Cu_2ZnSnS_4 (CZTS) THIN FILM GROWN BY ELECTROCHEMICAL DEPOSITION FOR SOLAR CELL

By

ELMOIZ MARGHNI MKAWI MRZOG

Thesis submitted in fulfillment of the requirements

for the degree of Doctor of Philosophy

March 2015

DEDICATION

***To my parents**: Thank you for teaching me to believe in myself, while always pushing me to do better. Your advice has helped me to make both the easy and hard decisions, and your support has given me the confidence to follow through.*

***To my beloved wife and kids**: Who suffered and sacrificed a lot during my absence from Sudan. Thank you for believing in me, and for allowing me to further my studies.*

Please do not ever doubt my dedication and love for you.

With respect

ACKNOWLEDGMENTS

All praise and thanks to Allah

I would like to acknowledge many people for their inspiration, mentoring, encouragement, and support. Without their invaluable help, I could not imagine how I would have completed my PhD. First of all, I owe the deepest gratitude to my advisor Professor Kamarulazizi Ibrahim for his encouragement, guidance, and support during the course of this dissertation research. In addition to his memorable stories delivered in our meetings, his enthusiasm and vision for the research have assisted and directed me to finish this PhD.

Along with this, a huge "thank you" goes to my co-supervisor Dr. Abd alsalam Mohammed for guidance through research challenges and the growth of the project. I am also very grateful to Universiti Sains Malaysia for providing financial support for my research and for giving me the chance to be a graduate assistant. I would like to thank all the staff from the School of Physics, Universiti Sains Malaysia, for providing a friendly environment in which I was able to conduct my project smoothly. I would like to thank the technicians of our School, especially the staff in the Nano Optoelectronics Research Laboratory, for their technical support and valuable contribution to my work. My thanks also go to the School of Chemistry at USM for providing me with the opportunity to use their laboratories and equipment.

Lastly, but by no means least, I would like to acknowledge my parents, my wife, and all my dear brothers and sisters in the Lord.

E.M.MKAWI

TABLE OF CONTENTS

LIST OF TABLES **Page**

LIST OF FIGURES

LIST OF SYMBOLS

T	Absolute temperature
α	Absorption coefficient
A	Area
D	Average crystal size
K	Boltzmann constant
μ	Carrier mobility
E_C	Conduction band edge
σ	Conductivity
Rc	Contact resistance
η	conversion effective
$m*$	Effective mass
E_F	Fermi level of semiconductor
F	Force
n	Free electron concentration
p	Free hole concentration
v	Frequency
R_H	Hall coefficient
V_H	Hall voltage
m_p	Hole effective mass
μ_p	Hole mobility
n	Ideality factor
P_{in}	Incident solar power
θ	Incident/Diffraction angle
d	Interplanar spacing of the crystal planes

a	Lattice constant along x-axis
c	Lattice constant along z-axis
I_m	Maximum current
J_m	Maximum current density
P_m	Maximum output power
$\emptyset_\mathrm{m}$	Metal work function
(hkil)	Miller indices
h	Planck’s constant
R	Resistance
ρ	Resistivity
A^{**}	Richardson’s constant
I_o	Saturation current
φ_B	Schottky barrier height
E_g	Semiconductor band gap
R_s	Series resistance
I_{SC}	Short circuit current
J_{SC}	Short circuit current density
R_{sh}	Shunt resistance
t	Thickness
τ	Time
$\mathrm{E_v}$	Valence band edge
V	Voltage
λ	Wavelength
w	Width

LIST OF MAJOR ABBREVIATIONS

AM1.5G	Air Mass 1.5 Global
Ar	Argon
CB	Conduction Band
CBD	Chemical Bath Deposition
CdS	Cadmium Sulfide
CE	Counter Electrode
CIGS	Copper Indium Gallium Sulfide ($Cu_2 ZnSnS_4$)
CTS	Copper Tin Sulfide (Cu_3SnS_4)
Cu	Copper
$Cu_2 S$	Copper (I) Sulfide
CuS	Cooper (II) Sulfide
CZTS	Copper Zinc Tin Sulfide (Cu_2ZnSnS_4)
CZTS-PVP	CZTS synthesized with the solvent polyvinylpyrrolidone
CZTS-EGL	CZTS synthesized with the solvent ethylene glycol
CZTS-OLA	CZTS synthesized with the solvent oleylamine
CZTS-ODE	CZTS synthesized with the solvent octadecene
CZTSe	Copper Zinc Tin Selenide ($Cu_2 ZnSnSe_4$)
CZTSSe	Copper Zinc Tin Sulfide Selenide ($Cu_2 ZnSn(S_x Se_{1-x})_4$)
EDA	Electrodeposition and annealing
EDX	Energy Dispersive X-Ray Spectroscopy
Eq	Equation
FF	Fill factor

FWHM	Full Width at Half Maximum
HCl	Hydrochloric acid
HRTEM	High-resolution transmission electron microscopy
H_2S	HHydrogen Sulfide
TO	Tin doped indium oxide
IV	Current-voltage characteristics
JCPDS	Joint Committee on Powder Diffraction Standards
J-V	Current density - Voltage
KCN	Potassium Cyanide
KOH	Potassium hydroxide
MS	Metal semiconductor
Mo	Molybdenum
MoS_2	Molybdenum disulfide
Mo -SLG	Soda-Lime glass coated with molybdenum
N_2	Nitrogen gas
NCs	Nanocrystals
nm	Nanometer
O	Oxygen
PV	Photovoltaic
RE	Reference electrode
RF	Radio frequency
RPM	Rotation per minute
RT	Room temperature
S	Sulfur

SAED	Selected Area Electron Diffraction
SCR	Space Charge Region
Se	Selenium
SEM	Scanning Electron Microscopy
Sn	Tin
SnS	Tin sulfide
STEM	Scanning Transmission Electron Microscopy
TCO	Transparent Conductive Oxide
TEM	Transmission Electron Microscopy
TFSC	Thin Film Solar Cell
UV–Vis	Ultraviolet–visible
VB	Valence Band
WE	Working electrode
XRD	X-ray diffraction
Zn	Zinc
ZnO	Zinc oxide
ZnO: Al	Aluminum doped zinc oxide
ZnS	Zinc sulfide

LIST OF PUBLICATIONS

International Journals (total IF =26.76)

1. **E. M. Mkawi**, K Ibrahim, M K M Ali, M A Farrukh, A S Mohamed, Influence of triangle wave pulse on the properties of Cu_2ZnSnS_4 thin films prepared by single step electrodeposition, Solar Energy Materials and Solar Cells 130 (2014) 91–98. IF 5.03.

2. **E. M. Mkawi**, K. Ibrahim, M.K.M. Ali, M.A. Farrukh, Nageh K.Allam, Influence of precursor salts on the properties of electrodeposition of Cu-Zn-Sn metal precursors and corresponding Cu_2ZnSnS_4-based solar cells **,**Solar Energy Materials and Solar Cells ,Accepted manuscript. **IF 5.03**.

