Investigation on the effect of cation substitution in $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ thin film solar cell

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**Investigation on the Effect of Cation Substitution in
 $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ Thin Film Solar Cell**

STENER LIE

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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STENER LIE

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

.....8 August 2019.....

Date

A handwritten signature in black ink, appearing to read 'Stener Lie', is positioned above a dotted line. The signature is stylized with a large 'S' and a long horizontal stroke.

.....
Stener Lie

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

8/8/2019

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Date

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Associate Professor Lydia Helena Wong

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journal(s) in which I am listed as an author.

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The contributions of the co-authors are as follows:

- Associate Professor Lydia Helena Wong provided the project direction and revised the manuscript drafts.
- I performed the thin film synthesis and characterization at School of Materials Science and Engineering and the Energy Research Institute @ NTU. I performed device fabrication and analysis at NTU and IBM T.J. Watson. I also analyzed the data and prepared the manuscript drafts.
- Dr Joel Ming Rui Tan assisted the Raman data collection and analysis at the School of Materials Science and Engineering.
- Mr Li Wenjie assisted in the fabrication of transparent conduction oxide.
- Dr Shin Woei Leow assisted and supervised the usage of spray pyrolysis technique at the Energy Research Institute @ NTU.
- Mr Mario Indra Sandi provided the initial preliminary work.
- Mr Tay Ying Fan assisted in the X-ray photoelectron spectroscopy data collection and analysis.

- Dr Douglas M. Bishop assisted in the photoluminescence study at the IBM T.J. Watson.
- Dr Oki Gunawan assisted and guided device characterization and analysis at the IBM T.J. Watson facilities

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- Dr Maxim Guc assisted the Raman data collection and analysis at the IREC Barcelona.
- Dr Victor Izquierdo-Roca assisted in manuscript revision for Raman analysis part,
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Abstract

Thin film solar cells technology based on $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) holds great promise due to the abundance of its constituent elements and their environmentally benign nature. In recent years, developments in achieving higher device performance have been halted due to the inherent Voc deficit of CZTSSe. This poses a huge setback for the successful industrialization of CZTSSe thin film solar cells. Many agreed that cation disordering which emerge due to Cu and Zn similarity in size and chemical environment, is one of the main causes of this issue. Recent progress in cation substitution of CZTSSe with other metals have shown promising result such as Ag with Cu and Cd with Zn. However, incorporation of these elements in CZTSSe is not ideal as they deviate from the earth-abundant and non-toxic motivation of CZTSSe.

This thesis aims to explore and understand the influence of novel cation substitution in CZTSSe solar cell and focus on optimizing the promising candidates by partial substitution. Firstly, screening and comparison between suitable cations such as Mn, Mg, Ni, Fe, Co, Sr and Ba were conducted and summarized to select ideal candidate for partial substitution study. These films were prepared by chemical spray pyrolysis in stoichiometric composition to investigate its intrinsic thin film properties. Following that, non-stoichiometric composition was fabricated to optimize the solar cell device performance. The screening concluded that Manganese (Mn), Magnesium (Mg), Barium (Ba) and Strontium (Sr) emerged as the promising cations as Zn substitute.

Next, Mn was partially substituted into CZTSSe in both sulfide and selenide system to optimize the photovoltaic performance. Mn has been chosen as the first novel cation based on its half-filled d-orbital in comparison with other transition metal candidates (e.g. Fe, Ni or Co) and larger ionic size mismatch with Cu. Effects of Mn substitution in $\text{Cu}_2(\text{Mn}_x\text{Zn}_{1-x})\text{Sn}(\text{S},\text{Se})_4$ (CMZT(S,Se)) thin films, with $x = 0.0-1.0$, on the film morphology, structure, and device performance was investigated. The highest device performance and the least defect density at the heterojunction interface was obtained at

$x=0.05$. Following that, double layered structure was fabricated by sol-gel spin coating method with variation in the CMZT(S,Se) layer thickness to further optimize the performance. In this structure, the sulfoselenide film showed the highest efficiency in this study due to reduced interface defect density, and increased hole mobility and photoluminescence intensities.

Mg was chosen as the second candidate for partial substitution as it is most stable as Mg^{2+} , unlike other multivalent transition metal cations. It is hypothesized that the single oxidation states help to reduce defects or secondary phases that could be formed due to the multivalent nature of other cations. In this thesis, the effect of Mg in CZTS solar cell was investigated by varying the amount of Mg from $Mg/(Mg+Zn) = 0.0 - 1.0$. Systematic phases transformation was observed from kesterite CZTS to monoclinic Cu_2SnS_3 as the Mg amount increase based on XRD and multiwavelength Raman study. The device performance improvement by Mg was apparent at $Mg/(Mg+Zn) = 0.05$. It is attributed to the improved bulk properties such as better charge collection, lesser amount of ZnS secondary phase and shallower acceptor defects level.

To summarize, this thesis provides systematic investigation of the effect of various cation substitutes for Zn. Our investigations on the positive effects of Mn and Mg as partial substitutes of Zn, which are among the first in literature, reveal that both cations reduced different types of defects in CZTS. Finally, based on our investigation, we conclude that the following design criteria should be considered when choosing a cation substitute for Zn: 1) it should possess d-orbital to form stable quaternary compound; 2) multiple oxidation states and partially filled d-orbital cations affect the conductivity and photovoltaic performance; 3) large cation radius difference with Zn result in structure and optoelectronic properties transformation; 4) partial (instead of full) substitution of Zn could lead to CZTS efficiency improvement.

Lay Summary

Total energy consumption in the world are increasing as world population increase and modernization occurs. Most of the energy sources are derived from fossil fuel such as gasoline, oil, coal, natural gas. The limitation of the supply and emission of greenhouse gases which create global warming has been the major concern to earth sustainability and human civilization. Many people agreed that renewable energy is the pathway to mitigate this issue and one form of it is solar energy. It is considered as the source of most energy resources in earth and is widely assessible everywhere in the world. To harness the energy, solar cell or photovoltaic is one of the established technologies to convert the solar energy into the form of electricity.

Photovoltaic material is a semiconductor material which can absorb light in the sunlight spectrum and generate electricity. The current most used technology in silicon semiconductor solar cell has several limitations in terms of cost and flexibility. Its heavy and bulky nature ensues higher transportation cost to cover remote area in the world [17]. To address this issue, thin film semiconductor technology comes as the promising solution due to its very thin thickness ($<1\ \mu\text{m}$ range) which enables flexibility deployment such as solar cell window or paint, mobile solar cell attached to daily equipment. CIGS and CdTe are the type of semiconductor technology which can compete with silicon performance and have the flexibility advantage. However, rarity (indium, gallium and tellurium) and toxicity (cadmium) for some of the elements create another issue. Therefore, CZTS come as the most ideal solution for these issues, but it struggles with low performance compare with its predecessor. Substituting one of its elements in Zn has been one of the promising pathways to improve the performance [18, 19].

This thesis addresses the problem of CZTS performance by incorporating novel, earth-abundant and non-toxic metal substitute. The screening of various suitable material has seen several promising candidates which has the potential to improve CZTS such as Mn and Mg. The thesis investigates the properties of various substitute candidates and in-depth study on the promising candidates.

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Abbreviations

AC	Alternating Current
AZO	Aluminum-doped Zinc Oxide
BEI	Backscattered Electron Images
CBD	Chemical Bath Deposition
CBM	Conduction Band Minimum
CCD	Charge Couple Device
CIGS	Copper Indium Gallium Selenide
CV	Capacitance-Voltage
CZTS	Copper Zinc Tin Sulfide
CZTSSe	Copper Zinc Tin Sulfoselenide
DFT	Density Functional Theory
DLCP	Drive Level Capacitance Profiling
DOS	Density of States
EDS	Energy Dispersive Spectroscopy
EDX	Energy Dispersive X-ray
EQE	External Quantum Efficiency
FESEM	Field Emission Scanning Electron Microscopy
FF	Fill Factor
FWHM	Full Width Half Maximum
GGA	Generalized Gradient Approximation
IBM	International Business Machines Corporation
ICDD	International Centre for Diffraction Data
IEA	International Energy Agency
ITO	Indium-doped Tin Oxide
IPA	Isopropyl Alcohol
IPCE	Incident Photon-to-Current Conversion Efficiency
IQE	Internal Quantum Efficiency
IREC	Institut de Recerca en Energia de Catalunya
IV	Current-Voltage

IVT	Current-Voltage-Temperature
JCPDS	Joint Committee on Powder Diffraction Standards
JV	Current Density-Voltage
KCN	Potassium Cyanide
NIR	Near Infrared
NTU	Nanyang Technological University
PCE	Power Conversion Efficiency
PEC	Photoelectrochemical cell
PL	Photoluminescence
PV	Photovoltaic
RF	Radio Frequency
SEI	Secondary Electron Images
SEM	Scanning Electron Microscopy
ST	Stannite
UV	Ultraviolet
VB	Valence Band
VBM	Valence Band Maximum
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

In this first chapter, the thesis overview is presented. Starting from the brief introduction of the study, followed by the hypothesis. The hypothesis is that the substitution of Zn^{2+} in $Cu_2ZnSn(S,Se)_4$ solar cell with other isoelectronic metal cations will improve its performance. Based on the hypothesis, objective and scope of the thesis are described, followed by summary of the content for each chapter. The purpose of this thesis is to investigate the effect of various cation substitution in $Cu_2ZnSn(S,Se)_4$. Research findings on the novel cation substitutes quaternary compound, Mn and Mg partial substitution properties are highlighted in the last part.

1.1 Hypothesis/Problem Statement

Energy is one of the essential components of our modern life, especially electricity. Thus, as population grows and modernization occurs in the world, the demands for energy will keep increasing. International Energy Agency (IEA) forecasted that due to rising incomes and an extra of 1.7 billion people, the global energy demand will grow up by quarter to 2040 [23]. Until now the primary energy source is fossil-fuel based energy, such as coal, oil and natural gas, and they account up to 81.1% total energy supply [2]. The problem with fossil fuel energy is not a renewable energy; it takes million years to reproduce it. A study predicted their lifetime are less than 100 years with some even less than 30 years left [24]. Carbon gas emission is the other issue for fossil fuel, as it is one of the main sources for global warming.

Figure 1.1 Total primary energy sources (TPES) outlook up to 2040 by International Energy Agency (IEA) [2]. Other refers to renewable energy such as geothermal, solar, wind, tide/wave.

Due to these predictions, renewable energy play an important role to satisfy the future energy requirement (**figure 1.1**). Various technology is intensively researched and one of the promising sources is solar energy. Photovoltaics (PV) / solar cells is the technology which enables us to harvest this solar energy into electricity. It is estimated that solar cells which cover 0.16% of the earth surface would be enough to satisfy the current energy demand [25]. Crystalline silicon solar cell has been the dominant technology and has

maintained at least 80% of market of PV technology in various countries [26]. For the past few years, thin film solar cells have emerged to be the alternative for the bulky and inflexible crystalline silicon solar cell. CuInGaSe₂ (CIGS) and CdTe have been the forefront of thin film solar cell which can compete with silicon. However, their precursor materials (indium, gallium and tellurium) are rare on earth's crust [27, 28], and toxic (cadmium) [29, 30]. Cu₂ZnSn(S,Se)₄ (CZTSSe) which has a similar electronic structure to CIGS with tunable band gap of 1-1.5 eV [25, 31] (within the optimum band gap for single junction cell ~ 1.34 eV [32]) and composed of non-toxic, earth-abundant element become the next best candidate as CIGS/CdTe replacement [33]. The most recent development of CZTSSe has achieved 12.6% efficiency by hydrazine and sputtering method [34-37].

Figure 1.2 Illustration of band diagram for CIGS and CZTS which highlight defect level and recombination mechanism due to band edge potential fluctuations [10].

Theoretically, the highest single junction efficiency for kesterite CZTS and CZTSe based on Shockley–Queisser (SQ) limit are 32.4% and 31.0% [38]. While CIGS has achieved high efficiency up to 23.35% [39], CZTS/CZTSSe performance lag behind due to open circuit voltage (V_{oc}) deficit ($E_g/q - V_{oc}$) [40-42] where E_g is the bandgap and q is the electron's charge. Several reasons have been proposed, such as severe band tail effects [43], secondary phases [36], and non-ideal interface [44]. Many reported the majority defects issue as one of the main reasons for the V_{oc} deficit [43, 45, 46]. The type of majority defects in CIGS and kesterite solar cell are different. Based on theoretical calculation [47],

V_{Cu} is a shallow defects and the majority of defects in CIGS, but in CZTS/CZTSSe, Cu_{Zn} antisite which has deeper defect level in band gap play the majority defects role. V_{Cu} is a defect where Cu move out of its lattice and leaving its position vacant, while Cu_{Zn} antisite is a defect where Cu replaces Zn in the lattice. It is a stable defect owing to cation disorder which are induced by the overlapping role and similar size of Cu and Zn (**figure 1.2**). Deeper defects level is unfavorable in solar cell, because they act as recombination centers and contribute to band potential fluctuation and tailing effects. This point defects also contribute in defects-complexes formation such as $(V_{Cu} + Zn_{Cu})$, $(V_{Zn} + Sn_{Zn})$, $(Zn_{Sn} + 2Zn_{Cu})$, $(2Cu_{Zn} + Sn_{Sn})$ which can act as non-radiative recombination center [47]. Precise chemical-stoichiometric control is important in tackling this issue because Cu-poor and Zn-rich composition is one common way to engineer high efficiency solar cell [48]. Many other engineering improvements such as surface treatment [49], anti-reflection coating [50], altering the buffer layers [51] have improved the efficiency but they are not tackling the main problem of the material and thus there has been no breakthrough in the power conversion efficiency.

Hypothetically, substitution of Zn in this structure with cation with similar oxidation states (e.g. Fe, Ni, Co, Mn, Mg, etc), should lead to defects reduction and an optimized amount of partial cation substitution could improve the PCE of CZTSSe solar cell. Some of the successful results are substitution of Zn with Cd [52-55] and Cu with Ag [14, 56, 57]. Both improvements are correlated to possible decrease in Cu_{Zn} antisite defects based on better carrier lifetime, sharp absorption edge and Voc improvement. However, these substitution methods are non-ideal and digress from the motivation in developing CZTSSe as earth-abundant and environmentally friendly solar cell. Although these findings supported the hypothesis, there is still a lack of understanding in the effect of other metal substitution to CZTS/CZTSSe structure. For instances, how other novel metal substitution could improve the efficiency and Voc, whether it removes the antisite defects or affect other issues in CZTS. Thus, understanding the effect of several cation substitutions to CZTS/CZTSSe structure is important to provide better solution to the bottleneck in CZTS/CZTSSe solar cell efficiency. In addition, knowledge on the optimum amount for different metal substitutes should also be explored. Beyond this optimized amount, phase separation or

phase transformation could take place and lead to different properties which compromises the solar cell performance. For example, p-type in CZTS comes from V_{Cu} , and exceeding 50% of Cu substitution with Ag will change it to n-type. Thus, to obtain PCE improvement, partial substitution is a promising pathway of keeping the electronic structure while providing defect passivation. From this study, a guiding principle on how to do effective cation substitution in CZTSSe will be discussed as well.

1.2 Objectives

This thesis aims to investigate the cation substitution effect in $Cu_2ZnSn(S,Se)_4$ thin films solar cell and understand the principles for selection of appropriate elements for effective Zn cation substitution in kesterite solar cell. To fulfill the objective, the scope of the thesis is as follows:

1. Synthesis, device fabrication and characterization of Zn full substitution with various metal X in Cu_2XSnS_4 solar cell (where X = Mn, Mg, Ni, Fe, Co, Sr and Ba) are conducted to correlate the physical, optoelectronic and device properties. This sub-study provides the necessary understanding of stable and suitable metal cations for the subsequent partial substitution study.
2. Assessing and understanding the effect of partial Mn-substitution in both sulfide and selenide CZTSSe solar cell. Various thin film and device characterizations are adopted to investigate its structural, optoelectronic and device junction properties.
3. Investigation of non-transition metal partial substitution by fabricating $Cu_2Mg_xZn_{1-x}SnS_4$ by a combination of thin film and device characterizations.

1.3 Dissertation Overview

The thesis addresses investigations of the cation substitution effect in $Cu_2ZnSn(S,Se)_4$ thin films solar cell. Various CXTS (X = Mn, Mg, Ni, Fe, Co, Sr and Ba) compounds, partial substituted CMnZTSSe and CMgZTS thin films are assessed as solar cell device. The outline of this thesis is given as:

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning the development of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ and its recent progress. Specifically, summary of the cation substitution study is also given.

Chapter 3 provides information on the fabrication methods and characterization techniques deployed including the basic principles of the characterization techniques. Rationale for the chosen methods are also described in the chapter.

Chapter 4 elaborates the thin film and device properties of CXTS ($\text{X} = \text{Mn}, \text{Mg}, \text{Ni}, \text{Fe}, \text{Co}, \text{Sr}$ and Ba) thin films. These thin films were fabricated by spray pyrolysis. The structural and phases of these film lead to categorization into three groups; tetragonal, trigonal and non-quaternary compound. $\text{Mn}, \text{Mg}, \text{Sr}$ and Ba compounds exhibit photovoltaic response which is positive indicator for possible partial substitution.

Chapter 5 elaborates the development of partially-substituted Mn into $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$. Two type of studies were performed; bulk partial substitution in both sulfoselenide and sulfide; and double-layered structure of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ and $\text{Cu}_2\text{Mn}_{0.15}\text{Zn}_{0.85}\text{Sn}(\text{S},\text{Se})_4$ for sulfide and sulfoselenide. This chapter exhibit the benefit of Mn partial substitution in reducing defects in buffer interface and how to optimize it.

Chapter 6 elaborates the development of partially-substituted Mg in $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ solar cells. The phase transformation from $x = 0.0$ to 1.0 was explained through multi-wavelength Raman study. The device properties were also discussed among different Mg contents.

Chapter 7 summarizes the findings in this thesis and provide information on the reconnaissance work on Ba and Sr partial substitution for future studies. Concluding remarks on the whole thesis is also presented here.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Demonstrating and summarizing unique differences and similarities among CXTS ($X = \text{Zn, Mn, Mg, Ni, Fe, Co, Ba, Sr}$) films through facile spray pyrolysis method. The samples are categorized into three groups based on distinct characteristics from XRD and Raman, namely: tetragonal structure (CZTS, CMnTS, CFeTS, CCoTS), trigonal structure (CBaTS and CSrTS), and non-quaternary compound (CMgTS and CNiTS). The difficulty in forming quaternary compound CMgTS and CNiTS is evident from poor grain quality, phase separation and gradual increase in light absorption.
2. Fabricating CBaTS and CSrTS thin film through spray pyrolysis for the first time. In addition, it is also the first report on CSrTS solar cell by any fabrication method. The trigonal structure and diode response from CBaTS and CSrTS were observed.
3. Fabricating Mn substitution in $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S,Se})_4$ solar cell based on low-cost spray pyrolysis technique. Incorporation of Mn in $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S,Se})_4$ structure induces structural, phase and optoelectronic transformation as the Mn content increases. A phase transformation from CZTSSe kesterite ($x = 0$) to CMnTSSe stannite ($x = 1$) is observed with mixed phase formed in between. At $x = 0.05$, reduction of interfacial defect density at $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S,Se})_4/\text{CdS}$ leads to improvement in fill factor and Voc.
4. Constructing double layer structure of double-layered CZTSSe and $\text{Cu}_2\text{Mn}_{0.15}\text{Zn}_{0.85}\text{Sn}(\text{S,Se})_4$ solar cell. Improvement in photovoltaic was shown by acquiring the benefit of $\text{Cu}_2\text{Mn}_{0.15}\text{Zn}_{0.85}\text{Sn}(\text{S,Se})_4/\text{CdS}$ and CZTSSe as back layer. The improvement was observed in sulfide and sulfoselenide system, but the latter achieves larger increase in Voc with better junction properties. The hall measurement and photoluminescence study show the improvement in carrier mobility and photoluminescence intensity which infer larger diffusion length and carrier lifetime.

5. Fabricating $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ solar cell through spray pyrolysis method. The effect of Mg on the improved performance in $\text{CMg}_x\text{Zn}_{1-x}\text{TS}$ solar cell was observed due to bulk properties improvement. Small amount of Mg substitution managed to enhance carrier mobility, create shallower acceptor defects level, and reduce ZnS secondary phase formation. Systematic study on structural and optoelectronic properties also exhibit phase transformation and carrier concentration increase from $x = 0.0 - 1.0$.

Chapter 2

Literature Review

This chapter outlines the knowledge about $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ solar cell and its progress in past decades. The properties of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ and its limitations and progress are explained in detail. Recent cation substitution study is also summarized, as well as the advancement of novel metal substitutes such as Fe, Mn, Ni, Co.

2.1 $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ as photovoltaic material

Figure 2.1 a) Quaternary crystal structure are derived from zinc blende structure. b) Relationship between binary, ternary, and quaternary semiconductors [5].

$\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) is a earth abundant solar cell compound which is derived from its predecessor CuInS_2 (CIS) chalcopyrite structure. Chalcopyrite structure is also a derivation from zinc blende structure of ZnS (space group $F\bar{4}3m$). Their basic structures are zinc blende structure which evolve to different type with substitution and addition of different cations. These compounds are categorized as chalcogenide due to having S or Se anions. In zinc blende ZnS , Zn^{2+} form II-VI binary structure, and then in CIS, Zn was substituted by a combination of +1 and +3 charges of Cu and In with an average charge of +2. Its structure is ternary I-III-VI₂. There are two thermodynamically stable position for Cu and In in the structure which are in (001) and (201) plane which result in CuAu-like (space group $P\bar{4}2m$) and chalcopyrite structure (space group $I\bar{4}2d$) respectively (**figure 2.1**) [5]. These structure are also favored because it satisfy the local charge neutrality where the anions are bonded with two group I and two group III cations [58]. These changes give more chemical freedom to chalcopyrite structure and made them viable for solar cell application due to having lower band gap, e.g. E_g of $\text{ZnS} \sim 3.5$ eV meanwhile E_g of CuInS_2

~ 1.5 eV [59] which correspond to theoretical photon to electron conversion efficiency of 32.4% (according to Shockley–Queisser estimation [60]). CIS is a p-type semiconductor due to Cu vacancy (V_{Cu}) is easily formed with low energy formation, providing hole carriers [61–63]. Cation substitution with other elements vary the band gap value as seen in CIS, gallium substitution with indium alters the intrinsic band gap from 1 eV to 1.7 eV (commonly known as CIGS [64]). Ga could easily replace In in the structure as both has +3 charge and the difference in size leads to changes in the band gap [65].

From chalcopyrite and CuAu-like structure, quaternary structure can be derived by replacing two group III cations by one group II and one group IV atom in these two structures, to form a $I_2-II-IV-VI_4$ compound. There are three structure from this derivation which satisfy local charge neutrality. They are kesterite (space group $\bar{I}4$) from chalcopyrite, stannite (space group $\bar{I}42m$) and PMCA (space group $P\bar{4}2m$) from CuAu-like structure (figure 2.1). From these three structures, CZTSs are found to have kesterite structure as the most stable structure. A theoretical calculation study shows that CZTS, CZTSe and mixed CZTSs adopt kesterite structure due to their lower formation enthalpy compare with stannite or PMCA [48, 66]. For CZTS, stannite and PMCA have higher formation energy by 2.86 meV/atom and 3.15 meV/atom respectively. The values are even higher for CZTSe, 3.79 meV/atom for stannite and 5.53 meV/atom for PMCA. This finding is also

Figure 2.2 Absorption coefficient and band gap of CZTS obtained experimentally [11].

supported by experimental result by neutron diffraction study which concluded that CZTS and CZTSe crystallize in kesterite structure [67].

Kesterite CZTS (JCPDS 026-0575) has lattice constant of $a=5.43 \text{ \AA}$, $c=10.83 \text{ \AA}$, with c/a ratio near 2 (1.999), space group $\bar{I}4$ [68]. It has a direct band gap in range of between 1.3 eV to 1.5 eV and a high absorption coefficient of over 10^4 cm^{-1} in the visible wavelength region (**figure 2.2**) [11, 69]. Its band gap is optimum as a photovoltaic material based on Shockley–Queisser limit which calculate the maximum theoretical efficiency of a solar cell in a single p-n junction around 33.7% at band gap of 1.34 eV. Besides crystal structure, band gap and absorption coefficient, Raman shift peaks of CZTS could also provide this compound fingerprint as some XRD peaks of CZTS are overlapping with ternary structure CTS and ZnS [11]. **Figure 2.3** shows the three most intense peaks at 28° , 47° and 56° are very similar between these compounds. The presence of CTS and ZnS as secondary can be difficult to recognized. Therefore, phase purity of the CZTS sample could be observed from Raman spectra because it can help to differentiates peaks from CZTS and secondary phases such as, Cu_xS , ZnS, Sn_xS , and Cu_2SnS_3 (CTS) (**table 2.1**) The main Raman peak in

Figure 2.3 Comparison between CZTS, Cu_2SnS_3 and ZnS XRD signature peaks [1].

CZTS which belong to A1 vibration mode is found at 339 cm^{-1} . There are also other peaks which belong to other vibrational mode in CZTS such as 289 cm^{-1} , 350 cm^{-1} and 370 cm^{-1} [70-72]

Table 2.1 Summary of Raman peaks of CZTS and possible secondary phases.

Phase	Raman scattering peak (cm^{-1})	References
CZTS	289, 339, 350, 370	[70-73]
Tetragonal Cu_2SnS_3	297, 337, 352	[74, 75]
Cubic Cu_2SnS_3	267, 303, 356	[74, 75]
Monoclinic Cu_2SnS_3	260, 292, 354	[7]
Orthorombic Cu_3SnS_4	318	[74, 75]
ZnS (zinc blende)	275, 352	[76]
SnS	160, 190, 219	[77]
SnS_2	314, 215	[77]
Sn_2S_3	32, 60, 307	[77]
Cu_{2-x}S	264, 475	[78]
MoS_2	288, 384, 410	[79, 80]

Resistivity for CZTS was reported in the range around $10^{-3}\text{ }\Omega\cdot\text{cm}$ to $10^{-1}\text{ }\Omega\cdot\text{cm}$ [81]. As for carrier concentration which was measured by hall measurement have been reported in several report is ranging from 10^{16} cm^{-3} to 10^{18} cm^{-3} [80, 82-84]. The reported carrier/hole mobility range from 0.1 to $30\text{ cm}^2\text{v}^{-1}\text{s}^{-1}$ [83-85], most likely due to different film quality (defects, secondary phase) and measurement details. The mobility is lower compared to its predecessor CIGS. The CIGS mobility is ranging from $1\text{ cm}^2\text{v}^{-1}\text{s}^{-1}$ for polycrystalline thin film up to $10^3\text{ cm}^2\text{v}^{-1}\text{s}^{-1}$ for single crystal [86].

Anion substitution of Se for S improves the efficiency of CZTS solar cell. Se with a bigger atomic size than S reduces the band gap up to 1 eV [31] which results in higher light absorption and leads to higher current density of the solar cell (theoretical maximum J_{sc} from $\sim 30\text{ mA/cm}^2$ to $\sim 50\text{ mA/cm}^2$ [87]). It also changes the conduction and valence band positions which improve its band alignment with the CdS buffer layer [88]. Se

incorporation through annealing in Se vapor also improves grain growth in the thin film. Bigger grain size extends the charge lifetime and carrier diffusion length [89]. The highest efficiency for pure sulfide CZTS is 11%, while CZTSSe is 12.6% [90].

