EFFECT OF POTASSIUM AND GERMANIUM DOPANTS ON OPTICAL, STRUCTURAL AND ELECTRICAL PROPERTIES OF COPPER ZINC TIN SULPHOSELENIDE SOLAR ABSORBER LAYER

MOHD SHAHRIL BIN SALLEH

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

Faculty of Science
Universiti Teknologi Malaysia

FEBRUARY 2020

DEDICATION

This thesis is dedicated to my beloved parents,
Hj. Salleh bin Ahmad and Zaila binti Sulaiman,
also my wife,
Dr. Nurul Hana binti Adi Maimun,
who taught me that impossible things may turn to possible,
and it come with strong passion and hard work.
It is also dedicated to my siblings and family,
who taught me that human is not perfect,
and effort to improve is beauty.

ACKNOWLEDGEMENT

This thesis is not come out in easy way, and thousand thanks to those great people, who never give up to lead and work with me. My sincere appreciation to my main supervisor, Dr. Kashif Tufail Chaudhary for the encouragement, guidance, critics and friendship. My co-supervisor, Dr. Safwan bin Abd Aziz, who is always very supportive and helping when it is needed. Not forgotten, my respectful research group leader, Professor Jalil bin Ali who never lost faith in me. Without their continued support and interest, this thesis would not have been the same as presented here.

I am also indebted to Universiti Teknologi Malaysia (UTM) Skudai, Universiti Tun Hussein Onn Malaysia (UTHM) and Malaysia-Japan Institute of Technology (MJIIT) for providing technical support and research facilities.

My fellow research groupmates, especially Elham bin Mazalan and Dr Mohamad Helmi bin Mubin, who should also be recognised for their support. My sincere appreciation also extends to all my colleagues and others who have provided assistance at various occasions. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them in this limited space.

Last but not least, million thanks to my family, who always at my side, in every occasion, ups and downs, laugh and cry, confident and lose hope. Thank you very much.

ABSTRACT

In present research, the role of Potassium (K) and Germanium (Ge) dopants in Copper Zinc Tin Sulphoselenide (CZTSSe) absorber thin solar film prepared using non-vacuum spray pyrolysis deposition technique has been investigated. K-doped CZTS precursor solution was prepared using one-pot approach with different concentrations of K (0.0, 0.5, 1.0, 1.5, 2.0 and 2.5) mol %, dissolved using dimethyl sulfoxide solvent. The solution was then sprayed on soda lime glass (SLG) substrate using ultrasonic spray coater at 300 °C. The deposited thin films were selenized in tube furnace using three-step temperature approach (300 °C, 500 °C and 550 °C) with 30 minutes ramping time in nitrogen environment. Deposited K-doped CZTSSe thin films were characterized by ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy and 3D microscope to determine the optical properties and thickness of K-doped CZTSSe structure. X-ray diffractometer was employed for the structural and crystallinity analyses, whereas field emission scanning electron microscope was used to study surface morphologies. Energy dispersive X-ray spectrometer was used to study the elemental composition of the film while Hall effect measurement system was used for measuring the charge carrier density. Based on results, 1.5 mol % of K-doped was selected for fabrication process of (K,Ge)-doped CZTSSe solar absorber layer. Same processes were performed to synthesize thin films except with different molar concentrations of Ge (10, 15, 20, 25 and 30)% in dimethylformamide as dissolving agent. The effects of different Ge concentrations were studied. UV-Vis-NIR spectra have shown high absorption coefficient which was more than 10000 cm^{-1} for each sample. The bandgap increased as the concentration of Ge was increased, which inferred the capability of Ge to tune the CZTSSe bandgap to increase the open circuit voltage. X-ray spectra showed better crystallinity at 25% and 30% of Ge dopant, while micrographs from field emission scanning electron microscope revealed that 25% Ge has better crystal growth. The charge carrier density in the absorber layer also increased with increase in dopant concentration. Based on the findings, (K,Ge)-doped CZTSSe thin film with 1.5 mol % K and 25% Ge has the best properties.

ABSTRAK

Dalam kajian ini, peranan dopan Potassium (K) dan Germanium (Ge) dalam penyerap filem tipis solar Kuprum Zink Tin Sulfoselenida (CZTSSe) yang disediakan menggunakan teknik pemendapan semburan pirolisis telah dikaji. Larutan pelopor K-dop CZTS disediakan dengan menggunakan pendekatan satu-periuk dengan kepekatan K yang berbeza (0.0, 0.5, 1.0, 1.5, 2.0 dan 2.5) mol %, dilarutkan menggunakan pelarut dimethil sulfoksida. Larutan tersebut kemudian disembur di atas substrat kaca soda kapur (SLG) menggunakan penyalut semburan ultrasonik pada 300 ºC. Filem tipis yang termendap diseleniumkan di dalam tiub relau menggunakan pendekatan suhu tiga-langkah (300 ºC, 500 ºC dan 550 ºC) dengan masa peningkatan 30 minit di dalam persekitaran nitrogen. Filem tipis termendap K-dop CZTSSe telah dicirikan dengan spektroskopi ultra ungu-cahaya tampak-infra merah dekat dan mikroskop 3D untuk menentukan ciri-ciri optik dan ketebalan struktur K-dop CZTSSe. Difraktometer sinar-X telah digunakan untuk analisis struktur dan hablur, manakala mikroskop elektron pengimbas pancaran medan digunakan untuk mengkaji morfologi permukaan. Spektrometer sinar-X penyebaran tenaga digunakan untuk mengkaji komposisi unsur filem tersebut manakala sistem pengukuran kesan Hall digunakan untuk mengukur ketumpatan pembawa cas. Daripada keputusan tersebut, 1.5 mol % K-dop telah dipilih untuk lapisan penyerap solar (K,Ge)-dop CZTSSe. Proses-proses yang sama dijalankan untuk menghasilkan filem tipis kecuali kepekatan molar Ge yang berbeza (10, 15, 20, 25 dan 30)% dalam pelarut dimethilformamida sebagai bahan pelarut. Kesan kepekatan Ge yang berbeza telah dikaji. Spektra ultra ungu-cahaya tampak-infra merah dekat menunjukkan pekali penyerapan yang tinggi melebihi 10000 cm^{-1} untuk setiap sampel. Lebar jalur juga bertambah apabila kepekatan Ge ditambah, yang menyimpulkan kebolehan Ge menala lebar jalur CZTSSe untuk meningkatkan voltan litar terbuka. Spektra sinar-X menunjukkan penghabluran yang lebih baik pada 25% dan 30% dopan Ge, manakala mikrograf-mikrograf dari mikroskop elektron pengimbas pancaran medan pelepasan mendedahkan bahawa 25% Ge mempunyai pertumbuhan hablur yang lebih baik. Ketumpatan pembawa cas dalam lapisan penyerap juga telah bertambah dengan pertambahan dopan. Berdasarkan dapatan, filem tipis (K,Ge)-dop CZTSSe dengan 1.5 mol % K dan 25% Ge mempunyai ciri-ciri yang terbaik.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AZO	-	Aluminium Zinc Oxide
CB	-	Conduction Band
CIGS	-	Cooper Indium Gallium Sulphide
CIGSe	-	Copper Indium Gallium Selenide
CIGSSe	-	Copper Indium Gallium Sulphoselenide
CIS	-	Copper Indium Sulphide
CISe	-	Copper Indium Selenide
CISSe	-	Copper Indium Sulphoselenide
CTO	-	Cadmium Tin Oxide
CZTGeS	-	Copper Zinc Tin Germanium Sulphide
CZTGeSSe	-	Copper Zinc Tin Germanium Sulphoselenide
CZTS	-	Copper Zinc Tin Sulphide
CZTSe	-	Copper Zinc Tin Selenide
CZTSSe	-	Copper Zinc Tin Sulphoselenide
DMF	-	Dimethylformamide
DMSO	-	Dimethyl Sulfoxide
EB	-	Electron Beam
EDX	-	Energy Disperse X-Ray
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infra-Red
GB	-	Grain Boundaries
IBM	-	International Business Machines Corporation
PV	-	Photovoltaic
SLG	-	Soda Lime Glass
UNSW	-	University of New South Wales
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