3. **E. M. Mkawi**, K. Ibrahim, M.K.M. Ali, M.A. Farrukh, Nageh K.Allam, Effect of complexing agents on the electrodeposition of Cu-Zn-Sn metal precursors and corresponding Cu_2ZnSnS_4-based solar cells, Journal of Electroanalytical Chemistry 735 (2014) 129–135. **IF 2.87**.

4. **E. M. Mkawi**, K. Ibrahim, M.K.M. Ali, K.A.M. Saron, M.A. Farrukh, A.S. Mohamed, Nageh K.Allam, Aqueous synthesis of visible-light photoactive cuboid Cu_2ZnSnS_4 nanocrystals using rotary evaporation, Materials Letters 125 (2014)195–197. **IF 2.27**.

5. **E. M. Mkawi**, K.Ibrahim, M.K.M Ali, M.A.Farrukh, A.S.Mohamed, Dependence of the properties of copper zinc tin sulfide thin films prepared by electrochemical deposition on sulfurization temperature**,** Journal of Materials Science Materials in Electronics 25 (2014) 857-863. **IF 1.97**.

6. **E. M. Mkawi**, K. Ibrahim, M.K.M. Ali, M.A. Farrukh, Nageh K.Allam, Solvent Solution-Dependent Properties of Nonstoichiometric Cubic Cu_2ZnSnS_4 Nanoparticles, Chemical Physics Letters 608 (2014) 393–397. IF 1.99.

7. **E. M. Mkawi**, K. Ibrahim, M.K.M. Ali, M.A. Farrukh, Nageh K.Allam, Influence of precursor thin films stacking order on the properties of Cu_2ZnSnS_4 thin films fabricated by electrochemical deposition method, Superlattices and Microstructures 76 (2014) 339–348. **IF 1.98.**

8. **E. M. Mkawi**, K. Ibrahim, M.K.M. Ali, K.A.M. Saron, M.A. Farrukh, Nageh K.Allam, Influence of substrate temperature on the properties of

electrodeposited kesterite Cu_2ZnSnS_4 (CZTS) thin films for photovoltaic applications, Journal of Materials Science: Materials in Electronics 26(2015) 222–228. **IF 1.97**.

9. **E. M. Mkawi**, K. Ibrahim, M.K.M. Ali, A S Mohamed, Dependence of Copper Concentration on the Properties of Cu_2ZnSnS_4 Thin Films Prepared by Electrochemical Method , International journal of electrochemical science 8 (2013) 359-368. IF 1.98.

10. **E. M. Mkawi**, K Ibrahim, M K M Ali, M A Farrukh, A S Mohamed, Electrodeposited ZnS precursor layer with improved electro-optical properties for efficient Cu_2ZnSnS_4 thin film solar cells, Journal of Electronic Materials, Accepted manuscript. **IF 1.67**.

11. E. M. Mkawi, K Ibrahim, M K M Ali, M A Farrukh, A S Mohamed, Synthesized and Characterization of Cu_2ZnSnS_4 (CZTS) Thin Films Deposited by Electrodeposition Method, Applied Mechanics and Materials 343 (2013) 85-89. IF -.

12. **E. M. Mkawi,** K Ibrahim, M K M Ali, M A Farrukh, A S Mohamed, The effect of dopant concentration on properties of transparent conducting Al-doped ZnO thin films for efficient Cu_2ZnSnS_4 thin film solar cells prepared by electrodeposition method **,**Applied Nanoscience, Accepted manuscript. **IF -**.

Conferences

1. **E.M. Mkawi**, K. Ibrahim ,M. K. M. Ali. M. A. Farrukh and Abdussalam Salhin Mohamed - Synthesized and characterization of Cu_2ZnSnS_4(CZTS) thin films deposited by electrodeposition method, the 2013 2nd International Conference on Sustainable Construction Materials and Computer Engineering (ICSCMCE 2013) June 1-2, 2013, Singapore.

Cu_2ZnSnS_4 (CZTS) FILEM TIPIS DITUMBUHKAN DENGAN ELEKTROKIMIA ENDAPAN UNTUK SURIA SEL

ABSTRAK

Sejak beberapa tahun kebelakangan ini, sebatian kuatenari Cu_2ZnSnS_4 (CZTS) menjadi tarikan sebagai bahan baru yang tidak toksik dan berkos rendah, dengan sifatnya yang amat sesuai bagi aplikasi filem atau saput nipis fotovoltan (PV). Dalam tesis ini, satu kaedah pemprosesan larutan berkos- efektif dibangunkan bagi penyerap saput nipis CZTS melalui pemendapan elektrokimia prekursor Cu, Zn, dan Sn pada substrat molibdenum (Mo)-bersalut kaca kapur soda (soda-lime glass,SLG), diikuti dengan rawatan haba dalam atmosfera sulfur. Kesan daripada parameter elektrokimia yang pelbagai terhadap sifat dan pertumbuhan saput nipis CZTS juga dikaji . Keputusan menunjukkan bahawa sifat saput nipis. Pengaruh denyut gelombang segi tiga terhadap sifat saput nipis mampu meningkatkan struktur dan morfologi sifat sampel melalui peningkatan peluang bagi elemen yang berlainan bersentuhan. Di samping itu, penggunaan trisodium sitrat sebagai agen pengkompleksan dalam larutan elektrolit dapat mengurangkan perbezaan di antara puncak penurunan Zn dan Cu sehingga 0.25 V. Kewujudan garam sulfat dalam elektrolit memudahkan pengurangan ion logam, dan meningkatkan penghasilan saput nipis. Empat prekursor berbeza yang terdapat dalam keadaan berjujukan dikaji dan tertib prekursor ditemui mempunyai kesan yang signifikan terhadap sifat saput nipis yang terhasil. Pengaruh suhu penyepuhlindapan (420–580 °C), suhu pensulfuran (250–400 °C), dan atmosfera (N_2 dan Ar (5%)) terhadap moforlogi dan struktur sifat saput CZTS yang terhasil dikaji. Penyepuhlindapan dalam atmosfera N_2 didapati

perlu bagi pertumbuhan bijirin. Penggunaan kimia prekursor yang sama, sintesis akueus daripada nanohablur Cu_2ZnSnS_4 kubik dan kuboid melalui sintesis solvohaba penyejatan putaran dikaji untuk mengesahkan keadaan penghabluran, jurang-jalur dan penyerapan secara langsung, dan ruang antar -satah daripada CZTS jenis -P. Pencirian sampel yang optimum (disimpan dengan sitrat trisodium) melalui belauan sinar X (XRD) menunjukkan orientasi pada satah (112), (220), (200) dan (312), mengesahkan struktur kesterit CZTS. Sampel mempunyai morfologi padat yang homogen, tanpa sebarang retak, dan saiz bijirin melebihi 1.5 μm. Pekali penyerapan saput adalah melebihi 10^4 cm^{-1} dan jurang-jalur nya meningkat kepada 1.48 eV. Kepekatan dan kelincahan saput CZTS adalah 4.5×10^{20} cm^{-3} dan 3.79 $cm^2V^{-1}S^{-1}$.Sel suria terbaik dengan struktur peranti gelas /Mo/CZTS/CdS/ZnO/Al:ZnO/Al yang diterbitkan daripada saput CZTS mempamerkan kecekapan penukaran awal 2.94%. Kajian ini menunjukkan fabrikasi saput nipis pada substrat molibdenum (Mo)-bersalut kaca soda kapur (SLG) adalah bermungkinan melalui pemendapan elektrokimia dengan aplikasi yang berpotensi dalam fotovolta sel suria .