In general, the CZTSSe device structure [31, 33, 34, 91] consist of; soda lime glass as substrate followed by Molybdenum (Mo) thin film on top of the glass with thickness of 500-1000 nm. As a back contact, Mo is proven to be stable under high temperature and reactive condition [92-94]. It is also a good carrier collector due to its low resistivity which is around $5 \times 10^{-5} \Omega \cdot \text{cm}$ or less [92, 95, 96]. Following that 1.0 to 2.0 μm thickness p-type CZTSSe is deposited. To form p-n junction, n-type CdS is deposited after the absorber layer with thickness around 50 nm. To collect the charge carriers, Sn:InO (ITO) or Al:ZnO (AZO) is deposited by sputtering with a thickness of 30-100 nm. In between CdS and ITO, a thin intrinsic ZnO (i-ZnO) layer is commonly deposited to prevent leakage as CdS is usually unable to uniformly cover the rough CZTSSe layer. The last part is an electrode to help conduct the carriers to the external circuitry. Ni/Al/Ag grid are usually used. These electrodes are also deposited on Mo layer to improve charge collection.

2.2 Problems in $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$

CZTS theoretically can achieve similar efficiency as its predecessor CIGS which already reach 23.35% [39]. Many studies conclude that Voc deficit is the main issue in achieving higher efficiency. The Voc of the highest efficiency CZTSSe device is only 60% of the maximum Voc value which equals to Voc deficit close to 0.6 V [97], larger than the Voc deficit of CIGS ($\sim 0.38 \text{ V}$ [98]). Voc value corresponds to the maximum amount of voltage that can be generated in a p-n junction under light illumination. In an ideal situation, the value is equivalent to the difference between Fermi levels of the p-type (absorber) and n-type (buffer) semiconductor. Therefore, the theoretical Voc maximum of a solar cell material is its band gap. Voc deficits in solar cells mainly comes from non-radiative recombination of photo-generated charge carriers in the bulk, interfaces or surfaces. Non-radiative recombination occurs when photo-generated carriers (electron or hole) recombine and the energy is released as phonon/thermal energy instead of photon (radiative

recombination). This recombination occurs primarily when photo-generated electrons or holes are trapped in mid-gap energy states (defects) in the band gap. Extra energy states in band gap are common in semiconductor and can be beneficial when it is introduced appropriately, for example external doping in Si. It creates energy states near the band level as defects which contributes extra charge carriers to material and making the Si a p-type or n-type semiconductor. The type of charge carriers, energy state depth and position are dependent on the type of defects. Unlike Si semiconductor, both CZTS and CIGS are p-type semiconductors due to intrinsic doping from their majority intrinsic defects creating energy states close to valence band. According to theoretical calculations [9], the majority of intrinsic defects for CIGS are Cu vacancy defects (V_{Cu}) whereas for CZTS is Cu-Zn antisite (Cu_{Zn}) defects. The calculation considers atomic chemical potential of cations and their relationship with each other. Cu_{Zn} antisite defects become majority carrier owing to the similarity between Cu and Zn play in the structure. Both have similar cation radius (Cu^+ :0.74 Å and Zn^{2+} :0.74 Å in 4-fold coordination) [99], they only differ by one electron in the s orbital. Due to these majority intrinsic defects, both CIGS and CZTS suffer from non-radiative problem and reflected by the V_{oc} deficit value. The problem is that the Cu_{Zn} antisite defects in CZTS has a deeper energy level in band gap and creates larger V_{oc} deficit [47].

Figure 2.4 Calculated defect formation energy as a function of the Fermi energy for $\text{Cu}_2\text{ZnSnS}_4$. Adapted from [4].

To understand the intrinsic defects in CZTS, theoretical study on the formation energy of the defects is important. The intrinsic defects in $\text{Cu}_2\text{ZnSnS}_4$ are usually assigned to several possible lattice defects, such as vacancies (V_{Cu} , V_{Zn} , V_{Sn} , V_{S}) interstitial defects (Cu_i , Zn_i) and antisite defects (Cu_{Zn} , Zn_{Cu} , Cu_{Sn} , Sn_{Cu} , Zn_{Sn} , and Sn_{Zn}). The concentration of these defects is dependent on their formation energy. The formation energy is influenced by the atomic thermodynamic chemical potential (growth conditions) [100] and the electron chemical potential (Fermi energy) [101, 102]. **Figure 2.4** shows the theoretical calculation of defects formation energy as a function of Fermi energy under thermodynamic stable chemical potential/growth condition [4]. As the Fermi energy moves up from the valence (0 eV) to conduction band (1.5 eV) (i.e., increase in the electron carrier concentration), the formation energy of the negatively charged acceptor defects such as V_{Cu} , Cu_{Zn} , and Zn_{Sn} decreases. On the other hand, the formation energy of positively charged donor such as Zn_{Cu} , Cu_i , and Sn_{Zn} increases as the Fermi energy shift to the conduction band because the

additional electron carriers in the system. The filled circles in figure 2.4 relates to the transition energy level or ionization level of these defects (i.e., from neutral to charged states). From figure 2.4, it is shown that the formation energies of most acceptor defects are lower than the donor defects which results in p-type conductivity for CZTS. The defect with the lowest energy formation is Cu_{Zn} antisite with neutral Cu_{Zn} at 0.01 eV and goes to negative formation energy at most of the Fermi energy level. The very small and negative formation energy is the reason that Cu_{Zn} antisite become the majority and dominant intrinsic defects in CZTS (especially at Fermi energy < 0.75 , where CZTS is formed). The other acceptors defects (V_{Cu} , V_{Zn} , Zn_{Sn} , Cu_{Sn}) might also be present in smaller concentrations due to their small difference with Cu_{Zn} antisite in formation energy (less than 1 eV).

Figure 2.5 Calculated intrinsic defects energy levels within the bandgap of $\text{Cu}_2\text{ZnSnS}_4$ [9].

In addition to the formation energy, the energy level of the defects also influences the performance of solar cell devices. **Figure 2.5** shows the intrinsic defects energy levels in CZTS. The Cu_{Zn} majority defects has energy level around 0.12 eV higher above the valence band and about 0.1 eV higher than V_{Cu} . The deeper energy level in Cu_{Zn} antisite was reported to be harmful to the V_{oc} [43, 45, 46]. The deeper energy level in the band gap decrease the carriers transition energy value to be lower than the band gap (band to defect transition) which correspond to lower V_{oc} . Deeper energy level defects act as harmful non-radiative recombination centers for free charge carriers in solar cells. As more energy is

required to remove the trapped carriers from these deep defects, their presence decreases the carrier lifetime and mobility. Therefore, it would be beneficial to decrease the quantity of Cu_{Zn} antisite and many studies agreed that having Cu-poor and Zn-rich composition can lower the amount of Cu_{Zn} antisite [69, 103]. At this composition, the amount of Cu_{Zn} antisite defects are lower because the lack of Cu in the system making it less favorable to occupy Zn position. It is also proven experimentally that this composition is required for high efficiency CZTS [69, 104-106]. Thus, other strategy which can reduce the Cu_{Zn} concentration should be conducted to further improve the CZTS efficiency.

Figure 2.6 The calculated valence and conduction band shifts caused by different defects-complexes in $\text{Cu}_2\text{ZnSnS}_4$. Red color is valence band, while green color is conduction band. Adapted from [9].

Besides point defects; some of the defects-complexes in CZTS might also contribute detrimental effect toward V_{oc} . Defects in CZTS have tendencies to form defect-complexes due to the ease of formation of the acceptor defects. The defects-complexes are usually acceptor-donor pair due to attraction of these opposite charged defects. These defect-complexes are influencing the local band edge alignment, thus creating band fluctuation where the band gap is not uniform throughout the samples [4]. **Figure 2.6** shows the calculated effect of these defect-complexes to band edge energy in CZTS. ($\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}$) pair is one of the most common defect-complexes due to the high population of Cu_{Zn} and Zn_{Cu} antisite. Both defects are acceptor and donor defects with the lowest formation energy,

respectively. Fortunately, their influence on the band edges is weak as shown by the slight band edge shift. However, the formation of other antisite pairs which involved Cu_{Zn} antisite such as $(2\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}})$ have detrimental impact on the electronic structure as it decreases the band gap by 0.4 eV (conduction band shifts down) which result in very low V_{oc} . Based on its formation energy [9], having low $\text{Cu}/(\text{Zn}+\text{Sn})$ and high Zn/Sn can prevent the formation of $(2\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}})$ clusters. However, inappropriate non-stoichiometric conditions or sub-optimal ratio might also enhance the probability of forming other defects-complexes such as $(\text{V}_{\text{Cu}} + \text{Zn}_{\text{Cu}})$, $(\text{V}_{\text{Zn}} + \text{Sn}_{\text{Zn}})$, $(\text{Zn}_{\text{Sn}} + 2\text{Zn}_{\text{Cu}})$, $(2\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Sn}})$ and also secondary phases which can act as non-radiative recombination center and reduce the photovoltaic performance [47]. Therefore, precise control of composition plays important role in achieving high performance in CZTS solar cell.

2.3 Cation substitution in $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$

The instantaneous occurrence of randomly distributed Cu and Zn atoms within the lattice (cationic disorder) which create Cu_{Zn} antisite is difficult to be avoided solely by process optimization [107]. This can be experimentally observed from the study in high quality single crystal CZTSSe which confirm both existence of Cu_{Zn} antisite and disorder in kesterite CZTSSe [72, 107-110]. One of the approach to solve the defects formation issue is to influence it by introducing new elements such as doping or substitution in the material. Doping and substitution terms can be defined by the concentration of the external element in the system. If the concentration of the element is lower than 1 mol. % it is considered as doping, while substitution or alloying is when the concentration exceeds 1 mol. % with or without changing the parent kesterite structure. Doping influence the electronic, electrical, charge transport and interface properties without changing the crystal structure of the host material. Substitution of isoelectronic cation can introduce ionic size mismatch, leading to a change in lattice parameters or crystal structure of the absorber, or change the optoelectronic band properties. The definition of doping and substitution are not strict scientific terms but both terms have been widely adopted by the kesterite community [19]. There are two types of doping, isoelectronic (i.e. with oxidation states matching to the cation oxidation states) and non-isoelectronic ones (e.g. Sb). Some notable cases include Na [111], Sb [112, 113] and Li [114, 115]. These dopants have proven to improve

crystallinity and grain size, for example antimony act as a good fluxing agent during annealing. Na and Li were proposed to passivate grain boundary and reduce interface recombination. of the possibility to alter the material properties. Substitution approach might be more impactful instead of doping, because of its possibility to alter the material properties. Recently, cation substitution has been suggested as a solution to tackle the Cu_{Zn} antisite problem in CZTSSe. Some of the recent results show improvement in performance for example cation substitution by Cd for Zn [52], Ag for Cu [56, 116], and Sn with Ge [117, 118]. Below is the summary of the three most notable studies of both partial and full cation substitution in CZTS:

(a) Cadmium Substitution

$\text{Cu}_2\text{CdSnS}_4$ is reported to have suitable properties as absorber in solar cells [119]. Cd which is a good flux agent is also used to partially substitute Zn. Partial substitution of Cd into CZTS (CZCTS) was also predicted have the capability to mitigate the issue of Cu_{Zn} and Zn_{Cu} antisite defects. Grain enlargement, reduction in secondary phases and sharper absorption edges (less band tailing) have been found with Cd substitution [52, 53, 120]. Cd has larger cation radius than Cu and Zn, but it is within same group with Zn in the periodic table, so it is expected to be suitable as Zn substitute. A theoretical study predicted a low level of Cd-doping can suppress disorder in the kesterite phase across all Cu concentrations [121]. Thus, Cd partial substitution in kesterite has been agreed as one of the most promising pathways to improve CZTS performance. The photovoltaic performance findings are also in agreement. Study by Su *et al.* have proven the ability of Cd partial substitution ($\text{Cd}/(\text{Cd}+\text{Zn})=0.4$) to enhance the photovoltaic performance from 5% to more than 9% in $\text{Cu}_2\text{Cd}_x\text{Zn}_{1-x}\text{SnS}_4$ [120]. Other results by Hao *et al.* [54] is also consistent where the efficiency was enhanced up to 11.5% by 40% Cd substitution through vacuum-based sputter method. Similarly, the enhancement is also observed in sulfoselenide system with $\text{Cd}/(\text{Cd}+\text{Zn})$ ratio = 0.13 which can achieve efficiency up to 11.2% [53].

(b) Germanium Substitution

Another cation substitution study in CZTS is Ge partial substitution for Sn to form $\text{Cu}_2\text{Zn}(\text{Sn}_{1-y}\text{Ge}_y)(\text{S}_x\text{Se}_{1-x})_4$ with $0 \leq y \leq 1$ [118, 122]. Introduction of germanium into the system from Ge-Se liquid phase which act as crystallization fluxing agent improves the grain growth [123]. In addition, incorporation of large amount of Ge into the CZTS system tailors of the band gap from 1.07 eV for CZTSe to 1.91 eV for CZGS [117]. Enhancement in photovoltaic performance is also seen at $(\text{Ge}/(\text{Ge}+\text{Sn})=0.3)$ from 7 to 10.1% [124]. In general, Ge partial substitution in kesterite has shown a great promise, with various device efficiencies improvement ranging from 6.8 to 12.3% [125-128].

(c) Silver Substitution

Other substitutes in CZTS solar cell is partial substitution of Cu by Ag. The increase in V_{oc} on both CZTS or CZTSe are evident in most of the reported studies [55-57, 97, 116, 129-131]. The introduction of Ag into the system which can suppress the concentration of Cu_{Zn} anti-site pair is regarded as the main cause of the V_{oc} improvement. The significantly higher radius of Ag^+ (1.14 Å) in comparison with Cu^+ (0.74 Å) contribute to the larger theoretical formation energy of Cu_{Zn} antisite defects and Ag-related defects complexes e.g. $(\text{Ag}_{\text{Zn}} + \text{Zn}_{\text{Ag}})$ and $(2\text{Ag}_{\text{Sn}} + \text{Sn}_{\text{Zn}})$ in $\text{Ag}_2\text{ZnSnS}_4$ (AZTS) [132-135]. Ag substitution with Cu have resulted in higher carrier lifetime and also sharper absorption edges [56]. These findings indicated that Cu_{Zn} antisite dominant defects were reduced. It is also in line with the improvement in efficiency as observed at 10% Ag substitution from 9% to 10% [56]. Band tailing effect is reduced with Ag partial substitution as observed by photoluminescence. Carrier concentration is also reduced and contributed to this efficiency improvement. However, the semiconductor property of the compound changes from p to n-type at $x > 0.5$. Following this initial positive results, various amount of Ag alloying, method and strategies have been reported in improving the efficiency ranging from 7.2% to the highest of 11.2% [55, 57, 116, 129, 133, 136, 137].

2.4 Emerging cation substitute for Zn in CZTS

Table 2.2 List of possible cation substitutes for Zn in $\text{Cu}_2\text{ZnSnS}_4$

Cations with +2 oxidation state		Electronic Configuration	Criteria			References
			Earth-abundant [138-140]	Non-toxic	Quaternary chalcogenide	
Alkaline Earth Metals (Group IIA)	Beryllium (Be)	$[\text{He}]2s^2$	✓	✗	✓*	[141, 142]
	Magnesium (Mg)	$[\text{Ne}]3s^2$	✓	✓	✓	[143-145]
	Calcium (Ca)	$[\text{Ar}]4s^2$	✓	✓	✗	[143]
	Strontium (Sr)	$[\text{Kr}]5s^2$	✓	✓	✓	[135, 146-148]
	Barium (Ba)	$[\text{Xe}]6s^2$	✓	✓*	✓	[149-152]
	Radium (Ra)	$[\text{Rn}]7s^2$	✗	✗	✗	
Transition Metals	Manganese (Mn)	$[\text{Ar}]4s^2 3d^5$	✓	✓	✓	[20, 153-155]
	Iron (Fe)	$[\text{Ar}]4s^2 3d^6$	✓	✓	✓	[156-158]
	Cobalt (Co)	$[\text{Ar}]4s^2 3d^7$	✓	✓	✓	[158-161]
	Nickel (Ni)	$[\text{Ar}]4s^2 3d^8$	✓	✓	✓	[21, 162, 163]
	Copper (Cu)	$[\text{Ar}]4s^1 3d^{10}$	✓	✓	✓(as Cu^+)	
	Zinc (Zn)	$[\text{Ar}]4s^2 3d^{10}$	✓	✓	✓	
	Palladium (Pd)	$[\text{Kr}]4d^{10}$	✗	✓	✗	
	Cadmium (Cd)	$[\text{Kr}]5s^2 4d^{10}$	✗	✗	✓	[119, 164, 165]
	Platinum (Pt)	$[\text{Xe}]6s^1 4f^{14} 5d^9$	✗	✓	✗	
	Mercury (Hg)	$[\text{Xe}]6s^2 4f^{14} 5d^{10}$	✗	✗	✗	
	Copernicium (Cn)	$[\text{Rn}]7s^2 5f^{14} 6d^{10}$	✗	✗	✗	
Post-Transition Metals	Germanium (Ge)	$[\text{Ar}]4s^2 3d^{10} 4p^2$	✗	✓	✓(as Ge^{4+})	[117, 135, 154]
	Tin (Sn)	$[\text{Kr}]5s^2 4d^{10} 5p^2$	✓	✓	✓(as Sn^{4+})	
	Lead (Pb)	$[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^2$	✓	✗	✗	
	Polonium (Po)	$[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^4$	✗	✗	✗	
Lanthanide	Europium (Eu)	$[\text{Xe}]6s^2 4f^7$	✗	✓	✗	
Actinides	Nobelium (No)	$[\text{Rn}]7s^2 5f^{14}$	✗	✗	✗	

Note: *metastable; *toxic as soluble compounds

Although the three notable cations substitute (Cd, Ag and Ge) have shown promising improvements, they are not the ideal substitute for CZTS_{Se} as it digresses from CZTS_{Se} research motivation of reducing the toxicity and scarcity of constituent elements in CdTe

and CIGS. There are several other possible cation substitutes with +2 charges for Zn which satisfy the octet rule, non-toxic and abundant in earth. **Table 2.2** listed all the possible cations with +2 from different type of cations such as alkaline earth metals, transition metals, post-transition metals, and rare-earth metals. The cations were screened based on three criteria to be suitable as environmentally friendly substitutes for Zn. The first criterion is their abundance in earth's crust. The cations' abundance data is based on United States Geological Survey (USGS) agency data, particularly based on the table report by Haxel *et al.* which summarize the abundance (atom fraction) of the chemical elements in Earth's upper continental crust [138-140]. The abundance in this study does not consider the production of the elements because it is affected by various factors such as economy and technology which can convolute the discussion. In this study, the elements are considered abundant when its abundance more than 10 atoms of element per 10^6 atoms of Si, or when they are not categorized as precious or rare-earth metals. The second criterion is their toxicity. The elements toxicity is based on their Globally Harmonized System of Classification and Labelling of Chemicals (GHS) identification [166] and safety data sheets (SDS). The toxicity is solely on the individual elements and does not consider the other compounds which include the elements (e.g. salt compound, organic ligand). The last criterion is their stability as quaternary compounds. This criterion is based on theoretical calculation or experimental findings in the literature which predict or show the possible formation of quaternary compounds with the cation substitute (references in the table). Therefore, based on their abundance, non-toxicity and stability predictions as quaternary compounds, transition metal within the same period, such as Mn, Ni, Fe, Co and group IIA cations (alkali earth metals), such as Mg, Sr, Ba are selected as possible ideal substitutes (marked in blue colors). All these cations have +2 oxidation states as their stable states and have different cation radius with Zn/Cu in 4-fold coordination [99, 167]. Following are the summary of these emerging cation substitutes for CZTS:

2.4.1 Iron Substitution

Figure 2.7 Schematic energy band diagram for CFTS with different buffer layer CdS, Bi_2S_3 , and Ag_2S . The line at 0 V represents the Fermi energy after contact [14].

One of the candidates as a substitute for Zn is Fe. Fe has oxidation state +2 with ionic radius $\text{Fe}^{2+} = 0.77 \text{ \AA}$ which is quite close to $\text{Zn}^{2+} = 0.74 \text{ \AA}$ in 4-fold coordination (the atom shares electrons with 4 neighboring atoms). When Fe replace Zn, it forms $\text{Cu}_2\text{FeSnS}_4$ (CFTS) compound with stannite crystal structure (ST), $I\bar{4}2m$ space group. The stannite structure has better symmetry in the structure which lead to less cationic disorder in comparison with kesterite CZTS [168]. Many reports on CFTS thin films fabrication based on different methods such as solvothermal [158], hot injection method [169], molecular method [170], spray pyrolysis [171]. CFTS has potential to be photovoltaic absorber based on its band gap (1–1.5 eV) and high absorption coefficient (10^4 cm^{-1}) in the visible spectrum range [18]. Few reports are published on CFTS as absorber for solar cell. One of them exhibit efficiency of 0.07% with glass/Mo/CFTS/CdS/i-ZnO/AZO structure based on RF magnetron sputtering [172]. A.J. Pal group managed to synthesize CFTS with SILAR method and achieved better solar cell efficiency of 2.95% by replacing the CdS buffer layer with Bi_2S_3 [14]. The pn-junction improvement was observed in CFTS/ Bi_2S_3 in comparison with CFTS/CdS and CFTS/ Ag_2S based on their energy band level alignment (see **figure 2.7**). In terms of partial substitution, limited study has been done on Fe partial substitution with Zn as solar cell material.

2.4.2 Manganese Substitution

Figure 2.8 Stannite crystal structure of $\text{Cu}_2\text{MnSnS}_4$ [20].

Mn is another substitute to replace Zn as it has oxidation state +2. At this oxidation state, the nature of half-filled $3d^5$ -orbitals in comparison with partially filled orbital of other transition metals (Fe, Ni or Co) is a positive point for Mn [173]. In addition, the ionic radius mismatch for 4-fold coordination between Mn^{2+} (0.80 Å) and Cu^+ (0.74 Å) is also the largest in comparison with the other transition metals (Zn^{2+} (0.74 Å), Fe^{2+} (0.77 Å), Co^{2+} (0.72 Å), and Ni^{2+} (0.69 Å)) [132]. Lastly, the benefit of Mn is its higher relative availability on earth than Zn [174]. $\text{Cu}_2\text{MnSnS}_4$ (CMnTS) has stannite phase with $I\bar{4}2m$ space group symmetry as its most stable structure [141] (see **figure 2.8**).

CMnTS can be an alternative absorber layer owing to its high absorption coefficient ($>10^4 \text{ cm}^{-1}$) and suitable direct band gap (1.0–1.4 eV) [158]. Some reports in the literature on the photovoltaic performance in CMnTSSe, however they are still quite poor ($<1\%$) [155, 175–177]. A record 0.83% PCE of CMnTS solar cell with composition ratio of $\text{Cu}/(\text{Mn} + \text{Sn}) \approx 0.8$ and $\text{Mn}/\text{Sn} \approx 1.1$ was synthesized based on two-step thermal evaporation. In sulfoselenide system, the record is 0.33% based on sol-gel technique [178]. One possible reason for these poor performances comes from the high majority carrier concentration ($\sim 10^{19} \text{ cm}^{-3}$) [176]. Partial substitution study on the thin film properties of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}$

$x\text{SnS}_4$ has been reported [179]. Nonetheless, no study has reported the effect of Mn to the solar cell device performance in $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ when the author started his PhD.

2.4.3 Nickel Substitution

Figure 2.9 Photovoltaic device structure diagram with glass/Mo/CNTS/CdS/Al-ZnO/Al architecture [21].

One of the other alternatives is Ni as a substitute for Zn. Ni has oxidation state +2 with smaller ionic radius as compared to Zn where the ionic radius of Ni^{2+} is $0.69 \text{ \AA}$ while Zn^{2+} is $0.74 \text{ \AA}$ [99]. Several experimental studies have been reported on CNTS based on various synthesis methods such as hot-injection, solvothermal and hydrothermal to obtain nanoparticle CNTS [163, 180-184]. Looking at its optical properties, CNTS has a similar electronic structure to CZTS with band gap of $1.5\sim 1.6 \text{ eV}$ and high optical absorption coefficient of $\sim 10^6 \text{ cm}^{-1}$ [21, 163, 180]. CNTS is calculated to have zinc blende crystal structure with the $\text{P}\bar{4}2\text{c}$ polytype as the thermodynamically most stable phase [21]. In terms of photovoltaic performance, there are two solar cell architectures which show photovoltaic response. The first architecture is glass/Mo/CNTS/CdS/Al-ZnO/Al which is commonly used in CZTS, however it only exhibits 0.09% efficiency (see **figure 2.9**) [21]. The other structure is by utilizing ZnS coated on ZnO nanorods. The ITO/ZnO-nanorods/ZnS/CNTS/Au architecture managed to exhibit better solar cell performance of 2.71% [22]. In terms of partial substitution, limited study has been done on Ni substitution with Zn.

2.4.4 Cobalt Substitution

Figure 2.10 Schematic diagram of device structure: (a) ITO coated glass substrate, (b) ITO patterning (c) ZnO seed layers (d) ZnO Nanorod arrays, (e) ZnS coated ZnO nanorod, (f) CCoTS on ZnS coated ZnO nanorod, (g) completed device with Au electrode [22].

Co is the other alternatives from transition metals as Zn replacement. Co has oxidation state +2 with smaller ionic radius but very close to Zn where the ionic radius of Co^{2+} is $0.72 \text{ \AA}$ while Zn^{2+} is $0.74 \text{ \AA}$. Several reports have shown the fabrication of $\text{Cu}_2\text{CoSnS}_4$ thin film using solution methods [158-161, 185]. Based on the study by Murali *et al.* [159], $\text{Cu}_2\text{CoSnS}_4$ thin films which were fabricated by spin casting solution route has stannite crystal structure (space group $I\bar{4}2m$) with band gap of 1.4 eV and absorption coefficient of 10^4 cm^{-1} . The fabricated thin films were shown to have potential as photodetector with current amplification from $\sim 1.9 \times 10^{-6} \text{ A}$ in the dark to $\sim 2.2 \times 10^{-5} \text{ A}$ at AM1.5 illumination. There have been no studies on utilizing $\text{Cu}_2\text{CoSnS}_4$ thin film as CZTS layer substitute in thin film solar cell application. However, $\text{Cu}_2\text{CoSnS}_4$ layers on top of ZnS coated on ZnO

nanorods in the ITO/ZnO-nanorods/ZnS/CCoTS/Au architecture yielded 3.23% (see **figure 2.10**) [22]. In terms of partial substitution, Pinto *et al.* reported $\text{Cu}_2\text{Co}_x\text{Zn}_{1-x}\text{SnS}_4$ films which were fabricated using solvothermal method and annealed to become kesterite $\text{Cu}_2\text{Co}_x\text{Zn}_{1-x}\text{SnS}_4$ [186]. However, the study concluded that due to secondary phase, further improvements in the film morphology and phase purity are required for solar cell application.

