showed that some grain boundaries were not as harmful as predicted and it can be engineered to be electrically benign, it would be more ideal to avoid having high density grain boundaries. An ideal grain size would be columnar grains as large as the film thickness similar to those obtained from co-evaporation technique. However, the solution-based approach introduce greater impurities during processing, which creates a drag force, slowing down grain boundary migration and dampening grain growth¹⁰⁸. Spray pyrolysed CIS films have very fine grains

(20-40 nm) due to its low processing temperature and higher impurity concentration (Chapter 4). This resulted in high density of grain boundaries, inclusive of high detrimental grain boundaries, which are parallel to the junction. Thus, additional processing is needed to enhance the grain size of spray pyrolysed CIS absorber layer.

Grain growth in thin film is normally associated with secondary grain growth as surface energy of the grain is dependent on its orientation¹⁰⁹. Different grain orientation would have different surface energy, resulting in grain growth along the orientation of the lowest surface energy. Hence, thin films would usually have better orientation as compared to powder samples. There are many factors which determine grain growth with temperature and grain boundary motion as the key factors affecting growth rate. Temperature controls the atomic diffusion of the individual elements which directly affects the rate of grain growth. Annealing is the simplest way to promote grain growth by providing energy surplus for atomic diffusion. Grain growth of $\text{CuIn}(\text{S,Se})_2$ is highly dependent on the annealing environment and temperature. Different annealing vapors, namely S, Se and Ar vapor, will affect the formation of intermediate liquid phase along grain boundaries which may assist in the atomic diffusion across grain boundaries. A series of annealing temperatures was selected, with larger extent of grain growth at higher temperatures. The films used have similar thickness to reduce the impact of thickness on growth rate. The extent of grain growth is determined by comparing the average grain size of the film after annealing. The distribution of grain size will also be analyzed to determine the type of grain growth, namely normal or secondary grain growth.

In CIS, Cu is the element with the highest diffusivity, which affects the activation energy on grain boundary motion⁷⁵. Similarly, inter-diffusion of Cu and In atoms are instrumental to the grain growth process of CIS¹¹⁰. Spray pyrolysed CIS film was prepared with a fixed

Cu/In ratio at 0.85 for all precursor solutions to minimize stoichiometric impact on grain growth. The vapors used for annealing are Se vapor, S vapor and Ar gas. The annealing process with the use of Se vapor is commonly termed as selenization, S vapor as sulfurization and Ar gas as Ar annealing. Se and S vapor are selected as they do not result in phase change. Se will replace S in CIS to form CISSe with a lower bandgap. CIS has a bandgap of 1.50 eV whereas CISe have a much lower bandgap of 1.05 eV. High efficiency CIGS devices have a bandgap of approximately 1.14-1.16 eV^{21, 38}. Selenization can also tune the bandgap to the required range by adjusting the Se incorporation. A CISSe film selenized under optimized conditions has a homogeneous selenium distribution throughout the film. Optimization of Se flux will result in CISSe with the optimal bandgap. However, bandgap grading of CISSe will not be considered in the study.

5.2 Effects of Annealing Atmosphere on Grain Growth

5.2.1 Ar annealing

Ar annealing of CIS films does not yield any significant grain growth (Figure 5.1). As-deposited CIS films are fine grained (average diameter 30 nm) with the top layer being less crystalline (Figure 5.1a). As the samples are left to cool immediately after spray deposition, there might not be sufficient time for formation of highly crystallized grains. A post spray heating of 2-3 min on the hot plate after spray deposition at 300°C can improve the overall crystallinity to form a monodisperse grain size distribution. However, this post-spray heating is usually avoided to prevent any stoichiometric change in the film as volatile binary compounds such as In₂S might be formed. Ar annealing of the CIS film at 500°C does not result in grain growth, as shown in Figure 5.1b. Increasing the temperature to 550°C for a longer duration of 1h does not produce any substantial grain growth either (average grain size ~ 50nm) (Figure 5.1c).

The XRD pattern of Ar annealed sample matches well with CuInS₂ (JCPDS no. 027-0159) and Mo (JCPDS no. 042-1120) (Figure 5.2). In addition, most of the previously observed β -In₂S₃ has been converted to CIS at high temperature. There is no significant increase in crystallinity or crystallite size which is consistent with the cross-sectional FESEM image (Figure 5.1b).

Ar annealing can only bring about minimal effect on grain growth even at high temperatures of 550°C. In addition, it might result in loss of In due to the volatility of binary phases such as In₂S that are formed during spray pyrolysis. Among the different batches of samples that were Ar annealed, there is an observable increase in Cu/In ratio after annealing by EDX in some of these samples, indicating a loss in In through volatile phases. This is more commonly observed in samples which are highly rich in In. In conclusion, Ar annealing is not a favorable process for grain growth. Therefore, annealing under other environment such as S or Se vapor should be used.

5.2.2 Sulfurization

CIS films were sulfurized at 500°C and 550°C for 1h which resulted in similar grain growth but with a polydispersed grain size (Figure 5.3). The small grains are approximately 100 nm but the large grains can grow up to around 300 nm. The polydisperse grain size indicates secondary grain growth⁷² which is common in thin films due to growth along preferred orientation. In addition, it is hypothesized that the growth is assisted by the formation of Cu_xS along grain boundaries during sulfurization. Sulfur vapor can easily seep through the grain boundaries of the CIS film, whereby it would react with Cu to form Cu_xS. Under high temperature and high S vapor pressure, there will be minute quantities of Cu_xS in the liquid phase which facilitates atomic transfer and grain boundary mobility. According to the phase diagram of Cu-S¹¹¹ system, at temperatures above 300°C, minute quantities of liquid phase

exist. These liquid phases will assist in CIS grain growth via liquid phase sintering¹¹², which is a more common technique used in sintering of ceramics. Liquid phase sintering is a sintering process which typically involves addition of a low melting point compound which melts before the matrix phase. The doped compounds reside and melt along grain boundaries, resulting in a liquid phase grain boundary. The presence of liquid phases considerably increases the atomic diffusion, resulting in larger extent of grain growth. Liquid state diffusion is normally 2-3 orders of magnitude higher than solid state diffusion. Hence, extensive grain growth can be observed in sulfurized CISSe as compared to Ar annealed samples. The level of grain growth is similar for both sulfurization temperatures of 500°C and 550°C which indicates that they may have the same amount of liquid phase. The final grain size of the sulfurized sample is still far from the desired size in the order of the thickness of film. Grain growth by liquid phase sintering is highly dependent on the amount of liquid phase. A much higher temperature, >813°C, is required to obtain large amount of liquid phase¹¹¹. At 507°C, liquid phase is only found when S concentration is as high as 99.98%. Therefore, the window whereby liquid phase is present is too narrow.

XRD pattern of sulfurized film matches well with CuInS₂ (JCPDS no. 027-0159) and Mo (JCPDS no. 042-1120) (Figure 5.4) without any new peaks detected. Cu_xS binary phases are absent and a significant increase in crystallinity is observed. Precursor solution is prepared with Cu/In ratio of 0.85, verified by EDX. As the film have a Cu/In ratio of 0.85, formation of Cu_xS binary phases are less probable. The presence of sulfur vapor prevents the loss of In from volatile phases by forming more stable In₂S₃. Hence, stoichiometry can be preserved after sulfurization.

Figure 5.1 Cross-sectional FESEM images of CIS films (a) as deposited, (b) Ar annealing at 500°C for 10 min and (c) Ar annealed at 550°C for 1 h.

Figure 5.2 XRD patterns of CIS (a) as sprayed and (b) Ar annealed at 500°C for 10 min.

Figure 5.3 Cross-sectional FESEM images of CIS films (a) as deposited, (b) sulfurized at 500°C for 1 h and (c) sulfurized at 550°C for 1 h.

Figure 5.4 XRD patterns of CIS (a) as sprayed and (b) sulfurized at 500°C for 1 hr.

Even though sulfurization does result in significant grain growth in CIS film, Se incorporation is necessary as the bandgap of CIS is too high to absorb the near infrared region of the solar radiation spectrum. In addition, the final grain size of the CIS films is still too small with a high density of grain boundaries parallel to junctions which are potential recombination centers. Further increase in temperature would not be possible due to softening of soda-lime glass substrate. Hence, exploration into annealing in Se environment is required.

5.2.3 Selenization

The selenization process involves annealing under Se vapor or H_2Se gas. Se vapor derived from evaporation of Se pellets was selected as a safer approach than the use of highly toxic H_2Se gas. In the selenization setup, the vapor pressure of Se can only be controlled by the selenization temperature and amount of Se source used. The amount of Se flux is found to have a major impact on the device properties¹¹³. Maximum Se flux has been proven to yield the best device properties, whereas insufficient Se would result in the extensive formation of

(In,Ga)_{Cu} defects, also known as N1 defect level, which are deep level traps. During selenization, Se replaces S in CuInS₂ to form CuIn(S,Se)₂ (CISSe) which enables the tuning of the bandgap from 1.50 eV (CuInS₂) to 1.05 eV (CuInSe₂), enabling absorption in the infrared region. Selenization temperature, duration and amount of Se used are the main factors affecting the S/(S+Se) ratio in the film. This substitution reaction is similar to the addition of Ga whereby a different In/(In+Ga) ratio allows bandgap tuning between 1.05 eV to 1.68 eV in Cu(In,Ga)Se₂ (CIGS)¹¹⁴.

Typical selenization of the spray pyrolysed films was conducted at 480-500°C for 10 min to observe grain growth and change in S/(S+Se) ratio. The temperature range of 480-500°C is optimal as it prevents the formation of thick MoSe₂, which affects the adhesion of absorber film onto the Mo substrate. The CIS film was selenized, forming CISSe without any phase change or binary compound, within the detection limits of instrument, as the XRD spectrum showed CISSe chalcopyrite peaks only (Figure 5.5a). During selenization, the high temperature provides sufficient energy for Cu atoms to diffuse and react with the β-In₂S₃ phase to form CIS, similar to Ar annealing and sulfurization process. Replacement of S by larger Se ion causes an increase in the lattice parameters and a shift in all the chalcopyrite peaks to the lower 2θ values. A clear shift in the (112) peak at 26.95° of the selenized sample was observed as compared to the sample before selenization at 27.90°. The (112) peak at 26.95° gives an estimated Se/(S+Se) of 0.27 according to Vegard's Law¹¹⁵. The FWHM of the peaks has decreased significantly after selenization, which corresponds to an increase in the crystallite size, consistent with cross-sectional FESEM image shown in Figure 5.5c with an average grain size of 500 nm. The extent of grain growth during selenization is significantly better than the sulfurized films even though selenization are conducted at much shorter duration. The mechanism of grain growth for CIS films which

undergo selenization or sulfurization is believed to be similar, which involves the formation of liquid phase which promotes grain growth by liquid phase sintering. The key difference is that the liquid phase which assisted in grain growth during selenization is Cu_xSe compound instead¹¹⁶, which is produced in a much larger amount than Cu_xS liquid phase in the case of sulfurization. According to the Cu-Se phase diagram¹¹⁷, there is a much higher window of Se concentration, where the liquid phase is present. At 523°C, the window for obtaining liquid phase is approximately from 99 at% Se and above, which is almost 50 times larger as compared to Cu-S system.