Cu_2ZnSnS_4 (CZTS) THIN FILM GROWN BY ELECTROCHEMICAL DEPOSITION FOR SOLAR CELL

ABSTRACT

Cu_2ZnSnS_4 (CZTS) quaternary compounds have attracted much attention in the last few years as an abundant new low-cost and non-toxic material with desirable properties for thin film photovoltaic (PV) applications. In this thesis, a cost-effective solution processing method is developed for the fabrication of CZTS thin film absorbers by electrochemical deposition of Cu, Zn, and Sn precursors on molybdenum (Mo)-coated soda-lime glass (SLG) substrate, followed by a heat treatment in sulfur atmosphere. The effects of varying the electrochemical deposition parameters on the properties and growth of the CZTS thin films were investigated. The influence of the triangle wave pulse on the properties of the CZTS thin films improves the structural and morphological properties of samples by increasing the opportunities for different elements to come into contact. Additionally, using trisodium citrate as the complexing agent in the electrolyte solution reduced the difference between the reduction peaks of Zn and Cu by up to 0.25 V. The presence of sulfate salts in the electrolyte led to easy reduction of the metal ions, and improved the thin film produced. Four different precursor stacking sequences were examined, and the ordering of the precursors was found to have a significant effect on the properties of the resulting thin films. The influence of the annealing temperature (420–580 °C), sulfurization temperature (250–400 °C), and atmosphere (N_2 and Ar (5%)) on the morphological and structural properties of the resulting CZTS films was

studied. Annealing in N_2 atmosphere was found to be necessary for grain growth. Using the same precursor chemistry, the aqueous synthesis of cubic and cuboid Cu_2 $ZnSnS_4$ nanocrystals by rotary evaporation solvothermal synthesis was investigated to confirm the crystalline state, direct band gap and absorption, and interplanar spacing of p-type CZTS. Characterization of the optimized sample (deposited with trisodium citrate) by X-ray diffraction (XRD) revealed a preferred orientation of the (112), (220), (200) and (312) planes, confirming the kesterite structure of CZTS. The sample had a homogeneous, compact morphology without any voids or cracks, and the grain size was more than 1.5 μm. The absorption coefficient of the films was over 10^4 cm^{-1}, and their band gap was increased to 1.48 eV. The carrier concentration and their mobility in the CZTS films were 4.5×10^{20} cm^{-3} and 3.79 cm^2 V^{-1} S^{-1}, respectively. The best solar cell with a device structure of glass/Mo/CZTS/CdS/ZnO/Al:ZnO/Al derived from the obtained CZTS film exhibited a preliminary conversion efficiency of 2.94%. The present study demonstrates the possibility of fabricating CZTS thin films on molybdenum (Mo)-coated soda-lime glass (SLG) substrates by electrochemical deposition with potential applications in photovoltaic solar cells.

CHAPTER 1

INTRODUCTION

1.1 The Energy Problem

According to recent studies, the global demand for energy is expected to increase by approximately 50% within the next 25 years. Fossil fuels such as natural gas, coal, and oil represent greater than 80% of world energy consumption. These fuels produce greenhouse gases upon combustion. In addition, the energy produced from these sources is becoming expensive. The search for sustainable alternatives is also driven by the increasing recognition that mankind's demand for energy is already causing changes in the climate that will have serious long-term consequences for the planet. For example, the energy sector produces 86.7% of the most greenhouse gases in the United States [1]. The most prevalent greenhouse gases are methane and carbon dioxide. These gases trap heat in the Earth's atmosphere by absorbing infrared radiation, which contributes to global warming [2]. Additionally, pollutant emissions, such as nitrous oxides and sulfur oxides, common to many fossil fuel sources have deleterious environmental effects and can lead to problems such as acid rain and smog. The fact that oil resources are expected to become exhausted within a relatively short period of time, the corresponding increase in prices of petroleum products, and the use of fossil fuel resources for political purposes will affect social and economic development worldwide [3]. Nuclear power plants also pose problems, related to fuel processing and the dumping of used fuel [4]. Electricity production is expected to continue to increase (from 17 PW h in 2009 to 28–35 PW h in 2035), and as a consequence the increased demand on fossil fuels, as well as possible problems from CO_2 emissions, are bound to increase wholesale electricity costs [5].

What is needed to combat these issues is real renewable energy, i.e., technologies based on energy that is inexhaustible. Those available on earth are geothermal energy, energy from the interaction of the earth and moon (tidal forces), and solar energy. The latter can be subdivided in to hydropower, wind power, biomass/biofuel, and photovoltaic/solar thermal power plants/solar heating systems (all these forms of energy can eventually be traced back to creation by the sun, i.e., solar energy). Global fossil fuel consumption based on world production data as of 2011 is shown in Figure 1-1.

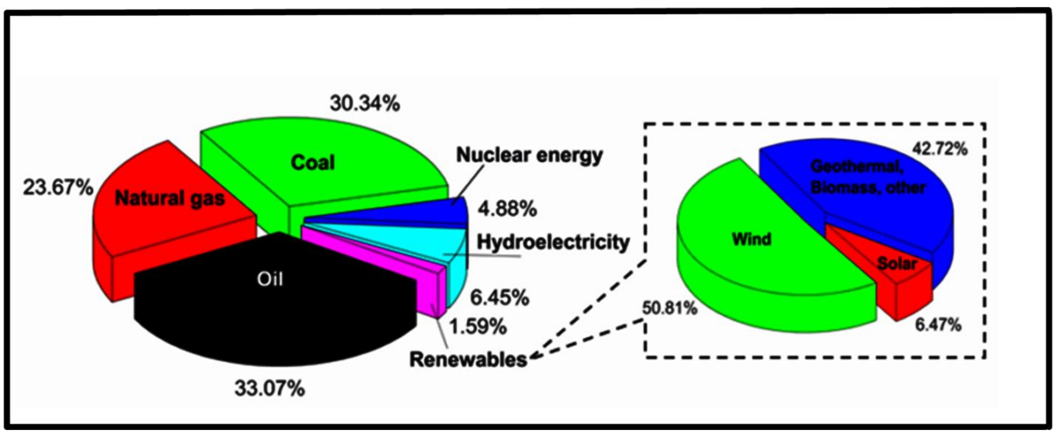

Figure 1.1 Fraction of world energy consumption by type of energy source in 2011. The inset shows share of energy consumption among renewable energies in 2011 [6].