2.4.5 Magnesium Substitution

Besides transition metal candidates (Mn, Fe, Ni or Co), group IIA can also be a novel cation substitute for Zn in CZTS. The multivalent properties of transition metals may form harmful deep level defects and group IIA element does not possess this issue [136, 187]. Mg is one of the viable candidates from this group which is very stable in +2 oxidation states, abundant and non-toxic. In addition, Mg also possess advantage compare with Zn because the Mg secondary phases such as MgS and MgSe are instable in solution. Meanwhile, the Zn-based secondary phases such as ZnSe and ZnS are prone to form during CZTSSe fabrication and their existence contribute to reduction in photovoltaic performance [145, 188]. Moreover, the amount of Mg availability in earth is also higher than Zn content [28].

There is a conflicting conclusion on $\text{Cu}_2\text{MgSnS}_4$ formation in the literature. A study predicted complete phase separation [131], while another predicted formation of stable phase [143]. Nevertheless, few groups reported experimentally fabrication of $\text{Cu}_2\text{MgSnS}_4$ nanoparticles and thin film by solution methods with kesterite structure (space group $I\bar{4}$) and bandgap from 1.63–1.76 eV [145, 189]. In terms of partial substitution, some experimental studies on Mg incorporation into $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ have been conducted using both vacuum and non-vacuum based method [145, 189–193]. $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ was fabricated by pulse laser deposition technique which exhibits p-type conductivity with band gap ranging from 1.3–1.5 eV [193]. One study exhibit enhancement in the grain sizes and increase of carrier concentration from 7.55×10^{16} to $6.4 \times 10^{18} \text{ cm}^{-3}$ at 20% of Mg substitution with Zn [191]. Other study partially substitute Cu with Mg in $\text{Cu}_2\text{ZnSnSe}_4$

which result in a significant hole mobility increase (36.5 to $120 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [190]. In terms of photovoltaic performance, Caballero *et al.* recently reported efficiency improvement from 5% to 7.2% for $\text{Cu}_2\text{Zn}_{1-x}\text{Mg}_x\text{Sn}(\text{S},\text{Se})_4$ at $x = 0.04$. It is attributed to reduced structural defects at this composition although phase separation was observed at high Mg content.

2.4.6 Barium Substitution

Ba is another candidate for Zn substitution. It comes from the group IIA and has very large ionic radius Ba^{2+} ($1.49 \text{ \AA}$) in comparison with Zn. Ba is calculated to form the $\text{Cu}_2\text{BaSnS}_4$ (CBTS) quaternary structures with trigonal structure (space group $P3_1$) and band gap of $1.7\text{--}2.1 \text{ eV}$ [148, 194]. It has out of the bandgap or very shallow Ba-related defects (V_{Ba} , Ba_i , Ba_{Cu} , Cu_{Ba} , Ba_{Se} , Se_{Ba} and Sn_{Ba}), except that Ba_{Sn} ($0.1\text{--}0.2 \text{ eV}$ higher than VBM). In addition, the formation energies of Ba-related antisite (Ba_{Cu} , Cu_{Ba}) are relatively higher than CZTSSe antisite defect. The high formation energy suggests the low disorder between the cations. Several studies have fabricated CBTS using vacuum based process [151, 195, 196]. The first CBTS device is obtained at 1.62% efficiency with device structure from CZTS solar cells, ITO/i-ZnO/CdS/CBTS/Mo/glass. Similar with CZTS, the incorporation of Se anions replacing S reduce the bandgap up to 1.5 eV which makes it closer to the optimal value for single-junction solar cell. The power conversion efficiency managed to reach the record efficiency of 5.2% [151]. Higher performance should be expected with future optimization and more in-depth understanding of the materials. In addition, CBTSSe has also been fabricated in solution-based process [152, 197] and shown promising results in photoelectrochemical water reduction technology too [149, 195]. In terms of partial substitution, limited study has been done on Ba partial substitution with Zn as solar cell material.

Chapter 3

Experimental Methodology

In this chapter, experimental procedure to synthesize and fabricate various thin film and solar cell devices are described including their selection reasoning. The description of these experimental methods should provide basic knowledge of the projects. In addition, the technical detail could provide information for future research in this field. Lastly, introduction of the characterization techniques (e.g. X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis absorption spectroscopy, Raman spectroscopy, energy dispersive X-ray spectroscopy (EDS), incident photon to charge carrier efficiency (IPCE) or external quantum efficiency (EQE), current-voltage measurement (I-V), hall measurement, photoluminescence (PL) spectroscopy, capacitance voltage (CV) measurement and X-ray photoelectron spectroscopy (XPS)) are presented and explained to give a broader knowledge of the techniques.

3.1 Rationale for selection

The projects described in **Chapter 4-6** adopted spray pyrolysis method to fabricate various cation chalcogenide Cu_2XSnS_4 ($\text{X} = \text{Zn, Mn, Mg, Ni, Fe, Co, Sr and Ba}$), $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn(S,Se)}_4$ and $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$. The reasons for choosing the fabrication methods are summarized below: (i) spray pyrolysis is a low-cost fabrication method which is scalable for industrial applications; (ii) spray pyrolysis is a facile and efficient method to fabricate novel thin film by simply changing the precursor material; (iii) various work using spray pyrolysis has proven to fabricate high quality CZTS solar cell.

In **Chapter 5**, spin coating is also chosen to deposit $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn(S,Se)}_4$ and $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$. It is a low-cost and simple method to tune the ratio of cations. This method has been reported to achieve one of the highest efficiency cation-substituted kesterite solar cell. In addition, the sequential deposition process enables control over the layer by layer composition.

In all three chapters, subsequent processes to fabricate good quality kesterite solar cells were adopted. After the film deposition by spray pyrolysis or spin coating, the film is subjected to annealing in S (sulfurization) or Se (selenization) environment, chemical bath deposition of CdS, sputtering for i-ZnO and transparent conducting oxide (Al-ZnO/In-SnO). Slight modifications of processing conditions (i.e. temperature, time, etc) were adopted to optimize the quality of different absorber thin films.

Detailed descriptions on the steps of these fabrication methods are listed in the following section.

3.2 Experimental methods

Figure 3.1 Schematic diagram of the fabrication procedure in this study.

Figure 3.1 shows an overview of the fabrication procedure in this thesis. In general, all the chapters are following the same procedure. The details and differences between procedures for different chapters are discussed at the specific sections below.

3.2.1. Fabrication of Cu_2XSnS_4

The samples were prepared by spray pyrolysis method. The precursor solution was made by dissolving copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.06 M), tin chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 0.036 M) and thiourea ($\text{CH}_4\text{N}_2\text{S}$, 0.64 M) into 50 cm^3 D.I. water. Following that, variation of cation with +2 oxidation states (0.044 M) was added, either zinc chloride (ZnCl_2), manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), nickel chloride (NiCl_2), iron (II) chloride (FeCl_2), cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) or barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$). All precursors were purchased from Sigma Aldrich with purity of 99.99%. There are two type of precursors made, the stoichiometric ratio ($\text{Cu molarity} = 0.072 \text{ M}$) and non-stoichiometric one. Deviation in the non-stoichiometric ratio were Cu-poor ($\text{Cu}/(\text{Zn}+\text{Sn}) = 0.75$) and X-rich ($\text{X}/\text{Sn} = 1.2$) composition which are common technique to decrease Cu-Zn antisite defects [69]. These ratios were optimized to obtain the highest CZTS efficiency for the spray pyrolysis procedure. Common salts were preferred because of their abundance and cost, especially chloride salts are chosen here due to their solubility and ease of dissociation into metal ions in aqueous solvent. Excess amount of thiourea was added above the stoichiometric ratio to compensate the S loss during spray pyrolysis. Dilute HCl (0.1 mol) was added to adjust the pH value to 2. It is to ensure solution stability and no precipitation appear during the spraying process. SnCl_2 in H_2O are prone to precipitate into SnO_2 which can disrupt the solution flow during spray [198, 199].

Before spray coating, Mo-coated glasses substrates were cleaned using Alconox® detergent, ethanol, isopropyl alcohol (IPA) and D.I. water in ultrasonic bath. **Figure 3.2** shows the schematic of the spray pyrolysis. Several important parameters such as hot plate temperature (723 K = 553 K substrate temperature), gas pressure (~138 kPa), solution flow rate (~0.027 cm^3/s), spray distance (0.45 m) and precursor concentration are optimized to obtain 1 μm thin film. Peristaltic pump controls the spray flow rate. Spray head was automatically moved in X and Y direction by motor controller to ensure uniform distribution on substrates.

Figure 3.2 Schematic illustration on spray pyrolysis process.

The as-deposited films were annealed in S-rich condition (sulfurization) at 873 K for 2400 s with 1800 s ramping from room temperature (~ 0.32 K/s) in two-zone tube furnace. The furnace setup is shown in **figure 3.3**. The setup was used for both sulfurization and selenization. The samples were placed in one zone and S source (~ 0.3 g) in other zone of

Figure 3.3 Schematic of two-zone furnace setup for high temperature annealing (top) picture of the setup (bottom)

the furnace with lower temperature (473 K). The chamber was coated with alumina coating as insulator to maintain the chamber temperature. Before sulfurization starts, purging with argon gas was done and then the tube was filled with Ar gas (~30 kPa). During annealing the valve were closed to maintain the chamber pressure and prevent leakage of gas.

Figure 3.4 Picture of standard sample configuration consist of 16 samples in 2x2 cm² substrate.

Following the thin film fabrication, solar cell device with configuration of Mo/CXTS/CdS/ITO/Ag-paste were made. Chemical bath deposition (CBD) of CdS buffer layer was operated at 353 K for 480 s. Cd(SO₄) (0.015 M), CH₄N₂S (0.75 M) and NH₄OH (28~30%) were used as precursor to obtain n-type CdS. Following that, Sn:InO (ITO) window layers were sputtered on top of CdS with a thickness around 100-200 nm. The devices were annealed at 573 K for 600 s in argon atmosphere (~30 kPa). The post device annealing was done to improve the device performance. Various reasons such as redistribution of Cu and Zn, recrystallization of CdS and ITO which improve absorber-buffer layer interface were attributed as the effect of these post device annealing [200-203]. After that the samples were manually scribed to make grid with each square have area of 0.16 cm² (active area of 0.15 cm²). Finally, Ag paste was put on top to act as electrode. **Figure 3.4** shows the picture of 16 samples in a 2x2 cm² substrate.

3.2.2 Fabrication of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ and $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$

3.2.2.1 Fabrication of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$

The samples fabrication of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ follows similar procedure as chapter 3.2.1. It is prepared by spray pyrolysis method with similar precursor and substrate preparation. The annealing method has several differences. The as-deposited CMnZTS were annealed in Se atmosphere (selenization) at 833 K for 1800 s with 600 s ramping (~ 0.9 K/s) to obtain CMnZTSSe thin films. While the Se source was heated to 673 K. In addition to the Se in the source zone (~ 0.3 g), extra Se pellet (~ 70 mg) put underneath the samples in the sample zone of the furnace. Before selenization starts, purging with argon gas was done and then the tube was filled with Argon gas (~ 30 kPa).

The solar cell configuration also differs with the intrinsic ZnO (i-ZnO) and Al:ZnO (AZO) as the transparent conduction oxide layers (glass/Mo/CMnZTSSe/CdS/i-ZnO/AZO/Ag-paste). 50 nm i-ZnO followed by 300 nm AZO were sputtered on top of CdS. The post device annealing was not conducted to the sulfoselenide system, because it degrades the intrinsic ZnO layer and provide leakage pathway which shunt the device. Similar amount of 16 samples (0.16 cm^2) were produced in a $2 \times 2 \text{ cm}^2$ substrate.

3.2.2.2 Fabrication of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$

The $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films preparation adopt different method which is sol-gel spin coating technique. The precursor solutions consist of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.36 M), $\text{MnCl}_2 \cdot 5\text{H}_2\text{O}$ / ZnCl_2 (0.25 M), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2M) and $\text{CH}_4\text{N}_2\text{S}$ (1.44 M) in 3 cm^3 of 2-methoxyethanol with ethanolamine and triethanolamine as additive. The precursors were stirred at 323 K for 3600 s until yellow transparent solutions were obtained. These precursors were taken in the ratio of $\text{Cu}/(\text{Zn}+\text{Mn}+\text{Sn}) = 0.8$ and $(\text{Zn}+\text{Mn})/\text{Sn}$ is 1.25 with excess $\text{CH}_4\text{N}_2\text{S}$. These ratios were different with the spray pyrolysis procedure and has been optimized to obtain highest CZTS efficiency by this spin coating procedure. Then the prepared solutions were spin-coated on molybdenum glass substrates at 314.16 rad/s for 30 s followed by preheating at 553 K for 180 s on a hot plate in air. This spin-coating was repeated thirteen

times to obtain around 1 μm thickness. Following this spin coating is the similar sulfurization, CBD and sputtering as mentioned previously to obtain glass/Mo/CMnZTS/CdS/ITO/Ag-paste configuration.

For the double-layered structure, several layers of CZTS were spin coated followed by $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$, starting from the control sample of 13 layers of CZTS, then proceeded by substituting 1 to 5 layers of CMZTS as the top layers while maintaining total of 13 layers. After that, the samples were annealed in similar procedure as mentioned previously. For sulfide film, they were annealed at 873 K for 2400 s in S atmosphere. For the sulfoselenide film, the films were annealed with Se atmosphere at 833 K for 1800 s.

3.2.3. Fabrication of $\text{Cu}_2\text{MgZnSnS}_4$

The fabrication of $\text{Cu}_2\text{MgZnSnS}_4$ is similar to chapter 3.2.1. The precursor solution consists of copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.06 M), magnesium chloride hexahydrate/zinc chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}/\text{ZnCl}_2$, 0.044 M), tin (II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 0.036 M) and thiourea ($\text{CH}_4\text{N}_2\text{S}$, 0.64 M) into 50 cm^3 D.I. water. Cu-poor ($\text{Cu}/(\text{Zn}+\text{Sn}) = 0.75$) and $\text{Mg}_x\text{Zn}_{1-x}$ -rich ($\text{Mg}_x\text{Zn}_{1-x}/\text{Sn} = 1.2$) composition was used. The as-deposited $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ samples were sulfurized at 873 K for 2400 s.

Following the spray pyrolysis is the similar sulfurization, CBD and sputtering as mentioned previously to obtain glass/Mo/CMgZTS/CdS/ITO/Ag-paste configuration. The devices were subjected to similar post device annealing at 573 K for 600 s. Similar amount of 16 samples (0.16 cm^2) were produced in a 2x2 cm^2 substrate.

3.3 Characterizations

Several characterization methods were done to both films and devices in chapter 4, 5 and 6 study, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis absorption spectroscopy, Raman spectroscopy, energy dispersive X-ray spectroscopy (EDS), incident photon to charge carrier efficiency (IPCE) or external quantum efficiency (EQE), current-voltage measurement (I-V), hall measurement, photoluminescence (PL)

spectroscopy, capacitance voltage (CV) measurement and X-ray photoelectron spectroscopy (XPS)

3.3.1. Scanning Electron Microscopy (SEM)

Figure 3.5 Electron-specimen interaction volume [12].

The morphology of the after-sulfurization/selenization thin films were investigated by field emission scanning electron microscopy (FESEM, JOEL, JSM-7600F). FESEM was operated in secondary electron imaging (SEI) mode with 5 kV accelerating voltage. SEM is a technique to obtain the morphology on the surface of sample by collecting the signal from electron-sample interaction. In SEM, electron is produced by filament cathode which is heated by a current. The electron is then accelerated and focused by condenser and objective lenses. These are electromagnetic lenses which able to alter electron trajectory as it passes by. As accelerated electron reaches the samples, electron-sample interaction yields various signals. The electrons will sweep across rectangular shaped area (called “Raster”), the signals generated from electron-sample interaction will be collected by different type of detectors according to their signals.

Figure 3.5 shows the various signals produced from electron-specimen interaction [12]. Secondary and backscattered electrons are the most commonly used signals in SEM. Secondary electrons are used to do topology imaging in SEI mode. Backscattered electrons

are used to distinguish different components in a multicomponent material in BEI mode. In this study, SEI mode is the focus. Secondary electrons are produced through inelastic scattering between k-shell in the atom and focused electron beam. Secondary electrons are low in energy and only obtainable near surface. These emitted secondary electrons are collected by detector. The most common detector is Everhart-Thornley detector. This detector has positively charged surface to attract secondary electrons and emit light as the secondary electrons are collected. Light is then guided by total internal reflection in a light pipe to a photomultiplier which converts the light to and amplifies it to an electronic signal and converted into digital image on screen. Beside surface images, SEM can also study the cross-section image of thin film by preparing and putting the samples on a specific sample holder. In this study, both cross section and plan view images from SEI mode were mainly characterized due to the focus to understand the thickness, thin film density, compactness, grain size and quality. Grain size distribution analysis were done by measuring the size of the grains (random sampling) from the both plan and cross section view using ImageJ software.

3.3.2 Energy Dispersive X-ray Spectroscopy (EDS)

EDS detector is attached to FESEM (FESEM, JOEL, JSM-7600F), so EDS measurement was also done concurrently with SEM by collecting the X-ray dispersion from electron bombardment. The accelerating voltage was increased to 20 kV to increase the signal produced. EDS is a quantitative and qualitative technique to investigate the chemical composition of a system. For EDS, the signals are produced in similar manner as SEM image, but in EDS, characteristics X-rays signal are used. Characteristic X-rays is X-ray waves which is emitted as electrons make transition from outer electron shells to the inner electron shells. One of the interactions that the accelerated and energetic electron beams made is excitation of electrons of the inner shells and leaves a vacancy. Thus, outer shells electron fills the vacancy and emit X-ray waves as the excess energy is released. The excess energy comes from the outer shells electrons which have higher energy than inner shells electrons. There various kind of characteristic X-rays which depend on which outer and inner shells the electron moves, for example if electron from L-shells (outer) move to K-

shell (inner), $K\alpha$ X-ray is emitted. The X-rays emitted during the process are collected by a detector, usually it is a solid-state X-ray detector which measure the relative abundance of emitted x-rays versus their energy. It creates a charge pulse that is proportional to the energy of the x-ray. The charges are sent and processed to a computer. It is displayed as the spectrum of x-ray energy versus counts. The energy of the emitted X-ray is unique, and it varies between elements as it depends on the elements' electron shells. Thus, identification of element can be carried out by collecting the characteristics x-ray signal and do comparison with reference spectra. From EDS, the ratio between elements can be analyzed to confirm the cation substitution in the thin film. However, several sources of inaccuracy in EDS [204] may include variation in sample qualities, instrumentation or data analysis. Insufficient signal counts can reduce the confidence in the chemical identification due to noise signal from sample contamination or local background. EDS quantitative analysis requires adequate amount of counts in the spectrum to have characteristic peak of interest above the background or contamination signals. Proper EDS energy calibration also needs to be done, if the energy calibration is not correct, then the X-ray peaks will appear in the wrong locations or increase error in calculation. The instrument also needs to be maintained and calibrated to avoid errors such as from inaccurate or instable electron beam. Inaccuracy from excessive dead time which cause an EDS spectrum with no peaks or "coincidence events" can occur when multiple X-rays enter at the same time are not recognized as distinct events and incorrectly placed in the EDS spectrum (energy histogram). Inaccuracy can also come from the software identification program for example because it is based on energy dispersive where some elements could have overlapping signal peak and misidentified.

EDS measurements were conducted on the plan view samples after high temperature annealing (sulfurization or selenization). To provide statistical confidence, the EDS measurements in this study were presented by the median value and standard deviation of each element's atomic percentage as well as their respective ratios from sampling of five different sampling area (x5000 magnification) within a sample. The median value is taken by averaging the five atomic percentage value. As for standard deviation the formula $s =$

$\sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}}$ (s = standard deviation, N = number of sampling, x_i = value of a sample item and $\bar{x}$ = mean value) were used.

3.3.3 X-ray Diffraction (XRD)

Figure 3.6 The reflected/diffracted incident X-rays on successive planes [3].

The material structure was determined by XRD (Bruker D8 Advance Diffractometer). In general, the definition of X-ray Diffraction (XRD) is phenomenon of scattering of incident X-rays by crystal atoms (atomic planes). These scattering X-rays produce diffraction pattern which contain crystal structure information of the system. Only coherent/elastic scattering are used in XRD, because it reflects the atomic arrangement, as the incoherent scattering is affected by other factors such as fluorescence. X-rays beam is used to characterize the crystal structure because their wavelength is comparable to inter-planar spacing of atoms. X-rays are diffracted by the atom (scattering points) that are arranged in planes on a space lattice that defines their arrangement in three dimensions. So, the crystal structure could be identified by collecting the diffracted pattern of the X-rays. However, there are many diffracted X-rays beam and according to the property of electromagnetic waves, waves can interfere with each other, so only diffracted X-rays which are in-phase or undergo constructive interference could be recorded. The signal in constructive interference can be propagated and detected by the detector, while the out of phase waves undergo destructive interference and eliminated. In general, the waves reflected by

successive lattice planes will not be in phase, but this condition can be satisfied by adjusting the incident beam angle. **Figure 3.6** shows geometrical representative of the in-phase diffraction by successive lattice planes. So, there is a certain angle which the constructive interference occurs, and high intensity signal will be received. From this signal, crystal plane identification can be done according to Bragg law:

$$n\lambda = 2d_{hkl} \sin(\theta)$$

where n is integer number, λ is X-rays wavelength, θ is the incident angle and d_{hkl} is the inter-planar distance between hkl planes. hkl is the notation of crystal plane according to miller indices. It represents the geometry of the planes.

In this study, XRD measurement was operated in two-theta configuration with glazing angle of 4° , voltage of 40 kV, current of 40 mA, and X-ray source: Cu K-alpha, 0.15418 nm (Bragg-Brentano). The measurement starts from two theta range of 10° to 80° with step size of $0.01^\circ/\text{S}$. This two-theta range is the range of kesterite, stannite or trigonal main peaks. However, some secondary phases' peaks are difficult to distinguish, because XRD result only show peaks which correlate with crystal structure, and secondary phases with same structure will have similar peaks. Rietveld analysis was also carried out using Fullprof software to obtain the lattice parameter.

3.3.4 UV-vis Absorption Spectroscopy

Absorption studies were conducted on Shimadzu UV-3600 with integrated sphere setup scanning range from 300 nm to 1500 nm. UV-Vis spectroscopy is a spectroscopy technique to obtain the material absorption spectra of a material which can lead to semiconductor bandgap determination after illumination of specific wavelength light. Before sample measurement, a baseline scan (substrate without samples) is performed. The value of bandgap can be determined by creating Tauc plot. In this plot, photon energy is plotted against the quantity $(\alpha h\nu)^{1/r}$, with $r = 1/2$ in this study because of direct band gap nature of these films. r is a quantity based on the nature of the energy transition in the band gap [205]. In Tauc plot, there is a linear region which denotes the onset of the absorption for the material. Thus, by extrapolating a linear line to the x-axis, the value of the band gap is

obtained (see **figure 4.3**). In this study, the samples were exfoliated from Mo substrate to glass substrate by using epoxy resin which was left overnight. Manual exfoliation was then performed to separate the glass/sample with the Mo [206, 207]. The exfoliation was conducted on the same samples used in other characterization to ensure consistent correlation across different characterization result.

3.3.5 Raman Spectroscopy

Raman spectroscopy measurement is also adopted to find any coexisting secondary phases which cannot be identified effectively by XRD. Raman spectroscopy measurement was conducted in two places, NTU and IREC. For NTU Raman, the excitation wavelength is 532 nm, it is conducted in Renishaw system 2000 with fast data acquisition setup and low penetration depth for surface characterization. For Raman scattering spectra designed in IREC, it were measured using the Horiba Jobin-Yvon FHR-640 spectrometer coupled with a CCD detector and excited by solid-state laser YAG:Nd (laser line 532 nm, 785 and 325 nm). Raman spectroscopy is a technique to obtain chemical information from a system through identification of the inelastic scattering phenomenon [208]. At the core of Raman spectroscopy theory is the idea that molecules in a material can vibrate and have vibrational energy states. When light shine to a material, the light can be absorbed, scattered or transmitted. Most of them are scattered, there are two types of scattering, elastic scattering and inelastic scattering. Scattering phenomenon can be described as when the molecule in the material are vibrated and excited by the photon to virtual vibrational energy states and then relax back to lower states. For elastic scattering/Rayleigh scattering, the molecule falls back to the initial vibrational energy states, but for inelastic scattering, the molecule falls back to either energy states above the initial states which is called stokes scattering or energy level below initial states which is called anti-stokes scattering. When the molecule falls back to lower states, they are also emitting light/photons according to the energy difference from the virtual and final states. These lights are signals which Raman spectroscopy used and collected. In Raman spectroscopy the signal is characterized by the difference between wavelength of incident photons/lights and scattered photons/lights, it is also called Raman shift (cm^{-1});

$$\bar{\nu} = \frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}}$$

Raman spectroscopy can identify chemical phases and composition of a system, because each chemical phases and composition carry a fingerprint. The inelastic scattering that occur are dependent on vibrational, electronic and rotational energy of the material. These variables are related to the atomic bonding and position in a phase, these atoms interaction with photons are unique. Thus, by analyzing the value of Raman shifts in the system and comparing it with literature, identification of material phases, secondary phases and contamination can be detected.

3.3.6 Current-Voltage Measurement (I-V)

Besides material characterization, device characterization was done through I-V measurement and IPCE. I-V measurement is a technique to measure the efficiency of a solar cell device. In I-V measurement, a solar simulator will shine light with 1 sun intensity and photon spectrum resembling the sun at AM1.5 (1 sun is a standard illumination at AM1.5, or 1 kW/m²). AM1.5 is a standard spectrum in solar cell measurement based on the air mass coefficient (AM) which correspond to the path length which light takes through the atmosphere and used to help characterize the solar spectrum after it traveled through the atmosphere. The 1.5 corresponds to a solar zenith angle of 48.2° and represent the overall yearly average solar angle for mid-latitudes [209]. Then, two probes (positive and negative) will connect to both electrodes to measure the current (I) and voltage (V) of the devices as light shines on it. The current comes from the excitation of charge carrier while voltage comes from bias in p-n junction. The measurement is also carried out by varying the current or voltage and measure the response in a form of I-V curve. From measurement under light, open circuit voltage (Voc), short circuit current (Isc), series resistance (Rs) and shunt resistance (Rsh) could be obtained. Voc and Isc comes from the device, Voc is obtained at current equals to zero or open circuit condition while Isc is obtained at zero bias or short circuit condition. From these two points, I-V curve is then obtained from the response by varying current and voltage under light illumination. Rs value represents the resistance that inhibit charge collection and is expected to be low,

while R_{sh} value indicates how the free charge carriers conduct within device. The free carriers are expected to mainly only conduct through the p-n junction to the electrode, when it is the case R_{sh} value is high, however if there is secondary phases or direct connection between electrodes which enable free carrier to flow through other path, R_{sh} value will be low. There is also another measurement which is called dark current measurement. It is a measurement of solar device under no light to obtain response in current or voltage as they are varied. From dark current, the material (absorber) characteristics could be understood, whether the material is shunting or too conducting, or its compatibility in making a p-n junction with buffer layer.