A	-	Absorbance
α	-	Absorption Coefficient
E_g	-	Energy bandgap
v	-	Energy frequency
I	-	Intensity of energy
h	-	Planck constant
d	-	Thin film thickness
c	-	Velocity of light
λ	-	Wavelength

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Solar energy, these two words have become a compulsory topic to most of the scientists all over the world in the field of renewable energy sources. Sun is an unlimited source of energy for earth, which can solve limited energy sources issues and reduce unnecessary fabrication and transmission losses (Mahjoubi, Bitri et al, 2017; Wallace, Mitzi and Walsh, 2017; Zakutayev, 2017). Since last three decades, different photovoltaic devices have been developed to convert solar energy into electrical energy. Starting from silicon based technology to thin film solar cells, scientists always struggled to find the best combination of materials including base materials, dopants and solvents, along with fabricating procedures which includes solution preparation and thin films deposition techniques to produce efficient final product (Abermann, 2013; Wallace et al, 2017; Yang, Mazalan et al, 2017). Since the silicon based solar panels are heavy, requires high material consumption and less economical, researchers turned their focus to thin film solar cells technology and known as the second generation solar cell (Suryawanshi, Agawane et al, 2013). The thin film technology is relatively simple, easy and capable to eliminate the unnecessary cost by reducing materials consumption with an advantage to deposit on different types of substrates such as glass, stainless steel and plastic (Zhou, Hsu et al, 2013; Song, Ji et al, 2014; Hsieh, Han et al, 2016; López-Marino, Sánchez et al, 2016; Diwate, Mohite et al, 2017; Liu, Huang et al, 2017; Rana, Kim et al, 2017). Currently, the main stream thin film solar cells are the amorphous silicon thin film, cadmium telluride (CdTe), copper indium selenide (CIS), copper indium gallium selenide (CIGS), the gallium arsenide and copper zinc tin sulphide (CZTS). Nevertheless, the cadmium and arsenic in cadmium telluride and gallium arsenide are toxic, while copper indium gallium selenide system contains rare indium element which make them an expensive approach to fabricate solar cells (Song et al, 2014; Pandiyan, Oulad Elhmaidi et al, 2017). Furthermore, CIGS technology was in questioned as they needed too long period to commercialize and failed to reduce the cost, while a supplier of CIGS PV module from United States faced bankruptcy (Song et al, 2014). These events open the door for CZTS thin film solar cell. Apart from insolvent of rare element, CdTe, CIS and CIGS are facing big challenges in the future development of solar cells such as green environment issues and economical fabrication processes, which give advantage to copper zinc tin sulphide (CZTS) thin film over other thin film solar cells (Song et al, 2014; Mahajan, Stathatos et al, 2018).

The CZTS is recognised as quaternary compounds in kesterite structure with direct band gap of 1.50 eV and high absorption coefficient (over 10^4 cm^{-1} in visible region). Thus, the CZTS materials can be utilized as absorption layer for thin film solar cells. Compared with the currently commercialized crystalline Si, CdTe and CIGS solar cells, CZTS has advantage of abundance in the earth crust and nontoxic characteristics. Hence, CZTS thin film is recognised as one of the potential candidate materials for thin film solar absorbing layer as it has the advantages that needed for an absorber layer (Riha, Parkinson and Prieto, 2009; Steinhagen, Panthani et al, 2009; Song et al, 2014; Gupta, Gupta and Mohanty, 2017).

In recent years, CZTS thin film solar cells have been successfully fabricated using vacuum-based approaches. However, the vacuum-based approaches are expensive and require a special and sophisticated equipment. As the fabrication cost is one of key challenge in solar industry, the non-vacuum deposition methods such as spray coating, spin coating, dip coating and doctor blade have been developed and are the current focus of scientist in solar cell field of research (Song et al, 2014). The achieved power conversion efficiency for CZTS solar cell at small scale is above 10% for non-vacuum deposition technique which is a quite encouraging achievement (Song et al, 2014). Here after, CZTS has attracted attention from industries for the commercial purposes. IBM collaborates with the subsidiary of Showa Shell-Solar Frontier (specialised in CIS thin film PV technology) to exploit non vacuum deposition technology for CZTS technology (Song et al, 2014). In 2012, Korea Daegu Gyeongbuk Institute of Science and Technology (DGIST) has refined a vacuum deposition coating suitable for the large-scale production. They had successfully fabricated the CZTS device with power conversion efficiency of 8% higher than the world's highest efficiency at that time, which gave this quaternary CZTS thin film solar cells a huge boost for the expansion of solar cell market (Song et al, 2014).

1.2 Problem Statement

Currently, IBM holds the world record for CZTSSe with 12.6% power conversion efficiency using hydrazine based solvent (Green et al, 2018). Unfortunately, hydrazine is known as explosive, hepatotoxic and carcinogenic chemical (Choudhary and Hansen, 1998; Gupta et al, 2017). To increase the power conversion efficiency of the devices, CZTS thin films are treated with selenium by changing CZTS structure to CZTSSe. Apart from the selenization, the efficiency of CZTS thin layer is also improved by introducing different dopants in CZTS host structure (Hsieh et al, 2016; Phuong, Katahara et al, 2016). Alkali-metals, such as sodium, lithium and potassium, have shown encouraging results towards the high performance (Hsieh et al, 2016; López-Marino et al, 2016).