1.2 Solar Energy

Solar energy is abundant, non-polluting, and able to provide a significant fraction of global energy demand. Current trends suggest that solar energy will play an essential role in future energy production. Perhaps the most promising renewable energy is solar energy, as it can potentially meet the world’s energy consumption. Indeed, solar energy alone has the capacity to meet all the planet's energy needs for the foreseeable future. The sun deposits ~120,000 TW of electromagnetic radiation on the surface of the Earth per year, a much greater amount than those of human needs. Covering just 0.16 % of the land on Earth with 10 % efficient solar conversion systems would provide 20 TW of power, which is nearly twice the world's present fossil fuel consumption (or the equivalent of 20,000 GW nuclear fission plants). However, photovoltaics have not yet reached so called grid parity, which means that electricity from solar cells is more expensive than energy from conventional sources like coal or gas. Consequently, further research is essential to increase the efficiency of solar cells and to make them cheaper. One approach for this is thin solar cells.

1.3 Thin Film Photovoltaics

Over recent years, the photovoltaics (PV) market has grown dramatically, and is completely dominated by products using silicon wafers. The two parameters often cited as the most important for solar cells are efficiency and cost. The cost of a Si solar cell is largely dependent on the cost of the Si wafer used in its fabrication. The high production cost and limited feedstock of silicon has sparked the photovoltaic community to search for new materials and technologies. Cheaper solar cells can only be produced using cheaper materials and low-cost fabrication methods. This is where thin film technology offers promising potential as an alternative to silicon photovoltaic technology [7]. Thin film solar cells are based on materials that strongly absorb sunlight, so that the cells can be very thin (1–3 µm), which reduces the demand for the raw material. The bottleneck for solar electricity to become a household energy source is mainly its cost. The cost of the Si wafer accounts for over 50 % of the total module cost. To eliminate this high cost component, silicon wafers may be replaced by thin films of semiconductors deposited onto a supporting substrate [8]. The main motivation for thin film solar cells is ability for high productivity and high speed manufacturing and low cost by using minimum material requirements . In the case of thin film solar cells, much less material is used compared with that required for crystalline silicon solar cells. Because the absorption coefficient of typical thin film absorber materials is ~100 times higher than crystalline silicon, a 100 times thinner layer of thin film material can absorb an equivalent amount of energy as crystalline silicon. For example, while 100 cm^3 (100 μm × 1 m × 1 m) crystalline silicon may be needed for a 1 m^2 solar cell, only 1 cm^3 is needed for a 1 m^2 thin film cell. In addition, thin film solar cells are less susceptible to the purity and crystallinity of their materials, and so the requirements on thin film solar cell materials are less stringent than for crystalline silicon solar cells [9]. Thus, thin film solar cells are cheaper to produce than silicon solar cells. Another advantage of thin film solar cells is that they can be fabricated on flexible materials like metal foils or polyimides, which allows for completely new applications [10]. Yet another advantage is that it is possible to adjust the band gap of thin film materials by varying their composition. Thus, a larger portion of the solar spectrum can be used and higher efficiency can be achieved, because the theoretical possible efficiency depends strongly on the band gap. The huge reduction in the active material requirements with respect to those of the standard technology allows a large decrease in device costs. Moreover, the large versatility in the device design and fabrication, owing to the wide choice of different substrates (rigid and flexible) and deposition techniques for the different device layers, allows precise engineering and optimization of the solar cell stack to enhance device performance [11]. Thin film PV has been therefore recognized as a promising strategy to obtain high efficiency and low cost PV devices, thus fulfilling the actual requirements of the increasing electrical demand.

1.4 Thin Film Photovoltaic Materials

Materials intended for thin film solar cells must fulfill some important conditions to be usable. The ideal materials should have high optical absorptivity to absorb sunlight (greater than 10^4 cm^{-1}). The term absorption coefficient can be defined as "the rate of decrease in the intensity of light as it passes through a given material". An essential precondition is of course a large absorption coefficient, as all (suitable) light should be absorbed in only a few micrometers [12] . Furthermore, the band gap should be in the range of roughly 1.0–1.6 eV to provide the theoretical opportunity to reach sufficient efficiencies. The bandgap should also be appropriate, ideally around 1.5 eV, to absorb a significant portion of the solar spectrum. Also needed is the ability to form a good electronic p–n junction with compatible materials.

Nevertheless, not all potentially suitable compounds can be used to produce viable solar cell materials. Many other conditions, including availability, possibility of industrial scale production, cost, and environmental safety (e.g., toxicity), have to be fulfilled. Recently, chalcogenide thin-film photovoltaic (PV) materials such as CdTe, $Cu(In,Ga)Se_2$ (CIGS), Cu_2ZnSSe_4 (CZTSe), Cu_2ZnSnS_4 (CZTS), and $Cu_2ZnSn(S,Se)_4$ (CZTSS) have attracted great attention owing to their ability to produce high efficiency, low cost, large area thin film solar cells (chalcogens are defined as all group 16 elements of the periodic table such as oxides, sulfides, tellurides and selenides).

Chalcogenide thin-film photovoltaics have seen significant improvements in device efficiency in the last 20 years, and have now reached mass production. In 2014, small area CIGS solar cells reached an efficiency of 20.9% (close to the record efficiency, 25 %, of bulk-crystalline Si solar cells [13]) and large-area modules with efficiency of about 13–14% are currently produced on an industrial scale. Even CdTe solar cells, which have a record efficiency of 10.1% for research cells and 16.1% for total area modules [14], already have an annual industrial production of more than 1.5 GW. Despite great developments in chalcogenide-based PVs, these technologies suffer from using toxic (Cd) and rare elements, such as In, Ga and Te, the high cost and scarcity of which could limit the sustainability of these technologies in the years to come [15]. Figure 1.3 shows the abundance of these materials in the earth's crust and their cost.

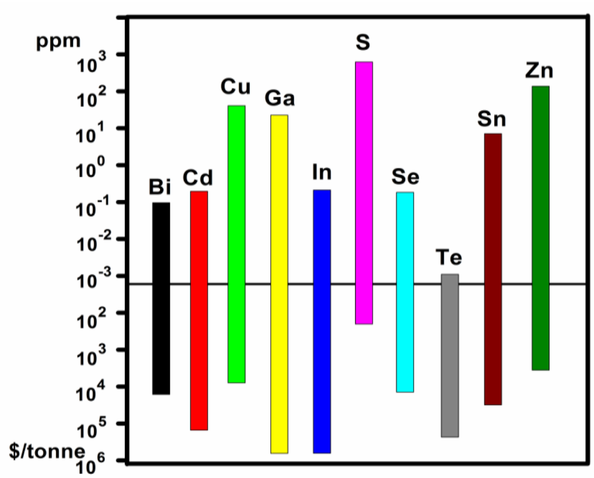

Figure 1.2 shows the abundance and cost of copper, zinc, tin and sulfur compared with those of some elements that are currently used to make thin film solar cells. The lowest abundance and highest cost element among the latter is tin (4 ppm and $3000/ton, respectively), which is still significantly better than the elements used in the current technologies (Cd, Te, In, Ga) [16].