In this study, I-V measurement were collected by Keithley 2612A SourceMeter as the current and voltage measuring tools while simultaneously provides current and voltage to system. The four solar cell parameters (V_{oc} , J_{sc} , efficiency and fill factor) from multiple devices are shown in box plot to provide statistical consistency. The specific number of samples in a study is mentioned in the respective discussions (minimum number of samples are 16 samples which is the number of samples per one batch of fabrication). The box range shows the standard deviation of the result with center line as the median value, the small rectangle shows the mean value, the cross sign shows the 1% lower limit and 99% upper limit of the data. The solar cell parameters for important cells (i.e., champion cells and control) including diode parameters such as ideality factor η_1 , reverse saturation current J_{01} , series resistance (R_s) and shunt conductance (G_{sh}) are extracted by Lambert-W curve-fitting method to a single diode model. [210] The single diode model is an equivalent circuit model for a single junction solar cell. The Lambert-W curve fitting method is a fitting technique based on the Lambert-W mathematical function which is also known as the product log function, which is able to solve problems where the variable is both as a base and an exponent (it is the inverse of $f(x) = xe^x$). The details of the usage of the Lambert-W function to fit and extract the parameters is explained in the study by Zhang *et al.* [210] The fitting and parameter extractions were performed by the software provided by IBM-PVX system.

Other important parameters, the measurement is carried out under 1.5 AM Illumination (international standard for light source in I-V measurement inside lab) at room temperature (San-EI Electric, XEC-301S solar simulator). In addition, current-voltage measurement with extra variable of temperature (IVT) can describe the dominant recombination mechanism in the solar cell. From V_{oc} vs temperature characteristics, the extrapolated V_{oc} intercepts at 0 K correspond to activation energy (E_A). If E_A less than the band gap ($E_A < E_g$), it means the recombination mechanism is dominated by interface recombination [211]. Meanwhile, when the Schottky-Read-Hall (SRH) recombination mechanism/trap-assisted recombination in space charge region dominates, the activation energy value is equal to band gap [212]. The reason is because at 0 K/low temperature region, the SRH recombination should be frozen out due to absence of thermal energy. Therefore, the activation energy in a material is solely based on the band gap energy. However, when the activation energy is less than band gap, it suggests the possibility of interface recombination at the p-n junction [211, 213, 214]. The IVT measurement for this study was conducted by IBM-PVX system, a solar simulator setup designed by IBM T.J. Watson solar cell group.

3.3.7 External Quantum Efficiency (EQE)

External quantum efficiency (EQE) is obtained from The PVE300 (Bentham) IPCE Instrument. Measurement were done from 300 nm to 1800 nm. EQE result measures the proportion of incident photons at each wavelength that is converted to carriers and collected as current by the PV cell. The Bentham PVE300 uses a xenon lamp and monochromator to illuminate the device with various wavelength and then excited carrier collected at the electrodes which connected to probes. There is step size and time for each wavelength increment or decrement. External in EQE means that the measurement is done by shining light from outside, so the measurement was done by comparing the current collected with all of incident photons. Meanwhile for internal quantum efficiency (IQE), it is a measurement of proportion between current collected and absorbed photons only. Below is the mathematical representation of both EQE and IQE;

$$EQE = \frac{\text{electrons/sec}}{\text{photons/sec}} = \frac{\text{current}/(\text{charge of one electron})}{(\text{total power of photons})/(\text{energy of one photon})}$$

$$IQE = \frac{\text{electrons/sec}}{\text{absorbed photons/sec}} = \frac{EQE}{1 - \text{Reflection-Transmission}}$$

In EQE, band gap of the material can also be obtained by differentiating the EQE curve with respect to its wavelength. A sharp slope change in EQE is the point where the energy from wavelength could convert into charge carriers/current which indicate the band gap. EQE result also explain how the charge collection of the overall devices.

3.3.8 Hall Measurement

Hall Measurement is defined by electric and magnetic forces and result in Lorentz force. A moving electron along electric field and perpendicular to magnetic field will experience a Lorentz force with direction normal to both electric and magnetic field. Lorentz force (F) can be calculated through this equation;

$$F = e(E + vB)$$

where e is the electronic charge, E is the electric field, v is the particle velocity, and B is the magnetic field. Accumulation of electrons which experienced Lorentz force will result in excess negative electrical charge on one side of the sample, drifting away from the current direction. The difference in charges results in Hall voltage (V_H) which can be calculated by below equation;

$$V_H = \frac{IB}{end}$$

where I is the current, B is the magnetic field, d is the sample thickness, n is carrier density and e is electron charge, from equation above we find the carrier density;

$$n = \frac{IB}{edV_H}$$

To obtain the carrier mobility, sample thickness (d) and resistivity (ρ) are required. Generally, Van der Pauw method is used to determine the resistivity. It is also known as four-point probe method, because it measures resistivity from probing four corners of the samples. Following that, the mobility of the carriers can be measured using equation below;

$$\mu = \frac{V_H d}{\rho IB}$$

Obtaining these two properties are important in studying the effect of cation substitution to CZTSSe, because it can prove the elimination of defects states based on the amount of carrier concentration. In this study, intrinsic doping from defects such as Cu vacancy or Cu-Zn antisite defects contribute as the majority carriers in the CZTSSe system, so reduction in carrier concentration could indicate reduction in defects. To achieve more accurate result, temperature dependent Hall measurement can be done to eliminate the effect of temperature. By lowering the temperature, the carrier concentration that is excited by the thermal energy can be eliminated. Therefore, intrinsic carrier concentration from the defects state can be obtained. In solar cell, an optimum amount of carrier concentration with high carrier mobility is preferred to achieve good carrier transport and device performance. An excessive amount of carrier concentration hinders the carrier transport and result in non-radiative recombination such as Auger recombination. Auger recombination is when an electron and a hole recombine, but the energy is given to a third carrier, an electron in the conduction band due to high amount of carriers[215]. As for carrier mobility, a low carrier mobility is not favorable for solar cell as it indicates carrier transport problem which may arises from non-radiative recombination such as from high density of mid-gap defects states in the system. Mid-gap defects states act as recombination center and eliminate the free carriers which should contribute to the photocurrent generation.

For this study, a rotating parallel dipole line AC Hall system was adopted as measurement tool. It is the novel invention from IBM system that generates pure harmonic, unidirectional and strong alternating magnetic field followed by lock-in detection of the Hall signal [207, 216, 217]. The measurement were conducted on exfoliated samples on quartz/glass substrate [206, 207].

3.3.9 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a non-destructive characterization technique to understand electronic properties of material, especially regarding electronic transition

through band gap. It reveals the recombination mechanism of the charge carriers, whether deep states play important role on it and band gap properties. In this study, photoluminescence measurements were recorded at room temperature using a 15 kHz pulsed 532 nm laser, a monochromator, and an InGaAs photomultiplier tube detector. The photoluminescence (PL) measurements were performed on bare absorber surface with Mo as substrate. PL spectroscopy's principle is as following; the sample is excited by a laser which results in the electrons excitation from valence to conduction band. Following that, electrons relaxation to the lowest energy level in conduction band, losing their energy via collisions. Subsequently, they recombine with holes in the valence band emitting light (band to band transition) [218].

A monochromator is usually used to analyze and record the emitted light. In the case of band to band transitions, emitted photons energy is equal to the band gap. If there are defect levels in the band gap, emitted photons energy is smaller by the defect activation energy. We thus learn about the energies of the defects within the band gap. Study of PL to understand defects need to be done in lower temperature, to inhibit the effect of thermal activated defects.

There are different types of transitions, which can be observed in photoluminescence measurements:

- Free electrons transition from conduction to valence band; which is known as band-to-band transitions.
- Free electrons transition from conduction/valence band to free acceptor/donor states; which is called free to bound transitions.
- Donor electrons transition to acceptor states produce positively charged donor and negatively charge acceptor; which is called donor-acceptor transitions.
- An excitonic transition which comes from electron-hole recombination in exciton. Exciton is quasi-particle consisting of free electron and free hole attracted to each other by coulombic force.

Each transition shows a characteristic temperature and intensity dependent behavior, so temperature and intensity dependent measurements can be used to differentiate between

the different transitions observed. After differentiating each transition, we can obtain the band gap and compare it to other band gap measurement values to look at the band-gap tailing states. We can also obtain the defect states energy level, and carrier lifetime from excitation to recombination. Carrier lifetime must be high enough for them to reach carrier's collector/electrode.

3.3.10 Capacitance-Voltage (CV) Measurement

Capacitance-voltage is one of the results from measurement of various electrical parameter such as capacitance, admittance, impedance and resistance, while external perturbation is introduced to the system. The perturbation could be in many forms for example alternating current (AC) signal, bias variation, temperature or light variation [219]. Generally, the variation of the electrical parameter quantities is observed when perturbation is introduced, or other electrical parameters are varied. Information on the type of response behavior of the device under such effect can lead to a good understanding of the efficacy of the electronic system. In thin film solar cell, depletion width from p-n junction is equivalent to a plate capacitor of the area A (cell area), with a plate distance of W (extension depletion region). Generally, there are two important values from thin film solar cell measurement, capacitance and admittance/impedance. Capacitance measures stored charges in the depletion width, while admittance is a measure of the easiness of a circuit or device to allow current to flow and impedance as its inverse is a measure of opposition to current flow.

By measuring the capacitance value in conjunction with an applied dc bias sweep, a spatially resolved defect distribution can be extracted and the depletion width can be estimated. The depletion width (x_d) can be determined by measuring capacitance at zero bias, followed by using $\epsilon_0 \epsilon A/C$ formula, where C is the measured capacitance, A is the device area, ϵ_0 is vacuum permittivity and ϵ is the dielectric constants for the absorber [13]. By measuring the admittance of the solar cell for a wide temperature range and varying the applied AC frequency, the energetic position of defect levels in the band gap, their capture cross-section and defect concentration can be derived.

In this study, capacitance-voltage (CV) and drive level capacitance profiling (DLCP) measurement were the focus. From capacitance voltage, charge density as a function of depletion width was derived at different voltage biases. Here the charge density includes bulk carrier density (free carrier density and the defect density), defects trap at space charge region and interface defects. The DLCP method introduce ac voltage amplitude variable dependence in examining the junction capacitance in addition to a range of dc bias. DLCP is considered a better measurement for bulk carrier density because it is only sensitive to bulk carrier density and defects trap at the space charge region compared to CV which is also sensitive to interface defects [220]. Thus, the apparent difference between these two charge density values is associated to interface defects. It was measured by HP 4192 impedance analyzer with ac frequency of 100kHz and voltage bias varying from +0.5 V to -6 V.

3.3.10 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB 220I-XL system under a base pressure of $< 5 \times 10^{-10}$ mbar. The source is a monochromatic Al K α (1486.6 eV) with a concentric hemispherical energy analyzer. The fitting and analysis are done on XPSPEAK41 software. XPS is a quantitative technique that provide elemental environment of the sample on surface. Based on photoelectric effect, photoelectrons are generated and emitted from sample surface during X-ray irradiation. Elemental, chemical states, and chemical composition can also be derived by analyzing elemental peak areas [221]. In this study, it is used to understand the oxidation states of the cations. Generally, the measurement is started by scanning a survey spectrum to observe all the existing elements on sample surface. Afterwards the high-resolution scan and fitting of certain elements is performed.

Chapter 4

Influence of Different Cation Substitutes of Zn on Structural, Optoelectronic and Photovoltaic Properties of CXTS Thin Films

In this chapter, screening of novel, low cost and non-toxic cation substitutes in CZTS is described. Based on octet rules and theoretical predictions on their quaternary compounds' stability, Mn, Mg, Ni, Fe, Co, Ba and Sr are selected as suitable candidates for Zn replacement. CXTS (X = Mn, Mg, Ni, Fe, Co, Ba, Sr) films were fabricated on Mo substrate by facile spray pyrolysis method. The resulting films demonstrates unique differences and similarities among each other. CMgTS and CNiTS have difficulty in forming the quaternary phases, CBaTS and CSrTS form trigonal structure. These findings are further elucidated by other characterization such as SEM-EDS, Hall measurement, UV-Vis spectroscopy and correlated with their device performances. Photovoltaic response was observed for CZTS, CMnTS, CMgTS, CBaTS and CSrTS. At the end, overall view on suitable cation substitutes for quaternary chalcogenide compound were discussed. This chapter provides insights in screening different cation substitutes for Zn in CZTS solar cell from the viable candidates using a simple fabrication spray pyrolysis method.

As mentioned in **chapter 1** and **2**, various cation substitutions are gaining interest to tackle the limitation in $\text{Cu}_2\text{ZnSnS}_4$ while maintaining its low cost and environmentally friendly advantages. There are several possible cation substitutes with +2 charges for Zn which satisfy these requirements (see table 2.2) such as Mn, Ni, Fe, Co, Mg, Sr, and Ba are selected as ideal substitutes. All these cations have +2 oxidation states as their stable states and have different cation radius with Zn/Cu in 4-fold coordination [99, 167]. Some of these substitutes quaternary compounds have been reported or predicted to be thermodynamically stable [21, 131, 136, 142, 144, 148, 222, 223]. However, there is no comprehensive comparison experimental study on different cations substitutes with +2 charges for CZTS with consistent variables such as similar synthetic method and characterization condition. Therefore, this chapter will focus on finding out the main differences of cation substitutes compound based on spray pyrolysis technique to fabricate CXTS ($X = \text{Mn, Mg, Ni, Fe, Co, Ba, Sr}$). These cations are selected based on their thermodynamic stability according to the theoretical prediction with some experimental evidence in the literature [143, 148, 224, 225]. This study may broaden the horizon and act as guideline for the alternative $\text{I}_2\text{-II-IV-VI}_4$ groups' solar cells. It will highlight the thin film properties between each cation according to their structural, phases, morphology and optoelectronic properties as well as their correlations to the photovoltaic performances based on CZTS thin film device structure.

4.1 Elemental composition of CXTS (X = Mn, Mg, Ni, Fe, Co, Ba, Sr)

Table 4.1 Elemental composition of CXTS from energy dispersive spectroscopy measurement

	Atomic Ratio (at%)				Ratio		
	Cu	X	Sn	S	Cu/ (X+Sn)	(X)/Sn	(Cu+X+Sn)/S
CZTS	23.19 ± 0.09	11.59 ± 0.16	13.79 ± 0.53	51.43 ± 0.62	0.91	0.84	0.94
CMnTS	23.11 ± 0.6	11.35 ± 0.15	12.51 ± 0.35	53.02 ± 0.99	0.97	0.91	0.89
CMgTS	20.8 ± 0.59	14.79 ± 2.37	11.53 ± 0.27	52.88 ± 1.63	0.80	1.29	0.89
CNiTS	22.84 ± 0.71	11.68 ± 0.4	13.97 ± 0.49	51.52 ± 0.3	0.89	0.84	0.94
CFeTS	25.12 ± 0.54	12.21 ± 0.33	12.53 ± 0.27	50.14 ± 0.62	1.02	0.97	0.99
CCoTS	24.75 ± 0.38	10.23 ± 0.17	13.2 ± 0.13	51.83 ± 0.43	1.06	0.78	0.93
CBaTS	24.07 ± 0.03	13.03 ± 0.2	11.18 ± 0.36	51.71 ± 0.23	0.99	1.17	0.93
CSrTS	20.03 ± 5.8	12.69 ± 5.03	15.64 ± 1.05	52.47 ± 2.06	0.76	0.88	0.91

The CXTS thin films were deposited on Mo coated glass by spray pyrolysis and sulfurization technique using the same procedure and parameters described in **chapter 3**. **Table 4.1** shows the chemical composition on the CXTS film based on the plan-view EDS. The CXTS thin films were fabricated in stoichiometry composition (stoichiometry in the precursor solution). The EDS results were averaged from five different areas of the samples to provide statistical confidence. Based on the standard deviations in table 4.1, most of the films shows lateral uniformity and homogenous chemical distribution in the bulk, except for CMgTS and CSrTS. Both compounds show higher standard deviation than the other cation substitutes which could indicate local distribution or phase separation for both CMgTS and CSrTS. The deviation from stoichiometry composition observed in the compounds (except CFeTS) may indicate the loss of these cations during high temperature

annealing. The cations loss as binary metal sulfides during the formation of quaternary compounds due to high temperature and low partial pressure of binary sulfides have been observed in CZTS[226].

4.2 Morphology of CXTS thin films

1)

2)

Figure 4.1 SEM cross section images (first) and plan-view images (second) of CXTS films where a) CZTS, b) CMnTS, c) CMgTS, d) CNiTS, e) CFeTS, f) CCoTS, g) CBaTS and h) CSrTS

Figure 4.1 show the SEM images of the CXTS thin films. Distinct morphology was observed for different cations. CZTS and CMnTS possess similar morphology of dense film made of mostly grains equivalent to their thickness. Meanwhile, CMgTS and CNiTS films consist of small grains which also result in layered structure for CMgTS. CCoTS and CFeTS films are dense and consist of large grains. However, the adhesion between the films and Mo substrate are poor as can be seen from the voids between them. Lastly, CBaTS and CSrTS exhibit the average largest grains (**figure A1**) compared to the other cations which might be related to its large ionic radius and trigonal structure [99, 148].

However, CSrTS also exhibit different type of morphology as seen from the plan-view SEM. This is related to the high standard deviation in EDS measurement which infer non-uniformity in the structure. Based on local EDS measurement, the large grain phase belongs to the CSrTS quaternary phase, while the small grains do not contain Sr (**figure A2**), thus possibly forming binary or ternary phases consisting of Cu-Sn-S. These small grains are also observed in CMgTS and CNiTS which might also be related to phases consisting of Cu-Sn-S.

4.3 Crystal structure and phase analysis of CXTS thin films

Figure 4.2 a) X-ray diffraction pattern (left) and b) Raman spectrum by 532 nm excitation wavelength (right) of CXTS films.

Figure 4.2a exhibits the diffraction pattern for the CXTS films and CZTS, CBaTS and CSrTS signature peaks from database. The peak at 40.5° corresponds to Mo which is used as substrate in this study. To further verify the phases of CXTS films, Raman spectroscopy study were also performed. Figure 4.2b shows the Raman spectra for the sulfurized CXTS

films. As shown in figure 4.2a, the XRD from CXTS films exhibit two distinct characteristics which can be classified into two group of crystal systems. The lower number of diffraction planes in CZTS, CMnTS, CMgTS, CNiTS, CFeTS and CCoTS indicates higher symmetry system. Meanwhile, the higher number of diffraction planes in CBaTS and CSrTS indicates lower symmetry system. These films can be categorized into tetragonal for higher symmetry system and trigonal group for lower symmetry system based the identification of their individual spectra with references spectra [131, 135, 141, 143, 148]. The detail of the identification will be elaborated further in the following paragraph.

In the tetragonal group, CZTS control sample exhibit the tetragonal structure which correspond to CZTS kesterite peaks (JCPDS 026-0575). The rest of the films in this group also exhibit similar strong diffraction peaks (for example reflections around 28° and 48°), which correspond to the CZTS database peaks (bottom black stick figure in figure 4.2a). This phenomenon is common for compounds with crystal system derived from zinc blende structure, including ZnS and Cu_2SnS_3 which also exhibit similar diffraction patterns [227-229] even though, there are differences in smaller intensity peaks such as at lower 2θ . In addition, there is also peak shift with different elements (see **figure A3**) with Mn show the leftmost and Co as the rightmost which correspond Mn having the largest ionic radius and Co as one of the smallest [99]. Peak shift is commonly found in substitution study due to the lattice strain introduced by elements with different ionic sizes [230-232].

Individual investigation was conducted on each films in the tetragonal systems (**figure A4**) and we found that CMnTS, CFeTS and CCoTS peaks correspond to their respective tetragonal peaks in database (JCPDS 051-0757 for CMnTS, JCPDS 044-1476 for CFeTS and JCPDS 026-0513 for CCoTS) [233, 234]. The increase in the background level at low 2θ for CFeTS and CCoTS which usually correspond to amorphous phase might be related to the adhesion problem as seen in figure 4.1e and f. These investigations were then verified by Raman. For CZTS, an intense peak at 338 cm^{-1} with broad shoulder peaks at 250, 287 and 370 cm^{-1} represent typical CZTS spectrum. [72, 235] For CMnTS, an intense peak at 328 cm^{-1} with shoulder peak at 345 cm^{-1} correspond with CMnTS spectrum in literature

[176, 236]. Additional small peaks at 150 and 220 cm^{-1} correspond to SnS [15]. Meanwhile for CFeTS and CCoTS, intense peaks at 319 cm^{-1} and 324 cm^{-1} matched with their typical spectra respectively [70, 161, 237] which show one intense peak related to tetragonal stannite structure.

The remaining films in the tetragonal group, CMgTS and CNiTS, are relatively more difficult to form compared to the rest. To date, the JCPDS database and Raman spectra of CMgTS are not available in literature. The main peaks of CNiTS correspond to JCPDS 026-0552, but these peaks also overlap with various secondary phases such as those from NiS₂ (grey circles) [238]. The observation of NiS₂ indicates the possible phase separation and difficulty in forming CNiTS phase. Deviation from the rest of tetragonal system were observed based on their Raman spectra. From Raman analysis, both CMgTS and CNiTS have double strong peaks at 291 cm^{-1} and 353 cm^{-1} which are related to ternary phase, monoclinic polymorph of Cu₂SnS₃ (CTS) [7]. There is an extra peak for CNiTS at 475 cm^{-1} which belong to NiS₂ [239], thus further verified its existence. In CNiTS, three typical strong main peaks of cubic CNiTS around 288, 320 and 343 cm^{-1} are not clearly observed in this study [21]. There might be a mixture of CNiTS or CMgTS and CTS for these two films, but the existence of the Mg and Ni quaternary compounds formation cannot be ascertained due to the high CTS intensity from Raman study.

The two remaining films are CBaTS and CSrTS which exhibit similar pattern in both XRD and Raman. Their diffraction peaks correspond to trigonal system of PDF#04-009-0392 and PDF#01-089-2481 respectively. Trigonal system has threefold axis of rotation in comparison with tetragonal with fourfold axis of rotation due to its angle $\neq 90^\circ$. By having less symmetry, more diffraction peaks in XRD are expected as it is observed for both CBaTS and CSrTS. Even though the substitution with Ba and Sr does not change the I₂-II-IV-VI₄ structure, the larger ionic size of Ba and Sr in the system induce large lattice distortion, thus making tetrahedral structure unstable and exhibit trigonal structure instead [148]. The atom coordination also differ from 4-fold coordination in tetragonal into more like 3-fold coordination between Cu-Sn-S surrounding Ba/Sr which have 8-fold coordination [135]. The difference between CBaTS and CSrTS originates from the larger

ionic size of Ba which shifts the peaks to lower angle compared to Sr. Even though the main peaks for most of the films correspond to their respective reference database, some secondary phases are undistinguishable with the main phases such as ZnS and Cu_2SnS_3 through XRD. Therefore, phases verification was conducted through Raman study. CBaTS and CSrTS, exhibit similar Raman spectra characteristic which correspond to their trigonal system with a right shift for CSrTS. The main peaks for CBaTS around 187, 250, 341, 366 and 380 cm^{-1} are comparable with the trigonal CBaTS spectrum from recent literature [152, 240, 241]. Even though there is no Raman data in literature as reference for CSrTS phase yet, based on theoretical prediction, it should possess similar structure as CBaTS and consequently similar main peaks should be observed. In figure 4.2b, the main peaks at 194, 273, 346, 375 and 388 cm^{-1} have similar spacing with different peak position as CBaTS peaks. This is due to different bond strength between the atoms but having similar lattice structure. The intensity for CBaTS peaks is higher than CSrTS owing to its phase purity. As SEM image in figure 4.1h show, phase separation is observed in CSrTS between the bottom layer and top layer. Phase separation is understandable due to the difficulty in trigonal CSrTS formation compared to trigonal CBaTS based on lower formation enthalpy and chemical potential window [148]. The Raman results does not show the secondary phases phenomenon due to the penetration depth of the 532 nm excitation wavelength ($\sim 50\text{ nm}$ [202]) on the sample.

4.4 Optoelectronic properties of CXTS thin films

Figure 4.3 a) absorption spectra for CXTS films and b) Tauc plot for band gap measurements.

Figure 4.3 summarizes the absorption and band gap measurements for the CXTS samples by UV-Vis spectroscopy. The absorption edge of CZTS, CMnTS, CBaTS and CSrTS show steep adsorption edge, while the rest have more gradual absorption edge. In addition, further classification can be done based on the absorption curve shape, which are CZTS and CMnTS (tetragonal), CMgTS and CNiTS, CFeTS and CCoTS, CBaTS and CSrTS (trigonal). As for CFeTS and CCoTS, although they belong to tetragonal structure, the partially filled orbital configuration differentiate their absorption spectra compared to half-filled orbital CMnTS and fully-filled orbital CZTS[136]. Meanwhile, CMgTS and CNiTS are similar as they possess multiple absorption edges which correspond to multiple band gaps due to polymorphism in Cu_2SnS_3 phases [7, 227]. Regarding the multiple absorption edges, CSrTS also exhibit low band gap absorption which can also be attributed to the Cu_2SnS_3 phase separation.

From the absorption curve, the band gap of these films are extracted based on tauc's plot as seen in figure 4.3b [242]. In this plot, energy is plotted against the quantity $(\alpha h\nu)^{1/r}$, with $r = 1/2$ for direct band gap and the extrapolation of distinct linear regime give us the band gap. The direct band gaps for CZTS and CMnTS are quite similar which is around 1.6 eV. CMgTS exhibit three gaps, which are 1.57 (correspond to orthorhombic Cu_3SnS_4 [75]), 1.1 and 1 eV. CNiTS also exhibit 1.1 and 1.05 eV band gaps which emphasize the occurrence of monoclinic Cu_2SnS_3 in both samples [7, 75]. CFeTS possess band gap of 1.2 eV which agrees with past study [243]. As for CCoTS, the band gap is estimated at 1.1 eV which is relatively smaller than the average reported values around 1.4-1.6 eV [160, 161, 185]. It might be due to different synthesis method and substrates in comparison with past study and previous characterization. Lastly, both CSrTS and CBaTS have estimated band gaps of 1.88 and 2.0 eV respectively. These values are comparable with both predicted and experimental results in literature [147, 148, 152], although, CSrTS also possess two small absorption edges at low energy (0.92 and 0.95 eV) which can be attributed to CTS phase.

Table 4.2 Summary of CXTS thin film characterization

Sample	Structure	Secondary phases	Band gap	Morphology	Hole Concentration (cm ⁻³)	Hole Mobility (cm ² /V.s)
CZTS	Tetragonal (kesterite) – $I\bar{4}$	–	1.6 eV	Grain size $\approx$ thickness	2.55×10^{15}	0.923
CMnTS	Tetragonal (stannite) – $I\bar{4}2m$	SnS	1.6 eV	Grain size $\approx$ thickness	2.56×10^{19}	0.501
CMgTS	–	Monolithic Cu ₂ SnS ₃ ,	1, 1.1, 1.57 eV	Small grains, non-uniform (layered)	2.92×10^{18}	1.083
CNiTS	–	NiS ₂ (cubic), Monolithic Cu ₂ SnS ₃	1.05, 1.1 eV	Small grains	1.97×10^{19}	1.579
CFeTS	Tetragonal (stannite) – $I\bar{4}2m$	–	1.2 eV	Poor adhesion with Mo	1.91×10^{19}	1.107
CCoTS	Tetragonal (stannite) – $I\bar{4}2m$	–	1.1 eV	Poor adhesion with Mo	2.95×10^{21}	0.466
CBaTS	Trigonal – P3 ₁	–	2 eV	Large grains, Grain size $\approx$ thickness	6.83×10^{15}	2.134
CSrTS	Trigonal – P3 ₂ 1	Cu-Sn-S phases	$\sim 0.92, \sim 0.95, 1.88$ eV	Large grain, non-uniform (island like)	2.14×10^{18}	2.762

Another characterization which is performed on these films are Hall measurement. All of the films possess p-type conductivity. The carrier concentration and mobility values are tabulated in **Table 4.2**. In terms of carrier concentration, CZTS and CBaTS have similar value around 10^{15} cm⁻³ which is suitable for solar cell material [207]. However, the other thin films possess carrier concentration $>10^{18}$ cm⁻³ which have been shown as an indicator for poor photovoltaic performances [176]. High carrier concentration generally decrease the carrier lifetime due to increased non-radiative recombination from defect traps or Auger recombination [244]. The high concentration for CMgTS, CNiTS and CSrTS may be attributed to CTS secondary phase [227]. High mobility is an important parameter to obtain longer diffusion length for better carrier transport [216]. In terms of mobility, all of the films have mobility around 0.5 – 2.7 cm²/V.s where CBaTS and CSrTS have the highest mobility.