It is highly preferred that the fabrication processes involve less toxic materials yet give high efficiency, which is the key challenge and requires attention in non-vacuum based solar cell thin layer deposition approaches (Ki and Hillhouse, 2011). The dimethyl sulfoxide (DMSO) is one of the effective solvent capable to replace hydrazine, as it is safer and low toxic (Ki et al, 2011; Haass, Diethelm et al, 2015; Xin, Vorpahl et al, 2015). This approach only requires earth abundant metal salts and has produced solar cells with over 10 % efficiency (Haass et al, 2015; Schnabel, Abzieher et al, 2015; Xin et al, 2015). DMSO also has high-boiling temperature (189 °C), which increases the drying time. This may improve the structure quality of absorber layer and enhances electrical properties of the thin film (Teichler, Perelaer and Schubert, 2013). Apart from DMSO, dymethylformamide (DMF) also has been used as a replacement to DMSO for certain materials, which are not dissolved in DMSO. DMF has boiling point 153ºC, a bit lower than DMSO, and still has similar characteristics with the later (Collord and Hillhouse, 2016). There are few other solvents such as monoethanolamine, ethylene glycol, oleylamine, trioctylphosphine oxide, oleic acid and octadecene have been used to prepare precursor solution (Zhou et al, 2013; Gupta et al, 2017). Although some of these solvents could dissolve much more materials, however, most of them are harmful, highly toxic, and environmentally hazardous as reported by Laboratory Chemical Safety Summary (LCSS) of National Institutes of Health (NIH), USA (Wang, Shen et al, 2017).

The doping of alkali metals group I, significantly improved the efficiency of copper-based solar cells (Ård, Granath and Stolt, 2000; Granath, Bodegård and Stolt, 2000; Igalson, Kubiaczyk et al, 2001; Rudmann, Bilger et al, 2003; Cho, Lee et al, 2012; Chirilă, Rienhard et al, 2013; Guo, Ford et al, 2013; Laemmle, Wuerz and Powalla, 2013; Pianezzi, Reinhard et al, 2013; Reinhard, Bissig et al, 2015; Jackson, Hariskos et al, 2015; Lepetit, Harel et al, 2016; Yang, Huang and Pan, 2017). The higher carrier concentrations and large grain size are two key parameters to enhance the efficiency of CZTSSe device (Hsieh et al, 2016). The alkali metals with small atomic size have higher ability to replace constituents of CZTSSe, and can increase the carrier concentrations. However, the alkali metals with large atomic size have large grains and less non-radiative combination due to the relative low melting point of binary selenides (Hsieh et al, 2016). Between the entire materials of +1 oxidation group, potassium (K) doped CZTS thin films have shown both high carrier concentration and large grain size (Hsieh et. al., 2016). However, to the best of the author's knowledge, no research has reported the synthesis of CZTSSe with power conversion efficiency higher than 12.6 % world record thin film solar cells (Green et al, 2018). This research gap highlights an opportunity to improve the efficiency of the CZTS solar thin layer.

Hence, in this research, K-doped CZTSSe thin film is prepared and optimized. The optimized K-doped CZTSSe is further doped with different concentrations of germanium (Ge) to study the role of Ge in thin film solar cells. It has been reported that Ge doping in CZTS thin films could improve the power conversion efficiency of solar cell devices, by replacing tin (Sn) atoms. Ge can prevent Sn from forming a +II oxidation state that has high possibility to form deep recombination centers in CZTS (Bag, Gunawan et al, 2012; Li, Shen et al, 2016). Ge doping also can tune the band gap in the crystal lattice of the thin film solar cells, which might help to optimize the band alignment of CZTS/CdS, without controlling the S/Se ratio for CZTSSe absorber layer (Chen, Walsh et al, 2013; Polizzotti, Repins et al, 2013; Kim, Kim et al, 2014; Kim, Hiroi et al, 2014; Hages, Levcenco et al, 2015; Khadka and Kim, 2015; Maeda, Kawabata and Wada, 2015; Xin et al, 2015; Khadka, Kim and Kim, 2016b). In some experiments, Ge has found to increase the grain sizes, at the same time reduced the grain boundaries and enhanced the crystal growth of CZTS thin films (Li et al, 2016; Sun, Shen et al, 2019). In addition, Ge also has the ability to increases the carrier lifetime and improves the carrier concentration (Hages et al, 2015).

1.3 Objectives of the Research

The general objective of this research is to study the role of Ge in optimized K-doped $Cu_2ZnSn(S,Se)_4$ thin absorber layer of solar cell device.

The specific objectives for this research are as follows:

1. To optimize the concentration of K in Cu_2ZnSnS_4 precursor solutions using dimethyl sulfoxide (DMSO) as the solvent and deposit as thin film on glass substrate using spray pyrolysis technique.
2. To investigate and optimize Ge as dopant in optimized K-doped $Cu_2ZnSn(S,Se)_4$ precursor using dimethylformamide (DMF) as the solvent and deposit the thin film using spray pyrolysis technique.
3. To measure the optical, structural, morphological and electrical properties of deposited K-doped $Cu_2ZnSn(S,Se)_4$ and (K,Ge)-doped $Cu_2ZnSn(S,Se)_4$ thin absorber layer.

1.4 Scope of the Research

K-doped Cu_2ZnSnS_4 precursor solution with different molar concentration of K = 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 mol % are prepared with DMSO solvent using one pot approach. K is chosen as doping material to the CZTSSe thin film solar cells as K may improve the crystal growth and minimize defects. For dissolving agent, DMSO is chosen because it is organic nature and low toxicity. These solutions then are deposited on the soda lime glass substrates using spray pyrolysis deposition technique to form thin films. Three-step temperature approach is performed during selenization process in the tube furnace. After selenization process, these thin films are characterized to optimize the concentration of K in $Cu_2ZnSn(S,Se)_4$ using UV-Vis-NIR Spectrophotometer, 3D Microscope Surface Profiler, X-Ray Diffractometer (XRD), Field Emission Scanning Electron Microscope (FESEM), Energy Disperse X-ray Spectrometer (EDX) and Hall Effect Measurement System (HEMS).