Spray pyrolysis of CIS film might form amorphous binary phases (Cu_xS or In_2S_3 etc.) that are not visible under XRD. Therefore, Raman spectroscopy was performed at random regions along the samples to check for binary phases. The Raman spectrum of the as-sprayed CIS sample before selenization (Figure 5.5 b) gives the dominant A_1 peak (295 cm^{-1}) of CIS with an additional shoulder peak (333 cm^{-1}) that is highly likely to be B_2 , E mode of CIS. The Raman spectrum is consistent with past reports on Cu-poor CIS film^{10, 104, 118}. Binary phases such as CuS and Cu_2S are not detected by Raman spectroscopy. $\beta\text{-In}_2\text{S}_3$ has close overlapping peaks (244 and 306 cm^{-1}) with E modes of CIS and are most probably overwhelmed by CIS peaks¹¹⁹ due to its low quantities. The selenized CISSe film shows dominant Raman peak at 174 cm^{-1} which belongs to A_1 mode of CISe and the B_2 , E mode of CISe at 214 cm^{-1} . Although the selenized film is a quaternary CISSe compound, which contains both S and Se atoms, the Raman peaks observed matches well with CISe database. This could be due to high Se content in CISSe which closely resembles the CISe environment. The peak observed at 174 cm^{-1} is slightly lower than the peak observed at $175\text{-}176\text{ cm}^{-1}$ on CISSe film fabricated using the hydrazine approach, possibly due to the different S/Se ratios¹²⁰. Similarly, selenization does not result in formation of Cu_xSe binary

phases as there is an absence of peaks at 260 cm^{-1} which is in agreement with the XRD results.

Selenization of spray pyrolysed CIS film resulted in large grain CISSe film (Figure 5.5c) with an average grain size of 500 nm, a significant improvement compared to Ar annealed or S vapor annealed samples. However, there was no distinct grain growth in CIS film that was spray pyrolysed on preheated Mo (Figure 5.6). The preheating of Mo substrate was to check for substrate degradation due to oxidation which had been shown to affect quality of the film deposited. Preheated Mo at 300°C followed by cooling the substrate back to 120°C before start of spray also yielded similar results on grain growth. Preheated Mo contains a layer of MoO_2 which possibly affects the nucleation and growth of CIS film during selenization. In addition, the formation of MoO_2 may inhibit Na diffusion from the substrate to the CIS film which in turn limits grain growth. However, further characterization is required to understand the impact of MoO_2 formation on Na diffusion. Hence, CIS film deposited on preheated Mo substrate is not suitable for device application.

Figure 5.5 (a) XRD and (b) Raman spectra of CIS (blue, before selenization) and CISSe (red, after selenization) and (c) Cross-sectional FESEM image of spray deposited sample with gradual heating after selenization at 480-500°C for 10 min.

Figure 5.6 Cross-sectional FESEM image spray pyrolysed CIS film on preheated Mo substrate and selenized at 480-500°C for 10 min. Red line shows interface between CISSe and Mo.

The stoichiometry of CISSe film is important as the $S/(S+Se)$ ratio affects the bandgap while impurities affect the film properties. EDX analysis does not reveal any impurities such as oxygen and carbon in the selenized CISSe film. Impurities restrict grain growth and affect the properties of the film. Organic solvent or organic binder materials (except thiourea), which contribute to C impurities in the film, were not used during the whole film fabrication process. Thiourea decomposes easily during the spray pyrolysis process and releases CO_2 . As the Mo and S peaks cannot be resolved under EDX, WDS was used to analyze the film composition. Results showed an average Cu/In ratio of 0.86 ± 0.01 (Table 5-1) which is close to the ratio of the prepared precursor solution (Cu/In=0.85). The selenized film was predominantly single phase $CuIn(S,Se)_2$ with a low $S/(S+Se)$ ratio of 0.23 ± 0.01 (Table 5-1). The estimated bandgap based on this ratio was 1.15 eV, which is close to the CIGS bandgap¹²¹ resulting in optimum absorption.

High temperature selenization can effectively enhance grain growth and achieve grain size close to the film thickness. It also allows reduction of the bandgap which allows greater absorption in the near infrared region. With further optimization on selenization parameters, grain growth can be enhanced further. As the Se flux directly affects the presence of liquid phase, optimization on the Se flux can lead to further enhancement in grain growth.

Table 5-1 Wave-dispersive X-Ray data of individual elements in CISSe film.

No.	Mo	S	Se	Cu	In	Cl	Total	Cu/In	S(S+Se)
1	8.49	10.99	36.64	19.97	23.04	0.86	100.00	0.87	0.23
2	0.98	10.92	40.25	22.11	24.82	0.92	100.00	0.89	0.21
3	6.96	11.19	36.94	20.81	22.96	1.14	100.00	0.91	0.23
4	0.68	10.03	38.93	23.16	25.76	1.43	100.00	0.90	0.20
5	5.39	10.45	38.42	20.95	23.93	0.87	100.00	0.88	0.21
6	18.85	11.30	33.48	16.08	19.36	0.93	100.00	0.83	0.25
7	12.17	11.43	35.80	18.04	21.57	0.99	100.00	0.84	0.24
8	11.26	11.07	36.25	18.20	22.31	0.91	100.00	0.82	0.23
9	12.74	10.87	36.03	17.34	22.00	1.02	100.00	0.79	0.23
10	0.57	10.42	39.29	22.63	25.84	1.25	100.00	0.88	0.21
								Avg:	Avg:
								0.859	0.227

5.3 Effect of Se Flux on Grain Growth during Selenization

The amount of Se added during selenization directly affects the selenium flux during selenization. As mentioned earlier, a higher concentration of Se would have higher tendency

to form liquid phase along grain boundaries. The level of Se flux can be controlled by the amount of Se used during selenization. A past report shows that the Se flux can affect the density of surface defects which impaired device performance¹¹³. A high Se flux was proven to promote larger grain growth in solution processed CIGSe devices by hydrazine approach¹¹³. However, spray pyrolysed CIS thin film contains low level of Cl impurities which resides along the grain boundaries. These Cl impurities provide a different grain boundary environment which might affect the grain growth. According to the Cu-Se phase diagram¹¹⁷, a minimum concentration of Se is required for liquid Cu_xSe to exist. However, previous studies do not quantify the Se flux. Here, an attempt to quantify the Se flux by evaporating fixed amount of Se by weight at a fixed temperature of 480°C was performed.

Selenization was carried out on spray pyrolysed CIS films at different Se vapor densities. The different vapor densities arise from evaporation of different masses of Se (15 mg, 20 mg, 25 mg and 30 mg). Yellowish brown Se vapor was observed to fill the inner selenization tube uniformly for 2 minutes after the temperature reaches 480°C. A maximum of 30 mg of selenium was vaporized as any further increase in Se mass to 35-40 mg results in residual Se. Hence, 30 mg of Se was close to the saturation vapor pressure. Saturation vapor pressure is obtained when Se is left on the selenization tube non-evaporated after the selenization process. The vapor pressure can be calculated based on the equation and coefficients revealed from study by Brooks¹²². High Se vapor close to the saturation vapor pressure is required to achieve significant grain growth (Figure 5.7) with a polydisperse grain size ranging from 400-600 nm. CIS films selenized with Se ranging from 15-25 mg produced similar extent of grain growth with much smaller grains capped at 100 nm. The significant grain growth at high Se vapor pressure further justified secondary grain growth occurred by liquid phase sintering during selenization. Liquid phase Cu_xSe exists at a very narrow

window of Se concentration which is close to the saturation vapor pressure. Selenization has to be done at a minimum of 30mg Se to obtain grain growth enhancement via liquid phase sintering. An increase in selenization duration would require higher amount of Se to be added as constant Ar flow is maintained within the main selenization tube. Optimization on selenium quantity is required to achieve desired grain growth effect when selenization duration parameter (temperature, duration etc.) changes.

Figure 5.7 FESEM images (Plan view) of CISSe film selenized with (a) 15 mg Se, (b) 20 mg Se, (c) 25 mg Se and (d) 30 mg Se at 480°C.

5.4 Conclusion

Grain growth of spray pyrolysed CIS thin film was conducted at different annealing temperature and environment. High temperature annealing of 500°C and above in inert Ar shows the least grain growth while annealing in reactive Se environment is most effective

for grain growth. It is concluded that inert environment annealing does not enhance grain growth even at high temperature because grain growth enhancement was observed for annealing under S and Se vapor due to the formation of liquid Cu_xS and Cu_xSe phases. Formation of liquid Cu_xSe is relatively easier than liquid Cu_xS , supported by information in the phase diagram of Cu-S and Cu-Se systems. Higher volume of liquid phase greatly enhances grain growth under Se vapor. Saturated or near saturated Se vapor has to be maintained for optimum liquid phase to exist, which eventually assist in grain growth by liquid phase sintering. The ease in the formation of liquid phase is instrumental to the grain growth of the film. With a deeper understanding of CISSe grain growth, large grains CISSe could be achieved by optimizing the selenization temperature under Se vapor. Although the grain growth from selenization is significant, it is still smaller than the target of similar grain size as the film thickness. Hence, there is a need to look into other methods for grain enhancement without the increase in annealing temperature in order to preserve the current thermal budget. The use of Sb doping is one method to promote grain growth of CISSe film and this is explored in the coming chapter.

Chapter 6

6. Sb doping in $\text{CuIn}(\text{S},\text{Se})_2$

6.1 Introduction

Grain growth in CISSe by thermal annealing under various environments (Ar, S or Se vapor) was shown in the previous chapter. Annealing in Se vapor has been shown to give the most significant grain growth by liquid phase sintering as compared to S vapor due to the larger existence of liquid phase. Although selenization results in large average grain size of 500 nm, it has not achieved the target grain size similar to the film thickness (approx. 800 nm). In CIGS, a higher copper content in films would lower the activation energy, resulting in larger grains after annealing as Cu has the highest diffusivity⁷⁵. Hence, Cu/In ratio is kept strictly within 0.80-0.85 for a fair comparison in grain size. Similarly, thickness is kept within variation of 100 nm to exclude the effect of thickness on grain growth. Typically, grain enhancement in CIGS was done by altering or deliberately creating a Cu-rich layer in the 3-stage co-evaporation technique^{37-38, 45} or use of binary nanoparticles to create Cu-rich phase⁸³. These Cu-rich regions promote the formation of Cu_xSe which melts and assists in liquid phase sintering during high temperature selenization or heat treatment. However, dual layer spray (Cu-rich layer followed by Cu-poor layer), or addition of nanoparticles, increase the complexity of the processing and create a larger stoichiometric variation in the final selenized film. Increasing annealing temperature or duration would form thicker MoSe_2 layer which increases the series resistance and most importantly, degrades the adhesion of absorber layer on Mo substrate.

Doping affects the mechanism of grain growth in silicon^{30, 123}. An optimal doping in silicon has been shown to improve grain growth of polycrystalline silicon. Na doping has been shown to promote grain growth in CIGS³. Similarly, antimony (Sb) doping has also been shown to produce significant grain size enhancement effect in CIGS thin films^{31-32, 79} with improved efficiency of 15.2%²¹ using hydrazine as the solvent. Sb doping may also enhance grain growth in spray pyrolysed CIS thin film by the same mechanism. However, the mechanism of grain growth is still unclear in the hydrazine system. It is proposed that Sb doping results in formation of low melting point compounds along grain boundaries which melt during annealing and provide a larger volume of liquid for liquid phase sintering. Sb was introduced into the precursor solution before spray deposition to study its doping effect on grain growth and diffusion in spray pyrolysed CIS films. Sb doping concentration can be controlled by varying the amount of Sb precursor added into the CIS precursor solution before spray pyrolysis. Similarly, Sb can be selectively introduced at the top, middle or bottom layer of the full CIS film by preparing different precursor solutions, which can be doped and undoped. Optimization on Sb doping level is required as over doping results in precipitation along grain boundaries which reduces grain boundary diffusion. Annealing on doped films at different atmosphere was conducted. A mechanism on the grain growth of CISSe by Sb doping was proposed to summarize the doping study.