In the last decade, many efforts have focused on the development of a new class of quaternary compounds as possible candidates to replace CIGS in thin film solar cells. These materials can be thought of as a derivation of the CIGS chalcopyrite structure obtained by a process known as “cross-substitution”, consisting of the replacement of one element (In or Ga in the present case) with two elements of different groups in the periodic table chosen to keep the ratio between the number of atoms and valence electrons fixed. The resulting materials are therefore quaternary compounds given by the chemical formula Cu_2-II-IV-VI_4 , where VI is a chalcogen element (S or Se) and II and IV represent divalent (Zn, Cd, Fe) and tetravalent (Sn, Ge, Si) elements, respectively. Among the possible Cu_2-II-IV-VI_4 compounds, kesterites $Cu_2ZnSn(S,Se)_4$ (CZTS(Se)) are the most studied, and the rapid improvement in their photovoltaic performance obtained in recent years makes them much more attractive.

Considerable work has recently been carried out on kesterite Cu_2 $ZnSnS_4$ (CZTS) to make it a good absorber layer for thin film solar cells and thermo-electric power generators [17, 18]. CZTS thin films are usually in a polycrystalline form consisting of kesterite crystal structures. CZTS has excellent physical properties, including a high optical absorption coefficient ($>10^{-4}$ cm^{-1}), direct band gap (1.4–1.5 eV), and low thermal conductivity. CZTS can be derived from the CIGS structure by the isoelectronic substitution of two In (or one In and one Ga) atoms by one Zn and one Sn atom. As a consequence, CZTS has some similar properties to those of CIGS. The availability of copper, zinc, tin and sulfur in the earth’s crust are much higher than that of indium (0.049 ppm [19], at 50, 75, 2.2. and 260 ppm, respectively, i.e., all the constituents of CZTS are abundant in the earth’s crust. Intrinsic point defects in CZTS make its conductivity p-type. The crystal structure of CZTS can tolerate some deviation from stoichiometry, making its deposition process easier. Moreover, grain boundaries in CZTS thin films are beneficial in enhancing minority carrier collection [20]. Theoretical calculations have shown that a conversion efficiency as high as 32.2 % [21] is possible for CZTS thin film solar cells with a CZTS layer of a few micrometers. To date, most of the solar cell devices based on p-type CZTS have been fabricated by sputtering or evaporation followed by annealing and sulfurization at high temperature (300–550 °C). To reduce the cost of these cells, it is necessary to develop alternate processing methods for their fabrication, such as solution based or electrochemical techniques.

1.5 Research Objectives

The principal goal of this research is to develop CZTS-based thin-film solar cells grown onto Mo-coated glass substrates by electrochemical deposition method.The sub objectives of this project can be summarized in the following :

1. To determine the optimal growth parameters that influence the structural, optical, and electrical properties of Cu_2SnZnS_4 (CZTS) thin film structures grown on Mo-coated glass substrates by electrochemical deposition.
2. To investigate the effects of annealing conditions including substrate temperature and sulfurization temperature on the properties of Cu_2SnZnS_4 (CZTS) thin film.
3. To investigate the synthesis and fabrication of Cu_2SnZnS_4 (CZTS) nanoparticle structures and films by solvothermal and rotary evaporation techniques under different conditions.
4. To evaluate the performance of solar cells incorporating the obtained CZTS thin film and its dependence on the growth parameters.

1.6 Originality of The Research Work

The originality of the study is supported by the following points.

a) The electrochemical deposition and growth of Cu_2ZnSnS_4 (CZTS) on Mo substrates is a new approach (the first report was published 5 years ago [22]) . This technique could provide a new insight into the use of semiconductor materials with good properties for photovoltaic applications.

b) This study is the first to report the use of triangle wave pulses to deposit CZTS thin film and its role in solving the problem of tin reduction during annealing treatment [23].

c) This study is the first to report a decrease in reduction potential between Cu and Zn elements of 0.25 V when trisodium citrate is used as a complexing agent.

d) This study is the first to report the effect of precursor salts on the stoichiometry of CZTS thin film.

e) This study is the first to report the use of a three-zone furnace to fabricate CZTS thin films to prevent loss of S during annealing and optimization of sulfurization temperature.

f) A review of contemporary studies of the synthesis of visible-light protective cubic Cu_2ZnSnS_4 nanocrystals and nonstoichiometric nanoparticles has not been conducted until now.

1.7 Outline of The Thesis

The thesis consists of eight chapters. An introduction to the energy problem, renewable energy, thin film materials, and Cu_2ZnSnS_4 (CZTS) thin film was presented in Chapter 1. This chapter also included the motivation, objectives and original contributions of this research, ending with this outline of the thesis. Chapter 2 consists of the literature review of the Cu_2ZnSnS_4 thin film deposition processes. In chapter 3, theoretical background of CZTS thin films, including its advantages, formation reactions, properties, and characteristics. PN Junctions and Solar Cells devices, principles of electrochemical deposition is discussed. Chapter 4 comprehensively describes the methodology and instrumentation used in the study. The results obtained from the research work are analyzed and discussed in Chapters 5, 6, and 7. Chapter 5 elaborates on the properties of Cu, Zn, and Sn metal precursors electrochemically deposited on Mo substrates under different conditions. Chapter 6 presents the results of investigations into the sulfurization and annealing treatment of the Cu, Zn, and Sn metal precursors under different conditions. Chapter 7 contains the experimental results of the synthesis of visible-light protective cubic Cu_2ZnSnS_4 nanocrystals and nonstoichiometric cubic Cu_2ZnSnS_4 nanoparticles via a rotary evaporation and solvothermal synthesis under different parameters. Chapter 8 is a summary of the work, in which important conclusions are highlighted. Future prospects of the work are also presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents the history and a survey of the relevant literature concerning CZTS thin film solar cells and the evolution of the efficiency of CZTS thin film solar cells. This chapter also describes the background of a variety of techniques used for the deposition of CZTS thin films.