The optimized K-doped Cu_2ZnSnS_4 is added together with different mol concentration of [Ge/(Ge + Sn)] % = 0, 10, 15, 20, 25, and 30 %, in DMF solvent using one pot approach. The solvent is changed from DMSO to DMF as there is precipitation formed in Ge-doped CZTS solution with DMSO solvent (Collord et al, 2016). Same processes of deposition and selenization of thin film are repeated for (K,Ge)-doped $Cu_2ZnSn(S,Se)_4$ thin films. The solar thin films with different concentrations of Ge are characterized by UV-Vis-NIR Spectrophotometer, 3D Microscope Surface Profiler, (XRD), (FESEM), (EDX) and (HEMS).

1.5 Significance of the Research

As the world now is critically looking for devices/systems for renewable energy with low cost fabrication process, earth abundant materials and environmental friendly, the present research findings will contribute towards the improvement of thin film solar cell devices and understanding of the role of K and Ge doping materials in CZTSSe solar cell absorber layer.

1.6 Thesis Structure

Chapter 1 includes the research background of CZTS thin film solar cells and its alloyed family, along with the advantages and problems related to CZTS solar cells. This chapter also includes the research objectives, scope of study, and the significance of the research.

Chapter 2 provides the literature review, which is directly and indirectly related to CZTS thin film solar cell technology. The details of CZTS and CZTSSe solar cell, its advantages and weaknesses, doping materials that may enhance the quality of the absorber layer, solvents that are suitable for dissolving related elements in precursor solution, also deposition methods are discussed briefly.

Chapter 3 includes the details of the research methodology that has been used to execute this research. The raw materials preparation of the precursor solution, the deposition technique to deposit CZTS thin film, selenization process and parameters involved in this research, for both K-doped CZTSSe and (K,Ge)-doped CZTSSe thin films are listed briefly. The chapter is ended with the flow chart as a summary for the research methodology.

Chapter 4 explains about characterization techniques used in studying (K,Ge)-doped CZTSSe absorber layer. Physical, chemical and optical properties of the thin films were measured by these techniques, while the data were analysed and discussed in this chapter.

Chapter 5 contains the conclusion drawn from results and future study and the recommendations in enhancing the CZTSSe thin film solar cells.

REFERENCES

Abermann, S. (2013) 'Non-vacuum processed next generation thin film photovoltaics: Towards marketable efficiency and production of CZTS based solar cells', *Solar Energy*. Elsevier Ltd, 94, pp. 37–70.

Akaki, Y., Komaki, H., Yokoyama, H., Yoshino, K., Maeda, K. and Ikari, T. (2003) 'Structural and optical characterization of Sb-doped $CuInS_2$ thin films grown by vacuum evaporation method', *Journal of Physics and Chemistry of Solids*. Elsevier, 64(9–10), pp. 1863–1867.

Ård, M. B., Granath, K. and Stolt, L. (2000) 'Growth of $Cu(In,Ga)Se_2$ thin films by coevaporation using alkaline precursors', *Thin Solid Films*. Elsevier, 361, pp. 9–16.

Bag, S., Gunawan, O., Gokmen, T., Zhu, Y. and Mitzi, D. B. (2012) 'Hydrazine-processed Ge-substituted CZTSe solar cells', *Chemistry of Materials*. ACS Publications, 24(23), pp. 4588–4593.

Barnes, I., Becker, K. H. and Patroescu, I. (1996) 'FTIR product study of the OH intiated oxidation of dimethyl sulphide: Observation of carbonyl sulphide and imethyl sulphoxide', *Atmospheric Environment*, 30(10–11), pp. 1805–1814.

Bhosale, S. M., Suryawanshi, M. P., Kim, J. H. and Moholkar, A. V. (2015) 'Influence of copper concentration on sprayed CZTS thin films deposited at high temperature', *Ceramics International*. Elsevier, 41(7), pp. 8299–8304.

Botti, S., Kammerlander, D. and Marques, M. A. L. (2011) 'Band structures of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ from many-body methods', *Applied Physics Letters*. AIP, 98(24), p. 241915.

Bourdais, S., Choné, C., Delatouche, B., Jacob, A., Larramona, G., Moisan, C., Lafond, A., Donatini, F., Rey, G., Siebentritt, S., Walsh, A. and Dennler, G. (2016) 'Is the Cu/Zn Disorder the Main Culprit for the Voltage Deficit in Kesterite Solar Cells?', *Advanced Energy Materials*, 6(12), pp. 1–21.

Boyle, J. H., McCandless, B. E., Hanket, G. M. and Shafarman, W. N. (2011) ‘Structural characterization of the (AgCu)(InGa)Se_2 thin film alloy system for solar cells’, *Thin Solid Films*. Elsevier, 519(21), pp. 7292–7295.

Boyle, J. H., McCandless, B. E., Shafarman, W. N. and Birkmire, R. W. (2014) ‘Structural and optical properties of (Ag,Cu)(In Ga)Se_2 polycrystalline thin film alloys’, *Journal of Applied Physics*. AIP, 115(22), p. 223504.

Carballeda-Galicia, D. M., Castanedo-Pérez, R., Jiménez-Sandoval, O., Jiménez-Sandoval, S., Torres-Delgado, G. and Zúñiga-Romero, C. I. (2000) ‘High transmittance CdO thin films obtained by the sol-gel method’, *Thin Solid Films*, 371(1), pp. 105–108.

Chagarov, E., Sardashti, K., Kummel, A., Lee, Y., Haight, R. and Gershon, T. (2016) ‘$Ag_2ZnSn(S,Se)_4$: A highly promising absorber for thin film photovoltaics’, *The Journal of Chemical Physics*. AIP Publishing, 144(10), p. 104704.

Chen, S., Gong, X. G., Walsh, A. and Wei, S. H. (2009) ‘Crystal and electronic band structure of Cu_2ZnSnX_4 (X = S and Se) photovoltaic absorbers: First-principles insights’, *Applied Physics Letters*. AIP, 94(4), p. 41903.

Chen, S., Gong, X. G., Walsh, A. and Wei, S. H. (2010) ‘Defect physics of the kesterite thin-film solar cell absorber Cu_2ZnSnS_4’, *Applied Physics Letters*. AIP, 96(2), p. 21902.

Chen, S., Yang, J.-H., Gong, X. G., Walsh, A. and Wei, S. H. (2010) ‘Intrinsic point defects and complexes in the quaternary kesterite semiconductor Cu_2ZnSnS_4’, *Physical Review B*. APS, 81(24), p. 245204.

Chen, S., Walsh, A., Gong, X. G. and Wei, S. H. (2013) ‘Classification of lattice defects in the kesterite Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ earth-abundant solar cell absorbers’, *Advanced Materials*. Wiley Online Library, 25(11), pp. 1522–1539.