6.2 Grain growth of Sb:CuIn(S,Se)₂ with different doping level

Sb is introduced into the CIS precursor solution before being spray pyrolysed on Mo-coated soda lime glass substrate. SbCl₃ was dissolved in acetone to form stock solution rather than direct addition into the precursor solution so as to prevent the formation of Sb₄O₅Cl₂ precipitate which is unfavorable for spray deposition. Acetone was selected as solvent for SbCl₃ as it is miscible in water. Sb₂S₃ is not selected as a doping source as it is not soluble in

water or common organic solvent (ethanol, acetone etc.).Sb was doped into CIS film at various doping level from as low as 0.1 mol% to 2.0 mol% with respect to In concentration. Grain growth is highly dependent on atomic diffusion of the individual elements of the compound. The films were subsequently selenized at high temperature to study the effect of Sb on grain growth. Selenization was carried out at 480°C on the Sb doped CIS films which resulted in grain growth enhancement (Figure 6.1) of the CISSe. High Sb doping of >1mol% (Figure 6.1 d-e) in CISSe films resulted in significant grain growth with grain size of approximately 600-800 nm, which is close to film thickness, as compared to the undoped sample with grain size approximately 300-400 nm (Figure 6.1 a). The grain size of undoped sample was slightly smaller than those reported in Chapter 5 due to larger thickness. Low Sb doping at 0.2 mol% and 0.5 mol% shows slight improvement in grain sizes at approximately 400-500 nm (Figure 6.1 b-c). The level of grain growth is similar to that of liquid phase sintering observed commonly in sintering of ceramics materials¹²⁴. As explained in the previous chapter, grain growth in CIGS/CISSe was enhanced by the formation of liquid Cu_xSe phase during selenization¹²⁵. However, as the Sb doped CIS layer has a fixed Cu/In ratio of 0.85, grain growth enhancement was probably due to the formation of low melting point Sb compounds which melt to generate higher volume of liquid phase to assist in the liquid phase sintering.

At low selenization temperature of 400°C, minimal grain growth observed. Hence, longer selenization duration of 1 h was used to amplify the effect of dopants on grain growth of Sb doped CIS. It was found that a doping level of ≥ 0.5 mol% Sb gives rise to larger grain growth as compared to undoped sample (Figure 6.2). Grain size similar to film thickness was finally achieved with doping level of 1.0 mol%. A low selenization temperature coupled with longer duration was used to obtain similar grain growth under high temperature

selenization. However, a higher level of doping is necessary. Lower doping levels (<2.0 mol%) may not have sufficient liquid phase for effective sintering. This might be due to the reduced formation of Cu_xSe which also assist in grain growth of undoped samples. Grain sizes in Sb doped CIS films are generally smaller than that in the hydrazine approach^{31, 79} which could be attributed to the presence of Cl impurities (1.0 at%) residing along grain boundaries which inhibits diffusion or reduce grain boundary mobility^{72, 108}. These Cl impurities could be traced back to the metal chloride (InCl_3 and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) precursors used in the preparation of precursor solution. The feasibility and ease in the formation of Sb compounds which melts during the sintering process might be possible reasons on the lower grain growth relative to the hydrazine approach which uses Sb_2S_3 directly. A separate spray pyrolysis study on the formation of possible Sb compounds will be revealed in the later section. Successful low temperature selenization enables spray pyrolysed CISSe to be deposited on flexible substrate such as polyimide which has a lower thermal tolerance.

Figure 6.1 Cross-sectional SEM images of Sb doped CIS with different doping levels of (a) undoped, (b) 0.2 mol%, (c) 0.5 mol%, (d) 1.0 mol% and (e) 2.0 mol% selenized at 480°C for 20 min.

Figure 6.2 Cross-sectional SEM images of Sb doped CIS with different doping levels of (a) undoped, (b) 0.2 mol%, (c) 0.5 mol%, (d) 1.0 mol% and (e) 2.0 mol% selenized at 400°C for 1 h.

XRD measurement on selenized Sb doped CISSe does not show any secondary phases (Figure 6.3). As the doping level was very small, secondary phase might be below the detection limits of the XRD instrument. As sprayed CIS film was not fully crystalline, there was no observable lattice parameter change. Similarly, the doping level was probably too small to be detected and the dopants would probably be rejected to the grain boundaries. However, increasing doping level resulted in increase in lattice parameter after selenization. XRD spectrum of selenized Sb doped CISSe showed a left shift to lower 2θ values as doping level increases from 1.0 mol% to 2.0 mol% (Figure 6.3a). This indicated an increase in Se incorporation in the film with higher doping level. It is highly possible that Sb reacts with Se alone or with other elements (Cu etc.) located at the grain boundary to form low melting point Sb-Se compounds. The melting of the Sb-Se compounds would further increase Se dissolution into the liquid grain boundaries. As a result, the liquid phase grain boundaries would be Se rich which facilitates Se incorporation into CIS matrix by diffusion. Over time,

substitution of S by Se takes place in CIS which forms CISSe with a high Se/(S+Se) ratio. The crystallinity and crystallite size have also increased with higher selenization temperature as indicated from a higher peak intensity and narrower FWHM (Scherrer equation¹⁰³). An increase in crystallite size would also indicate an increase in grain size as observed from the cross-sectional FESEM images. External quantum efficiency (EQE) measurements of completed CISSe devices selenized at 500°C showed a red-shift in absorption edge which corresponds to a lower bandgap, when doping level is increased from 1.0 mol% to 2.0 mol%, further justified the higher Se/(S+Se) ratio in the film (Figure 6.3b). The effect of Sb doping on the optical properties of CISSe would be discussed in greater detail in Chapter 7.

CISSe with different doping level ranging from 0.2 mol% to 2.0 mol% were selenized but does not reveal significant differences in Se incorporation as the selenization duration was shorter. CISSe doped with Sb displayed a preferred grain growth in the (204)/(220) plane (Figure 6.4) after selenization. The introduction of Sb in CISSe promoted a preferred orientation growth in (204)/(220) plane which was also observed in Sb doped CIGS by hydrazine approach³¹. However, in spray pyrolysed films, the changes in grain orientation were not as significant. This could be due to the higher Cl impurities residing at grain boundaries which inhibit grain rotation during liquid phase sintering. In addition, the increase in secondary grain orientation of (204)/(220) was found to be optimum at a doping level of 1% regardless of selenization temperature (Table 6-1). Over-doping might provide higher liquid phase for sintering but may also contain other Sb precipitates which may in turn hinder grain rotation. Lower selenization temperature gave higher (204)/(220) orientation which could be due to lower diffusion of Na into CISSe at 400°C as Na was found to promote growth in the (112) plane¹²⁶.

Figure 6.3 (a) XRD spectrum of CISSe with different doping level and selenization parameters, and (b) EQE measurements of CISSe with 2 different doping levels which are selenized at 500°C for 10 min.

Figure 6.4 XRD spectrum of CISSe with different doping level selenized at (a) 480°C for 20 min and (b) 400°C for 20 min.

Table 6-1 List of (112)/(204) grain orientation ratio in CISSe doped with different Sb concentration.

Ratio (112)/(204)		
Doping lvl (mol%)	480°C 20min	400°C 20min
0.2	3.16	2.24
0.5	2.75	2.20
1.0	2.78	2.04
2.0	3.01	2.24

6.3 Time-of-Flight Secondary Ion Mass Spectrometry analysis on CISSe film

As the dopant distribution might provide greater insight on dopant diffusion of CISSe during selenization, elemental depth profile information of the CIS and CISSe absorber layer was characterized by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)¹²⁷. Qualitative analysis could be drawn from the results but not quantitative results due to different ionization phenomena and matrix effects¹²⁷ between CISSe and CIS. The depth profile of Sb dopants for annealed samples indicated that Sb was homogenously incorporated throughout the film, excluding top and bottom interfaces, with a slight intensity fluctuation near the top surface probably due to the spray process or measurement artifact (Figure 6.5). The elemental profile near the film interface will not be discussed due to possible measurement artifact. The depth profile of Sb for pristine sample indicated two peaks near the front interface. This could be due to localized Sb aggregation that arises from the deposition process. Depth profile of Sb on the selenized CISSe film shows an even distribution of Sb within the main bulk of film with segregation of Sb near the back interface (slight spike in Sb intensity). The number of Sb counts obtained near the back interface is on average 2-3 times larger than the main bulk depending on selenization condition. The

detailed plot of the elemental depth profile data (Figure 6.6) gives a better illustration that the segregation behavior is near the Mo/CISSe interface as the Mo intensity rises rapidly around the Sb spike region. This distinct dopant segregation behavior reveals the presence of an additional driving force for diffusion of Sb towards the Mo/CISSe interface. A probable driving force would be a reaction between the diffusing Sb species with the Mo substrate, which consumes Sb resulting in low Sb concentration near the Mo/CISSe interface. The S and Se intensities are very consistent throughout the bulk of the film, indicating a conversion of CIS to CISSe with Se replacing S uniformly through the film. There is also a spike in S intensity along the CISSe/Mo interface at longer selenization condition indicating the formation of MoS_2 . As the concentration of Sb is extremely low, 1 mol% of In, relative to the other elements (Cu, In, S, Se and Mo), the depth profile data does not provide any evidence of Sb compound formation that could be the driving force for segregation behavior of Sb. Although a clear phase segregation of Sb is observed near the back interface, there was no observable adverse electronic impact on the completed Sb doped CISSe devices as compared to undoped samples (details in Chapter 7).

The selenization was homogenous with uniform S/(S+Se) ratio throughout the bulk film at 400°C (Figure 6.6). Hence, there will not be any graded bandgap in the CISSe film after selenization. The concentration of In fluctuates down the depth while concentration of Cu was generally more consistent. The fluctuation in In profile could be due to formation of ordered defect compounds (ODC). However, ODC are localized defects with low concentration and has negligible impact on bandgap. Cu, being the species with the highest diffusivity, can easily diffuse throughout the entire film to ensure a uniform distribution. Formation of Cu_xSe phase after selenization was highly unlikely as there is no peak in concentration throughout the Cu-poor CISSe film. The film is kept Cu-poor during precursor

preparation and as Cu and In compounds formed during film deposition are non-volatile, an average Cu/In ratio of CISSe within the range of 0.80-0.85 is expected.

Figure 6.5 SIMS depth profile study illustrating the Sb counts detected in logarithmic scale with respect to sputter time for pristine CIS film (blue) and CISSe film after selenization at various conditions (400°C for 10 min, red; 480°C for 10 min, green; 480°C for 30 min, violet).

Figure 6.6 SIMS depth profile study of major elements detected in CIS/CISSe film (a) before selenization, (b) selenized 400°C for 10min, (c) selenized 480°C for 10min and (d) selenized 480°C for 30min.

6.4 Effect of Additional Concentration Gradient on $\text{CuIn}(\text{S,Se})_2$ Grain Growth

As the grain growth behavior was coupled with diffusion and segregation of Sb towards the CISSe/Mo interface (section 6.2), a steeper Sb concentration gradient is hypothesized to provide an additional driving force for diffusion. Selective doping of Sb by spray pyrolysis of Sb doped precursor solution and undoped precursor solution to create a single Sb:CIS layer (top, middle or bottom) is shown in Figure 6.7. This design creates a concentration gradient across the film which enables effective study on the diffusion of Sb compound on grain growth after selenization. The increased diffusion will enable rapid formation of liquid phase along grain boundaries down the depth of film and enable effective liquid phase sintering.