In summary, based on structural characterizations, the emerging material CBaTS and CSrTS are successfully formed for the first time using this solution based method as most study has been limited to vacuum based method, although non-uniformity occurs in CSrTS. We found that only CMgTS and CNiTS seems to be not forming quaternary compounds based on the XRD and Raman spectra which shows formation of ternary (Cu_2SnS_3) and secondary phases (NiS_2). While some CXTS films are not optimal yet (poor adhesion and secondary phases), this study shows the potential of spray pyrolysis method to screen and fabricate novel kesterite films in a systematic and quick manner.

4.5 Light J-V measurement discussion on CXTS Solar Cells

Figure 4.4 Device parameters for stoichiometry CXTS solar cell as a function of X cations.

Solar cell devices (Mo/CXTS/CdS/i-ZnO/ITO/Ag-paste) were fabricated and measured to further figure out the effect of different cations on the photovoltaic performance. **Figure 4.4** shows the statistical results for the device performance parameters including power

conversion efficiency (η), fill factor (FF), short-circuit current (J_{sc}), and open-circuit voltage (V_{oc}) as a function of different cation. The results are averaged of 16 samples to provide statistical consistency. Only the aforementioned absorber CXTS films were replaced, the remaining layers are identical as mentioned in solar cell fabrication method in **chapter 3**. In figure 4.4, the solid outline and dashed outline with stripped fill represent solar cell devices after post device annealing and before, respectively. CZTS, CMnTS, CMgTS, CBaTS and CSrTS show noticeable photovoltaic response after post device annealing. This is a positive indicator that these cations are suitable to partially substitute Zn. CBaTS and CSrTS shows the highest efficiency, V_{oc} and J_{sc} compared to the rest of the films. On the other hand, both pre-anneal and post annealed devices show that CNiTS, CFeTS and CCoTS does not produce photovoltaic response, even though some literature reported photovoltaic response for these three compounds [14, 21, 22, 172]. Several reasons can be attributed to this contradictory result; firstly, the CNiTS does not seem to form based on the characterization in this study. Secondly, the morphology of CFeTS and CCoTS are not similar with the reported study. The poor adhesion with Mo may create an issue for photovoltaic device. Lastly, in the reported literature, the evident photovoltaic performance for these three compounds are observed in different structure, such as using different buffer layer (Bi_2S_3 for CFeTS [14]) and in a sensitized solar cell structure (ZnO/ZnS nanorods [22]). Although post device annealing helps to improve the photovoltaic performance for the stoichiometric CZTS, CMnTS, CMgTS, CBaTS and CSrTS, the device parameters for all the samples are relatively low in comparison with high performing CZT(S,Se) devices. One possible reason especially for CZTS is the non-optimal composition ratio where stoichiometric ratio has been proven to be less optimal to achieve high performing CZTS solar cell [69, 245]. Therefore, another set of CXTS samples were fabricated with different cation ratio, Cu-poor ($Cu/(X+Sn) = 0.75$) and X-rich ($X/Sn = 1.2$), which was shown to generate better photovoltaic performance [69, 245-247].

Figure 4.5 Device parameters for Cu-poor and X-rich CXTS solar cells as a function of X cations.

Figure 4.5 shows the statistical device parameters for the non-stoichiometric (Cu-poor and X-rich) CXTS solar cells. In this set of results, there are overall improvement for the five CXTS films which shows photovoltaic response in comparison with the stoichiometric films. Voc is increased for all the films which may correspond to the Cu-poor effect in controlling carrier transport and lifetime as shown chalcopyrite CIGS [248, 249]. The highest improvement is achieved by CZTS as this non-stoichiometric ratio is chosen based on one of the best performing ratio using spray pyrolysis method [187]. Meanwhile, the post device annealing in this set of samples also exhibit improvement similar with previous finding [200-203] except for CBaTS which show negative impact. Redistribution of the cations and anions were commonly observed as the effect of these post device annealing. The CBaTS does not show similar improvement which might be because CBaTS has a much more ordered structure than CZTS and hence [135, 250] the post device annealing disrupts the structure instead of improving it. Based on these different conditions, non-stoichiometry conditions show more promising results with CBaTS as the highest average

efficiency among the cation substitutes followed by CSrTS, CMgTS and CMnTS. The fill factor of the post device annealing non-stoichiometry films are similar, but they have different Voc and Jsc values. CBaTS, CMgTS and CSrTS have higher Jsc value while CMnTS and CBaTS have higher Voc value. As for CNiTS, CCoTS and CFeTS, there are no photovoltaic response observed in any of the conditions. The J–V characteristics of the respective CXTS “champion” cells under one sun illumination is shown in **figure 4.6**. These cells were taken from the non-stoichiometric and post annealed set of samples, except for CBaTS (before post anneal). The CNiTS, CFeTS and CCoTS displayed an ohmic response which illustrate non-diode response from these materials. Among these cells, CZTS as a reference performs the best with efficiency of 5.66%. CBaTS exhibits the second-best performing cells and the best among the substitutes. The low Jsc for CBaTS is expected due to its high band gap, but the Voc is quite low with respect to the band gap. In comparison with the literature, the highest efficiency CBaTS is achieved at 1.7% with Voc ~0.2 V higher than in this study [152]. The Voc deficit might be due to unoptimized cation ratio or deposition parameters. Nevertheless, this result is comparable with the highest reported and further optimization should be able to improve the performance. As for CMnTS, this efficiency ($\eta = 0.56\%$) is also not far behind the record in literature ($\eta =$

Figure 4.6 J-V curve for the “champion” cell from each of the CXTS films.

0.91%) [251]. In fact, the V_{oc} and fill factor in this study is slightly higher than the record, but the J_{sc} is lower by $\sim 3 \text{ mA/cm}^2$ which could be improved by thickness optimization. It should be noted that the PV of CMgTS and CSrTS are most likely attributed from the CTS secondary phases as the former phases cannot be observed in Raman and XRD.

4.6 Charge collection in CXTS Solar Cells

Figure 4.7 External quantum efficiency for CXTS solar cells with their respective extracted band gap and J_{sc} . Each CXTS films (represented by different colors) have two EQE response, solid line represents the post annealed film response and dashed line represents pre-annealed film response.

To further understand the charge collection on these films, external quantum efficiency measurements were performed on the non-stoichiometric CXTS devices. From **figure 4.7**, only CZTS, CMnTS, CMgTS (only post anneal sample), CBaTS and CSrTS shows quantum efficiency signal which is consistent with the photovoltaic response. Similarly, the trend among the CXTS films also correspond with their respective photovoltaic

performances. The EQE of CMgTS and CSrTS show extended gradual decreasing slope which should correspond to the presence of low band gap secondary phase such as CTS. Its absorption edge was observed in UV-Vis. Meanwhile, the sharp drop around 600 nm for CBaTS indicate low band fluctuation and tailing which is an issue in CZTS [47, 252]. From the EQE response, the band gap and the integrated photocurrent is also extracted as shown in the inset table. The band gaps can be estimated using the first peak of $dEQE/dE$ curves (where $E = hc/\lambda$) [212]. Band gap determination by EQE is only performed on CZTS, CMnTS, CBaTS and CSrTS due to the poor charge collection and no clear absorption edge for the rest of the films. The band gap values are consistent with the UV-Vis estimation, however there is a slight discrepancy between the measured J_{sc} and the extracted J_{sc} from EQE. The discrepancy might be due to the light intensity difference between the two measurements which affect the charge generation especially for poor performing cells that suffer from light dependency issues [253, 254]. The higher intensity in IV measurement induces slightly higher J_{sc} in JV curve because the light-induced current leakage as these cells suffer from high shunt conductance which can be observed from the apparent slope near the J_{sc} in figure 4.6 [176]. The high shunt conductance comes from poor junction properties such as interface defects and secondary phases.

4.7 Discussions on different substitutes in CXTS

Figure 4.8 Schematic diagram of cation substitute selection for Zn in $\text{Cu}_2\text{ZnSnS}_4$

After performing both thin film and solar cell device characterizations on various CXTS, there are several interpretations on different type of cation substitute for Zn in CZTS. **Figure 4.8** summarizes the methodology for cation selection and categorization of this study. From these various characterizations, several design considerations on the different cation substitutes include:

1. *The metallic substitute must have d-orbitals to replace Zn and form stable quaternary compound.* The lack of d-orbital seems to be the reason why CMgTS is not forming. Even though d-orbital of Zn does not play important role in CZTS conduction and valence band formation, it still contributes to the density of states formation [13]. Similar case for the remaining cations in this study (Fe, Co, Mn, Ba and Sr), their d-orbital also contributes in density of states formation of CFeTS, CCoTS, CMnTS, CBaTS and CSrTS [135, 141, 150, 224, 255]. Even in CMnTS, Mn d-orbital play more important role as it hybridize with S p-orbital to form conduction band minimum (CBM) formation [256].
2. *The multiple oxidation states from the transition metal candidates (Fe, Ni, Co and Mn) seems to influence the conductivity of the films.* These quaternary compounds possess large majority carrier concentration ($>10^{18} \text{ cm}^{-3}$). Only CMnTS has diode response owing to its more stable and less detrimental half-filled $3d^5$ -orbitals (**table 4.3**). According to Pauli Exclusion principles, five valence electron in Mn $3d^5$ -orbitals fill the orbital with parallel spin which increase the intrinsic stability in comparison with the partially filled orbital in Fe, Ni or Co [173]. The situation will be more stable if the substitute has fully filled orbital as observed in Cd. Other than the multiple oxidation states, the magnetic properties that these compounds possess might affect charge transport or conductivity [154, 162, 237, 257]. Intrinsic magnetism which can arise due to internal electric field in the junction might affect the free carrier transport pathway as seen in Hall effect [258].

Table 4.3 Electron configuration for transition metals at +2 oxidation state

Elements	Electron configuration	Notes					
Zn ²⁺	[Ar] <table><tr><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td></tr></table> 3d ¹⁰	↑↓	↑↓	↑↓	↑↓	↑↓	Fully filled d-orbital
↑↓	↑↓	↑↓	↑↓	↑↓			
Mn ²⁺	[Ar] <table><tr><td>↑</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr></table> 3d ⁵	↑	↑	↑	↑	↑	Half filled d-orbital
↑	↑	↑	↑	↑			
Fe ²⁺	[Ar] <table><tr><td>↑↓</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr></table> 3d ⁶	↑↓	↑	↑	↑	↑	Partially filled d-orbital
↑↓	↑	↑	↑	↑			
Ni ²⁺	[Ar] <table><tr><td>↑↓</td><td>↑↓</td><td>↑</td><td>↑</td><td>↑</td></tr></table> 3d ⁷	↑↓	↑↓	↑	↑	↑	Partially filled d-orbital
↑↓	↑↓	↑	↑	↑			
Co ²⁺	[Ar] <table><tr><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑</td><td>↑</td></tr></table> 3d ⁸	↑↓	↑↓	↑↓	↑	↑	Partially filled d-orbital
↑↓	↑↓	↑↓	↑	↑			
Cd ²⁺	[Kr] <table><tr><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td></tr></table> 3d ¹⁰	↑↓	↑↓	↑↓	↑↓	↑↓	Fully filled d-orbital
↑↓	↑↓	↑↓	↑↓	↑↓			

3. *Large ionic difference on the substitute (Ba/Sr and Zn) result in different quaternary crystal structure and optoelectronic properties.* The trigonal structure and larger band gap were observed in CBaTS and CSrTS. This tranformation might benefit the cation ordering which was indicated by the sharp slope in CBaTS EQE.
4. *For subsitute which has similar structure between its secondary phase and quaternary phase such as CNiTS, the fabrication needs to be done in more controlled method.* CNiTS has been predicted and fabricated to have stable quaternary compound [163, 180-184]. However, phase separation into CTS and NiS₂ occurred in this study. One possible reason is Ni has the smallest ionic radius in 4-fold coordination which increases the likelihood of Ni leaving the lattice. Moreover, CNiTS has a stable P4̄2c polytype cubic phase which has similar stable phase with its secondary phase NiS₂, so it can be more difficult to obtain the quaternary compound [9]. Thus, the reaction

kinetics during growth of CNiTS must be carefully controlled to obtain pure quaternary compound.

Based on these characterizations and considerations, several cations substitutes are selected for further study on partial substitution. Manganese (Mn), Barium (Ba) and Strontium (Sr) are suitable candidates. They satisfy the low cost and non-toxic motivation of CZTS and the requirements to replace Zn and form quaternary compound with notable photovoltaic responses. Magnesium (Mg) was also selected for partial substitution study even though it does not seem to form quaternary compound, as it exhibits notable photovoltaic response.

4.8 Conclusions

In summary, investigation on the effect of different cation substitutes for Zn in CZTS has been performed using spray pyrolysis method. Initial screening of candidates based on their abundance, non-toxicity and stability predictions as quaternary compounds results in Mn, Mg, Ni, Fe, Co, Ba and Sr as potential candidates. Their thin film and device properties were investigated. XRD and Raman analysis managed to categorize the samples into three groups; tetragonal structure (CZTS, CMnTS, CFeTS, CCoTS), trigonal structure (CBaTS and CSrTS), and non-quaternary compound (CMgTS and CNiTS). The existence of low band gap monolithic Cu_2SnS_3 were apparent in CMgTS and CNiTS samples. Lack of d-orbital and the need of controlled fabrication for CMgTS and CNiTS respectively seem to be the reason of difficulty in forming quaternary compounds.

Distinct morphology was observed for different substitutes where CZTS, CMnTS, CBaTS and CSrTS show large grain size, while CMgTS, CNiTS, CFeTS and CCoTS show smaller grains with layered or poor interface. This finding is consistent with notable photovoltaic response for CZTS, CMnTS, CBaTS, CSrTS and ohmic response for CNiTS, CFeTS and CCoTS. The high hole concentration ($>10^{18} \text{ cm}^{-3}$) due to multiple oxidation states from their partially filled d-orbital seems to be the reason of non-diode response for CNiTS, CFeTS and CCoTS. CMgTS is the only exception which shows photovoltaic response even though it possesses smaller grains and does not seem to form quaternary compounds. Although the efficiency is still low, the photovoltaic response and the formation of stable

quaternary compound for CMnTS, CBaTS and CSrTS shows the potential and suitability as cation substitute to further improve CZTS. In addition, from EQE measurement, the CBaTS also show sharper slope compared to CZTS near the band gap which indicate improvement in band fluctuations and tailing. There are several ways to improve the photovoltaic response for these cation substituted devices, such as finding the optimized stoichiometry ratio (e.g. the cations ratio) for each compounds, optimizing the annealing parameters and/or different device configuration (e.g. different buffer layers). In addition, based on these findings, partial substitution by Mn, Ba, Sr and Mg in CZTS could also provide positive improvement and new understanding in improving CZTS solar cell.

Chapter 5

Understanding the Mn Substitution Effect on the Intrinsic Properties of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ Photovoltaic Devices

Mn is one of the potential candidates for Zn substitution in CZT(S,Se). This chapter reports novel and in-depth study on $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ films fabricated by spray pyrolysis and spin coating. Partial substitution of Mn in the bulk of CZT(S,Se) induces structural and optoelectronic transformation within $x = 0.0 - 1.0$. Both sulfide and selenide system show efficiency improvement with 15% and 5% of Mn substitution respectively. They show superior charge collection in the short wavelength and larger depletion width compared to the control samples. Furthermore, by using a double layer structure of CZT(S,Se) and CMZT(S,Se) the photovoltaic performance was further improved to achieve the highest performing cell due to superior charge transport, charge collection and junction properties. This chapter demonstrates the advantage of having partial Mn substitution in boosting kesterite photovoltaic performance.

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Lie, S., et al., *Improving the Charge Separation and Collection at the Buffer/Absorber Interface by Double-Layered Mn-Substituted Czts*. Solar Energy Materials and Solar Cells, 2018. **185**: p. 351-358.

5.1 Introduction

Among the candidates discussed in **chapter 4**, Mn is one of the promising cations to replace Zn as it is relatively more abundant than Zn [174]. Mn is stable at oxidation state +2, because of the half-filled $3d^5$ -orbitals consist of five parallel spin d -orbitals. This state is intrinsically more stable than the partially filled orbital Fe, Ni or Co [173]. Regarding the ionic size, Mn also offer the largest size mismatch as Mn^{2+} 's (0.80 Å) size in 4-fold coordination is the largest in comparison with Cu^+ (0.74 Å), Zn^{2+} (0.74 Å), Fe^{2+} (0.77 Å), Co^{2+} (0.72 Å) and Ni^{2+} (0.69 Å) [132]. Lastly, photovoltaic responses are observed for $\text{Cu}_2\text{MnSnS}_4$ (CMTS) and $\text{Cu}_2\text{MnSn}(\text{S},\text{Se})_4$, even though they are quite poor (< 1 %) [155, 175, 176, 236]. CMTS is stable in stannite structure and has similar high absorption coefficient and direct band gap compared to CZTS [153, 158]. In addition to bulk CMTS study, partial substitution of Mn should be investigated as partial substitution of Ag and Cd have shown success so far [52, 56, 231]. Therefore, in this chapter, partial substitution of Mn with Zn on both sulfide and selenide-based are investigated by fabricating $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ through spray pyrolysis and spin coating method as described in **chapter 3**. The effect of alloying different amount of Mn into CZT(S,Se) are investigated in terms of the structure, morphology, optoelectrical and device properties. Our “champion” cells were achieved with $x = 0.15$ and 0.05 for sulfide and selenide based respectively. Detailed opto-electrical characterizations were performed on these champion cells to understand the performance limiting factors. Finally, a double-layered structure of CMZT(S,Se) and CZT(S,Se) was fabricated to take advantage of the improved interfacial properties of CMZT(S,Se).

5.2 Partial substitution of Mn with Zn in selenide condition (CMZT(S,Se))

As an initial part of the study, partial substitution of Mn with Zn was performed on CZTSSe by spray pyrolysis technique. The Mn was distributed homogeneously in the absorber layer by mixing it in the precursor solution with variation of $\text{Mn}/(\text{Mn}+\text{Zn})$ ratio. Following that, in-depth thin film and device analysis were performed to figure out the influence of Mn in

the system. Similar partial substitution study was performed on sulfide-based CZTS to figure out the difference between the sulfide and selenide-based.

5.2.1 Structural and phase transformation of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$

Figure 5.1a shows XRD results of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ thin films for $x = 0$ to $x = 1$. Most of the observed peaks can be correlated with the planes from CZTS (JCPDS#26-0575), CMTS (JCPDS#51-0757), CZTSe (JCPDS#26-0868), CMTSe (JCPDS#26-0542), Mo and MoSe₂ [233]. The first observation from the graph is the misalignment with the reference database peaks. This is due to left shift which is attributed by larger size element of Mn and Se substitution with Zn and S. Introduction of larger ionic radius elements affect the lattice parameter and spacing of the structure, induce lattice stress and strain, thus decreasing the angle of diffraction [50]. Transformation from the kesterite CZTSSe into stannite CMTSSe with increasing x is suggested by the distinct signature of the (204) and (312) plane peak splitting in stannite [120]. This phenomenon is also supported by the abrupt peak shift from $x = 0.2$ to $x = 0.4$ and $x = 0.8$ to $x = 0.1$ (**figure B1**) which suggest possible intermediate phases of these two structures in between the phase transformation. Furthermore, lattice parameters were extracted through Rietveld refinement analysis on samples with $x = 0, 0.2, 0.4, 0.8$ and 1.0 (**figure B2**) using FullProf software. The a -axis and c -axis are increased as Mn substitute Zn from $a=5.658 \text{ \AA}$ (CZTSSe) to $a=5.736 \text{ \AA}$ (CMTSSe), and from $c=11.259 \text{ \AA}$ (CZTSSe) to $c=11.345 \text{ \AA}$ (CMTSSe). Abrupt changes are observed in the lattice parameter from $x = 0.2$ to $x = 0.4$ and $x = 0.8$ to $x = 0.1$ which correspond the peak shift. This observation might be related to the solid solubility limit of Mn (20%) in the CZTSSe structure. According to Hume-Rotherford theory [259], complete substitutional solid solution can only be performed with element which its atomic size difference is less than 14-15%. For Mn ($1.61 \text{ \AA}$) substitution with Zn ($1.42 \text{ \AA}$), the atomic size difference is $\sim 13.4\%$. Therefore, the Mn dissolution within CZTSSe structures for up until around 20% and formation of CMTSSe and CZTSSe intermediate phases (CMZTSSe) at $0.2 < x < 0.8$ is conceivable. Despite Rietveld refinement limitations on thin film samples, the analysis indicates that CZTSSe is kesterite, CMTSSe is stannite, and at $0.2 < x < 0.8$, there is a possibility of having intermediate (CMZTSSe) phases.

Figure 5.1 a) X-ray diffraction spectra and b) Raman spectroscopy for $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S,Se})_4$ thin films ($x = 0.0-1.0$)

Figure 5.1b depicts the Raman spectra for CMZTSSe films. Further curve fitting was carried out (**figure B3**) to reveal hidden peaks. Three main peaks which correspond to CZTSe [260] or CMTSe [261] were observed around 174 (B mode), 198 (A mode) and 236 cm^{-1} (B mode). In addition, the peaks around 330 cm^{-1} (A mode) correspond to CZTS [262] or CMTS [261]. The A mode signals are more dominating because it is related to the vibration of anion atoms [70], as for the B symmetry mode is related to cation and in CZTS case, it is sensitive to the Cu/Zn and Cu/Sn atomic planes movements [263]. Due to Raman sensitivity towards element vibration, chemical ratio variation will alter the spectra profiles which are apparent in these samples. Furthermore, shifts to the lower wavenumber were also observed with the increase of Mn substitution which indicate Mn incorporation to the lattice as observed similarly in the literature [179]. In addition, several hidden peaks around 220 cm^{-1} and 235 cm^{-1} ($x = 0$ and $x \geq 0.8$) are also observed from the fitted Raman curve. These peaks coincide with secondary phases, the 220 cm^{-1} coincide with SnS peaks which is a volatile compound commonly formed during high temperature annealing. As for peaks around 235 cm^{-1} , it might be related to ZnSe and MnSe [264]. The appearance of both phases is attributed to the Zn and Mn rich condition at $x = 0$ and $x \geq 0.8$ respectively.

5.2.2 Morphology and elemental composition of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$

Figure 5.2 (a-h) exhibits cross section images of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ thin films after the selenization process. The average thickness of the films is around 1000 nm which is still lower than the best performing CZTSSe (2000nm) [50]. In terms of grain size, it ranges from 400 nm to 1000 nm which is also observed from plan-view sides (**Figure B4**). The overall films are compact and dense, except for $x = 0.2$ and 0.4 where some voids are visible in conjunction with small grains. The largest grain size is obtained at $x = 0.05$ where it extends throughout the film thickness. Concurrently, this composition also results in the best device performance. It is due to fewer grain boundaries which facilitate better charge transport as grain boundaries can act as barrier during charge transport [265]. Various

Figure 5.2 (a-h) Cross section SEM images of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ thin films ($x = 0.0-1.0$).

thickness of Mo is observed for different composition due to different growth of MoSe_2 layers during selenization which is difficult to control. The thickest Mo is spotted at $x = 1$, which indicates thicker MoSe_2 growth in CMTSSe. The appearance of MoSe_2 is commonly found in high performance CZTSSe [34]. Although several studies report that MoSe_2 is detrimental, some studies argue that it is necessary at the interface, especially for band alignment [266]. Nevertheless, overgrowth of MoSe_2 as seen in $x = 1$ is deemed unfavorable and detrimental for charge collection [267].

Table 5.1 Elemental compositions of the $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ thin films

x	Chemical Composition (at%)						Composition Ratio			
	Cu	Mn	Zn	Sn	S	Se	Cu / (Mn+Zn+Sn)	(Mn+Zn) / Sn	Se / (S+Se)	Mn / (Mn+Zn)
0	20.09 ± 1.10	0.00	12.81 ± 1.85	11.22 ± 1.45	8.31 ± 3.62	47.46 ± 2.93	0.85	1.15	0.85	0.00
0.05	21.84 ± 0.98	0.86 ± 0.26	13.11 ± 1.55	12.06 ± 0.95	7.19 ± 2.08	44.36 ± 2.05	0.84	1.16	0.86	0.06
0.1	19.05 ± 0.69	1.12 ± 0.32	11.65 ± 1.23	11.48 ± 1.11	8.93 ± 1.83	47.79 ± 1.60	0.79	1.1	0.84	0.09
0.2	20.20 ± 0.94	2.41 ± 0.59	10.54 ± 0.81	12.22 ± 0.76	10.15 ± 3.28	44.48 ± 5.66	0.80	1.06	0.81	0.18
0.4	19.77 ± 1.06	5.27 ± 0.35	8.38 ± 0.80	11.21 ± 1.16	10.45 ± 4.14	44.85 ± 4.85	0.80	1.23	0.81	0.38
0.6	22.12 ± 0.33	7.01 ± 0.86	5.72 ± 0.5	11.63 ± 1.55	8.96 ± 0.82	44.57 ± 1.89	0.92	1.10	0.83	0.56
0.8	22.49 ± 1.11	8.88 ± 1.09	4.01 ± 0.63	12.22 ± 0.57	9.95 ± 0.84	42.46 ± 3.22	0.90	1.05	0.81	0.69
1	23.64 ± 0.90	12.04 ± 1.82	0.00	12.33 ± 1.23	8.24 ± 2.16	43.76 ± 4.01	0.98	0.98	0.84	1.00

Table 5.1 exhibit elemental composition from energy dispersive spectroscopy (EDS) measurement from the surface of absorber layer after selenization. The measurements were presented by the median value and standard deviation of each element's atomic percentage as well as their respective ratios from sampling of five different points (x5000 magnification) within each sample. The incorporation of Mn into the system is proven by Mn/(Mn+Zn) ratio which reflect to the intended ratio in precursor. Furthermore, Cu-poor and Zn/Mn-rich conditions are maintained throughout all ratios, except for $x = 1$. S and Se have higher variance at $x = 0.2$ and 0.4 in comparison with other composition. These

variations might be due to the smaller grain and voids observed in SEM. It also suggests less Se incorporation into the system which can reduce the grain growth as Se promote grain growth [268]. In addition, the larger standard deviation may also be the effect of phase transformation which occurred around this composition as the alteration of the structure may affect Se incorporation.