Chirilă, A., Reinhard, P., Pianezzi, F., Bloesch, P., Uhl, A., Fella, C., Kranz, L., Keller, D., Gretener, C. and Hagendorfer, H. (2013) ‘Potassium-induced surface modification of Cu(In,Ga)Se_2 thin films for high-efficiency solar cells’, *Nature Materials*. Nature Research, 12(12), pp. 1107–1111.

Cho, D.-H., Lee, K. S., Chung, Y. D., Kim, J. H., Park, S. J.and Kim, J. (2012) 'Electronic effect of Na on Cu(In,Ga)Se_2 solar cells', *Applied Physics Letters*. AIP, 101(2), p. 23901.

Choudhary, G. and Hansen, H. (1998) 'Human health perspective of environmental exposure to hydrazines: A review', *Chemosphere*. Elsevier, 37(5), pp. 801–843.

Collord, A. D. and Hillhouse, H. W. (2016) 'Germanium Alloyed Kesterite Solar Cells with Low Voltage Deficits'. *Chemistry of Materials.* ACS Publications, 28, pp. 2067–2073.

Courel, M., Valencia-Resendiz, E., Andrade-Arvizu, J. A., Saucedo, E. and Vigil-Galán, O. (2017) 'Towards understanding poor performances in spray-deposited Cu_2ZnSnS_4 thin film solar cells', *Solar Energy Materials and Solar Cells*. Elsevier, 159, pp. 151–158.

Crépieux, A. and Bruno, P. (2001) 'Theory of the anomalous Hall effect from the Kubo formula and the Dirac equation', *Physical Review B - Condensed Matter and Materials Physics*, 64(1), pp. 1–16.

Diwate, K., Mohite, K., Shinde, M., Rondiya, S., Pawbake, A., Date, A., Pathan, H. and Jadkar, S. (2017) 'Synthesis and Characterization of Chemical Spray Pyrolysed CZTS Thin Films for Solar Cell Applications', *Energy Procedia*. The Author(s), 110(December 2016), pp. 180–187.

Du, H., Yan, F., Young, M., To, B., Jiang, C. S., Dippo, P., Kuciauskas, D., Chi, Z., Lund, E. A. and Hancock, C. (2014) 'Investigation of combinatorial coevaporated thin film Cu_2ZnSnS_4. I. Temperature effect, crystalline phases, morphology, and photoluminescence', *Journal of Applied Physics*. AIP, 115(17), p. 173502.

Dudchak, I. V and Piskach, L. V (2003) 'Phase equilibria in the Cu_2SnSe_3–$SnSe_2$–ZnSe system', *Journal of alloys and compounds*. Elsevier, 351(1), pp. 145–150.

Engelke, U. F. H., Tangerman, A., Willemsen, M. A. A. P., Moskau, D., Loss, S., Mudd, S. H. and Wevers, Ron A. (2005) 'Dimethyl sulfone in human cerebrospinal fluid and blood plasma confirmed by one-dimensional 1H and two-dimensional 1H-13C NMR', *NMR in Biomedicine*, 18(5), pp. 331–336.

Erslev, P. T., Lee, J. W., Hanket, G. M., Shafarman, W. N. and Cohen, J. D. (2011) 'The electronic structure of $Cu(In_{1-x}Ga_x)Se_2$ alloyed with silver', *Thin Solid Films*. Elsevier, 519(21), pp. 7296–7299.

Ford, G. M., Guo, Q., Agrawal, R. and Hillhouse, H. W. (2011) 'Earth Abundant Element $Cu_2Zn(Sn_{1-x}Ge_x)S_4$ Nanocrystals for Tunable Band Gap Solar Cells: 6.8% Efficient Device Fabrication', *Chemistry of Materials*. ACS Publications, 23(10), pp. 2626–2629.

Gershon, T., Gokmen, T., Gunawan, O., Haight, R., Guha, S. and Shin, B. (2014) 'Understanding the relationship between $Cu_2ZnSn(S,Se)_4$ material properties and device performance', *Mrs Communications*. Cambridge University Press, 4(4), pp. 159–170.

Gershon, T., Shin, B., Bojarczuk, N., Hopstaken, M., Mitzi, D. B. and Guha, S. (2015) 'The Role of Sodium as a Surfactant and Suppressor of Non-Radiative Recombination at Internal Surfaces in Cu_2ZnSnS_4', *Advanced Energy Materials*. Wiley Online Library, 5(2).

Gershon, T., Lee, Y. S., Antunez, P., Mankad, R., Singh, S., Bishop, D., Gunawan, O., Hopstaken, M. and Haight, R. (2016) 'Photovoltaic materials and devices based on the alloyed kesterite absorber $(Ag_xCu_{1-x})_2ZnSnSe_4$', *Advanced Energy Materials*. Wiley Online Library, 6(10).

Ghediya, P. R. and Chaudhuri, T. K. (2015) 'Doctor-blade printing of Cu_2ZnSnS_4 films from microwave-processed ink', *Journal of Materials Science: Materials in Electronics*, 26(3), pp. 1908–1912.

Giraldo, S., Neuschitzer, M., Thersleff, T., López-Marino, S., Sánchez, Y., Xie, H., Colina, M., Placidi, M., Pistor, P. and Izquierdo-Roca, V. (2015) 'Large efficiency improvement in $Cu_2ZnSnSe_4$ solar cells by introducing a superficial Ge nanolayer', *Advanced Energy Materials*. Wiley Online Library, 5(21).

Gokmen, T., Gunawan, O., Todorov, T. K. and Mitzi, D. B. (2013) 'Band tailing and efficiency limitation in kesterite solar cells', *Applied Physics Letters*. AIP, 103(10), p. 103506.

Granath, K., Bodegård, M. and Stolt, L. (2000) 'The effect of NaF on $Cu(In,Ga)Se_2$ thin film solar cells', *Solar Energy Materials and Solar Cells*. Elsevier, 60(3), pp. 279–293.

Green, M. A., Hishikawa, Y., Dunlop, E. D., Levi, D. H., Hohl-Ebinger, J. and Ho-Baillie, A. W. Y. (2018) 'Solar cell efficiency tables (version 52)', *Progress in Photovoltaics: Research and Applications*, 26(7), pp. 427–436.

Group, R., Division, S. and Berkeley, L. (2009) 'Materials Availability Expands the Opportunity for Large-Scale Photovoltaics Deployment', 43(6), pp. 2072–2077.

Gunawan, O., Gokmen, T. and Mitzi, D. B. (2014) 'Suns-VOC characteristics of high performance kesterite solar cells', *Journal of Applied Physics*. AIP Publishing, 116(8), p. 84504.

Guo, H., Li, Y., Guo, X., Yuan, N. and Ding, J. (2018) 'Effect of silicon doping on electrical and optical properties of stoichiometric Cu_2ZnSnS_4 solar cells', *Physica B: Condensed Matter*. Elsevier Ltd, 531(October 2017), pp. 9–15.