Selectively doped CIS films are prepared with a higher thickness (1300-1500 nm) and selenized to observe the grain growth. A higher film thickness increases the time for dopant diffusion throughout the film and reduces grain growth. Grain growth was observed with a different grain size distribution with different positions of doping layer. Sb doped from the top layer shows large grain growth (Figure 6.7a) for the layers below the doped region. Similar grain growth behavior was observed for Sb doped near Mo/CISSe interface (Figure 6.7c) with larger average grain size at the doped region. The Sb doped layer sandwiched by two undoped CIS layers shows little grain growth throughout the bulk of the film with the minimal grain growth near the top surface and CISSe/Mo interface (Figure 6.7c). Generally, there are few main possible causes for a different grain size distribution across the depth of the film. The possibility of localized Cu rich layer, resulting in difference in grain growth is low as Cu is highly diffusive and shown to be well distributed before selenization process (Figure 6.6a). Similarly, Se vapor diffuses into the film easily, resulting in a uniform distribution of S and Se throughout the film. Hence, there would be a similar level of liquid Cu_xSe formed where there is no difference in growth rate. Thus, the diffusion of Sb dopant would be the main cause for the different grain growth. The level of doping (0.5 mol%) is insufficient to fill all the grain boundaries of the film. This results in the top layer of CISSe having insufficient liquid phase for recrystallization and growth of the grains as the liquid phase would diffuse down the film through the grain boundaries by capillary action rapidly after it is formed and retained near the CISSe/Mo interface due to segregation effect. This would also explain the similar behavior for CIS film with Sb doped at the bottom near the Mo whereby the liquid phase is retained at the lower layers while allowing for longer duration of recrystallization and growth. The segregation of Sb at the CISSe/Mo interface retains dopants towards the interface, resulting in a gentler concentration gradient towards

the top of film. Uniform grain growth behavior was observed for the sample with Sb doped layer sandwiched between two undoped layers. There is no distinct difference in grain size along the depth of the film except for regions near both interfaces as the Sb compounds diffuse in both directions which provides an even spread in the liquid across the central layers of the film.

The doping level was reduced to 0.1 mol% to have a clear observation of grain growth along with Sb diffusion direction. The low selenization temperature (400°C) study shows that the grains start to grow from the top where the Sb is located and slowly moves downwards as Sb diffuses downwards (Figure 6.8). Se would have diffused evenly into the film forming CISSe after 10 min. After 20 min of selenization, there is still barely any grain growth due to the low temperature and doping level. Upon approaching 30 min, grain growth was observed at the top layer where the Sb is located. Diffusion of Sb is relatively slow due to the low doping level with a gentle concentration gradient between the doped and undoped region. After 60 min of selenization, significant grain growth was observed for the bulk of the film with a thin layer at the bottom which remains relatively much smaller. This is evident that the Sb brings about grain growth as it diffuses downwards.

The doping of Sb at the top would be most effective with adequate grain growth as there is a preferred downwards diffusion of Sb. Doping at the bottom interface has reduced diffusion towards the top due to the segregation of Sb at the bottom. Separate experiment was conducted with separate batches of thinner films (600-800 nm) that was fabricated with Sb doped at the top at various concentrations (0.1, 1.0 and 2.0 mol%). They were selenized under the same condition and samples doped ≥ 1.0 mol% of Sb achieved big grain sizes of which is similar to the thickness (Figure 6.9 b-c). The grain size of 2.0 mol% Sb CISSe film might seem to have smaller grain sizes than that doped with 1.0 mol% due to a rough

cleavage surface. The grain size of lightly doped sample (0.1 mol%) is in the range of 300-500 nm, which is comparable to the undoped sample (Figure 6.9a). With sufficient doping, secondary grain growth will take place by liquid phase sintering during selenization. Large grain with size similar to thickness (Figure 6.9b) was achieved with shorter selenization duration.

Figure 6.7 Schematic diagram on selectively Sb doped layer along the depth of CIS film (left column) and cross-sectional FESEM images of selenized film. Selenization conducted at 480°C for 10 min on the different spray design (a) Sb:CIS/CIS/CIS/Mo, (b) CIS/Sb:CIS/CIS/Mo and (c) CIS/CIS/Sb:CIS/Mo. The Sb:CIS have a doping level of 0.5 mol%. Black dashed line marks the interface between two different grain size distributions with depth while red dotted line marks CISSe/Mo interface at back contact.

Figure 6.8 Cross-sectional FESEM images of selective Sb doped (0.1 mol%) at top layer of CISSe and selenized at 400°C for (a) 20 min, (b) 30 min and (c) 60 min.

Figure 6.9 Cross-sectional FESEM images of selective Sb doped at top of CIS with different doping level (a) 0.1 mol%, (b) 1.0 mol% and (c) 2.0 mol% selenized at 480°C for 10 min.

6.5 Effect of Annealing Environment on Grain Growth

Grain growth enhancement is observed in Sb doped CISSe selenized at 400°C. Different doping level brings about different degrees in grain enhancement but the mechanism of grain growth is still an open question. The Se vapor present during selenization may potentially play an important role on the grain growth. To understand the effect of annealing environment on grain growth, a series of annealing studies under various annealing environments and temperatures were conducted. We hypothesize that the dopants form low melting point Sb compound(s) which assist in grain growth by liquid phase sintering. However, Sb selectively doped at different layers within CIS did not show any grain growth

after Ar annealing at 480°C. The results suggested the formation of low melting point Sb compound(s) occurring in the presence of Se vapor only (Figure 6.10). In order to prove this point, sulfurization was conducted at low temperature of 400°C for 60 min which is the same parameter used for low temperature selenization, with a slightly higher doping level than the optimal 1 mol% used, in presence of additional diffusion gradient (Figure 6.11). A higher doping level is deployed to enhance grain growth effect as sulfurization induces lower grain growth than selenization. Similarly, there is minimal grain enhancement observed after sulfurization. An attempt to increase the sulfurization parameter to 550°C for 60 min result in slightly improved grain growth observed in CIS film with Sb doped at the top layer of the film as compared to other doping positions or undoped film (Figure 6.12). It was evident that Sb induced grain growth would only occur in the presence of Se vapor. Hence, there is a high possibility of reaction between Sb and the Se vapor. A literature search of the possible compounds that can be formed is listed in Table 6-1. Sb_2Se_3 has a bulk melting point of 611°C and is highly unlikely to be responsible for grain growth enhancement. The most probable compound would be Cu_3SbSe_4 with a much lower bulk melting point of 426°C. The melting point is potentially lower due to the nanoscale dimensions along grain boundaries. Hence, it is possible that Cu diffuses from the bulk and reacts with Sb in Se vapor to form Cu_3SbSe_4 at the grain boundaries.

Figure 6.10 Cross-sectional FESEM image of Ar annealed Sb doped film (1.5 mol%) at (a) top layer, (b) middle layer and (c) bottom layer at 480°C for 60 min.

Figure 6.11 Cross-sectional FESEM images of sulfurized CIS 1.5 mol% Sb doped at different layer b) top layer, c) middle layer and d) bottom layer at 400°C for 60 min.

Figure 6.12 Cross-sectional FESEM images of sulfurized CIS a) without doping and 2.0 mol% Sb selectively doped at different layer b) top layer, c) middle layer and d) bottom layer at 550°C for 60 min.

Table 6-2 Melting temperature in bulk form of Sb metal and its binary to ternary chalcogenides.

Compound	Melting point (°C)
Sb	630.6
Sb ₂ S ₃	550
Sb ₂ Se ₃	611
CuSbS ₂	535 ¹²⁸

CuSbSe₂	480 ¹²⁹
Cu₃SbS₄	556.9 ⁸²
Cu₃SbSe₄	426.9 ¹³⁰

6.6 Cu-Sb-S Spray Pyrolysis

The formation of Cu₃SbSe₄ which melts to form liquid phase along grain boundaries assisting in grain growth is highly possible. In order to understand the feasibility of its formation, a series of Cu-Sb-S spray is performed.

This was similar to the usual CIS spray with the substitution of In precursors with Sb precursors. A clear precursor solution for spray was not possible due to Sb₄O₅Cl₂ complex formation when SbCl₃ dissolved in acetone was added to aqueous mixture of CuCl₂ and thiourea. This complex formation was not observed in the previous doping study as the doping concentration was too low. The complex formation affects the spray pyrolysis process slightly by formation of a less uniform film. As the amount of Cu that diffuses to the grain boundaries was unknown, the Cu/Sb ratio was varied between Cu poor (Cu/Sb=0.33) and Cu rich (Cu/Sb=3.0) with another sample having the same ratio as the CIS spray (Cu/Sb=0.85). CuSbS₂ (JCPDS No. 44-1417) was formed predominantly regardless of the Cu/Sb ratio of the precursor material (Figure 6.13). Other impurities peaks found could be traced to Cu_xS with the Cu poor film having the most Cu_xS. The Cu poor sample has the highest concentration of Sb with most of them still in amorphous state, probably due to the formation of complex which are still relatively stable during spray pyrolysis. High temperature selenization resulted in formation of highly crystalline Cu₃SbSe₄ (JCPDS No. 25-0263) which was predicted to be the compound responsible for grain enhancement during selenization (Figure 6.14). Sb₂Se₃ is formed as a reaction byproduct during selenization which is highly dependent on the amount of Sb introduced. Sb₂Se₃ has a high

melting point which will potentially inhibit grain growth when formed at the grain boundary.

The chemical equations illustrating the formation of CuSbS_2 and Cu_3SbSe_4 are shown below:

In addition to Cu_3SbSe_4 , Sb_2Se_3 peaks (JCPDS No. 15-0861) was also detected. The amount of Sb_2Se_3 formed was proportional to the amount of Sb added in the precursor solution. Sb_2Se_3 has a high melting point and would exist in the solid form along grain boundaries during selenization which in turn hinders grain growth. Thus, over-doping of Sb can restrict grain growth. Cu source arises from the diffusion of Cu from CIS which could be the limiting factor in the formation of Cu_3SbSe_4 . In these doping studies, the amount of dopants added was very low, which would probably limit the formation of liquid phase Cu_3SbSe_4 during selenization. Doping level of 2.0 mol% might be high as it begins to restrict grain growth in the (204)/(220) plane (Section 6.2). Thus, increasing doping level would provide higher volume of liquid phase for liquid phase sintering of CISSe. However, over-doping above the optimum level will result in Sb_2Se_3 formation which has much higher melting point and might reduce grain growth.

Figure 6.13 XRD spectrum of Cu-Sb-S spray pyrolysis on Mo substrate with different Cu/Sb ratio.

Figure 6.14 XRD spectrum of Cu-Sb-S spray pyrolysis with different Cu/Sb ratio that was selenized at 480°C for 10min.