2.2 Evolution of CZTS Thin Film Solar Cell Efficiency

CZTS material was first introduced into solar cell applications in 1988 by Ito and Nakazawa. They successfully fabricated a heterodiode of CZTS and cadmium tin oxide (CTO) thin films on a stainless steel substrate [24]. That produced an open circuit voltage (V_{OC}) of 165 mV under AM1.5 illumination. Katagiri et al. [25] reported the fabrication of a CZTS thin film solar cell with the structure Mo/CZTS/CdS/ZnO:Al on soda lime glass substrate by sulfurization of electron beam deposited Cu/Sn/Zn stacked precursors. Their device showed a power conversion performance of 0.66% and an V_{OC} of 400 mV. In the same year, a best conversion efficiency of 2.3% and V_{OC} of 470 mV was achieved by Friedlmeier et al. [26] using CZTS as a good light absorber layer in a similar structure to that of Katagiri's device, prepared by the sulfurization of co-deposited Cu-Zn-Sn films. Katagiri et al. recorded a new CZTS device efficiency of 2.63% by varying the method of the sulfurization of the Cu/Sn/ZnS stacks [27]. The efficiency was increased to 5.45 % in 2003 by the same group using different annealing conditions [28]. And further improved to 6.7 %

in 2008 by soaking the thin films in deionized water to etch the metal oxide particles in the CZTS layer [29]. A CZTS thin film solar cell with a conversion performance of 9.6% was attained in 2010 by Mitzi et al., who used a hydrazine precursor solution and sulfurization to deposit CZTS active layers via a spin-coating technique [30]. and further improved the efficiency of their cell to 10.1 % in 2011[31]. Obtained by the same group, the most recent record efficiency of CZTS thin film solar cells is 11.1%, according to the available literature.

2.3 CZTS Thin Film Deposition Techniques

Different deposition methods have been used to fabricate CZTS thin films, including evaporation, sputtering, spin coating, and screen printing. These methods can be divided into two main categories, vacuum-based techniques and solution-based techniques. In this section these technique are reviewed.

2.3.1 Vacuum-Based Techniques

Vacuum based deposition techniques are popular methods of obtaining high quality thin film devices owing to the high uniformity of the produced films. These techniques include coating of the integral atoms of the CZTS material onto a substrate either by sputtering or by evaporation/co-evaporation of target sources under optimized conditions (pressure and temperature). The advantages of these techniques include the good and simple control of the chemical composition of the thin films, and good reproducibility. Nonetheless, the final CZTS thin films are normally obtained by high temperature sulfurization of the deposited stacks of metals, metal sulfides, or a combination of the two. These procedures are usually slow and may require several hours for thin film growth and annealing.

2.3.1.1 Sputtering Techniques

Several sputtering techniques have been widely employed in previous studies to deposit CZTS thin films for solar cell applications such as argon beam, ion beam, DC, RF, hybrid, and reactive magnetron sputtering.

For example, Ito and Nakazawa used CZTS pressed targets to fabricate thin films by an argon beam sputtering technique without an annealing process. The resulting CZTS thin film had a stannite structure, a band gap of 1.45 eV, and an obtained V_{OC} of 165mV [25]. However, the efficiency of the device was not reported. Later on, Tanaka et al. [32] employed hybrid sputtering technology to deposit Sn/Zn/Cu precursor layers which were then annealed at different temperatures with sulfur flux. The CZTS phase formed at 350 °C. The produced films had a direct band gap of 1.5 eV, absorption coefficient higher than 10^4 cm^{-1}, and a high rate of Zn losing when heated over 450 °C. CZTS solar cells with an efficiency of 5.7% have been fabricated by reactive co-sputtering of Cu, SnS, and Zn in an atmosphere containing 20% concentrated H_2S by Katagiri et al [29]. The best performance of the resulting solar cell device was obtained at component material ratios of Cu/(Zn+Sn) = 0.87, Zn/Sn=1.15, and S/(Cu+Zn+Sn) = 1.18 [33]. Fernandes et al [34] used DC magnetron sputtering to deposit CZTS thin films and sulfurized them in N_2 atmosphere at 525 °C. Zhang et al.[35] formed CZTS thin films by sequential sputtering of Cu, Zn, and Sn from metallic targets using ion beam sputtering, then sulfurized the stacked Cu/Sn/Zn precursors on soda lime glass (SLG) substrates without heating the substrates. Proper sulfurization was achieved in $S_2 + N_2$ flux at 550 °C for 3 h.

The best reported efficiency for sputtered CZTS solar cells is 7.6 %, obtained by Fukano et al [36]. This value was obtained by annealing at 580 °C for 30 min under 20 % H_2S balanced with N_2. In addition, Fukano et al. also reported that CZTS films fabricated from a three-layer (ZnS/Sn/Cu (top)) precursor displayed higher quality than those obtained from a four-layer (ZnS/Sn/Cu/ ZnS (top)) precursor.

2.3.1.2 Evaporation

Evaporation techniques have been the preferred method of numerous academic researchers owing to previous achievements of good absorber materials using various evaporation technologies such as electron beam (EB) evaporation, co-evaporation, fast evaporation, and thermal evaporation. CZT precursors deposition by evaporation can be achieved by two different approaches:

(i) single step simultaneous deposition of all precursors followed by sulfurization

(ii) two step, sequential deposition of metallic precursors, e.g., Cu–Zn–Sn/Cu–Zn–Sn–Cu or Cu–ZnS–SnS, followed by sulfurization/annealing.

The first study of CZTS thin film fabrication by an evaporation technique was reported by Katagiri et al. in 1997 [25] They sulfurized Zn/Sn/Cu layers at 500 °C for 1–3 h under a $N_2 + H_2S$ (5%) atmosphere. The precursor layers were deposited by electron beam evaporation with a substrate temperature of 150 °C. A device with a structure of glass/Mo/CZTS/CdS/ZnO/Al produced from the resulting CZTS thin films exhibited a conversion efficiency of 0.66 %. Katagiri et al. also reported that replacing Zn with ZnS in the initial precursor stack significantly improved the adhesion of the film material to the Mo/SLG substrate. This development offered solar cells with an efficiency of 5.45%, V_{OC} of 582 mV and short circuit current (J_{SC}) of 15.5 mA/cm [25]. Kobayashi et al.[33] used EB evaporation and sulfurized the resulting films at a temperature of 510–550 °C, and obtained a best efficiency of 4.53%, V_{OC} of 629 mV, J_{SC} of 12.53 mA/cm^2 and FF of 0.58 at 520 °C [37]. Wang et al. [38] used a thermal co-evaporation technique to deposit elements simultaneously onto the same substrate at 110 °C, and annealed them at 540 °C for 5 min in sulfur atmosphere. The produced solar cell with thickness of 650 nm and structure of glass/Mo/CZTS/CdS/i-ZnO/ITO/Ni–Al grids exhibited a V_{OC} of 587 mV, J_{SC} of 17.8 mA/cm^2, FF of 65 % and efficiency of 6.8 %. Tanaka et al [39], deposited CZTS thin films by co-evaporation of Cu, Zn, Sn, and S precursors and obtained growth along the [112] plane with an increasing grain size with substrate temperature between 400 and 600 °C. In a later study, they investigated the influence of CZTS thin film composition on the structure and electrical properties[40] . In another study, CZTS films deposited on Mo coated SLG substrates at 110 °C by thermal evaporation technique and annealed on a hot plate at 540 °C for 5 min were used to fabricate a solar cell device with a layer arrangement of SLG/Mo/CZTS/CdS/i-ZnO/Al:ZnO that displayed an efficiency of 6.8% ,V_{OC} of 587 mV, J_{SC} of 17.8 mA/cm^2 and FF of 65% [38] . More recently, Shin et al.[41] deposited CZTS thin film based solar cells on Mo coated SLG substrates by a thermal evaporation method. After annealing at 570 °C for 5 min in air, the device showed an efficiency of 8.4%, V_{OC} of 661 mV, J_{SC} of 19.5 mA/cm^2 and FF of 65.8%.