5.2.3 Optoelectronic properties of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$

Figure 5.3 a) Photoluminescence (PL) spectra (normalized) as a function of energy (black axis) and band gap as a function of $\text{Mn}/(\text{Mn}+\text{Zn})$ for $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ (blue axis). b) Plot of bandgap and photoluminescence (PL) peaks and the energy difference between them marked with red star as a function of $\text{Mn}/(\text{Mn}+\text{Zn})$

Figure 5.3a shows the photoluminescence response and band gap of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$. The band gap values are extracted from UV-Vis measurement by Tauc plot method (**Figure B5**). Band gap bowing is observed with maximum point at $x = 0.2$. The band gap increases initially from 1.11 eV (CZTSSe) to 1.2 eV ($\text{CM}_{0.2}\text{Z}_{0.8}\text{TSSe}$) and then decrease to 1.03 eV (CMTSSe). Bowing effects or nonlinearity dependence in band gap are commonly found in alloying semiconductor compound [269-272]. This phenomenon can be related to the changes in the band formation on the system. In CZTS or CZTSSe system, Cu $3d$ and S/Se $3p$ -states antibonding is responsible for the upper valence band formation, while Sn $5s$ and S/Se $3s3p$ -states hybridization is responsible for the bottom conduction band formation [48]. However, there is a difference in CMTS and CMTSSe band formation. For the upper valence band, it is mainly formed by Cu $3d$ and S/Se $3p$ -states with additional contribution from Cu and Mn $5d$ -states hybridization, as for the

bottom conduction band, it is mainly formed by Mn $5d$ -states and S/Se $3p$ -states [231]. Mn play a role in the band edge formation in comparison with Zn. The band gap increase might be due to small amounts of Mn weakening the hybridization between Sn and S/Se in the conduction band. However, the small quantity of Mn may not be hybridized with S/Se to replace Sn as the primary cation for the conduction band formation. As the Mn content increases, the hybridization between Mn and S/Se becomes more dominant and thus stronger hybridization which results in band gap decrease at $x > 0.2$. Furthermore, larger ionic size Mn also contributes to the smaller band gap as similarly observed with Cd substitution [231].

The photoluminescence (PL) measurements were performed at room temperature on bare absorber surface (Mo as substrate) with significant atmospheric exposure. In addition, they were etched for 180 s in KCN prior to PL measurements which was performed to improve the PL signal from the samples. The etching help to recover PL signal which generally are expected to decrease from sample exposure and aging, but this process generally does not change the PL peak position. PL signals are observed from $x = 0.0$ - 0.6 and they are quenched above $x = 0.6$. The PL peak position change in agreement to the band gap trend except for the drop at $x = 0.1$. The PL intensity decay as Mn increases with quenched signal at $x \geq 0.6$ suggest high non-radiative recombination and lower carrier lifetime. Non-radiative recombination generally occur due to defect level in the band gap, which leads to lower carrier lifetime [273]. Furthermore, defect near the band edges can also results in band tailing effects. Both band gap defects and band-tailing contribute to the V_{oc} deficit as observed in CZTSSe [34]. Another observation from PL is the difference between PL peak position and band gap energy level ($E_g - \text{PL peak}$) which can determine the absorber quality, depth of acceptor defects which arise band tailing problem. A good performing solar cell generally have minimal band-tails which exhibit PL peak at the bandgap energy [97]. From Figure 3(b), the 5% Mn shows a slight reduction in the PL and the bandgap difference from pure CZTSSe, i.e. 40 meV to 30 meV which infer absorber quality improvement and possible band-tailing reduction. However, the difference between PL and bandgap energy are increasing at $x = 0.1$ - 0.6 compared to CZTSSe ($x = 0$) which suggests increase in defects level near the band edge of these samples. Another metric to assess the absorber is

the shape of PL graph and full width half maximum (FWHM) is one of the variables to quantify it. It correlate with the potential fluctuation near electronic transition [43]. In Figure 5.3a, the FWHM exhibit negligible changes at $x = 0-0.1$ while at $x \geq 0.2$, the FWHM is decreasing which may indicate less energy fluctuations. However, based on the large E_g – PL peak compare to FWHM, the deeper transition level should be more detrimental compare to $x = 0.05$ sample.

Figure 5.4 Hole concentration and hole mobility as a function of Mn/(Mn+Zn) ratio

Figure 5.4 displays the majority carrier concentration and mobility of CMZTSSe as a function of Mn/(Mn+Zn). All of the samples exhibit p-type conductivity based on the AC Hall measurement (see chapter 3) [216]. Significant increase in carrier concentration is observed as Mn content increase, except for the small drop at $x = 0.05$ which is accompanied by small increase in hole mobility. Increase in carrier mobility result in larger diffusion length which leads to better carrier transport provided that the carrier lifetime is high. The carrier concentration and mobility values for CZTSSe is in agreement with reported high efficiency CZTSSe in literature [34, 213]. Similarly, the high carrier concentration is also reported for CMTSSe using same measurement technique [176]. This high carrier concentration may correlate with large number of defects as observed in PL for high Mn samples. The elemental composition difference especially the higher

$\text{Cu}/(\text{Mn}+\text{Zn}+\text{Sn})$ ratios at $x \geq 0.6$ may partly contribute to the high carrier concentration due to the changes in defects concentration such as Cu vacancy (V_{Cu}) or antisite defects (Cu_{Zn}). However, it should not result in huge increase as observed. One other possible reason is due to the elemental properties of Mn, specifically the half-filled $3d^5$ orbital in comparison with fully filled $3d^{10}$ orbital (Zn). Although Mn^{2+} is the most stable state due to parallel single electron spin in $3d$ orbitals, the unpaired electron can still act as carrier traps and forming other oxidation states, such as Mn^{4+} or Mn^{7+} . In addition, due to the splitting of the d-orbitals in tetrahedral systems into two sets of energy levels (t_{2g} and e_g), it may facilitate electrons to leave some of the orbitals which increase the oxidation states of Mn [274]. Moreover, cation radius will decrease as the increase in oxidation states [275], the smaller cation radius of Mn will result in an ease of antisite formation between Cu-Mn as observed between Cu-Zn. The Mn oxidation states evolution is indicated by the x-ray photoelectron spectroscopy (XPS) measurement (**figure B6**) which exhibit shoulder peaks around Mn $2p$ peaks for CMTS ($x = 1.0$). These shoulder peaks generally correspond to change in chemical environments surrounding Mn such as oxidation states change. Therefore, the evolution of Mn oxidation states may introduce extra carriers in the system.

5.2.4 Device performance of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$

Figure 5.5 Device parameters a) η , b) FF, c) J_{sc} and d) V_{oc} versus the Mn content for $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ thin film solar cells. The “champion” cell parameters are marked by red stars.

To investigate Mn effect on device performance, solar cell devices with structure of Mo/CMZTSSe/CdS/i-ZnO/AZO/Ag-paste were fabricated and measured. **Figure 5.5** displays the average (black square box) and standard deviation of four device parameters; efficiency (η), fill factor (FF), short-circuit current (J_{sc}), and open-circuit voltage (V_{oc}) as a function of Mn/(Mn+Zn). These data were collected from three batches (16 cells per batch) to provide statistical credibility. The efficiency shows non-linear dependency toward Mn/(Mn+Zn) ratio with $x = 0.05$ as the highest performing ratio. This efficiency improvement from CZTSSe can be attributed to the V_{oc} improvement and fill factor improvement. This indicates there is an improvement in the charge separation and collection. This result is in conjunction with the larger grain size, small increment in band gap, lower carrier concentration and higher carrier mobility which can be attributed to the

improvement.

Figure 5.6 a) J-V curves, b) CV and DLCP measurement for $\text{CM}_x\text{Zn}_{1-x}\text{TSSe}$ devices with $x = 0$ and 0.05. We use relative dielectric constant $\epsilon_r = 8.5$ which is close to CZTSe [6]. The dashed line indicates the zero bias voltage. c) V_{oc} vs temperature (T) under 1 sun. d) EQE measurement for $\text{CM}_x\text{Zn}_{1-x}\text{TSSe}$ with $x = 0$ and $x = 0.05$.

Table 5.2 Diode model J-V parameters for the highest CZTSSe and $\text{CM}_{0.05}\text{Zn}_{0.95}\text{TSSe}$.

Devices	Efficiency (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	Fill Factor (%)	η_1	J_{01} (A/cm ²)	R_s (Ohm.cm ²)	G_{sh} (mS/cm ²)
$x = 0$	6.42	28.8	0.39	57.8	1.88	9.57×10^{-6}	0.86	4.9
$x = 0.05$	7.59	28.9	0.43	61	1.91	4.25×10^{-6}	0.81	2.7

Following that, device performance is decreasing at $x > 0.05$. This reduction is due to significant reduction in J_{sc} and fill factor. The samples at higher Mn content ($x > 0.4$) suffer

from poor charge collection and lower carrier lifetime due to increase in non-radiative recombination as observed by PL and high carrier concentration ($\sim 10^{17}$ - 10^{18} cm^{-3}). High carrier concentration absorber tends to suffer from high shunt conductance (G_{sh}) and narrow depletion width which result in poor charge collection. This is shown by the shunted profile, high G_{sh} and ideality factor JV curve of CMTSSe (**figure B7**). High shunt conductance around short circuit current can be observed even in the dark condition which indicate intrinsic shunt problem in the absorber. The poor interface with thick MoSe_2 and secondary phases might also contribute to poor performances.

Further analysis was performed on the highest performing $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ cell by comparing the JV curve with the control CZTSSe device. The J–V characteristics with their extracted device parameters are shown and tabulated in **Figure 5.6a** and **table 5.2**. Besides the four device parameters, diode model parameters such as ideality factor η_1 , reverse saturation current J_{01} , series resistance (R_s) and shunt conductance (G_{sh}) are extracted by Lambert-W curve-fitting method to a single diode model [210]. The $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ exhibit smaller J_{01} , R_s and G_{sh} in comparison to CZTSSe which lead to V_{oc} and fill factor improvement. FF improvement is mainly due to decrease in shunt conductance which could be related to absorber quality improvement as observed in the previous findings. However, the fill factor ($\approx 61\%$) and diode ideality factor (1.91) are still relatively poor in comparison with the best CZTSSe solar cell in literature [34]. This might be due to voltage dependent collection problem and recombination losses which could be due to the different defect properties of the film arising from difference in synthesis method [34]. Capacitance-voltage (CV) and drive level capacitance profiling (DLCP) measurements were also performed on these samples. The results are shown in figure 5.6b as charge density (N_x) vs distance (x) with voltage bias from +0.5 to -6 V. In CV, the definition of charge density includes bulk carrier density (free carrier density and defect density), defects traps at space charge region and interface defects. As for DLCP, it only includes bulk carrier density and defects trap at the space charge region but does not include interface defects [13]. Therefore, the difference between the two charge density values correspond to interface defects in the junction. In this study, the $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ cell exhibit smaller difference compared to CZTSSe. In addition, a reduction in overall charge density for the champion device is also

observed which emphasize the interface improvement by Mn. Regarding the depletion width (x_d), it is determined by $\varepsilon_0\varepsilon A/C$ at zero bias, where C is the capacitance, A is the device area, ε_0 is vacuum permittivity and ε is the dielectric constants for the absorber [13]. The depletion width (x_d) for $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ is wider than that of CZTSSe (i.e. ≈ 340 nm vs 290 nm, respectively). The wider depletion region is generally associated with better charge separation between the electron-hole pairs generated which leads to higher V_{oc} . Furthermore, the carrier density at large negative bias (correspond to bulk carrier concentration) for the $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ ($\approx 1 \times 10^{14} \text{ cm}^{-3}$) is consistent with carrier concentration from Hall measurement ($\approx 2 \times 10^{14} \text{ cm}^{-3}$). Another observation from external quantum efficiency (EQE) of these two cells shows charge collection improvement in the short wavelength region ($<700\text{nm}$) for the $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ device which is in agreement with lower interface charge density found in the DLCP/CV study. As for the charge collection in long wavelength region ($>700\text{nm}$), $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ have lower charge collection compared to the CZTSSe which leads to similar J_{sc} value between the two. Although the $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ cell has higher depletion width, its thicker film may reduce charge collection at longer wavelength due to increases the collection path and recombination probability. This finding indicates that having CZTSSe as the backside absorber may be more beneficial and having double layer of pure- CZTSSe and Mn-substituted CZTSSe should improve the performance further.

Further device characteristic of the champion $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ is investigated through temperature dependent current-voltage study (IVT). The V_{oc} vs. temperature (T) plot is shown in Figure 5.6c. The remaining parameters such as efficiency, J_{sc} and FF vs temperature are also plotted in **figure B8**. The measurement was performed on an aged and exposed sample thus the efficiency has slightly dropped. From V_{oc} vs temperature graph, the activation energy (E_A) can be extracted by extrapolating V_{oc} at 0 K. The E_A value for $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ is around 1.05 eV while it is around 1.00 eV for CZTSSe . The activation energy for $x = 0.05$ is still less than the band gap ($E_A < E_g$) which infer that the recombination mechanism is dominated by interface recombination [212]. Compared to the Schottky-Read-Hall (SRH) recombination mechanism in space charge region which dominates when the activation energy value is equal to band gap [211]. However, a

noteworthy $\Delta(E_g - E_A)$ lower value of ~ 0.07 eV is obtained for $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ in comparison with control sample (~ 0.11 eV) and it is also comparable with record CZTSSe cell, ~ 0.1 eV [34]. From figure B8, the efficiency increases initially as we decrease the temperature and then drops at ~ 200 K for $x = 0.05$, while the control sample drops at higher temperature ~ 225 K. These drops come from the collapse in J_{sc} and FF, as less carriers are being generated and transported due to insufficient thermal energy. This phenomenon is generally observed with the increase in series resistance which leads to carrier freeze-out at low temperature [213]. Overall, the device performance was improved mainly due to less interface recombination in the CdS/CMZTSSe interface as observed by larger charge collection at short wavelength in figure 5.6d which is also supported by the finding from the difference between CV and DLCP value.

Moving forward, further optimization could be performed as J_{sc} , V_{oc} and fill factor values are still relatively low. The double layer structure should be able to improve the performance further as indicated by EQE. This optimization could harness the positive charge collection of both CZTSSe and CMZTSSe. Furthermore, study on the partial substitution of Mn with Zn in pure sulfide-based samples should also be investigated to enhance the understanding of Mn substitution in kesterite system.

5.3 Partial substitution of Mn with Zn in sulfide condition (CMZTS)

The second part of this study is to investigate partial substitution of Mn with Zn in sulfide based CZTS. Spin coating method was used in this study instead of spray pyrolysis to ensure the Mn effect does not rely on deposition method and to establish for further study on double layer structure. Similarly, Mn salt was mixed in the precursor solution with various $\text{Mn}/(\text{Mn}+\text{Zn})$ ratio and then spin coated uniformly on substrate. Following that, screening of thin film and device analysis were performed to find out similarity and differences of Mn in the sulfide system compared to sulfoselenide system.

5.3.1 Morphology and elemental composition of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$

Table 5.3 Elemental composition of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films

x	Composition (%at)					Mn/(Mn+Zn)	Cu/(Zn+Mn+Sn)	(Zn+Mn)/Sn
	Cu	Mn	Zn	Sn	S			
0.0	20.9 ± 0.17	0.0	13.1 ± 0.43	11.5 ± 0.08	54.5 ± 0.63	0.0	0.85	1.14
0.15	20.3 ± 0.41	1.6 ± 0.07	9.6 ± 0.13	10.7 ± 0.06	57.9 ± 0.33	0.14	0.93	1.04
0.20	19.6 ± 0.06	2.1 ± 0.07	9.2 ± 0.12	10.6 ± 0.0	58.6 ± 0.09	0.19	0.89	1.07
0.40	20.5 ± 0.25	4.0 ± 0.11	7.0 ± 0.06	11.2 ± 0.16	57.3 ± 0.54	0.36	0.93	0.98
0.60	22.0 ± 0.76	4.8 ± 0.24	4.6 ± 0.14	11.7 ± 0.13	57.0 ± 1.10	0.51	1.05	0.80
0.80	24.8 ± 0.29	5.3 ± 0.12	2.9 ± 0.36	12.3 ± 0.17	54.7 ± 0.22	0.65	1.21	0.66
1.0	26.3 ± 1.75	5.7 ± 0.33	0.0	13.4 ± 0.83	54.6 ± 2.86	1.0	1.38	0.42

Table 5.3 exhibit the elemental composition for CMZTS with various Mn/(Mn+Zn) ratio after sulfurization. The EDS results were tabulated based on the average atomic percentage value and standard deviations from different spot of the samples to ensure statistical confidence. The EDS results verify the lateral uniformity and homogenous bulk distribution through this deposition method based on the low standard deviations (± 3 at%). The Mn/(Mn+Zn) ratio at $x = 0.15$ -0.40 maintain the Cu-poor and Zn/Mn-rich composition from the precursor ratio. However, the amount of Mn is lesser than the precursor solution at $x \geq 0.40$ which is also observed before sulfurization (**figure B9**). This observation infers the limitation on formation of Mn complex for higher amount of Mn in the precursor solution through this spin coating method. Different type of Mn precursor or extra additives might be required to form complex in high Mn as reported in previous study [179]. The Mn loss for these samples leads to Cu-rich or Mn-poor condition and increase the likelihood of secondary phases formation [69]. In addition, the excess of Cu is unfavorable for solar cell due to possible defects formation such as Cu interstitials (Cu_i) or Cu_{Mn} antisite

[276]. Extra defects will result in higher hole concentration which are unfavorable for the minority carrier diffusion. Further optimization is required to obtain desired composition for higher Mn content for this spin coating method.

Figure 5.7 Plan-view SEM of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ with a) $x = 0$, b) $x = 0.15$, c) $x = 0.2$, d) $x = 0.4$, e) $x = 0.6$, f) $x = 0.8$, g) $x = 1.0$ and h) cross-section SEM of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ sample.

Figure 5.7 exhibit plan-view SEM images of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ after sulfurization. The grains sizes are varied from one micrometer to tens of nanometers. The grains are well defined and crystallized for $x \leq 0.6$. However, poor grain quality is observed for $x \geq 0.8$ due to the less developed grains and voids. This might be due to the significant composition

difference which comes from non-optimized fabrication technique for high Mn content films. Other than that, there is no significant changes in the thickness and cross-sectional morphology with different Mn content. The film thickness is found to be around 1 μm as shown by a representative image in figure 5.7h. In comparison with spray pyrolysis technique, the spin coating technique generally exhibit more uneven surface and less compact films. It might be related to the nature of lateral spreading deposition compare with vertical growth in spray pyrolysis.

5.3.2 Structural and phase transformation of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$

Figure 5.8 X-ray diffraction pattern of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ thin film at $x = 0.0 - 1.0$.

Figure 5.8 exhibits the XRD patterns for $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}$ films. Most of the significant peaks corresponds to either CZTS or CMTS signature peaks. There are no significant different peaks position with the database compared with sulfoselenide system. There is no sign of notable secondary peaks at $x = 0.0 - 0.8$, although some secondary phases such as ZnS and Cu_2SnS_3 are generally undistinguishable with CZTS. Peaks at $2\theta = 40^\circ$ belong to the molybdenum (Mo) peak. At $x = 0$, the dominant peaks at $2\theta = 28.5^\circ$ and 47.4° are in agreement with (112) and (220) planes of CZTS kesterite [277]. Peaks were shifted slightly

to lower angle from 28.5° to 28.3° for the (112) plane following the increase in Mn content as observed in **figure B10**. It infers the crystal lattice expansion due to the larger ionic size Mn substituting Zn [99]. At the other end ($x = 1$), stannite crystal structure of CMTS is observed as indicated by double peaks at $2\theta = 47.8^\circ$ (figure B10) which is shown in reference (JCPDS No. 51-0757) [278]. The double peaks denote stannite (220) and (204) planes of stannite instead of single peak which is usually shown in kesterite [15]. However, low stannite peaks intensity signifies the low crystallinity of the deposited CMTS. This observation is in conjunction with small grain sizes and poor grain quality as observed in SEM. Furthermore, additional peak splitting at $2\theta = 28.3^\circ$ and 40° peaks may suggest the presence of secondary phases at $x = 1.0$.

Raman scattering was performed to examine the presence of secondary phases in the CMZTS absorber, especially the overlapping secondary phases with CZTS in XRD such as ZnS or Cu_2SnS_3 [261]. **Figure B11** displays the Raman spectra for CMZTS for different Mn composition. Overall, no notable secondary peaks were observed for all ratios. The dominant peaks around 332 cm^{-1} and 282 cm^{-1} correspond to both CZTS and CMTS phases respectively [70, 262]. The 332 cm^{-1} peak are shifted to the lower wavenumber for CMZTS at $0.4 \leq x \leq 0.8$ which suggests weaker bond stretching force constant due to crystal lattice expansion upon substitution [279]. Secondary phase peaks such as cubic ZnS (352 cm^{-1}), cubic Cu_2SnS_3 (303 cm^{-1} and 356 cm^{-1}) or Cu_{2-x}S (475 cm^{-1}) were not observed [15]. However, due to the surface sensitivity of Raman measurement, the possibility of secondary phases around the back contacts is plausible, especially based on the large composition difference at high Mn content in comparison with the stoichiometric ratio in EDS. In addition, multiwavelength excitation might be required to fully confirm that secondary phases do not exist in the samples, because certain secondary phases such as ZnS is only sensitive to UV-Raman.

5.3.3 Device performance of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$

Figure 5.9 Device parameters a) η , b) J_{sc} , c) V_{oc} and d) FF as a function of the Mn content for $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ (data for each condition are taken from 16 solar cell devices).

Solar cells with Mo/CMZTS/CdS/ITO/Ag-paste structure was fabricated to observe the effect of Mn on CMZTS device. The optimum average power conversion efficiency was achieved at 5.20% for $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$, an increase from 4.40% of CZTS (**figure 5.9a**). All three parameters exhibit improvements from the control samples, especially J_{sc} . Screening process around $x = 0.15$ were conducted which verify the optimum ratio (**figure B12**). As the Mn concentration increase ($x \geq 0.15$), the efficiency of the solar cell gradually decreases before sharply declining at $x = 0.6$. This finding is consistent with the observation from the thin film characterization. In comparison with sulfoselenide system, the optimum amount of Mn substitution is higher which might be due to the less lattice constraint that S element contribute compared to larger anion in Se.

Figure 5.10 a) External quantum efficiency of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ and b) band gap determination through $d\text{EQE}/dE$ graph for $x = 0-0.4$.

The EQE measurements were performed on these devices to determine origin of J_{sc} improvement (**figure 5.10a**). The highest quantum efficiency was observed for $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$. Short wavelength collection ($<600\text{nm}$) increment is observed for $x = 0.15$ and 0.2 in comparison with CZTS ($x = 0$). Meanwhile, the longer wavelength charge collection ($>600\text{nm}$) has similar quantum efficiency with CZTS. This suggest absorber-buffer layer interface improvement with Mn as observed similarly in sulfoselenide system. Abrupt drop in EQE for $x \geq 0.6$ explain the J_{sc} drop in device performances. Low charge collection can be attributed to either poor charge transport due to carrier recombination and high defects density, or poor junction [176], or secondary phases from non-stoichiometric ratio.

The band gap determination was also conducted based on EQE. The band gaps are determined using the first peak of $d\text{EQE}/dE$ graph (where $E = hc/\lambda$) [212]. However, band gap determination by EQE is only suitable for notable charge collection. Therefore, only samples for $x \leq 0.4$ were analyzed. Insignificant changes in band gap ($1.57 \text{ eV} \pm 0.01$) were observed at $x = 0.0-0.4$. This agrees with the theoretical study on band structure of $\text{I}_2\text{-II-IV-VI}_4$ quaternary semiconductors which states that substitution of group-II cation, such as Zn with Mn, theoretically, should not affect the band gap [131]. It is slightly different

than the sulfoselenide system where there are some changes in band gap even in low Mn substitution. This might be due to the difference between S and Se as anion which is the main contributor to the band edges formation.

5.4 Double-layered structure of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ and $\text{Cu}_2\text{Mn}_{0.15}\text{Zn}_{0.85}\text{Sn}(\text{S},\text{Se})_4$ for sulfide and sulfoselenide-based system

Figure 5.11 Device parameters a) η , b) J_{sc} , c) V_{oc} and d) FF as a function of $\text{Cu}_2\text{Mn}_{0.15}\text{Zn}_{0.85}\text{SnS}_4$ layers (data for each condition are taken from 16 solar cell devices).

The findings from EQE and J-V curve suggest the charge collection improvement at the absorber-buffer interface for both spin coated $\text{Cu}_2\text{Mn}_{0.15}\text{Zn}_{0.85}\text{SnS}_4$ and spray pyrolysis $\text{Cu}_2\text{Mn}_{0.05}\text{Zn}_{0.95}\text{Sn}(\text{S},\text{Se})_4$. As for the back interface, CZTS performs similarly well or even better charge collection while having similar band gap. Therefore, in this last part of study, investigation on double layered structures of CZT(S,Se) as the back layer and

$\text{CM}_{0.15}\text{Z}_{0.85}\text{T}(\text{S},\text{Se})$ as the top layer using spin coating method. Investigation was performed for sulfide based, followed by comparison with the sulfoselenide films.

5.4.1 Device optimization on double layer structure in sulfide-based system

The double-layered structure was fabricated with a total of 13 layers which is equivalent to 800-1000 nm thickness. The $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ layers were deposited and substituting the top layers with various number of layers (2,3, 4 and 5 layers). The control samples for both CZTS and $\text{Cu}_2\text{Mn}_{0.15}\text{Zn}_{0.85}\text{SnS}_4$ ($\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$), were also fabricated within the same batch (16 samples) with the rest of samples to provide data reliance. **Figure 5.11** exhibit the device parameters for the various $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ thickness in the double-layered structure. As $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ layer increase, a gradual increase in average efficiency is observed from the 4.40% of CZTS to the optimal performances of 5.35% at CZTS + 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ (30% of overall thickness). The increase in J_{sc} from 15.75 mA/cm^2 to 17.55 mA/cm^2 is the main contributor for the device performance improvement. Regarding the V_{oc} , a slight improvement is observed at both CZTS + 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ and bulk $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$. In comparison with 5 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ and bulk $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$, the optimal 4 layers shows the highest average efficiency and J_{sc} with similar V_{oc} and FF. Based on the notable device differences and cross-section SEM-EDS (**figure B13**), most of the Mn-substituted layers remain on top of the absorber and forming composition gradient, instead of diffusing homogenously in the bulks and forming $\text{CM}_x\text{Z}_{1-x}\text{TS}$ with $x \leq 0.15$ which was observed to perform less than the double layer. Subsequent device analysis was performed on the 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ device in comparison with CZTS and bulk $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$.

Figure 5.12 a) Current density-voltage (J-V) and b) external quantum efficiency (EQE) for CZTS, CZTS + 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ and bulk $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$.

Table 5.4 Diode model J-V parameters for the highest CZTS, CZTS + 4 layer of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ and bulk $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$

Devices	Efficiency (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	Fill Factor (%)	η_1	J_{01} (A/cm^2)	R_s (Ohm.cm^2)	Gsh (mS/cm^2)
CZTS	4.70	15.87	0.59	50.32	3.47	1.75×10^{-5}	1.57	5.21
CZTS + 4 $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$	5.73	17.86	0.60	53.27	2.61	1.79×10^{-6}	0.93	7.69
$\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$	5.30	16.33	0.60	53.45	2.74	2.39×10^{-6}	0.99	6.17

The J-V graph of the “champion” CZTS + 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$, CZTS and bulk $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ are depicted in **figure 5.12**. Their extracted device parameters based on single diode model are tabulated in **table 5.4**. The diode model parameters were extracted using Lambert-W curve-fitting method [210]. The CZTS + 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ possess the lowest η_1 , J_{01} and R_s which confirm better p-n junction quality compared to control samples. FF improvement is also observed due to decrease in series resistance and diode parameters which may indicate better junction interface. However, the champion device still suffers from low fill factor (FF) and high ideality factor. The high diode ideality

factor (>2) does not represent the any carrier generation mechanism in typical p-n junction according to Sah-Noyce-Shockley [280], but it can be described as coupled defect level recombination mechanism according to other theory [281]. In addition, parameter extraction based on Lambert-W can obtain high ideality factor especially in high resistance sample [282]. Nevertheless, this double layer strategy able to maximize the benefit of CMZTS in comparison with the pure CZTS.