6.7 Proposed Grain Growth Mechanism

There are two main modes of grain growth that are commonly used to describe grain growth behavior and final grain size. They are (1) normal grain growth whereby the grain size distribution follows a monomodal model throughout the heat treatment process and abnormal grain growth, (2) secondary grain growth, with a bimodal grain size distribution at the intermediate stage of the heat treatment process⁷². Grain growth of Sb doped CISSe belongs to secondary grain growth with a clear distribution of both large and small grains, which are evident from the cross-sectional images of low temperature selenized CISSe film (Figure 6.2). The bimodal grain size distribution is consistent in low temperature selenized samples but less obvious in high temperature selenized sample as the rate of grain growth under high temperature is significantly faster and the cross-sectional images shows monomodal grain size which signify the end phase of grain growth by liquid phase sintering. Unlike undoped samples with a uniform grain size distribution observed throughout the film, Sb doped CISSe results in the formation of large grains at certain regions during selenization. Similar grain growth effect was observed in the sintering of ceramics¹³¹⁻¹³² by liquid phase sintering resulting in secondary grain growth.

Sb doping aims to create liquid phase easily for liquid phase sintering of CISSe. Sb dopants are naturally rejected to the grain boundaries as impurities during the deposition process, which is a common behavior for dopants. There was no evidence of Sb dopants being doped inside the crystal lattice as there is no observable change in lattice parameters. The rapid and fast segregation behavior of Sb to the back contact after selenization further justifies that the dopants along grain boundaries are highly mobile. Along the grain boundaries, the dopants can react with diffusing species from the bulk materials of the absorber layer (Cu, In or S) or

from annealing vapors during selenization or sulfurization to form compounds which melts at temperatures below sintering temperature. The liquid phase, having higher diffusion, resulted in increase in grain boundary mobility and allows for effective diffusion of atoms across grain boundaries. Undoped CISSe can achieve significant grain growth by liquid phase sintering due to the existence of liquid Cu_xSe formed during selenization. However, liquid Cu_xSe will exist only at extremely high Se concentration which might be hard to achieve. Sb doping resulted in the formation of Cu_3SbSe_4 during selenization which has a bulk melting point of 427°C along grain boundaries (Figure 6.15). Unlike Cu_xSe , Cu_3SbSe_4 melts during selenization, forming liquid grain boundaries. The capillary action will draw the liquid to pores and enable densification of grains over time. A liquid phase grain boundary would increase the elemental diffusion of atoms across these grain boundaries as diffusion across liquid was significantly higher than solid state diffusion. Dissolution of atoms into the grain boundaries and precipitation along another site would occur easily. The formation of Sb_2Se_3 does not assist in grain growth due to its high melting point of 611°C which is beyond the softening point of glass. Hence, Sb_2Se_3 formation should be avoided as it will remain in the solid state throughout the selenization process and create a drag force¹⁰⁸, impeding grain growth. It is worth noting that the valence of Sb in Cu_3SbSe_4 is $3+$, which is similar to the valence of Sb from the precursor solution¹³³.

The liquid phase sintering effect on Sb doped CISSe was also observed at selenization temperature of 400°C which further justifies the existence of Cu_3SbSe_4 as it is the only possible compound with a bulk melting temperature slightly above 400°C . Melting point of Cu_3SbSe_4 may be lowered due to the lower dimensions of grain boundaries¹³⁴⁻¹³⁷. Annealing of Sb doped CIS under inert Ar atmosphere did not result in any grain growth at 480°C as Cu_3SbSe_4 would not be formed without Se vapor. During spray process, Sb dopants would

probably react with Cu^+ and S^{2-} to form CuSbS_2 residing along the grain boundaries. Annealing under a reactive annealing vapor allows the formation of binary (Sb_2S_3 , Sb_2Se_3 when Sb is in excess etc.) or ternary compounds (Cu_3SbS_4 , Cu_3SbSe_4 etc.). Sulfurization of the CIS film requires temperatures up to 550°C to observe a difference in the grain growth between doped and undoped sample as both Cu_3SbS_4 and Sb_2S_3 (present in excess of S) have much higher melting points in the bulk phase of 550°C or above.

Figure 6.15 Schematic diagram on the mechanism of grain growth of Sb doped CISSe by liquid phase sintering.

6.8 Conclusion

It was hypothesized that Sb dopants formed low melting point secondary compounds which melts easily creating liquid phase to assist in liquid phase sintering of CISSe thin film. Sb doped CISSe resulted in significant grain enhancement achieving the target of having final grain size similar to film thickness. Increase in doping level from 0.2mol% to 2mol% resulted in grain enhancement of different magnitude. Doping level of $\geq 1\text{mol}\%$ is optimal to achieve grain size of the order of the film thickness at high temperature selenization. Furthermore, higher Sb doping increases Se incorporation in CISSe, resulting in a lower

bandgap. The Sb compounds might either be Se rich or assists in Se dissolution to form Se rich grain boundaries, which promotes Se incorporation during annealing. Low temperature selenization requires much higher doping level to generate larger volume of liquid phase for sintering. Selective doping of Sb at the top of the CIS thin film generates additional diffusion gradient which enhances diffusion rate and promote grain growth. Diffusion of dopants and doping level are the main parameters controlling the growth of CISSe during annealing. Sb dopants react with Se vapor and diffusing Cu species from the CIS bulk to form low melting point compounds, generating additional liquid phase during annealing to assist in atomic diffusion of elements across grain boundaries, promoting grain growth. Spray pyrolysis of Cu, Sb and S precursors formed CuSbS_2 which was later converted to Cu_3SbSe_4 after selenization. This confirms Cu_3SbSe_4 as the species responsible for grain growth in Sb doped CISSe and confirms the hypothesis. Having a low melting point, Cu_3SbSe_4 melts easily contributing to the liquid phase required for liquid phase sintering. A detailed mechanism on grain growth of CISSe was also shown to illustrate Sb doping assisted liquid phase sintering of CISSe thin film. Large grains CISSe of the order of film thickness is successfully achieved with the mechanism of grain growth explained. Further characterization on Sb doped CISSe absorber layer is conducted and discussed in the next chapter which includes deeper analysis on the electronic and optical properties of completed devices.

Chapter 7

7. The effect of Sb doping on optoelectronic properties of $\text{CuIn}(\text{S,Se})_2$

7.1 Introduction

Sb doping has been shown to promote grain growth by liquid phase sintering during selenization in spray pyrolysed CISSe in Chapter 6. However, the effect of doping on electrical or optical properties is still not understood. It was reported that Sb doping resulted in an improvement on device J-V characteristics for hydrazine processed CIGSe films³¹. Sb doped films have shown a highly preferred (220)/(204) orientation which may possibly affect defect density which resulted in better photovoltaic performance. However, evaporated CIGSe film doped with thin Sb layer near the Mo interface resulted in decrease in device J-V characteristics¹³⁸. Hence, the effect of doping on the film properties is highly dependent on the film fabrication methodology and the method the dopant is introduced.

As CISSe is mainly used for photovoltaic applications, it is important to understand the effect of doping on the optical and electrical properties of the film. As the doping concentration is low, formation of CuSbS_2 is unlikely in the bulk film. Even if it is formed, it would probably have little effect on optical absorption. However, the doping concentration affects the Se incorporation during selenization which controls the bandgap of CISSe. Sb doping on spray pyrolysed CISSe film has shown grain growth enhancement with lower grain boundary density which may enhance the photovoltaic performance due to lower probability of recombination along grain boundaries. Sb doped CISSe devices with uniform

doping and top layer doping were fabricated to compare device J-V characteristics with undoped devices. A higher diffusion of dopants due to a larger concentration gradient would probably assist in grain growth and result in larger grains with lower recombination. TEM studies on FIB prepared cross-sectional Sb doped CISSe film were conducted to investigate Sb segregation effect, formation of ordered defect compounds and porosity in film. Low temperature PL was used to study the defects of Sb doped CISSe. In addition, pump probe studies were conducted on CISSe film with different level of doping to gain a deeper understanding on carrier lifetimes. Conducting atomic force microscopy (C-AFM) was conducted to investigate the effect of Sb doping on conduction path. Carrier properties of Sb doped CISSe on glass substrate were investigated with Hall Effect measurements.

7.2 Sb doping on optical absorption and bandgap of CIS

Spray pyrolysis of Sb doped CIS would probably form CuSbS_2 along the grain boundaries. CuSbS_2 has a much higher bandgap of 1.69 eV¹³⁹ which would result in absorption increase around 733 nm when a substantial amount is formed. However, optical absorbance does not indicate any increase in absorption around 730 nm for CIS film doped with Sb up to 2.0 mol% (Figure 7.1a). As CIS is a direct bandgap material, the bandgap of the Sb doped CIS can be obtained from the intercept of the gradient, plot of $(a \cdot \text{energy})^2$ against energy, with the x-axis (where “a” refers to absorbance). As Sb dopants are typically rejected to the grain boundaries, there would not be any optical effect on the CIS bandgap. However, with a large amount of dopants, formation of CuSbS_2 is highly possible as shown by Cu-Sb-S spray (Chapter 6). The bandgap derived from the UV-vis absorption spectra of as-deposited CIS films with different doping level, 0.5 mol% Sb to 2.0 mol% Sb, are in the range of 1.48-1.52 eV, which is in the range of pure CIS film. Hence, Sb dopants do not replace In to form CuSbS_2 . The variation in the intensity of the samples is an effect of thickness variation but

would not affect the derived bandgap. The thickness of sample is expected to be around 100nm with 10nm variation between batches due to limitation on deposition methodology.

Figure 7.1 (a) UV-Vis absorption of as sprayed CIS with different doping level and (b) Plot of $(\alpha \cdot \text{energy})^2$ against energy to determine the bandgap of material. α refers to absorbance.

7.3 Sb doping on device J-V Characteristics and structural properties

Sb doping has been shown to enhance grain growth of CISSe absorber layer. CISSe thin film that was uniformly doped with Sb was made into complete device, with an undoped sample acting as a control. J-V curves of Sb doped CISSe (blue and green) shows that Sb doped devices have superior properties compared to the undoped sample (black) (Figure 7.2). J-V characteristics are displayed in Table 7-1. When Sb was introduced with a doping level of 0.3 mol%, there is a significant increase (13%) in V_{oc} accompanied with measurable improvement in FF . Further increase in doping level to 1.0 mol% increases V_{oc} and J_{sc} , with the bulk increment arising from J_{sc} (16%). A higher Sb doping results in lower series resistance of the completed device, which is consistent with larger grain size and lower grain boundaries of the CISSe absorber layer. The series resistance dropped by more than 75% as

doping level increases to 1.0 mol%. Grain boundaries are amorphous, contain defects, dopants and impurities (Cl etc.), which act as resistive layers, increasing the series resistance of device. In addition, grain boundaries are believed to be potential recombination centers^{23, 140}. With lower grain boundaries and lower recombination velocity, carrier diffusion length would increase which correspond to more charge carriers being collected, resulting in increase in current density.

An enhanced Sb diffusion gradient was created with 1.0 mol% of Sb doped at the top layer of the CISSe film (Top-doped 1.0Sb:CISSe) resulting in larger grain growth as compared to uniform doping (Figure 7.3). Top-doped CISSe film has a larger grain size of 500-600 nm as compared to 400-500 nm for uniformly doped film. Although the average doping level for the top-doped CISSe film (0.3 mol%) was much lower than the uniform doping CISSe film (1.0 mol%), the additional diffusion gradient promotes grain growth and improve the J-V characteristics, resulting in improvement in device efficiency. The largest increase arises from FF (13%) followed by V_{oc} (9%) and the lowest increase comes from J_{sc} (5%). Similarly, top layer doped CISSe film significantly outperforms uniformly doped film with the same average doping level of 0.3 mol% by absolute increase in power conversion efficiency to 8.23% (Table 7-1). External quantum efficiency measurements of the Sb doped devices are shown in Figure 7.4a. CISSe device with lower Sb doping of 0.3 mol% has lower absorption in the infrared region due to a larger bandgap of 1.15 eV as compared to the 1.0 mol% uniformly doped and top-doped CISSe (Figure 7.4b) which has a bandgap of 1.0 eV. Hence, the increased infrared absorption of higher Sb doped CISSe films results in a higher J_{sc} . Bandgap approximation is estimated from the near band edge section of the EQE data²¹. The top layer doped and uniformly doped CISSe have the same bandgap even though the average doping level throughout the whole film is different. This shows that the doping level

at the top of the absorber layer would determine the amount of Se incorporation during selenization. In Chapter 6, a higher doping level results in higher Se incorporation. This could be due to the formation of Cu_3SbSe_4 , which is rich in Se, and dissolution of Se into the liquid grain boundaries resulting in higher diffusion of Se from grain boundaries to the bulk of the grain, increasing the overall Se content in the CISSe film. The calculated current density of the various devices from EQE values are similar with the values measured from solar simulator ($\pm 5\%$ error) under one sun condition.