2.3.1.3 Pulsed Laser Deposition Technique

Pulsed laser deposition (PLD) is one of the best methods of producing very good quality layers of complex compositions, and has advantages including simplicity, clean deposition (owing to the use of a high vacuum chamber), and deposition of highly enhanced crystal structures owing to the high energy and flexibility in the engineering plan.

Sekiguchi et al.[42] benefited from this technique to fabricate the first epitaxially grown CZTS films on GaP substrate. Moriya et al.[43] employed a KrF pulsed laser with a wavelength of 248 nm to form CZTS thin films for solar cell applications after annealing in N_2 atmosphere at different temperatures (300–500 °C), and obtained a efficiency of 1.74 % from a sample treated at 500 °C in 2007.

2.3.2 Solution-Based Techniques

The various vacuum techniques were the established methods of producing CZTS thin films for several decades, then the majority of researchers switched to low-cost deposition techniques (non-vacuum approaches) in subsequent years. Vacuum routes are mostly expensive and consume more time and energy than non-vacuum approaches, which are less costly, simpler, and offer high material output with lower time and energy cost. As a result, there has been a recent unexpected growth in CZTS thin films solar cell fabrication by non-vacuum techniques; therefore, solution-based fabrication will be an important direction for future research. These solution-based techniques are briefly described below.

2.3.2.1 Precursor-Ink Based Approach

The sol–gel method is the foremost of the ink-based approaches, and was first introduced as a method of fabricating CZTS thin films by Tanaka et al [44]. They prepared a CZTS solution by using the elemental powders of coper, zinc, tin and sulphur, with stirring at 45 °C for 1 h, and then spin-coated and dried the resulting film in air at 300 °C. This method was repeated by Yeh et al [45],who added an annealing process in N_2+H_2S atmosphere at 500 °C for 1 h and studied the effect of the preparation (synthesis and annealing) temperatures on the properties of the resulting CZTS thin films. In other work, Ki et al. spin-coated CZTS films from a solution of copper chloride, zinc chloride, tin chloride and thiourea dissolved in 70:30 deionized water/ethanol and stirred at 40 °C for 30 min. The spin-coated films were annealed at 580 °C for 2.5 min and used to fabricate a solar cell with a structure of glass/Mo/CZTS/CdS/ZnO/ITO/Ni-Al that exhibited an efficiency of 4.1% [46]. Todorov and his group reported the coating of crack-free CZTS films onto glass substrates by reacting metal salts (complexed with triethnolamine) with dissolved elemental sulfur in ethylene glycol at 170 °C for 3 h [47] .

Zhou et al. [48] used a very easy and cheap technique known as screen printing (SP) to print CZTS layers from ink prepared from powders of copper, zinc, tin, and sulfur onto Mo coated polyimide. The resulting solar cell with the structure polyimide/Mo/CZTS/CdS/Al:ZnO/Al showed an efficiency of 0.49%, V_{OC} of 386 mV, J_{SC} of 4.76 mA/cm^2, and FF of 0.27.

Many previous works have reported the preparation of CZTS thin films by chemical bath deposition (CBD) methods, such as the fusing of Cu atoms into films by an ion exchange method [49], synthesis of nanocrystalline CZTS by a drop method [50], synthesis of CZTS nanorods via controlled evaporation from a solution source [51], and synthesis of CZTS nanocrystals by high temperature arrested precipitation. In the last case, copper acetylacetonate, zinc acetate, tin chloride dehydrate, and elemental sulfur were reacted in oleyamine at 280 °C for 1 h under an inert atmosphere, and the solar cell fabricated from the obtained nanocrystals exhibited an efficiency of 0.23%, V_{OC} of 321 mV, J_{SC} of 1.95 mA/cm^2 and FF of 0.37 .

The most impressive result obtained for CZTS photovoltaics prepared by a solution based method was reported by Xin et al [52] .They fabricated a dye sensitized solar cell with N719 ruthenium based dye, a TiO_2 layer on FTO, a CZTS absorber layer on FTO, and an ionic liquid electrolyte that exhibited an efficiency of 7.37%, V_{OC} of 800 mV, J_{SC} of 17.7 mA/cm^2, and FF of 52.2%.

2.3.2.2 Spray Pyrolysis

The spray pyrolysis deposition (SPD) method is considered to have the greatest simplicity, easiest handling, and best reproducibility of the large area coating techniques. It can be a suitable method for industrial commercial production because it does not require a vacuum at any step of the fabrication process, which is the most pronounced advantage of the technique. In spite of these advantages, spray pyrolysis has not been widely used for the creation of CZTS thin films.

Nakayama and Ito [53] prepared CZTS thin films by a spray pyrolysis technique for the first time in 1996. They sprayed a solution of CuCl, $ZnCl_2$, $SnCl_4$, and thiourea dissolved in 50:50 DW/ethanol onto SLG substrates at temperatures from 280 to 360 °C. Prabhakar and Jampana [54] also used this method and determined the conductivity of the sprayed CZTS films, reporting that the conductivity increased with

Na-diffusion from SLG and Cu-deficiency in the sprayed CZTS. The effect of Na-diffusion was found to be stronger than that of Cu-deficiency, and the conductivity of the film increased by an order of magnitude when SLG was used instead of borosilicate glass.

2.3.2.3 Electrodeposition technique

Electrodeposition is one of most attractive solution-based techniques, and has been commonly applied to the growth of solar cell absorber layers of several materials, such as CdTe, CZTS and CIGS [54, 55]. The preparation of CZTS thin films by electrodeposition is usually achieved in one of two ways, namely the sequential electroplating of precursors or the single step electrodeposition of precursors. Both of these are followed by sulfurization using different sulfur sources, such as pure S vapor, S_2+N_2 and S_2+Ar, at annealing temperatures between 300 and 600 °C. The first CZTS film solar cell prepared by an electrochemical deposition method was reported by Scragg et al., with efficiency of 0.8%. Electrochemically deposited metal stack Zn/Sn/Cu was sulfurized by S vapor at 550 °C for 2 h. They added that the low efficiency of the obtained solar cell was caused by a high series resistance and a high shunt conductance [22].

Araki et al. [56] synthesized CZTS thin films by annealing co-electrodeposited Cu-Zn-Sn films in S atmosphere for 2 h. Slightly Zn-rich films gave the best device efficiency, 3.16%. Copper (II) sulfate pentahydrate, zinc sulfate heptahydrate, tin (II) chloride dihydrate, and tri-sodium citrate dihydrate were used for the co-electrodeposition. The co-electrodeposited films did not exhibit any phase separation after annealing.