Lastly, the EQE results were examined to verify the J_{sc} improvement from both layers (figure 5.12b). The increase in charge collection were observed at short wavelength for both 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ and bulk $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ as predicted based on the indication of interface improvement with CdS. The collection was only reduced for bulk $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ in the long wavelength region. It also the only sample who possess slightly higher band gap (1.54 eV) and gentler slope in comparison with CZTS (1.53 eV).

5.4.2 Comparison between double layer structure in sulfide and sulfoselenide system

Following the optimization in sulfide system, similar investigation was performed in sulfoselenide system. **Figure 5.13** exhibit both sulfide and sulfoselenide samples as a function of Mn-substituted layers. Due to the lower band gap of sulfoselenide system, the overall J_{sc} are significantly higher and the V_{oc} are less than the sulfide ones. The first difference is that a smaller number of layers (2 layers/15% of overall thickness) is needed to obtain the optimum performance. This finding is consistent with the previous finding where smaller amount of Mn substitution is required in the bulk for sulfoselenide (5%) compared to sulfide (15%) film. Secondly, the increase in performance of the sulfoselenide system is also accompanied by significant increase in V_{oc} , J_{sc} and FF compared to only notable J_{sc} increase in sulfide system. The V_{oc} increase by ~ 0.1 V on average without band gap changes. Together with the large increase in fill factor, it infers the improved bulk and junction properties for sulfoselenide film.

Figure 5.13 Device parameters a) V_{oc} , b) η , c) J_{sc} and d) FF as a function of either $\text{Cu}_2\text{Mn}_{0.15}\text{Zn}_{0.85}\text{SnS}_4$ or $\text{Cu}_2\text{Mn}_{0.15}\text{Zn}_{0.85}\text{Sn}(\text{S},\text{Se})_4$ layers (data for each condition are taken from 16 solar cell devices).

Figure 5.14 a) J-V graphs and b) external quantum efficiencies of CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTSSe.

Table 5.5 Diode model J-V parameters for the “champion” CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTSSe cell.

Devices	Efficiency (%)	Jsc (mA/cm ²)	Voc (V)	Fill Factor (%)	η_1	J ₀₁ (A/cm ²)	Rs (Ohm.cm ²)	Gsh (mS/cm ²)
CZTS	4.70	15.87	0.59	50.32	3.47	1.75×10^{-5}	1.57	5.21
CZTS + 4 CM _{0.15} Z _{0.85} TS	5.73	17.86	0.60	53.27	2.81	3.41×10^{-6}	0.86	6.76
CZTSSe	6.42	28.8	0.39	57.80	1.88	9.57×10^{-6}	0.86	4.93
CZTSSe + 2 CM _{0.15} Z _{0.85} TSSe	8.74	31.7	0.47	58.57	1.50	1.33×10^{-7}	1.37	2.47

To further evaluate the differences between sulfide and sulfoselenide systems, diode analysis was performed for the highest performing cell in each sample. **Figure 5.14** exhibit the photovoltaic response and the quantum efficiencies for the CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTSSe. The diode parameters are extracted by Lambert-W method in **table 5.5**. The ideality factor of sulfoselenide films are within $1 < \eta_1 < 2$ which infer the recombination mechanism can be described as a single diode junction, while sulfide films have $\eta_1 > 2$ which indicate more complex recombination mechanism [280, 281]. This finding is consistent with the bulk Mn-substitution study. Furthermore, the double layer structure reduces the ideality factor which indicate improvement in diode behaviour toward band to band recombination. Reduced dark saturation current (J₀₁) is observed in both systems, but significant decrease is observed for sulfoselenide which leads to larger Voc increase. In general, the shunt conductance for sulfoselenide are lower than sulfide film with the lowest shunt conductance corresponds to the highest performing cell.

Regarding the charge collection, improvement in short wavelength (<700 nm) with constant charge collection in long wavelength region is also observed in the sulfoselenide films. In terms of band gap, there are no notable changes for the double layered samples from their respective control samples. The main difference between the sulfide and sulfoselenide is observed in the different collection near the CdS region for sulfide film with similar thickness. The sulfide samples might have a thinner CdS as a result of Cd

diffusion into the absorber owing to the post annealing process in sulfide films. Lastly, the smaller J_{sc} from quantum efficiency compared with the J_{sc} from the JV curve suggests that the samples might have poor light or voltage dependent charge collection.

Figure 5.15 Charge density as a function of distance derived from capacitance-voltage (CV) measurement for CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTSSe.

To assess the p-n junction quality, capacitance-voltage measurements were performed with +0.5 V to -3V voltage bias. **Figure 5.15** depicts the derived space-charge density from the CV sweep as a function of distance. Due to different anions, two values of relative

permittivity are used, ϵ is 6.7 for sulfide films and 8.5 for sulfoselenide (assuming that small amount of Mn as cation does not affect the permittivity) [6, 13]. From figure 5.15, both 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ and 2 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TSSe}$ increases the depletion width (x_d) from control samples with larger increase for sulfide film. The larger depletion region width improves charge separation and collection which is in agreement with the improved EQE and J_{sc} [116]. The depletion width in sulfoselenide films are larger than sulfide films which might be related to the thinner CdS as observed in EQE. As for the charge density, notable decrease was only observed for sulfoselenide film from $1.08 \times 10^{17} \text{ cm}^{-3}$ (CZTSSe) to $3.43 \times 10^{16} \text{ cm}^{-3}$ (CZTSSe + 4 $\text{CM}_{0.15}\text{Z}_{0.85}\text{TSSe}$). Based on the DLCP-CV difference, this decrease comes from interface defect density reduction which was also observed in sulfide film but with smaller magnitude. In addition, all of the samples possess similar charge density values ($\sim 10^{16} \text{ cm}^{-3}$) in DLCP measurements which highlight Mn effects in the interface.

Figure 5.16 a) V_{oc} as a function of temperature (T) under 1 sun measurement and b) dark shunt conductance as a function of temperature for CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTSSe.

The V_{oc} vs. temperature (T) plot for “champion” devices were plotted in figure 5.16a. The extrapolated V_{oc} at 0 K (E_A) values were also depicted in the figure. The values for sulfide films are significantly lower than their respective band gap in comparison with sulfoselenide. Since the activation energy are less than band gap ($E_A < E_g$), this suggests

interface recombination is the dominant recombination mechanism [283]. The double layer structure increase the E_A which indicates reduction in interfacial barrier height that eases the charge transport through the junction [284]. Meanwhile, for sulfoselenide films, the activation energy is closer to band gap ($E_A \approx E_g$) which suggests space charge recombination [211]. The drop in V_{oc} at lower temperature is generally attributed to increase in series resistance due to carrier freeze-out effect or an energetic barrier to collection at the interface [212]. However, the drop for both control samples occurs at higher temperature which suggests possibility of higher barrier effect especially at front junction. From figure 5.16b, the dark shunt conductance (G_{SD}) decreases with lower temperature for all samples due to thermal energy decrease [285]. Both double layer structure in sulfide and sulfoselenide have lower shunt conductance even at low temperature. At low temperature, the value originates solely from intrinsic shunt

Figure 5.17 Photoluminescence (PL) spectra (normalized) as a function of energy (eV) for CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTSSe.

conductance, while at high temperature, the trapping-detrapping also contribute to shunt conductance [285]. Lower shunt conductance infers less shunt pathway for leakage current which is due to defect density reduction at the junction.

Table 5.6 Hole concentration and hole mobility for CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTSSe.

Devices	Hole concentration (cm^{-3})	Hole mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
CZTS	1.71×10^{15}	0.3305
CZTS + 4 $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$	2.65×10^{15}	0.4973
CZTSSe	2.52×10^{15}	0.3041
CZTSSe + 2 $\text{CM}_{0.15}\text{Z}_{0.85}\text{TSSe}$	6.51×10^{14}	2.102

Thin film characterization was also performed to further explain the improvement difference in double layer structures of sulfide and selenide films. From **figure 5.17**, the PL spectra of selenide films show closer ΔE ($E_g - \text{PL peak}$) and lower FWHM values than sulfide. These findings are expected due to the shallower majority acceptor defects Cu_{Zn} antisite defect level and weaker charge trapping complex defects such as $(2\text{Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}})$ in selenide-based CZTSe compared with the deeper position in the gap for sulfide-based CZTS as the PL peaks position and FWHM can be related to the acceptor defects properties [9]. Both double layer structures help to reduce energy fluctuation as indicated by FWHM reduction. The larger amount of Mn in the sulfide-based film affect the defect level as observed by photoluminescence peak shift slightly to higher energy level and closer to band gap. These findings suggest Mn in sulfide films also help reduce band-tailing induced by defect states which have deeper Cu_{Zn} defects level in sulfide based CZTS. The double layer selenide film does not exhibit notable change in ΔE , but the PL intensity is significantly higher compared to control sample (**figure B14**).

Regarding the carrier concentration and mobility, all samples have comparable hole concentration based on the AC hall measurement tabulated in **table 5.6**. This finding is also consistent with the DLCP values at high negative bias. The double layer selenide film reduce the carrier concentration and increase hole mobility significantly from the control sample. This finding suggests the possible increase in minority carrier mobility as the high majority carrier mobility may indirectly stipulate high minority carrier mobility [286]. In

conjunction with larger PL intensity, these findings indicate improved diffusion length which may contribute to less carrier recombination and better charge transport properties for sulfoselenide film.

Overall, this study shows that the improvement by Mn substitution near buffer interface can be optimized through double layer structure in both sulfide and sulfoselenide films. It provides higher improvement in the sulfoselenide film junction and additional improvement in charge transport properties.

5.5 Conclusions

In summary, this chapter provides in-depth analysis on Mn partial substitution in both CZTS and CZTSSe. The structural transformation of CZTSSe kesterite, $\text{C}(\text{M},\text{Z})\text{TSSe}$ stannite and CMTSSe stannite were observed at $x = 0.2$ and $x = 0.8$. The increase in Mn content affect the charge density, mobility and carrier lifetime in CMZTSSe. The best photovoltaic device is obtained in $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ with improvements in depletion width, Voc, and Fill factor. The improved open circuit voltage (Voc) and fill factor (FF) are attributed to the improved shunt resistance and carrier transport due to less defect density especially in CdS/CMZTSSe interface. It also has the lowest carrier concentration, improved carrier mobility and shallower acceptor defects level compared to control sample. However, when Mn content is more than 5% ($x > 0.05$), the efficiency was reduced due the significant increase of carrier density and non-radiative recombination as suggested from PL. The poor interface with thick MoSe_2 and secondary phases might also contribute to poor performances.

Following that in sulphide system, $\text{CM}_x\text{Z}_{1-x}\text{TS}$ solar cell devices (with $0 < x < 1$) have been fabricated by spin coating method. Thin film characterization such as SEM-EDS, XRD and Raman confirm Mn substitution in CZTS thin films. The largest device improvement is obtained in $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ owing mainly from improved Jsc. Similar to sulfoselenide film, short wavelength collection is improved which indicates an improved absorber/CdS interface.

Lastly, further optimization by double-layered structure of CZTS and $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ were obtained based on the better collection in short wavelength from $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ and better back-contact collection by CZTS. The highest efficiency was obtained at 5.73% at CZTS + 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ in comparison with control samples of CZTS and $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$. In sulfoselenide system, the double layer structure managed to achieve the highest performing cell at 8.74% with 2 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TSSe}$. The Mn-substituted top layer increase depletion width and short wavelength collection which correlates with better charge separation and collection. The magnitude of improvement in double layer sulfoselenide film is larger due to the better junction properties with lowest ideality factor and dark saturation current. In addition, charge transport was also improved as observed by increase in PL intensity, CV-DLCP and large carrier mobility. Although the champion cell in this study (8.74%) is lower than the best reported CZTSSe (12.6%), further improvement in the synthesis method and film quality such as annealing in SnS vapor, post selenization chemical etching and $\text{In}_2\text{S}_3/\text{CdS}$ buffer layer could be done to further increase the champion cell in this study. Overall, we believe the partial Mn substitution provides an alternative pathway to improve the performance of kesterite solar cell.

Chapter 6

Study on Structural Transformation and Enhanced Carrier Transport by Mg Incorporation in CZTS Solar Cell

To avoid the multivalence issue from transition metal substitute, Mg is proposed as a possible Zn substitute. In this chapter, the effect of Mg incorporation was investigated by systematically varying the content of Mg in $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ solid solution. Low Mg content ($\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$) improves the power conversion efficiency from CZTS. The improvement was attributed to the better carrier transport properties based on lesser amount of ZnS secondary phase, higher carrier mobility, and shallower acceptor defects level. Detailed analysis by multiwavelength Raman spectroscopy reveals the phase transformation pathways as the Mg content increase.

*This section published substantially as Lie, S., *et al.*, *Improving Carrier Transport Properties of Czts by Mg Incorporation with Spray Pyrolysis*. ACS Applied Materials & Interfaces, 2019.

6.1 Introduction

Mg is another viable candidate as Zn substitute which is very stable in +2 oxidation states in comparison with other multivalent novel transition metals (e.g. Mn, Fe, Ni or Co) which may provide harmful deep level traps [136, 187]. Mg is also abundant and non-toxic, its quantity in earth's crust is naturally higher than Zn [28]. Another advantage of Mg is the possible reduction in the existence of secondary phases compared to Zn based on the instability of Mg binary phases in solution. As for Zn binary phases such as ZnSe and ZnS, they are well known to be present in CZTSSe which lead to reduced photovoltaic performance [188]. However, MgS and MgSe are instable in solution condition [145], therefore their existence should be limited.

Based on the finding in **chapter 4**, photovoltaic performance was also detected from the fully substituted CMgTS compound. A recent study also reported device improvement by Mg partial substitution for sulfoselenide-based $\text{Cu}_2\text{Zn}_{1-x}\text{Mg}_x\text{Sn}(\text{S},\text{Se})_4$ at $x = 0.04$ which is attributed to reduced structural defects. So, in this chapter, partial substitution of Mg was explored to understand its effect on the thin film transformation and photovoltaic response of sulfide-based CZTS. Spray pyrolysis is used as fabrication method in this study due to its facile, low-cost and ease of composition control especially for novel substitution study. The morphology, crystal structure and phases of the $\text{Cu}_2\text{Zn}_{1-x}\text{Mg}_x\text{SnS}_4$ ($x = 0.0-1.0$) thin films were investigated and correlated with photovoltaic device characteristics. A combination of multiwavelength Raman and XRD is used to analyze the crystal and phase formation pathways in the thin films as Mn substitute Zn. Small amount of Mg ($\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$) was found to be the optimal condition for photovoltaic device, while large Mg amount were detrimental. This improvement was further explained by the finding in Photoluminescence (PL) and capacitance-voltage (CV) measurements.

6.2 Elemental composition and morphology of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$

Table 6.1 Elemental composition of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films

x	Composition (at%)					Cu/(Zn+Mg+Sn)	(Mg+Zn)/Sn	Mg/(Mg+Zn)
	Cu	Mg	Zn	Sn	S			
0.0	18.51 ± 0.14	0	12.78 ± 0.17	11.53 ± 0.32	57.19 ± 0.49	0.76	1.11	0
0.05	18.64 ± 0.69	1.04 ± 0.11	11.30 ± 0.20	11.04 ± 0.23	58.00 ± 0.97	0.80	1.12	0.08
0.10	18.53 ± 0.45	1.72 ± 0.1	11.39 ± 0.37	10.99 ± 0.55	57.38 ± 0.92	0.77	1.19	0.13
0.20	20.52 ± 0.18	3.73 ± 0.48	10.68 ± 0.41	11.16 ± 0.66	53.91 ± 0.58	0.82	1.29	0.26
0.40	21.46 ± 0.52	9.62 ± 0.46	9.91 ± 1.13	15.12 ± 0.42	43.8 ± 0.3	0.62	1.28	0.49
0.60	22.78 ± 0.79	13.52 ± 1.78	5.94 ± 1.39	15.15 ± 2.58	42.6 ± 2.37	0.66	1.29	0.69
0.80	21.17 ± 1.37	15.15 ± 1.21	2.64 ± 0.33	14.47 ±2.04	47.24 ± 1.50	0.66	1.23	0.85
1.0	22.59 ± 1.49	19.12 ± 0.96	0	15.31 ± 1.07	42.98 ± 1.35	0.66	1.25	1

To confirm the Mg presence in the film, the composition of the samples was measured by surface energy dispersive spectroscopy (EDS) measurement. **Table 6.1** values represent the average results of several measurement with its standard deviation to provide statistical confidence of the composition. The highest elemental atomic percentage standard deviation is $\approx 2\%$ which should justify the films homogeneity produced by spray pyrolysis. The findings also confirm the Mg presence in the films after sulfurization as shown by Mg/(Mg+Zn) ratio. Notable changes were observed at $x \geq 0.4$ where the samples are very Cu-poor (from Cu/(Zn+Mg+Sn) ratio) and lack of S content compared to the other

composition. In addition, composition measurement was also conducted across the thickness of these films to investigate the lateral elemental distribution (see **figure C1**). It revealed the homogenous distribution of all elements throughout the film thickness.

Figure 6.1 FESEM cross section images of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films with a) $x = 0$, b) $x = 0.05$, c) $x = 0.1$, d) $x = 0.2$, e) $x = 0.4$, f) $x = 0.6$, g) $x = 0.8$ and h) $x = 1.0$.

Figure 6.1 displays the cross-section images of the $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films as a function of Mg content. The average thickness for $x \leq 0.2$ is estimated to be around 700-1000 nm. Thickness increase was notably observed to more than 2000 nm as the amount of Mg increases ($x \geq 0.4$). It might be due to the evident degradation of the film compactness and porosity which leads to voids in between grains. The ease of secondary

phases formation at these compositions may also cause the thickness increase [287]. The largest grain size was observed at $x = 0.05$ which is also the composition for the highest device performance. It might be due to relation between fewer grain boundaries and better charge transport [265]. The grains at $x \leq 0.2$ were larger, denser and more compact in comparison with smaller grains and layered structure for $x \geq 0.4$. Furthermore, voids were also evident in these films especially at $x \geq 0.8$. These observations were also shown and in consistent with the plan-view images of these films (**figure C2**). **Figure C3** displays the grain size distribution on these films based on the area and diameter. Quantitative analysis on the grain size distribution was conducted to present the grain sizes comparison among these thin films.

6.3 Structural and phases transformation of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$

Figure 6.2 X-ray diffraction pattern of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin film ($x = 0.0-1.0$).

Figure 6.2 depicted the diffraction patterns for $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ films at $x = 0.0-1.0$. Molybdenum (Mo) substrate signature peaks were observed at $2\theta = 40.5^\circ$ for all the films. For CZTS ($x = 0$), the dominant peaks are matched with signature peaks of kesterite CZTS (JPCDS No. 26-0575) [277]. From $x = 0.0$ up to $x = 0.6$, peak decreases were evident at 23.1° which is identified as the (110) plane of the kesterite CZTS. In terms of peak full

width half maximum (FWHM), an evident increase is observed which infers crystalline quality degradation of kesterite CZTS phase [265]. This observation agrees with the decrease in grain size as Mg increase for $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ at $x \geq 0.4$ via SEM. In addition, there is an intensity increase for $x = 0.4\text{--}1.0$ at 16.0° , 17.6° , 10.8° and 32.1° which correspond to the presence of the Cu_2SnS_3 monoclinic phase [7]. Moreover, the appearance of peak at 29.2° might indicate the presence of texturized SnS phase. In all compositions, the most dominant peak around 28.5° which correspond to (112) plane in CZTS, does not show notable shift. This suggests that there is no relation between cell lattice parameters with Mg substitution, or insignificant Mg incorporation into CZTS structure. The detailed representation which shows the reference ICDD database for the possible different phases is presented in **figure C4**. At high Mg content, the small peaks at 34° and 43° may indicate the presence of MgS and MgO. However, strong overlap of different possible phases among $\text{Cu}_2(\text{Zn,Mg})\text{SnS}_4$, Cu-Sn-S ternaries and sulfide binaries secondary phases in the XRD diffraction pattern complicate the separation of each phases, therefore multiwavelength Raman scattering measurement and analysis were conducted to better help distinguish them.

Figure 6.3 a) Raman scattering spectra of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films. In the bottom the fingerprint spectra of Cu_2SnS_3 [7], Cu_3SnS_4 [15] and MoS_2 [16] are presented; b) distribution of the phases in $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films according to the analysis of Raman scattering spectra.

Raman scattering spectra were conducted on bare absorber surface without any surface treatment at four points for each sample. The spectrum for all samples is displayed in **figure 6.3a**. For the control sample at $x = 0$, typical kesterite CZTS phase spectrum was clearly pertained [72, 235], which signify good crystalline quality sample, low full width at half maximum (FWHM), in agreement with FESEM images. The spectra remain similar with Mg increase up to $x = 0.2$. Fitting of the most intense peak at 338 cm^{-1} by Lorentzian curve shows inconsequential change of the peak position and FWHM (**figure C5**). This peak is expected to shift to the higher wavenumber as a lighter cation (Mg) substitute Zn [288, 289]. Moreover, quaternary compounds solid solution formation generally result in noticeable increase of the FWHM at $\sim 10 \%$ concentration of the substituted cation [288, 289], which was not observed in this case for the $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ system up to $x = 0.2$,

(the dark yellow spheres in the **figure C5**). These findings infer only small amount of Mg may be incorporated in the $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ solid solution for x up to 0.2.

Notable change in the Raman spectra of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films start to occur after further increase of Mg content ($x \geq 0.4$). The A symmetry peak of kesterite type compound [72] which is the most intense peak exhibited a red shift, followed by a blue shift and accompanied with significant increase in FWHM, and final disappearance at $x = 1.0$. This finding was also in conjunction with the appearance of extra Raman peaks, which start to be identified at $x = 0.4$. These new peaks are related to two ternary phases, monoclinic polymorph of Cu_2SnS_3 [7], orthorhombic polymorph of Cu_3SnS_4 [15], and to the MoS_2 [16] compound. The ternary phases might be formed due to the reduced amount of Zn at $x \geq 0.4$ and incapability of Mg to form the quaternary compound which results in excessive Cu, Sn and S atoms. In contrast, the MoS_2 phase at the back contact was detected when it is not expected due to the low penetration depth of the 532 nm excitation wavelength (~ 50 nm [202]) in comparison with the film thickness. A possible explanation could be the presence of holes which is observed from the SEM figures, enable the detection of Raman signal from MoS_2 at CMgZTS/Mo interface [290]. It should be noted that only in a Zn-free ($x = 1.0$) sample that the peaks of ternaries and MoS_2 phases were detected, and hence confirming that the $\text{Cu}_2\text{MgSnS}_4$ compound is not formed in the present study. This finding is also consistent with the previous results for sulfoselenide system [192], where mixture of ternary and binary phases was found for the $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ thin films at high Mg content, and with the theoretical predictions of phase separation for pure Mg based quaternary compound [131]. It is worth mentioning that $\text{Cu}_2\text{MgSnS}_4$ [193] and $\text{Cu}_2\text{MgSnSe}_4$ [291] compounds have been reportedly formed. However, a detailed analysis of their data could also be interpreted as mixture of ternary phase and Mg based binary phase instead of the quaternary phase proposed by the authors [193]. In addition, insufficient evidence of the presence of the quaternary phase formation were presented in ref. [291], except of XRD patterns, where ternary and quaternary phases are difficult to be resolved.

Additional investigation on the secondary phase formation in $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films were conducted by complementary measurements of Raman spectra under 785 and 325 nm excitation wavelength (see **figure C6**). The usage of 785 nm excitation laser line able to detect additional ternary phases such as $\text{Cu}_2\text{Sn}_3\text{S}_7$ and Cu_4SnS_4 [7] in the thin films especially for the high Mg content. An intense peak of ZnS secondary phase were detected by the 325 nm excitation wavelength in the samples with $x \leq 0.2$. The relative distribution of these phases as a function of Mg content in $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ is depicted in figure 6.3b. In the top figure the relative amount of Cu_2SnS_3 and Cu_3SnS_4 are presented, as measured under 532 nm excitation wavelength, while the bottom figure displays the absolute intensity of LO peak of the ZnS phase, as measured under 325 nm excitation wavelength. These observations are in line with XRD observation. However, the MgS and MgO binary phases which was speculated from XRD analysis are not detected (see figure C4). It might be because they are wide band gap and transparent semiconductors (for MgS $E_g > 4.5$ eV [292], for MgO $E_g = 7.8$ eV [292]), which are difficult to be detected even with the 325 nm excitation laser. Furthermore, instead of forming binary phases, there is a possibility that the excess of Mg segregate as metallic Mg in the interstitial positions, in the grain boundaries or at the back of the absorber layer. Another possibility is that the presence of Mg results in more Zn atoms occupying Cu sites and/or Mg replacing Cu. However, to confirm the structure of of Mg-substituted CZTS, a careful neutron diffraction study is needed.

6.4 Optoelectronic properties of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$

Figure 6.4 a) Carrier concentration (black) and hole mobility (blue) for $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ as a function of $\text{Mg}/(\text{Mg}+\text{Zn})$; b) photoluminescence (PL) spectra (normalized) of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ at $x = 0.0-0.2$.

Figure 6.4a displays the carrier concentration and hole mobility value of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ as a function of $\text{Mg}/(\text{Mg}+\text{Zn})$ which were obtained by rotating parallel dipole line magnet AC Hall setup [216, 293]. The values for control sample in CZTS is comparable with reported findings on high efficiency CZTS measured by the same technique [116, 294]. For all these samples, p-type is observed as the majority carrier. At $x = 0.0-0.2$, the hole concentration is within the order of 10^{15} cm^{-3} , and then an increase is observed when $x \geq 0.4$. In terms of the hole mobility, a small increase is noted at $x = 0.05$ which might indicate the carrier transport improvement. The abrupt increase at $x = 0.4$ is consistent with the notable changes observed in SEM, XRD, EDS and Raman. Additionally, at $x \geq 0.4$, there is an indication of high number of defects or impurities based on the high carrier concentration and small hole mobility which might be due to the higher amount of Mg.

Figure 6.4b displays the photoluminescence spectrum of the $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ absorber samples. The samples were treated by air annealing in a dry box with low controlled humidity for 600 s at 553 K and then slowly cooled (hot plate cooled for around 3600 s) to room temperature. This treatment was reportedly shown to reduce cation disorder in CZTS and beneficial to improve open circuit voltage which leads to improved PL signal [206]. PL signal can only be detected from samples with low Mg content ($x = 0.0-0.2$) and the other compositions do not yield any PL response. The quenched PL signals at $x \geq 0.4$ suggest non-radiative recombination or lower carrier lifetime problem as observed previously [273]. This observation might correlate with the high carrier concentration and presence of ternary phases as observed in AC Hall and Raman measurements, respectively. Another metric from the PL is the difference between PL peak position and band gap (ΔE) which translate as quantity to measure bulk absorber quality and depth of band states near band edge [295]. For this study, the band gap is taken from EQE based on its first derivative peak from **figure C7**. From figure 6.4b, a slight reduction of ΔE value is observed with $x = 0.05$, from 0.21 to 0.18 eV. This phenomenon is usually related to the absorber quality improvement and possible reduction in the depth of acceptor defects for kesterite solar cell [56].