Figure 7.2 J - V curves of best performance doped and undoped CISSe devices selenized at 500°C for 10 min under 1 Sun AM1.5G light condition and at dark condition. (Black) undoped device; (blue) uniform doped 1.0 mol% Sb CISSe; (red) top-doped 1.0 mol% Sb CISSe; (green) uniform doped 0.3 mol% Sb CISSe.

Table 7-1 *J-V* Characteristics of doped and undoped CISSe devices.

	V_{oc} (mA)	J_{sc} (mA/cm ²)	FF (%)	η (%)	R_{sh} (Ω)	R_s (Ω)	Cell Area (cm ²)
Undoped CISSe	349.6	24.25	50	4.22	566.8	45.2	0.120
Uniform doped 0.3Sb:CISSe	394.3	24.23	55	5.26	898.4	20.4	0.106
Uniform doped 1.0Sb:CISSe	411.5	28.07	55	6.41	677.5	8.7	0.110
Top-doped 1.0Sb:CISSe	447.6	29.50	62	8.23	1405.3	7.9	0.116

Figure 7.3 Cross-sectional FESEM images of Sb doped CISSe devices selenized at 500°C for 10 min with (a) uniform doped 1.0 mol% Sb and (b) top-doped 1.0 mol% Sb.

Figure 7.4 (a) External quantum efficiency, EQE, measurements of Sb doped CISSe devices selenized at 500°C for 10 min and (b) bandgap determination plot of near band edge section from EQE data.

Low temperature selenization at 400°C was carried out displaying the J-V characteristics for both top layer doped and uniformly doped sample (Figure 7.5). The uniformly doped device has a higher V_{oc} but lower J_{sc} , which is the opposite to that of top layer doped device. The higher V_{oc} could be due to a more uniform Sb distribution in the bulk film and a greater segregation of Sb at the back interface. Series resistances for both devices are high, in the range of 40 - 50 Ω , due to smaller grain growth at lower selenization temperatures. Calculated J_{sc} from EQE curves are comparable to measured values with a slightly larger error margin of 10% (Figure 7.6a). Uniform doped and top-doped low temperature devices have comparable PCE of 3.61% and 3.47% respectively. The thicknesses of both devices are approximately 1.0 μm . The bandgap for both devices are similar in the range of 1.13-1.14 eV (Figure 7.6b). Hence, optical light absorption of both devices is similar with comparable J_{sc} . At low selenization temperature, the Se vapor pressure is much lower, resulting in slow Se incorporation to form CISSe. Long selenization duration of 1 h is used to provide longer

time for grain growth but is still insufficient to achieve large grains and lower series resistance. The grain size distribution is polydisperse with certain regions having large grain size (>100 nm) while other regions having significantly smaller grain size (50 nm) (Figure 7.7). A polydispersed grain size distribution was characteristic of secondary grain growth by liquid phase sintering, which was discussed in Chapter 6. However, the incorporation of Sb enables fabrication of CISSe devices with flexible substrate as lower temperature selenization can be used to yield reasonable grain growth. In addition, the formation of resistive MoSe₂ is significantly reduced under low temperature selenization as observed from cross-sectional images (Figure 7.7).

Figure 7.5 J - V curves of best performance Sb doped CISSe devices selenized at 400°C for 1 h under 1 Sun AM1.5G light condition and at dark condition. Uniform doped 1.0 mol% Sb CISSe (solid line) top-doped 1.0% Sb CISSe (dotted line).

Figure 7.6 (a) External quantum efficiency EQE measurements of Sb doped CISSe devices selenized at 400°C for 1 h and (b) bandgap determination plot of near band edge section from EQE data.

Figure 7.7 Cross-sectional FESEM images of Sb doped CISSe devices selenized at 400°C for 1 h with (a) uniform doped 1.0 mol% Sb and (b) top-doped 1.0 mol% Sb.

A different batch of Sb doped CISSe device with a lower doping level of 0.2 mol% and selenized at 480°C with a power conversion efficiency (PCE) of 5.0% was prepared for TEM structural analysis. The cross-section of the sample was prepared by FIB to ensure a smooth surface. However, there are numerous small and bright regions in the film which

might affect device properties (Figure 7.8a). These bright regions are unlikely to be due to presence of binary compounds during processing as they are not detected by XRD or Raman spectroscopy. EDX line scan was conducted across one of the bright regions which show a sharp drop in all the elements across the bright region (Figure 7.8b & c). Further EDX scan across the other regions indicated similar drop in elemental compositions. Hence, these bright regions are actual porosity within the film. Presence of porosity indicated insufficient grain growth and densification during liquid phase sintering. With sufficient liquid phase during sintering, the liquid phase would fill the pores via capillary action enabling grain growth. Porosity limits device performance as these pores are highly resistive and potential recombination sites. Higher Sb doped films with less pores resulted in significant reduction in device series resistance from 45.2 Ω for undoped CISSe to 8.7 Ω in uniform doped 1.0 mol% Sb CISSe. A lower series resistance combined with smaller bandgap of Sb doped sample improves carrier transport which contributed to the increase in J_{sc} from 24.25 mA/cm² to 28.07 mA/cm². Sb could be detected from the EDX scan but the counts are very low and there is no observable strong segregation behavior unlike the SIMS result discussed in Chapter 6. There is also significant background count of Cu which originates from the Cu grid used.

SAED pattern along [110] zone axis on the various grains of the CISSe device shows two different diffraction patterns with the majority of the grains having a tetragonal chalcopyrite structure similar to CISE/CIS (Figure 7.9a). However, one of the grains showed an unknown diffraction pattern with extra diffraction spots that is possibly a superstructure of the dominant chalcopyrite structure (Figure 7.9b). HRTEM image on a selected grain of CISSe was shown with the measured lattice fringes matching well with the diffraction pattern of tetragonal chalcopyrite CISSe (Figure 7.9c). The unknown superstructure was the first to be

observed in CISSe and is believed to be a result of ordered defect compounds (ODC). A different superstructure with fewer diffraction spots has been previously observed on Cu poor CIGS¹⁴¹. A lower number of diffraction spots on CIGS indicated a lower order of superstructure with the ordered defect believed to be $\text{Cu}(\text{In,Ga})_3\text{Se}_5$. Hence, the superstructure observed in CISSe may be a 3 times superstructure, possibly due to localized Cu deficient CISSe forming ODC, but further investigation is required. SAED patterns were obtained from other Sb doped CISSe films, including 2.0 mol% doped sample, and showed the common tetragonal chalcopyrite structure. The presence of ODC is unlikely to be a result of Sb introduction but more of localized ODC formation. Presence of ODC is detrimental to device properties and should be kept at a minimum by increasing and optimizing Cu/In ratio in CISSe.

Figure 7.8 (a) TEM cross-sectional image of Sb doped CISSe device, (b) EDX line scan on a magnified section of the cross-sectional image, and (c) Plot of EDX line scan displaying counts of individual elements present except sulfur.

Figure 7.9 Selected Area Diffraction Pattern (SAED) on different grains of Sb doped CISSe thin film showing a (a) tetragonal chalcopyrite structure, (b) superstructure, and (c) HRTEM image of CISSe.

7.4 Carrier recombination and defects study of Sb doped CISSe film

Carrier recombination is the main factor limiting device performance. In solution-processed CISSe thin film by spray pyrolysis, the type of defects and recombination mechanism might be different to that of a film deposited by vacuum approach. Low temperature (78 K) photoluminescence (PL) measurement was conducted on 2.0 mol% Sb doped CISSe to understand the mechanism of recombination. The PL measurements were conducted at excitation wavelength of 532nm on Sb doped CISSe on Mo substrate without any CdS buffer layer. PL data showed a blue shift with increasing laser intensity (Figure 7.10a), which is a signature of donor-acceptor pair (DAP) recombination, observed in Sb doped CIGS films fabrication by vacuum approach¹³⁸. The shift in peak intensity to lower wavelength is a result of a lower average distance between the donor and acceptor, which were involved in the recombination process as the excitation power increases from 1 mW to 10 mW. However, the observed blue shift of approximately 22 meV per decade increase in excitation power might be a result of potential fluctuation in the material^{138, 142}. DAP recombination would normally result in minor blue shift of 1-2 meV per decade of

excitation power¹⁴². A much larger magnitude of shifting, of the orders of 10 meV with higher excitation power, would be observed in the case of potential fluctuation. The potential fluctuation arises from a strong fluctuation in conduction and valence bands, which resulted from random distribution of high density of charged defects. It was reported that a higher S/(S+Se) ratio in material would result in higher potential fluctuation, inferring a higher density of charged defects when the film is S rich¹⁴². In the measured Sb doped CISSe films, S/(S+Se) is approximately 0.10, which corresponds to a high potential fluctuation and high defect density in the sample. The PL intensity can be fitted with the power law equation as shown below:

$$I \propto P^m \dots\dots\dots (8)$$

Whereby I refers to the PL intensity, P is the excitation power and m is the coefficient of power law. The power law linear fit gives a value of $m > 1$, indicating excitonic recombination (Figure 7.10b) is dominant within material. In other materials whereby $m < 1$, recombination is mainly defects recombination. The single peak at around 0.96eV indicated In_{Cu} as the dominant donor defect, similar to past PL reports on Sb doped and undoped films¹³⁸, due to a low Cu/In ratio of 0.85. However, V_{Se} donor defect observed in Sb doped CIGS film¹³⁸ was not prominent in spray pyrolysed CISSe. Presence of intrinsic In_{Cu} and V_{Se} defects limits the V_{oc} of devices¹⁴³. Hence, Sb doping does not result in greater Se loss during selenization which could be the main reason for improvement in J-V characteristics in as-fabricated Sb doped CISSe films as compared to co-evaporated CIGS film. Temperature dependent PL measurement shows a significant blue shift and peak broadening with increasing temperature (Figure 7.11a). This is similar to temperature dependent PL of undoped CIGS¹⁴⁴. The equation for temperature relation with PL intensity is given as below¹⁴⁵:

$$I(T) = I_o \left(1 + c_1 e^{-\frac{E_1}{k_B T}} + c_2 e^{-\frac{E_2}{k_B T}} \right)^{-1} \dots\dots\dots (9)$$

where I_0 is the intensity extrapolated at $T = 0$ K, E_1 and E_2 refers to the separation energy of non-radiative channels from their radiative states, and k_B is the Boltzmann constant. As PL measurement was not conducted below 80 K, a single exponential fit ignoring c_2 term in equation (9) of the PL intensity quenching gives rise to separation energy of 35 meV (Figure 7.11b), similar to past report on CIGSSe films¹⁴². It is the energy of non-radiative channels that is separated from the radiative state involved in the PL emission that quenches PL at high temperature.