Guo, Q., Ford, G. M., Yang, W. C., Hages, C. J., Hillhouse, H. W. and Agrawal, R. (2012) 'Enhancing the performance of CZTSSe solar cells with Ge alloying', *Solar Energy Materials and Solar Cells*. Elsevier, 105, pp. 132–136.

Guo, Q., Ford, G. M., Agrawal, R. and Hillhouse, H. W. (2013) 'Ink formulation and low-temperature incorporation of sodium to yield 12% efficient $Cu(In,Ga)(S,Se)_2$ solar cells from sulfide nanocrystal inks', *Progress in Photovoltaics: Research and Applications*. Wiley Online Library, 21(1), pp. 64–71.

Gupta, I., Gupta, P. and Mohanty, B. C. (2017) 'Synthesis of non-hydrazine solution processed $Cu_2(ZnSn)S_4$ thin films for solar cells applications', *AIP Conference Proceedings*, 1832, p. 080024.

Haass, S. G., Diethelm, M., Werner, M., Bissig, B., Romanyuk, Y. E. and Tiwari, A. N. (2015) '11.2% Efficient Solution Processed Kesterite Solar Cell with a Low Voltage Deficit', *Advanced Energy Materials*, 5(18), pp. 1–7.

Hages, C. J., Levcenco, S., Miskin, C., Alsmeier, J. H., Abou-Ras, D., Wilks, R. G., Bär, M., Unold, T. and Agrawal, R. (2015) 'Improved performance of Ge-alloyed CZTGeSSe thin-film solar cells through control of elemental losses', *Progress in Photovoltaics: Research and Applications*. Wiley Online Library, 23(3), pp. 376–384.

Hsieh, Y. T., Han, Q., Jiang, C., Song, T. B., Chen, H., Meng, L., Zhou, H. and Yang, Y. (2016) 'Efficiency Enhancement of $Cu_2ZnSn(S,Se)_4$ Solar Cells via Alkali Metals Doping', *Advanced Energy Materials*, 6(7), pp. 1–6.

Igalson, M., Kubiaczyk, A., Zabierowski, P., Bodegård, Marika. and Granath, K. (2001) 'Electrical characterization of $ZnO/CdS/Cu(In,Ga)Se_2$ devices with controlled sodium content', *Thin Solid Films*. Elsevier, 387(1), pp. 225–227.

Ito, K. (2014) *Copper zinc tin sulfide-based thin film solar cells*. John Wiley & Sons.

Jackson, P., Hariskos, D., Wuerz, R., Kiowski, O., Bauer, A., Friedlmeier, T. M. and Powalla, M. (2015) 'Properties of $Cu(In,Ga)Se_2$ solar cells with new record efficiencies up to 21.7%', *physica status solidi (RRL)-Rapid Research Letters*. Wiley Online Library, 9(1), pp. 28–31.

Jiang, M. and Y, X. (2013) 'Cu_2ZnSnS_4 Thin Film Solar Cells: Present Status and Future Prospects', *Solar Cells - Research and Application Perspectives*, (May).

Jiang, Y., Yao, B., Li, Y., Ding, Z., Luan, H., Jia, J., Li, Y., Shi, K., Sui, Y. and Zhang, B. (2018) 'Structure, optical and electrical properties of $(Cu_{1-x}Ag_x)_2ZnSn(S,Se)_4$ alloy thin films for photovoltaic application', *Materials Science in Semiconductor Processing*, 81(March), pp. 54–59.

Johnson, M., Baryshev, S. V., Thimsen, E., Manno, M. Zhang, X. Veryovkin, I. V., Leighton, C. and Aydil, E. S. (2014) 'Alkali-metal-enhanced grain growth in Cu_2ZnSnS_4 thin films', *Energy & Environmental Science*. Royal Society of Chemistry, 7(6), pp. 1931–1938.

Kamoun, N., Bouzouita, H. and Rezig, B. (2007) 'Fabrication and characterization of Cu_2ZnSnS_4 thin films deposited by spray pyrolysis technique', *Thin Solid Films*, 515(15 SPEC. ISS.), pp. 5949–5952.

Khadka, D. B. and Kim, J. (2015) 'Band Gap Engineering of Alloyed $Cu_2ZnGe_xSn_{1-x}Q_4$ (Q= S, Se) Films for Solar Cell', *The Journal of Physical Chemistry C*. ACS Publications, 119(4), pp. 1706–1713.

Khadka, D. B., Kim, S. and Kim, J. (2016) 'Ge-alloyed CZTSe thin film solar cell using molecular precursor adopting spray pyrolysis approach', *RSC Adv.*, 6(44), pp. 37621–37627.

Khadka, D. B., Kim, S. Y. and Kim, J. H. (2016) 'Effects of Ge Alloying on Device Characteristics of Kesterite-Based CZTSSe Thin Film Solar Cells', *Journal of Physical Chemistry C*, 120(8), pp. 4251–4258.

Ki, W. and Hillhouse, H. W. (2011) 'Earth-Abundant Element Photovoltaics Directly from Soluble Precursors with High Yield Using a Non-Toxic Solvent', *Advanced Energy Materials*. Wiley Online Library, 1(5), pp. 732–735.

Kim, I., Kim, K., Oh, Y., Woo, K., Cao, G., Jeong, S. and Moon, J. (2014) 'Bandgap-Graded $Cu_2Zn(Sn_{1-x}Ge_x)S_4$ Thin-Film Solar Cells Derived from Metal Chalcogenide Complex Ligand Capped Nanocrystals', *Chemistry of Materials*. ACS Publications, 26(13), pp. 3957–3965.

Kim, J., Hiroi, H., Todorov, T. K., Gunawan, O., Kuwahara, M., Gokmen, T., Nair, D., Hopstaken, M., Shin, B., Lee, Y. S., Wang, W., Sugimoto, H. and Mitzi, D. B. (2014) 'High efficiency $Cu_2ZnSn(S,Se)_4$ solar cells by applying a double in $2S_3$/CdS Emitter', *Advanced Materials*, 26(44), pp. 7427–7431.

Krunks, M., Leskela, T., Mannonen, R. and Niinisto, L. (1998) 'Thermal Decomposition of Copper(I) Thiocarbamide Chloride Hemihydrate', *Journal of Thermal Analysis,* 53, pp 355–364.

Kumar, M., Dubey, A., Adhikari, N., Venkatesan, S. and Qiao, Q. (2015) 'Strategic review of secondary phases, defects and defect-complexes in kesterite CZTS–Se solar cells', *Energy Environ. Sci.* Royal Society of Chemistry, 8(11), pp. 3134–3159.