6.5 Effect of Mg substitution in CZTS device properties

Figure 6.5 Device parameters (η , J_{sc} , V_{oc} and FF) as a function of $\text{Mg}/(\text{Mg}+\text{Zn})$ for $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ solar cell.

Solar cell devices with architecture of $\text{Mo}/\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4/\text{CdS}/\text{i-ZnO}/\text{ITO}/\text{Ag-paste}$ were fabricated and measured to figure out Mg effect in CZTS device. **Figure 6.5** exhibit the statistics of their device parameters as a function of Mg content. The results were averaged from 32 cells of two batches. The composition with highest performing conversion efficiency in this set of samples is $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$ ($x = 0.05$). In comparison with control sample CZTS, an increase in average efficiency by 1% is accompanied by the increase in the rest of the parameters. The maximum J_{sc} and fill factor were achieved at the same composition, as for the maximum V_{oc} was achieved at $x = 0.1$. This suggests the bulk properties improvement which is also observed in the optoelectronic measurement for $x = 0.05$ with the assumption that other variables such as process

parameters and other layers are constant and unaffected. Increase in Mg content results in a notable decrease of the binary ZnS phase amount, which leads to overall improvement of solar cell performance. In contrary, the Mg may also form binary phases or metallic Mg segregations which reduces the compactness of the films, and consequently reduces the J_{sc} and fill factor. Further Mg increase at $x \geq 0.4$, all device parameters abruptly decrease due to emergence of the ternary secondary phases and substantial increase in majority carrier concentration. Such a significant increase in hole carrier density might lead to a very narrow depletion width and short lifetime, thereby lower the minority carrier diffusion length. Lastly, there is a small photoconversion efficiency in the Zn-free ($x = 1.0$) device which probably due to the photovoltaic response of the Cu_2SnS_3 compound [7, 227].

EQE measurements (figure C7) on each of the devices reveals the highest quantum efficiency at $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$, which is an improvement from control CZTS sample ($x = 0$). At higher Mg content ($x > 0.05$), the quantum efficiency depicts smaller charge collection in comparison with the control CZTS. This is consonance with the high carrier density for these samples which leads to narrow depletion width and low collection efficiency. This EQE results also elucidate the sudden J_{sc} decrease for $x > 0.2$. Furthermore, the effect of Mg incorporation on the band gap is also analyzed. The analysis is conducted based on the first derivative of EQE at $x \leq 0.2$. Insignificant band gap changes ($1.54 \text{ eV} \pm 0.01$) were shown at $x = 0.0$ - 0.2 . This finding can be interpreted that Mg cation does not affect band edges formation for CZTS system and theoretical prediction also conclude similarly [131]. Finally, at $x = 1.0$, small quantum efficiency is observed which originated from the presence of low bandgap Cu_2SnS_3 [227].

Figure 6.6 a) J-V curves for the highest CZTS and $\text{CMg}_{0.05}\text{Zn}_{0.95}\text{TS}$; b) Spatial charge density as a function of depletion width which is derived from CV measurement for CZTS and $\text{CMg}_{0.05}\text{Zn}_{0.95}\text{TS}$. The relative dielectric constant $\epsilon_r = 6.7$ [13]. The dashed vertical line indicates zero bias voltage.

Table 6.2 Device parameters which extracted from diode model for the highest CZTS and $\text{CMg}_{0.05}\text{Zn}_{0.95}\text{TS}$

Devices	Efficiency (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	Fill Factor (%)	n_1	J_{01} (A/cm ²)	R_s ($\Omega\cdot\text{cm}^2$)	G_{sh} (mS/cm ²)
CZTS	5.10	17.35	0.61	47.97	2.91	7.61×10^{-7}	5.20	7.18
$\text{CMg}_{0.05}\text{Zn}_{0.95}\text{TS}$	6.73	17.19	0.67	59.37	2.6	1.81×10^{-7}	4.90	2.95

The comparison between the ‘champion’ $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$ device with the control CZTS device is presented in **figure 6.6a** and accompanied by the extracted diode model parameters in **table 6.2**. The parameters are extracted using Lambert-W curve-fitting in a single-diode model [210]. The champion device’s fill factor ($\approx 59\%$) is relatively low, but it is comparable with the high efficiency CZTS fabricated by spray pyrolysis from literature [137, 198, 296]. The high diode ideality factor of > 2 is commonly found for device with coupled defect level recombination mechanism [281]. The n_1 , J_{01} and R_s are comparatively lower with the control samples which suggest Mg effect in improving the bulk absorber quality. Additionally, the V_{oc} increase by ~ 0.05 V despite the small reduction in bandgap

(~0.015 eV difference) may also due to the small amount of Mg contribution in reducing the Voc deficit [136].

To investigate the junction properties, capacitance-voltage (CV) measurement were conducted on the highest performing cells with voltage bias of +0.5 to -4 V. Figure 6.6b exhibit the space-charge density as a function of distance for both $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$ and CZTS cells which are derived from the CV sweep based on the relation in the literature [297]. The depletion width at zero bias for $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$ is shorter compared with CZTS (i.e. ≈ 106 and 170 nm, respectively). Depletion width is related with the charge separation and collection quality of the generated electron-hole pairs. Despite having smaller depletion width, $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$ in this study performs better than CZTS. This infers the better absorber quality in collecting the charges which most probably due to larger carrier lifetime or diffusion length [34]. Better diffusion length is also pointed out by the higher hole mobility in $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$. Although the minority carrier diffusion length is directly influenced by minority carrier mobility, the high majority carrier mobility can be indirectly translated into high minority carrier mobility [286]. The charge density value is also in line with carrier concentration value from Hall measurement. Furthermore, both samples have similar carrier density value in high reverse bias condition which imply that despite having similar charge density, small amount of Mg improves the bulk quality intrinsically to improve the performance. The Voc vs. temperature (T) and Jsc vs temperature (T) plots of the champion $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$ are plotted in **figure C8**. From the plot, the activation energy (E_A) for both $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$ and CZTS are ≈ 1.55 and ≈ 1.5 eV respectively. The activation energy for $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$ is closer to the band gap which imply the space charge recombination ($E_A \approx E_g$) [211], while for CZTS, other limiting factors such as interface recombination or band tailing may still be more dominant [283].

The improvement for $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$ in this study has similarity with the improvements by alkali metal doping studies (such as Na or K) [298-300]. Grain size enhancement and electronic properties improvement which results in enhanced photovoltaic performance are also shown from those studies. Additionally, the small

amount of the element ($<10\%$) reiterate the usual amount of alkali doping. However, there is a decrease of Zn that compensate the increase in Mg in this study which also contribute to the improvement. The slight changes in structural and optoelectronic properties also suggest small incorporation of Mg into lattice rather than act as an interstitial dopant. Overall, in this chapter, the effect of Mg incorporation has shown to improve the bulk properties of CZTS in terms of hole mobility, shallower acceptor defects level, less amount of ZnS and better charge collection. Detailed study on the band energetics could also provide more further improve the device performances.

6.6 Conclusion

The effect of partial Mg substitution in CZTS on thin film properties and device performance have been examined. The facile spray pyrolysis method has successfully integrated Mg into CZTS film while preserving respectable Zn and Mg precursor ratio in the film. SEM images shows abrupt transformation of the film quality between $x = 0.2$ and 0.4 . These changes correspond with other changes such as appearance of secondary phases as observed in XRD and Raman spectra, significant increase in carrier concentration, quenched PL signal and significant drop in photovoltaic performance. Multiwavelength Raman analysis of the $\text{Cu}_2\text{Zn}_x\text{Mg}_{1-x}\text{SnS}_4$ solid solutions unveils that only limited amount of Mg is integrated in the compounds, which result in the secondary phases appearance at higher Mg content. The prominent observation was shown by small substitution of Mg in $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$ which give rise to improvement in all photovoltaic parameters. At this composition, the improvements come from the bulk properties such as higher carrier mobility, shallower acceptor defects level, less amount of ZnS and higher charge collection. The highest performance was obtained at 6.73% in $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$, which is a remarkable increase from 5.10% of the highest control-CZTS cell. Efforts to reduce secondary phases by optimizing fabrication method such as sulfurization and post-device annealing could further improve the efficiency of the champion cell. Detailed study on the band energetics could also help in understanding of Mg effect in kesterite solar cell and selecting a more suitable buffer layer with better band alignment to further improve device

performances. Based on this study, we found that the effect of small amount Mg incorporation as a viable route to improve the CZTS solar cell performance.

Chapter 7

Discussion and Future Work

This chapter provides concluding remarks for the whole thesis including reconnaissance and future works in this topic. The discussion on the major results on novel cation substituted quaternary compounds, Mn substituted, and Mg substituted kesterite are summarized. It highlights the unique characteristics of different quaternary compounds, findings from the Mn and Mg partial substitution studies. Based on the finished work in the thesis, reconnaissance and future works on the possibility of Ba and Sr partial substitution, Sn substitution and double cation substitution are discussed. In conclusion, partial substitution using earth abundant and non-toxic elements can be a promising pathway in solving kesterite performance limitation.

7.1 Discussions

This thesis started by addressing the demand of alternative flexible and environmentally friendly solar cell technology with CZTSSe as the candidate of choice. The limitation in the performance of CZTSSe solar cell due to the similarity of Cu-Zn atomic size is introduced in **chapter 1** and explained in detail in **chapter 2**. Recent solution through cation substitution of Ag and Cd have shown promising improvements but these substitutes are less ideal for CZTSSe due to their scarcity and toxicity issues. Thus, as stated in **chapter 1**, the objective of this thesis is to investigate novel cation substitution in CZTSSe with cations which are non-toxic and abundant. Several candidates for Zn substitution with similar oxidation states but different ionic radii are selected and identified. Screening process in full substitution of Zn with the novel elements, followed by understanding and optimizing the partial substitution for the promising candidates (Mn and Mg) to achieve improved photovoltaic responses are the general scope of the study. Detailed explanations on the hypothesis and thesis overview are presented in **chapter 1**.

As a start of finding the ideal candidate for Zn substitution, study on various quaternary chalcogenide compounds with different +2 cations were conducted. In **chapter 4**, the cations were selected based on their compound's stability from theoretical and experimental studies in literature. **Chapter 4** has successfully identified and categorized the formation of different compounds by fully substituting Zn with Mn, Mg, Ni, Fe, Co, Sr and Ba. From structures and phases perspective, the samples can be categorized into three groups; 1) tetragonal structure (CZTS, CMnTS, CFeTS, CCoTS), 2) trigonal structure (CBaTS and CSrTS), and 3) non-quaternary compound (CMgTS and CNiTS). From these three groups, CZTS, CMnTS, CMgTS, CBaTS and CSrTS exhibited photovoltaic response which is a positive indicator for further partial substitution study. The detailed discussions on the possible requirement to form stable and photoactive cation substituted quaternary chalcogenide compounds are given in **chapter 4**. To date this systematic comparison using the same film deposition method is not available in literature and will be a useful contribution to this field.

Chapter 5 summarizes the follow up in-depth analysis on partial substitution study of Mn. Mn partial substitution in both sulfide and sulfoselenide CZTSSe systems ($\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$) were fabricated by spray pyrolysis and spin coating. Incorporation of Mn into CZTSSe induce structural transformation from kesterite to $\text{C}(\text{Mn},\text{Zn})\text{TSSe}$ stannite at $x = 0.2$. The increase in Mn content especially at high Mn content ($x > 0.2$) also increase carrier concentration significantly. For the first time, photovoltaic device improvement is observed in $\text{CMn}_{0.05}\text{Zn}_{0.95}\text{TSSe}$ and $\text{CMn}_{0.15}\text{Zn}_{0.85}\text{TS}$ with improvements in depletion width, Voc, fill factor and Jsc. The improved parameters are attributed to the improved shunt resistance and carrier transport due to less defect density especially in $\text{CdS}/\text{CMnZTSSe}$ interface as observed by short wavelength collection improvement from EQE. Further optimization by creating double layer of CZTSSe + CMnZTSSe managed to achieve the highest performing cell at 5.73% for CZTS + 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ and 8.74% with 2 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TSSe}$. The magnitude of improvement in sulfoselenide film is larger due to the higher quality junction properties. This study proved the capability of Mn as novel substitute which improves CZTSSe defect properties especially at the interface.

In **chapter 6**, the effect of Mg substitution in CZTS is shown by successfully fabricating $\text{Cu}_2\text{Zn}_x\text{Mg}_{1-x}\text{SnS}_4$ with spray pyrolysis technique. First report on the systematic transformation by Mg substitution in the morphology, structural and electronic properties are described in detail. XRD and Raman investigations unveil that limited amount of Mg is incorporated in the $\text{Cu}_2\text{Zn}_x\text{Mg}_{1-x}\text{SnS}_4$ solid solution, which result in the secondary phases appearance at higher Mg content. Similar to Mn, a small substitution of Mg in $\text{Cu}_2\text{Mg}_{0.05}\text{Zn}_{0.95}\text{SnS}_4$ improved the photovoltaic performance. The improvements come from the bulk properties such as higher carrier mobility, shallower acceptor defects level, less amount of ZnS and higher charge collection. This study again shows the effectiveness of partial substitution in enhancing kesterite solar cell efficiency by improving the bulk defect properties.

Overall this thesis has demonstrated a systematic study in selecting and investigating novel cation substitution in CZTSSe to enhance its photovoltaic performance. In the thesis, small

amount of Mn and Mg substitution has been proven to be promising substitutes. However, Ba and Sr, additional promising candidates from the screening remain to be explored. Some reconnaissance investigation and other possible strategies such as Sn substitution and double cation substitution will be discussed in the following sections.

7.2 Reconnaissance and future works

7.2.1 Partial substitution of Zn with Sr and Ba

The remaining promising candidates to be studied are barium (Ba) and strontium (Sr). Both elements are more abundant than Cu and Zn in the earth's crust [301], the only issue is possible toxicity from dissolved Ba^{2+} [302]. These two candidates are predicted to mitigate Cu-Zn antisite formation due to their atomic difference with Zn. Elements with distant location in the periodic table might induce structural changes which lead to changes in optoelectronic properties, as was indeed observed in chapter 4. Therefore, partial substitution of Ba and Sr in CZTS could be a compromised solution where the tetragonal structure of CZTS is preserved while using Ba and Sr to mitigate the Cu-Zn antisite formation. In this thesis, some preliminary work on Sr and Ba partial substitution in CZTS has been conducted using spray pyrolysis method. It highlights the structural and morphology properties as well as their photovoltaic performances.

From the reconnaissance work, several preliminary findings were observed. The Ba partial substitution exhibit a more controlled and incremental transformation in comparison with Sr due to the stability and uniformity of the phases. It might be related to the ease of CBaTS formation compared to CSrTS as predicted based on its chemical potential [148]. The phase separation and segregation were observed in Sr partial. Both cations seem to be difficult to incorporate and create mixed solid solution, but they prefer to form their trigonal phase separately. This was observed in the $\text{Cu}_2\text{Ba}_x\text{Zn}_{1-x}\text{SnS}_4$ / $\text{Cu}_2\text{Sr}_x\text{Zn}_{1-x}\text{SnS}_4$ device parameters and thin film properties which has non-linear dependency with Ba/Sr content. The large difference in elemental properties such as radius (Ba^{2+} (1.49 Å), Sr^{2+} (1.32 Å) with Cu^{1+} (0.91 Å) and Zn^{2+} (0.88 Å) [99]) and electron configuration, and the different crystal

structure (trigonal vs tetragonal) for Ba and Sr might be the possible reasons. However, small amount of Ba/Sr incorporation seems to exhibit some enhancement in device performances. For future study, different formation pathway could be explored for example by using sequential deposition or vacuum based fabrication to incorporate these cations into CZTS. In addition, focusing more on optimizing the pure CSrTS and CBaTS might also be beneficial to figure out their novel properties which can help to solve and understand the performance limiting factors in CZTS.

7.2.2 Sn substitution

In addition to the issue of Cu_{Zn} antisite, some studies suggested Sn related defects in CZTS might lead to Voc deficit [118, 124, 303]. The possible reduction of Sn^{4+} due to the presence of chalcogen vacancies (S or Se) is predicted to introduce deep defects in the band gap [303]. In addition, the Sn_{Zn} is also proposed as a “killer defect” due to its electron trapping/detrapping nature [9, 47]. Although the amount of this defect is small due to nature of Zn-rich composition in high performance CZTS solar cell, the formation of this defect cannot be neglected [106]. In addition, the volatility of Sn compounds (binary or ternary) has been reported especially Sn-loss during the high temperatures process of kesterite formation [304, 305]. As mentioned in **chapter 2**, Ge substitution has been one of the promising substitutes for Sn. Ge has more stable +4 oxidation states than Sn [167], thus less likely to get reduced and form the deep defects[306]. However, fabrication of notable performing Ge-substituted CZTSSe has been limited to nanocrystal or vacuum based method and in the presence of Se [118, 122, 123, 125, 126, 307]. Therefore, further study on sulfide-based Ge substitution or study on various Sn substitute could be beneficial and provide more knowledge in improving CZTS solar cell.

7.2.3 Multiple cation substitution

As mentioned in **chapter 2**, Voc deficit issues in kesterite solar cell are complex and originated from various issues. In addition, various cation substitution studies have also indicated improvements with different mechanism and targeting different defects in kesterite solar cell [52, 56, 116-118, 150, 151]. Even in this study, Mn and Mg substitution

which similarly substitute Zn exhibit improvements in different area. The Mg substitution improve the bulk properties and reduction in secondary phases while Mn enhances the interface and pn-junction quality. Therefore, one possible way to further improve the kesterite performance is to apply multiple cation substitutions. Recent study has shown synergistic effect of double cation substitution of Ag for Cu and Cd for Zn [55]. In this study, Cd improves acceptor defect properties, and Ag reduces the non-radiative bulk recombination. It should be noted that introduction of multiple promising cation substitute to the system can also increase the degree of improvements from one substitution. A study reported that introduction of potassium (K) alone does not improve CZTSSe, but a combination of K and Na result in the highest performance [308]. Therefore, investigation on various combination of other promising substitutes could provide new insight to further improve the device performances.

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List of Publications

- **Stener Lie**, Lydia Helena Wong, *et al.*. Reducing interfacial defect density of CZTSSe solar cell by Mn substitution, *Journal of Materials Chemistry A*, 2018, 6 (4), 1540-1550.
- **Stener Lie**, Mario Indra Sandi, Ying Fan Tay, Wenjie Li, Joel Ming Rui Tan, and Lydia Helena Wong. Investigation of Jsc Improvement in Solution Processed $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ with Efficiency of $> 5\%$, *Solar Energy Materials and Solar Cells*, 2018, 185, 351-358.
- **Stener Lie**, *et al.*. Improving Carrier-Transport Properties of CZTS by Mg Incorporation with Spray Pyrolysis. *ACS Applied Materials & Interfaces* (2019).
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- Asim Guchhait, **Stener Lie**, *et al.*. Enhancement of Open Circuit Voltage of Solution Processed $\text{Cu}_2\text{ZnSnS}_4$ Solar Cell with 7.2% Efficiency by Incorporation of Silver, *ACS Energy Letters*, 2016, 1 (6), 1256-1261.
- Ying Fan Tay, Sing Yang Chiam, **Stener Lie**, *et al.*. Solution processed kesterite $\text{Cu}_2\text{Cd}_{0.4}\text{Zn}_{0.6}\text{SnS}_4$ photocathode for efficient solar hydrogen evolution from neutral water. *Joule*, 2018, 2 (3), 537-548.
- Wenjie Li, Joel Ming Rui Tan, Shin Woei Leow, **Stener Lie**, Shlomo Magdassi, Lydia Helena Wong. Recent Progress in Solution-Processed Copper-Chalcogenide Thin-Film Solar Cells. *Energy Technology*, 2018, 6 (1), 46-59.
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APPENDIX A

Figure A1 Grain size distribution for CXTS thin films based on area (top) and diameter (bottom)

Figure A2 Local EDS measurement for CSrTS at large grains area (left) and small grains area (right)

Figure A3 Normalized XRD peaks for CXTS compounds at 26° - 30°

Figure A4 XRD pattern of CXTS films with each respective reference patterns (excluding CMgTS, no reference available).

APPENDIX B

Figure B1 The XRD of 112 peaks for $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ thin films.

R-Bragg Average = 7.4% ; $\chi^2 = 4.5$

Phases	Crystal Parameter	Space Group	Site	x	y	z	Occ
CZTSSe	a=b=5.6580 Å, c=11.2594 Å	<i>I-4</i> Tetragonal	Zn	0.0000	0.0000	0.0000	1
			Sn	0.0000	0.0000	0.5000	1
			Cu	0.0000	0.5000	0.2500	1
			Cu	0.0000	0.0000	0.0000	1
			S	0.2490	0.2410	0.1279	0.1
			Se	0.2490	0.2410	0.1279	0.9
Mo	a=b=c=3.1496 Å	<i>Im-3m</i> Cubic	Mo	0.0000	0.0000	0.0000	1

R-Bragg Average =8.8% ; $\chi^2 = 6.0$

Phases	Crystal Parameter	Space Group	Site	x	y	z	Occ
CMZTSSe	a=b=5.6574 Å, c=11.2708 Å	<i>I-42 m</i> Tetragonal	Zn	0.0000	0.0000	0.0000	0.8
			Sn	0.0000	0.0000	0.5000	1
			Cu	0.0000	0.5000	0.2500	1
			Mn	0.0000	0.0000	0.0000	0.2
			S	0.2417	0.2417	0.1317	0.1
			Se	0.2417	0.2417	0.1317	0.9
Mo	a=b=c=3.1496 Å	<i>Im-3m</i> Cubic	Mo	0.0000	0.0000	0.0000	1

R-Bragg Average =9.9% ; $\chi^2 = 4.9$

Phases	Crystal Parameter	Space Group	Site	x	y	z	Occ
CMZTSSe	a=b=5.6855 Å, c=11.3531 Å	<i>I-42 m</i> Tetragonal	Zn	0.0000	0.0000	0.0000	0.6
			Sn	0.0000	0.0000	0.5000	1
			Cu	0.0000	0.5000	0.2500	1
			Mn	0.0000	0.0000	0.0000	0.4
			S	0.2417	0.2417	0.1317	0.1
			Se	0.2417	0.2417	0.1317	0.9
Mo	a=b=c=3.1504 Å	<i>Im-3m</i> Cubic	Mo	0.0000	0.0000	0.0000	1

R-Bragg Average =9.2% ; $\chi^2 = 5.2$

Phases	Crystal Parameter	Space Group	Site	x	y	z	Occ
CMZTSSe	a=b=5.6911 Å, c=11.3521 Å	<i>I</i> -42 <i>m</i> Tetragonal	Zn	0.0000	0.0000	0.0000	0.2
			Sn	0.0000	0.0000	0.5000	1
			Cu	0.0000	0.5000	0.2500	1
			Mn	0.0000	0.0000	0.0000	0.8
			S	0.2417	0.2417	0.1317	0.1
			Se	0.2417	0.2417	0.1317	0.9
Mo	a=b=c=3.1523 Å	<i>Im</i> -3 <i>m</i> <i>Cubic</i>	Mo	0.0000	0.0000	0.0000	1

R-Bragg Average =7.2% ; $\chi^2 = 5.2$

Phases	Crystal Parameter	Space Group	Site	x	y	z	Occ
CMTSe	a=b=5.736 Å, c=11.3450 Å	<i>I</i> -42 <i>m</i> Tetragonal	Mn	0.0000	0.0000	0.0000	1
			Sn	0.0000	0.0000	0.5000	1
			Cu	0.0000	0.5000	0.2500	1
			S	0.2451	0.2451	0.1286	0.1
			Se	0.2451	0.2451	0.1286	0.9
Mo	a=b=c=3.147 Å	<i>Im</i> -3 <i>m</i> Cubic	Mo	0.0000	0.0000	0.0000	1

Figure B2 Rietveld Refinement on CM_xZ_{1-x}TSSe thin film as a) x = 0 b) x = 0.2 c) x = 0.4 d) x = 0.8 and e) x = 1.0

Figure B3 Raman Fitting using Gaussian Method on $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S,Se})_4$

Figure B4 Plan view SEM of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$

Figure B5 Tauc Plot for $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S},\text{Se})_4$ from UV-Visible Light absorption measurement

Figure B6 Mn 2p scan for $\text{Cu}_2\text{MnSn}(\text{S},\text{Se})_4$ from X-ray Photoelectron Spectroscopy

Devices	Efficiency (%)	Jsc (mA/cm ²)	Voc (V)	Fill Factor (%)	η_1	J_{01} (A/cm ²)	R_s (Ohm.cm ²)	Gsh (mS/cm ²)
100% Mn	0.91	12.67	0.21	34.14	6.534	53×10^{-3}	0.00	16.6

Figure B7 IV curve for $\text{Cu}_2\text{MnSn}(\text{S,Se})_4$ under dark and illuminated conditions

a)

b)

Figure B8 I-V-T measurement for $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{Sn}(\text{S,Se})_4$ with a) $x=0$ b) $x=0.05$

Figure B9 Elemental composition of $\text{Cu}_2\text{MnSnS}_4$ before sulfurization by SEM-EDS

Figure B10 a) The XRD of (112) peaks for $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films; b) double peaks of (220) and (204) planes for $\text{Cu}_2\text{MnSnS}_4$

Figure B11 Raman scattering for $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ with $x=0, 0.15, 0.2, 0.4, 0.6, 0.8$ and 1.0

Figure B12 Device performances for $x = 0-0.3$ $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films

Figure B13 Cross-section SEM-EDS of CZTS + 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$.

Figure B14 Photoluminescence intensity of CZTSSe (black) and CZTSSe + 2 CMnZTSSe (blue)

APPENDIX C

Figure C1 Cross section SEM images of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films with their respective EDS line scans at a) $x = 0$, b) $x = 0.05$, c) $x = 0.1$, d) $x = 0.2$, e) $x = 0.4$, f) $x = 0.6$, g) $x = 0.8$ and h) $x = 1.0$

Figure C2 Plan-view SEM images of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films with a) $x = 0$, b) $x = 0.05$, c) $x = 0.1$, d) $x = 0.2$, e) $x = 0.4$, f) $x = 0.6$, g) $x = 0.8$ and h) $x = 1.0$

Figure C3 Grain size distribution for $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films based on area (top) and diameter (bottom)

Figure C4 X-ray diffraction pattern of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin film ($x = 0 - 1.0$). In the bottom is list of the signature peaks of possible quaternary, ternary and secondary phases from ICDD database.

Figure C5 Position and FWHM of the A1-like peak in $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films.

Figure C6 Raman scattering spectra of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films measured under 785 (left) and 325 (right) nm excitation wavelength. In the right spectra the first (LO), second (2LO) and third (3LO) order of main ZnS peak are indicated.

Figure C7 External Quantum Efficiency of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$

Figure C8 a) V_{oc} vs temperature (T) and b) J_{sc} vs T under 1 sun measurement of $\text{Cu}_2\text{Mg}_x\text{Zn}_{1-x}\text{SnS}_4$ for $x = 0.0-0.2$