Pump probe measurements of CISSe doped with various Sb doping level result in different transmittance and lifetimes (Figure 7.12). A higher doping level reduces ΔT , differential transmittance, intensity and increases lifetimes, where T is 2 mV. A fitting of the decay curves gives two lifetimes, namely t_1 and t_2 , with t_2 magnitude an order higher than t_1 (Figure 7.13). Increase in Sb doping increase lifetimes, t_1 and t_2 , with an optimum t_2 value at approximately 1.0 mol% of doping level. As 1.0 mol% doped CISSe has a higher preferred orientation in (220)/(204) direction, which corresponds to lower non-radiative recombination centers, t_2 would likely be a measure on non-radiative recombination. Hence, t_1 would probably be a measure of defect related recombination along grain boundaries.

Figure 7.10 (a) Low temperature PL measurement of 2.0 mol% Sb CISSe film at 78 K and (b) Plot of integrated intensity against P_{exc}/P_{max} .

Figure 7.11 (a) Temperature dependent PL measurement of CISSe film from 80 K to 300 K and (b) PL intensity quenching with function fitting.

Figure 7.12 Pump probe measurement on CISSe films with different doping level.

Figure 7.13 Plot of lifetime against doping level for Sb:CISSe films showing (a) first lifetime, t_1 and (2) second lifetime, t_2 .

7.5 Electron transport in Sb:CISSe devices

Conducting AFM was employed to investigate the conducting path of CISSe thin film. Topographical and conductivity scans on the surface of 2.0 mol% doped CISSe show that the electrons conduct mainly through the grain boundaries. The surface of CISSe is rough which makes the grain boundaries distinct (Figure 7.14 a,c). The conductivity mapping

under positive bias showed that electrons are transported mainly through the grain boundaries under the dark (Figure 7.14 b,d) which is consistent with undoped CIGS sample¹⁴⁶. Similar conductive mapping was done on 1.0 mol% top-doped CISSe device by probing the transparent conductive oxide (TCO) layer under positive and negative bias conditions. Under positive bias, the dark and light maps are identical (Figure 7.15 a,b). This indicates that there is no leakage current in the CISSe device. As the illuminating light from the AFM stage is weak, there was only a slight increase in the intensity of the current. Under negative bias condition, the current detected was minimal in the dark with a further decrease in current under illumination (Figure 7.15 c,d). In an ideal device, there would not be any current under negative bias condition and an identical current map under positive bias condition indicates negligible current leakage. Hence, the CISSe film quality was good with room for improvement to reduce current conduction under negative bias condition.

Figure 7.14 (a) Surface topography mapping and (b) conductivity mapping on Sb:CISSe thin film under positive 200 mV bias. (c) Surface topography and (d) conductivity scan at a new region under same positive bias. Brighter contrast in topography/conductivity scan indicates higher height/current.

Figure 7.15 Conducting AFM mapping on transparent conducting oxide layer of Sb:CISSe device with a 8.2% efficiency under (a),(b) positive bias and (c),(d) negative bias conditions. (a),(c) mappings are obtained under dark condition whereas (b),(d) mappings are obtained under illumination of light from AFM stage.

7.6 Carrier properties of Sb doped CISSe

The carrier properties of the CISSe film will directly influence the electrical properties of the completed CISSe device. Carrier mobility and density will determine the conductivity and semiconductor properties of the film. Hall Effect measurement of CISSe film selenized over a temperature range of 480-520°C gives good mobility range of 4-6 cm²/Vs and carrier density of 10⁷ (Table 7-2), which are comparable to the CIGS film of NREL (National Renewable Energy Laboratory)¹⁴⁷. The sheet resistance and resistivity of the CISSe film are

also similar to NREL CIGS film. Although CISSe and CIGS are two different materials, they have similar structure and bandgap. Sb doping was introduced and has shown superior device J-V characteristics. However, Hall Effect measurement on Sb doped CISSe thin films do not give better carrier properties. Sb doped samples selenized at 500°C with doping level from 0.2 mol% to 2.0 mol% were measured and compared with undoped sample (Table 7-3). The sample with 0.5 mol% Sb doping has poorer properties as compared to other doped samples, probably due to processing issues, which resulted in inferior quality of film. In general, doped samples result in a lower carrier mobility and density but higher sheet resistance and resistivity of film. In addition, increase in doping concentration does not result in any observable difference in each of the individual properties measured. Lower carrier density of 10^{16} observed shows that the Sb doped CISSe behaves more like a semiconductor. The lower carrier density could be due to reduction of Na diffusion into CISSe film due to competing Sb diffusion. A lower carrier density would lead to lower carrier recombination and scattering as observed by an increase in device V_{oc} as doping level increases (Table 7-1). Although lower carrier mobility will reduce carrier diffusion and collection, a reduced recombination probability due to lower carrier density might render the effect of carrier mobility less significant. However, there might be a high discrepancy between the measured values and the actual properties of the CISSe film as the Hall measurement samples are deposited on soda-lime glass, which is non-conductive, instead of Mo. The absence of Mo layer also affects the diffusion of Na into the CISSe film. During selenization or high temperature annealing process, a higher Na diffusion into the film occurred, which may have affected film properties^{126, 148-149}. Na doping has been reported to increase hole concentrations¹⁴⁹ and enhances the formation of point defects¹²⁶. Furthermore, there is strong competition between the upward diffusing Na species against downward

diffusing Sb atoms. This would reduce Sb diffusion and segregation towards the bottom contact which would affect grain growth. However, presence of Na was found to be necessary for grain growth enhancement in Sb doped CIGS³⁴. The absence of Mo layer, with a different interfacial energy, may also affect the segregation behavior of Sb. Hence, the Hall Effect measurement data could only serve as a guide on the carrier properties as there is a need for further characterization to confirm the observed trend. Other characterization techniques recommended for carrier properties study of CISSe films are Deep Level Transient Spectroscopy (DLTS), Impedance or Admittance and Time-resolved photoluminescence (TRPL).

Table 7-2 Hall Effect measurement data on undoped CISSe selenized at different temperature for 10 min.

Undoped			
Selenization Temperature (°C)	480	500	520
Resistivity ($\Omega\text{-cm}$)	3.05	3.02	2.38
Mobility (cm^2/Vs)	6.03	4.04	4.14
Density (cm^{-3})	3.39E+17	5.12E+17	6.33E+17
Hall Coeff. (cm^3/Coul)	18.4	12.2	9.87
Sheet Number (cm^{-2})	2.03E+13	3.07E+13	3.80E+13
Sheet Res. (Ω/cm^2)	5.09E+04	5.04E+04	3.97E+04
Type of Carriers	Holes		

Table 7-3 Hall Effect measurement data on doped and undoped CISSe selenized at 500°C for 10 min.

Sb Doping level	Undoped	0.2	0.5	1.0	2.0
(mol%)					
Resistivity ($\Omega\text{-cm}$)	3.05E+00	3.36E+02	1.37E+04	4.54E+02	6.34E+02
Mobility (cm^2/Vs)	6.03	2.68	0.72	1.54	1.76
Density (cm^{-3})	3.39E+17	1.64E+16	3.19E+15	2.79E+16	3.08E+16
Hall Coeff. (cm^3/Coul)	1.84E+01	4.46E+03	1.08E+04	4.51E+02	1.21E+03
Sheet Number (cm^{-2})	2.03E+13	4.92E+11	9.57E+10	8.37E+11	8.85E+11
Sheet Res. (Ω/cm^2)	5.09E+04	1.12E+07	4.57E+08	1.51E+07	2.11E+07

7.7 Conclusion

Optical and electrical properties of CISSe absorber material are important for its use in photovoltaic applications. Sb incorporation does not alter the bandgap of the material but the formation of secondary Sb compounds increases the Se incorporation, resulting in Se rich CISSe, which has a lower bandgap. A lower bandgap improves optical absorption in the infrared region resulting in higher J_{sc} . In addition to grain growth enhancement in CISSe absorber layer, Sb doping results in better device J-V characteristics. V_{oc} , J_{sc} and FF increases with higher Sb doping. A steep Sb doping concentration gradient in CISSe by selective top layer doping further increases grain growth resulting in improvement of J-V characteristics which led to the record efficiency of 8.2% on spray pyrolysed CISSe film.

Further device optimization can be achieved by selection of other precursor solutions such as nitrates or acetates instead of chlorides to remove Cl impurities, addition of Ga to increase bandgap, spray a film with a graded bandgap or increase the thickness of absorber film. Structural analysis of device cross-section under TEM reveals a number of voids in the film, porosity issues, and presence of ordered defect compounds, which limits carrier transport and collection. Higher doping level reduces porosity and significantly reduces series resistance of device resulting in better charge transport. Photoluminescence measurement shows a strong potential fluctuation at low temperature, probably due to high S content in the film. Power law linear fit shows the recombination mechanism to be excitonic. As the CISSe film is Cu poor, In_{Cu} remains as the dominant donor defect, similar to other PL reports on undoped films. In addition, Se loss was not observed in selenized CISSe film as V_{Se} donor defect is not prominent from PL. The low presence of V_{Se} donor defect could be the main reason for better J-V characteristics as compared to co-evaporated CIGS films. PL intensity quenching fit shows separation energy of 35 meV, similar to reported CIGSSe film. Pump probe measurement shows that Sb doping enhances carrier lifetimes. The increased carrier lifetimes can be attributed to lower DAP and non-radiative combination with increase doping level. Lower recombination probability improves carrier transport which result in a higher V_{oc} and J_{sc} in Sb doped devices. Conducting AFM mapping on Sb doped CISSe device shows the grain boundaries as the main conducting pathway for electrons and the presence of negligible leakage current. In addition, Sb doping results in lower carrier density and carrier mobility which might lead to reduced recombination. In conclusion, Sb doping in CISSe is favorable as it enhances electrical properties resulting in improved device performance.

Chapter 8

8. Conclusion and Future Work

8.1 Overall Summary

A few methods were explored to achieve an environmentally friendly solution-based CIS thin film. The initial focus was on nanoparticle synthesis with both chalcopyrite and wurtzite phase CIS synthesized by a solvothermal approach. High temperature stable wurtzite phase was successfully synthesized at low temperature with ethylenediamine as the solvent under excess sulfur environment. Using the dual amine approach, the synthesis temperature of metastable wurtzite phase CIS is successfully reduced. However, the wurtzite phase is thermally unstable and will convert to the chalcopyrite phase at elevated temperatures. Binary Cu_9S_5 and In_2S_3 nanoparticles were synthesized and spray deposited to form a film. However, the sole use of nanoparticles results in a non-uniform and rough film which shift focus towards film formation from precursor solution. Hence, spray pyrolysis of aqueous precursor solution was deployed and resulted in a uniform and dense CIS film. The oxidation of Mo substrate was overcome by deposition of CIS precursor as a barrier layer. However, the average grain size of the CIS film is too small, which will result in extensive recombination along grain boundaries. The hybrid approach of incorporating nanoparticles into precursor solution for spray pyrolysis succeeded in inducing significant grain growth during selenization. However, the hybrid approach involves complex processes which require precise experimental control. Hence, precursor solution spray is selected as the methodology for CIS film fabrication as it is simple, direct and does not involve toxic solvents or chemicals.