Laemmle, A., Wuerz, R. and Powalla, M. (2013) 'Efficiency enhancement of $Cu(In,Ga)Se_2$ thin-film solar cells by a post-deposition treatment with potassium fluoride', *physica status solidi (RRL)-Rapid Research Letters*. Wiley Online Library, 7(9), pp. 631–634.

Lafond, A., Guillot-Deudon, C., Vidal, J., Paris, M., La, C. and Jobic, S. (2017) 'Substitution of Li for Cu in Cu_2ZnSnS_4: Toward Wide Band Gap Absorbers with Low Cation Disorder for Thin Film Solar Cells', *Inorganic Chemistry*, 56(5), pp. 2712–2721.

Laghfour, Z., Aazou, S., Taibi, M., Schmerber, G., Ulyashin, A., Dinia, A., Slaoui, A., Abd-Lefdil, M. and Sekkat, Z. (2018) 'Sodium doping mechanism on sol-gel processed kesterite Cu_2ZnSnS_4 thin films', *Superlattices and Microstructures*. Elsevier B.V., 120, pp. 747–752.

Lepetit, T., Harel, S., Arzel, L., Ouvrard, G. and Barreau, N. (2016) 'Coevaporated $KInSe_2$: A Fast Alternative to KF Postdeposition Treatment in High-Efficiency $Cu(In,Ga)Se_2$ Thin Film Solar Cells', *IEEE Journal of Photovoltaics*. IEEE, 6(5), pp. 1316–1320.

Li, J., Shen, H., Chen, J., Li, Y. and Yang, J. (2016) 'Growth mechanism of Ge-doped CZTSSe thin film by sputtering method and solar cells', *Phys. Chem. Chem. Phys.* Royal Society of Chemistry, 18(41), pp. 28829–28834.

Li, J. V., Kuciauskas, D., Young, M. R. and Repins, I. L. (2013) ‘Effects of sodium incorporation in Co-evaporated $Cu_2ZnSnSe_4$ thin-film solar cells’, *Applied Physics Letters*. AIP, 102(16), p. 163905.

Li, W., Liu, X., Cui, H., Huang, S. and Hao, X. (2015) ‘The role of Ag in $(Ag,Cu)_2ZnSnS_4$ thin film for solar cell application’, *Journal of Alloys and Compounds*. Elsevier, 625, pp. 277–283.

Li, W., Su, Z., Tan, J. M. R., Chiam, S. Y., Seng, H. L., Magdassi, S. and Wong, L. H. (2017) ‘Revealing the Role of Potassium Treatment in CZTSSe Thin Film Solar Cells’, *Chemistry of Materials*, 29(10), pp. 4273–4281.

Lin, C. C. and Li, Y. Y. (2009) ‘Synthesis of ZnO nanowires by thermal decomposition of zinc acetate dihydrate’, *Materials Chemistry and Physics*, 113(1), pp. 334–337.

Lin, X., Madhavan, V. E., Kavalakkatt, J., Hinrichs, V., Lauermann, I., Lux-Steiner, M. Ch., Ennaoui, A. and Klenk, R. (2017) ‘Inkjet-printed CZTSSe absorbers and influence of sodium on device performance’, *Solar Energy Materials and Solar Cells*. Elsevier B.V., (September), pp. 0–1.

Liu, F., Huang, J., Sun, K., Yan, C., Shen, Y., Park, J., Pu, A., Zhou, F., Liu, X., Stride, J. A., Green, M. A. and Hao, X. (2017) ‘Beyond 8% ultrathin kesterite Cu_2ZnSnS_4 solar cells by interface reaction route controlling and self-organized nanopattern at the back contact’, *NPG Asia Materials*. Nature Publishing Group, 9(7), p. e401.

Liu, X., Feng, Y., Cui, H., Liu, F., Hao, X., Conibeer, G., Mitzi, D. B. and Green, M. (2016) ‘The current status and future prospects of kesterite solar cells: a brief review’, *Progress in Photovoltaics: Research and Applications*, 24(6), pp. 879–898.

López-Marino, S., Sánchez, Y., Espíndola-Rodríguez, M., Alcobé, X., Xie, H., Neuschitzer, M., Becerril, I., Giraldo, S., Dimitrievska, M., Placidi, M., Fourdrinier, L., Izquierdo-Roca, V., Pérez-Rodríguez, A. and Saucedo, E. (2016) ‘Alkali doping strategies for flexible and light-weight $Cu_2ZnSnSe_4$ solar cells’, *J. Mater. Chem. A*, 4(5), pp. 1895–1907.

Ma, T., Jiang, G., Liu, W. and Zhu, C. (2015) 'Sodium doping effects on the crystalline and electrical properties of $Cu_2ZnSnSe_4$ thin films', *Solar Energy*. Elsevier Ltd, 115, pp. 413–418.

Maeda, T., Kawabata, A. and Wada, T. (2015) 'First-principles study on alkali-metal effect of Li, Na, and K in Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$', *physica status solidi (c)*. Wiley Online Library, 12(6), pp. 631–637.

Mahajan, S., Stathatos, E., Huse, N., Birajdar, R., Kalarakis, A. and Sharma, R. (2018) 'Low cost nanostructure kesterite CZTS thin films for solar cells application', *Materials Letters.* Elsevier B. V., 210, pp. 92–96.

Mahjoubi, S., Bitri, N., Bouzouita, H., Abaab, M. and Ly, I. (2017) 'Effect of the annealing and the spraying time on the properties of CZTS thin films prepared by the "Spray sandwich" technique', *Applied Physics A: Materials Science and Processing*, 123(6).

Mitzi, D. B., Gunawan, O., Todorov, T. K. and Barkhouse, D. A. R. (2013) 'Prospects and performance limitations for Cu–Zn–Sn–S–Se photovoltaic technology', *Phil. Trans. R. Soc. A*. The Royal Society, 371(1996), p. 20110432.

Mule, A., Vermang, B., Sylvester, M., Brammertz, G., Ranjbar, S., Schnabel, T., Gampa, N., Meuris, M. and Poortmans, J. (2017) 'Effect of different alkali (Li, Na, K, Rb, Cs) metals on $Cu_2ZnSnSe_4$ solar cells', *Thin Solid Films*. Elsevier B.V., 633, pp. 156–161.

Nagaoka, A., Miyake, H., Taniyama, T., Kakimoto, K., Nose, Y., Scarpulla, M. A. and Yoshino, K. (2014) 'Effects of sodium on electrical properties in Cu_2ZnSnS_4 single crystal', *Applied Physics Letters*. AIP, 104(15), p. 152101.