Ennaoui et al.[57] reported a novel low cost technique for the preparation of CZTS thin film absorber layers for solar cell applications. First, they prepared Cu–Zn–Sn precursor layers on Mo coated SLG substrates using single step electrochemical deposition from an alkaline electrolyte bath containing Cu(II), Zn(II), and Sn(IV) metal salts, which were further reacted with Ar/H_2S to form CZTS thin films. A solar cell fabricated using these CZTS thin films with the configuration glass/Mo/CZTS/CdS/ZnO/Ni–Al showed an efficiency of 3.4% (V_{OC} = 563 mV, J_{SC} = 14.8 mA/cm^2 and FF = 41%).

Pawar et al. [58] demonstrated a single step co-electrodeposition of S along with the CZTS component metals from $CuSO_4$, $ZnSO_4$, $SnSO_4$, and $Na_2S_2O_3$ (sulfur source) in an aqueous electrolytic bath at room temperature. The as-deposited films were annealed in an Ar atmosphere at 550 °C for 1 h for grain growth, and did not require any post deposition sulfurization step. The bandgap of the film annealed at 550 °C was found to be 1.50 eV.

Ahmed et al.[59] developed a three-step method: i) sequential electroplating of Cu/Zn/Sn or Cu/Sn/Zn stacks; ii) annealing of the stacks at low temperature (210–350 °C) under N_2 to produce homogeneous alloys; iii) annealing of these well-mixed CuZn and CuSn alloys at 550–590 °C in sulfur atmosphere for 5–15 min to allow the formation of CZTS. Secondary phases such as Cu_2S, SnS, and Cu_2SnS_3 were found in the annealed samples when the annealing temperature was lower than 580 °C. They proposed that the secondary ZnS and Cu_2SnS_3 phases reacted to form CZTS when the annealing temperature was above 580 °C. Solar cells made from the CZTS samples prepared by sulfurization at 585 °C for 12 min showed efficiencies as high as 7.3%.

This is the highest efficiency reported to date for a pure CZTS-based solar cell prepared by electrodeposition.

This study involves the synthesis of CZTS-based solar cell prepared by electrodeposition method. This method is simple , inexpensive compared to other complicated vacuum based methods, allows fine control of the product composition, high throughput and very much cost effective for synthesis of quaternary chalcogenide thin film PV materials.

CHAPTER 3

THEORETICAL BACKGROUND

3.1 Interdiction

This chapter presents the general principles and theory of the various aspects of this research. It starts with a description of the physical and chemical properties of Cu_2SnZnS_4 thin film. The fundamental principles of electrochemical deposition and cyclic voltammetry are addressed. Furthermore, the basic concepts of the devices fabricated in this thesis, which include p–n junctions, are discussed. This is followed by a brief discussion of the basic principles of solar cell devices. In addition, this chapter addresses the principles underlying the operation of the fabrication and characterization equipment, as well as how to use theoretical equations to find the values of the parameters that describe the properties of the thin films and the performance of the devices.

3.2 Characteristics of Cu_2 $SnZnS_4$ Thin Film

CZTS (copper zinc tin sulfide, with formula Cu_2SnZnS_4) solar cell research has been conducted extensively in recent years mainly because it is composed of elements that are not only inexpensive, but also non-toxic. CZTS is a p-type semiconductor, and is used as an absorber material in solar cells. In contrast, the elements used in the more common copper indium gallium selenide (CIGS) solar cells are both expensive and toxic. The reason CZTS cells are inexpensive is because the elements that comprise these cells are found abundantly in the earth's crust [60]. This allows the low-cost manufacture of solar cells in high volumes. While researchers have been able to produce CIGS cells of high efficiency, the efficiency of CZTS cells is not comparable. However, in addition to being inexpensive and non-toxic, CZTS offers good optical and electronic properties. Thus, it is considered to be a promising semiconductor material for use in solar cells.

3.2.1 Structural Properties

Crystallographically, CZTS has two main structures, recognized as the kesterite type and stannite type structures. These two structures are alike except for the dissimilar arrangements of their 'Cu' and 'Zn' atoms (Figure 3.1). The structural differences are related to a different order in the cation sublattice: Kesterite, with space group *I*4, is characterized by alternating cation layers of CuSn, CuZn, CuSn, and CuZn at z=0, 1/4, ½, and 3/4, respectively, whereas in the stannite structure, with *I*4m symmetry, ZnS layers alternate with Cu_2 layers. Tin and sulfur ions occupy the same lattice positions in both structures. However, CZTS materials usually appear in kesterite phase because it is more thermodynamically stable than the stannite phase [60, 61]. However, the energy difference between the kesterite and stannite type structures is very small; only about 3 meV per atom, indicating that the stannite type structure may also be obtained under standard preparation conditions.

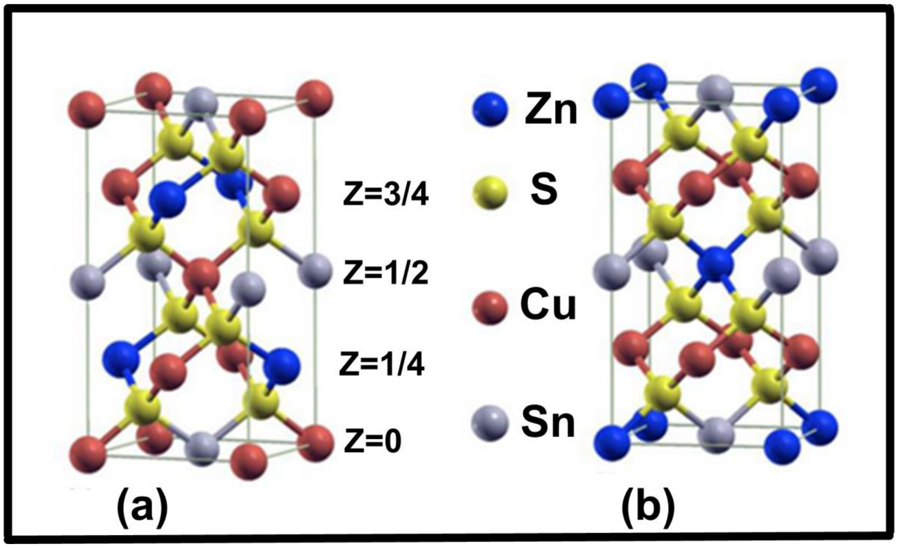

Figure 3.1 Schematic representations of the kesterite (a) and stannite (b) structures [62]

Kesterite materials (Kesterite is defined a sulfide mineral with a formula $Cu_2(Zn,Fe)SnS_4$) belong to the family of chalcogenides. Some examples of this group include sphalerite (ZnS), chalcopyrite (e.g., $CuInS_2$), and kesterite (e.g., Cu_2ZnSnS_4) as shown in Figure 3.2 [30]. The option of replacing the rare and expensive indium with cheap and available Sn and Zn, while retaining main semiconductor properties such as nearly the same energy gap as that of the highly successful chalcopyrite absorber materials, makes CZTS attractive for large-scale photovoltaics manufacturing.