Spray pyrolysed CIS was annealed under various environments, namely S, Se and Ar, to investigate the effect of annealing environment on grain growth. Ar annealing proved ineffective in grain growth while annealing in Se vapor, also known as selenization, results in the most significant grain growth. Both annealing in S and Se vapors resulted in grain growth, due to the formation of liquid Cu_xS and Cu_xSe phases. The presence of these liquid phases promotes grain growth by liquid phase sintering. Formation of liquid Cu_xSe phase is easier than Cu_xS phase, as suggested from the Cu-S and Cu-Se phase diagrams. This is because Cu_xSe requires a much lower concentration of Se in the environment. The extent on grain growth is dependent on ease and availability of liquid phase for sintering. Maximum Se flux was proven to result in the largest extent of grain growth. Although selenization can promote significant grain growth, the grain size of CISSe is still relatively smaller than those fabricated by vacuum approach. Hence, Sb is introduced to further enhance grain growth.

Sb was shown to enhance grain growth significantly during selenization. A grain size of similar magnitude as the CISSe film thickness was achieved with optimal doping level of 1% or more. A higher doping level promotes higher Se incorporation on top of increased grain growth. This could be due to formation of Se rich grain boundaries as Cu_3SbSe_4 is formed along grain boundaries which may enhance dissolution of Se into the grain boundaries. Cu_3SbSe_4 is believed to be formed, which melts at low temperature, providing additional liquid for liquid phase sintering. Lowering selenization temperature requires more abundant doping to achieve similar grain growth shown in high temperature selenization. Selective doping at specific layer to create Sb diffusion gradient proved to be effective in enhancing grain growth. Grain growth is highly dependent on diffusion of Sb dopant. Spray pyrolysis of Cu, Sb and S precursor solution formed CuSbS_2 film, which effectively converts to Cu_3SbSe_4 upon selenization. This proved the existence and formation of low melting point

Cu_3SbSe_4 compounds which are responsible for enhancing grain growth via liquid phase sintering.

Sb doped CISSe absorber film was characterized to understand doping on optoelectronic properties of the film. The bandgap of the CISSe lowers with higher Sb doping due to increase in Se incorporation. The grain growth enhancement in Sb doped CISSe absorber resulted in better device J-V characteristics. In addition, an additional Sb doping concentration gradient created by selective doping enhances grain growth together with device J-V characteristics leading to a record efficiency of 8.2% on spray pyrolysed CISSe film. Structural analysis identified a large number of porosity and presence of ordered defect compounds, which may affect carrier transport within the film. Porosity arises due to insufficient liquid phase present for effective sintering. High potential fluctuation was observed at low temperature photoluminescence measurement due to high S content in film, similar to past reports. There is a significant blue shift in PL peak with increasing excitation power and power law fitting shows recombination to be excitonic. Equation fitting on the PL intensity quenching at high temperature gives separation energy of 35 meV. The pump probe measurement data indicated a higher carrier lifetime with increased doping. The increased carrier lifetime is a result of lower combination with Sb doping. Grain boundaries are the main conducting pathway for electrons. There is also a negligible leakage current in the completed device. Hall Effect measurement shows a lower carrier density and carrier mobility with Sb doping, which might lead to reduced recombination and higher V_{oc} in doped device. Hence, Sb doping in CISSe is favorable as it improves device performance by enhancing its electronic properties. Other dopants that are capable of forming liquid phase at low temperature would probably be effective in enhancing the grain growth of CISSe.

8.2 Scientific Contribution and Novelties

The scientific contribution of the thesis is highlight as shown below:

- I. Decrease in wurtzite synthesis temperature by the use of dual amine as solvent.
- II. Development of new method to conduct spray pyrolysis in ambient without oxidation by multi-stage spray pyrolysis.
- III. Reveal the mechanism of grain growth with the aid of Sb: Sb doping forms Cu_3SbSe_4 compound during selenization which contribute to additional liquid phase that improves grain growth in CISSe by liquid phase sintering (LPS)

8.3 Future Directions

The research results have provided significant insight on the grain growth and the role of Sb on the grain growth in CISSe. However, more work could be done to have a deeper understanding on the material and the effect of doping on the properties of the film. Some of the possible suggestions are listed below:

- I. Use of other dopants such as Bi to investigate the formation of low melting point compound which promotes grain growth by liquid phase sintering.
- II. Detailed studies on the cause of the dopant segregation behavior at the back contact. Determine the possibility of compound formation at the back contact which drives segregation behavior.
- III. Investigate the effect of Sb segregation on the types of defect formed and the impact of defects on device physics.

- IV. Investigate the effect of over-doping on the structural, electrical and optical properties of the CISSe film.

8.3.1 Alternative dopants to enhance grain growth of CISSe

Grain growth enhancement observed in Sb doped CISSe was shown to be a result of formation of low melting point secondary phases which assist in liquid phase sintering. These secondary phases, being in liquid phase during heat treatment, enhance atomic transfer and diffusion between grain interior and grain boundaries. Hence, formation of secondary phases is the key to grain growth enhancement. The choice of dopant element should not be limited to Sb. A brief screening for alternative elements on the periodic table shows Bismuth, Bi, as a promising alternative. Preliminary studies had shown similar grain enhancement effect on Bi doped CIGS films¹⁵⁰. As Bi and Sb are in the same group of the periodic table, they share similar chemical properties. Bi could readily react with Cu and Se to form a range of Cu-Bi-Se compounds, with certain compounds having potentially lower melting point than Cu_3SbSe_4 . In addition, Bi metal has a much lower melting point of 272°C as compared to Sb of 631°C , resulting in Bi to be an effective sintering agent if the dopant, normally introduced in the form of metal salt, is able to be reduced to a metal. In addition, Cu-Bi-Se compounds such as Cu_3BiSe_4 may potentially have a low melting point. This would generate a higher if not similar volume of liquid phase under the same heat treatment condition for liquid phase sintering. Further investigations should be carried out to determine any Cu-Bi-Se compound formation and the melting points of the compounds formed. Among the same group of elements under the periodic table, phosphorus, P, could also be an alternative to Sb and Bi but the use of Arsenic should be avoided as it has a high toxicity.

8.3.2 Dopant segregation behavior

The Sb dopant was found to segregate near the back contact Mo substrate. The degree of Sb segregation varies with different processing and doping methodology. Although dopant depth profiling by SIMS has consistently shown a higher level of Sb near the back contact, the driving force of the segregation behavior is still not understood. These Sb dopants react to form low melting point Cu-Sb-Se compounds which assisted in liquid phase sintering. However, little information is available on the decomposition and vaporization possibility of Cu-Sb-Se compounds. Cross-sectional TEM characterization was conducted but unable to identify secondary compound formation along the grain boundaries or near the Mo interface as the dimensions are too small to be characterized properly with the current technology. A possible hypothesis for Sb segregation would be reaction between Cu-Sb-Se compounds with Mo or MoSe₂, which consistently requires Sb enhancing diffusion. This can be investigated by modification on the sample preparation for characterization. Instead of the normal cleaving methodology to observe the sample cross-section, the film can be delaminated from the substrate for surface sensitive characterization such as auger electron spectroscopy or X-ray photoelectron spectroscopy. In addition, modeling and simulation can be employed to emulate and understand the segregation behavior with different doping level and position of doping.

8.3.3 Sb Segregation on defect formation and device physics

Sb introduction and segregation can introduce new defects along the grain boundaries and interface. Similarly, it can reduce defect density and lowers recombination probability. According to *J-V* measurement of completed devices, Sb introduction increase the V_{oc} of the devices consistently. The observed V_{oc} improvement is a result of lower recombination along grain boundaries and at the interface. In addition to the elimination of grain

boundaries by grain growth significantly reduces recombination. However, the formation of defects along the back interface whereby segregation is observed may introduce new defects which can be electrically detrimental but was overshadowed by a significant reduction in recombination due to lower grain boundaries. Characterization techniques such as deep-level transient spectroscopy, DLTS, and PL can be used to study defect formation and density. Knowledge on role of Sb on defects will enable defect modeling to improve carrier properties of the absorber layer.

8.3.4 Over doping on structural, optical and electrical properties of CISSe

A common effect of excessive doping, or over doping, is precipitation. Under low Sb doping (≤ 2.0 mol%), formation of CuSbS_2 during spray pyrolysis is low. Hence, the dopants will be rejected to the grain boundaries to assist in liquid phase sintering during heat treatment. However, a high level of doping would possibly forms CuSbS_2 and CuInS_2 . They have very different crystal structure with CuSbS_2 having an orthorhombic structure and CuInS_2 having a tetragonal structure. A high level of Sb doping would precipitate CuSbS_2 and a wider doping level study would give the doping level when precipitation starts to yield. In addition, a higher doping level would enhance grain growth further and reduce porosity due to a higher level of grain densification during selenization. CuSbS_2 has a much larger bandgap of 1.70eV^{139} than CIS of 1.50eV . Selenization would result in the formation of Cu_3SbSe_4 which has a narrow bandgap of 0.31eV^{82} and CISSe which has a bandgap of around 1.10eV . As the bandgap of the two compounds are very different, the absorption spectra will also be affected. Similarly, excessive Sb doping can affect the electrical properties of CISSe. Precipitation of Cu_3SbSe_4 at grain boundaries will affect carrier transport and might be potential recombination centers. Excessive segregation of Sb might introduce greater defects along the back interface which may significantly impact the carrier

transport. Hence, a wide range of studies had to be conducted to investigate the effect of excessive doping on the properties of the CISSe absorber layer.

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List of Publications

1. **Ho, J. C. W.**; Batabyal, S. K.; Pramana, S. S.; Lum, J.; Pham, V. T.; Li, D.; Xiong, Q.; Tok, A. I. Y.; Wong, L. H., Optical and Electrical Properties of Wurtzite Copper Indium Sulfide Nanoflakes. *Materials Express* **2012**, 2, 344-350.
2. Cai, Y.; **Ho, J. C. W.**; Batabyal, S. K.; Liu, W.; Sun, Y.; Mhaisalkar, S. G.; Wong, L. H., Nanoparticle-Induced Grain Growth of Carbon-Free Solution-Processed CuIn(S,Se)₂ Solar Cell with 6% Efficiency. *ACS Appl. Mater. Interfaces* **2013**, 5, 1533-1537. (co-author, equal contribution)
3. **Ho, J. C. W.**; Zhang, T.; Lee, K. K.; Batabyal, S. K.; Tok, A. I. Y.; Wong, L. H., Spray Pyrolysis of CuIn(S,Se)₂ Solar Cells with 5.9% Efficiency: A Method to Prevent Mo Oxidation in Ambient Atmosphere. *ACS Appl. Mater. Interfaces* **2014**, 6, 6638-6643.
4. Zeng, X.; Tai, K. F.; Zhang, T.; **Ho, C. W. J.**; Chen, X.; Huan, A.; Sum, T. C.; Wong, L. H., Cu₂ZnSn(S,Se)₄ kesterite solar cell with 5.1% efficiency using spray pyrolysis of aqueous precursor solution followed by selenization. *Sol. Energy Mater. Sol. Cells* **2014**, 124, 55-60.
5. Li, Z.; **Ho, J. C. W.**; Lee, K. K.; Zeng, X.; Zhang, T.; Wong, L. H.; Lam, Y. M., Environmentally friendly solution route to kesterite Cu₂ZnSn(S,Se)₄ thin films for solar cell applications. *RSC Advances* **2014**, 4, 26888-26894
6. **Ho, J. C. W.**; Zhang, T.; Lee, K. K.; Batabyal, S. K.; Tok, A. I. Y.; Wong, L. H., Mechanism of Sb induced grain growth in solution-processed CuIn(S,Se)₂ thin films. (Under preparation)