Nateprov, A., Kravtsov, V. C., Gurieva, G. and Schorr, S (2013) 'Single crystal X-ray structure investigation of $Cu_2ZnSnSe_4$', *Электронная обработка материалов*. Институт прикладной физики Академии наук Молдовы, (5).

Nguyen, T. H., Harada, T., Nakanishi, S., Ikeda, S. (2016) ‘Cu_2nSnS4-based thin film solar cells with more than 8% conversion efficiency obtained by using a spray pyrolysis technique’, in *2016 IEEE 43rd Photovoltaic Specialists Conference (PVSC)*, pp. 0470–0472.

Olekseyuk, I. D., Gulay, L. D., Dydchak, I. V., Piskach, L. V., Parasyuk, O. V. and Marchuk, O. V. (2002) ‘Single crystal preparation and crystal structure of the $Cu_2Zn/Cd,Hg/SnSe_4$ compounds’, *Journal of Alloys and Compounds*. Elsevier, 340(1), pp. 141–145.

Olekseyuk, I. D., Dudchak, I. V and Piskach, L. V (2004) ‘Phase equilibria in the Cu_2S–ZnS–SnS_2 system’, *Journal of alloys and compounds*. Elsevier, 368(1), pp. 135–143.

Pandiyan, R., Oulad Elhmaidi, Z., Sekkat, Z., Abd-lefdil, M. and El Khakani, M. A. (2017) ‘Reconstructing the energy band electronic structure of pulsed laser deposited CZTS thin films intended for solar cell absorber applications’, *Applied Surface Science*. Elsevier B.V., 396, pp. 1562–1570.

Park, J.-S., Yang, J. H., Ramanathan, K., Wei, S. H. (2014) ‘Defect properties of Sb- and Bi-doped $CuInSe_2$: The effect of the deep lone-pair s states’, *Applied Physics Letters*. AIP Publishing, 105(24), p. 243901.

Patel, K., Kheraj, V., Shah, D. V., Panchal, C. J. and Dhere, N. G. (2016) ‘Cu_2ZnSnS_4 thin-films grown by dip-coating: Effects of annealing’, *Journal of Alloys and Compounds*, 663, pp. 842–847.

Pathan, H. M., Desai, J. D. and Lokhande, C. D. (2002) ‘Modified chemical deposition and physico-chemical properties of copper sulphide (Cu_2S) thin films’, *Applied Surface Science*, 202(1–2), pp. 47–56.

Patil, P. S. (1999) ‘Versatility of chemical spray pyrolysis technique’, *Materials Chemistry and Physics.* Elsevier Science S. A., 59, pp. 185–198.

Phan Thi, K. L., Anh Tuan, D., Huu Ke, N., Anh Le, T. Q. and Hung, L. V. T. (2017) 'Effect of thickness and sulfur-free annealing atmosphere on the structural, optical and electrical properties of Cu_2ZnSnS_4 thin films prepared by dip-coating technique', *Journal of Sol-Gel Science and Technology*. Springer US, pp. 1–8.

Phuong, L. Q., Katahara, J. K., Yamashita, G., Nagai, M., Ashida, M., Hillhouse, H. W. and Kanemitsu, Y. (2016) 'Impact of alkali doping on carrier transport in $Cu_2ZnSn(S,Se)_4$ thin films for solar cell applications', *2016 IEEE 43rd Photovoltaic Specialists Conference (PVSC)*, pp. 0027–0030.

Piacente, V., Foglia, S. and Scardala, P. (1991) 'Sublimation study of the tin sulphides SnS_2, Sn_2S_3 and SnS', *Journal of alloys and compounds*. Elsevier, 177(1), pp. 17–30.

Pianezzi, F., Reinhard, P., Chirilă, A., Nishiwaki, S., Bissig, B., Buecheler, S. and Tiwari, A. N. (2013) 'Defect formation in $Cu(In,Ga)Se_2$ thin films due to the presence of potassium during growth by low temperature co-evaporation process', *Journal of Applied Physics*. AIP, 114(19), p. 194508.

Polizzotti, A., Repins, I. L., Noufi, R., Wei, S. H. and Mitzi, D. B. (2013) 'The state and future prospects of kesterite photovoltaics', *Energy & Environmental Science*. Royal Society of Chemistry, 6(11), pp. 3171–3182.

Pontes, F. M., Longo, E., Leite, E. R. and Varela, J. A. (2001) 'Study of the dielectric and ferroelectric properties of chemically processed $Ba_xSr_{1-x}TiO_3$ thin films', *Thin Solid Films.* Elsevier Science B. V., 386, pp. 91–98.

Prabeesh, P., Saritha, P., Selvam, I. P. and Potty, S. N. (2017) 'Fabrication of CZTS thin films by dip coating technique for solar cell applications', *Materials Research Bulletin*. Elsevier Ltd, 86, pp. 295–301.

Prabhakar, T. and Jampana, N. (2011) 'Effect of sodium diffusion on the structural and electrical properties of Cu_2ZnSnS_4 thin films', *Solar Energy Materials and Solar Cells*. Elsevier, 95(3), pp. 1001–1004.

Rana, T. R., Kim, J. H., Sim, J. H., Yang, K. J., Kim, D. H. and Kang, J. K. (2017) 'Fabrication and device characterization of potassium fluoride solution treated CZTSSe solar cell', *Current Applied Physics*. Elsevier B.V, 17(10), pp. 1353–1360.

Rana, T. R., Shinde, N. M. and Kim, J. (2016) 'Novel chemical route for chemical bath deposition of Cu_2ZnSnS_4 (CZTS) thin films with stacked precursor thin films', *Materials Letters*, 162, pp. 40–43.

Rawat, K. and Shishodia, P. K. (2016) 'Enhancement of photosensitivity in bismuth doped Cu_2ZnSnS_4 thin films', *Phys. Status Solidi RRL.* Wiley Online Library, 5, pp. 1–5.

Redinger, A., önes, K., Fontané, X., Izquierdo-Roca, V., Saucedo, E., Valle, N., Pérez-Rodríguez, A. and Siebentritt, S. (2011) 'Detection of a ZnSe secondary phase in coevaporated $Cu_2ZnSnSe_4$ thin films', *Applied Physics Letters*. AIP, 98(10), p. 101907.

Reinhard, P., Bissig, B., Pianezzi, F., Avancini, E., Hagendorfer, H., Keller, D., Fuchs, P., Döbeli, M., Vigo, C. and Crivelli, P. (2015) 'Features of KF and NaF postdeposition treatments of Cu(In,Ga)Se_2 absorbers for high efficiency thin film solar cells', *Chemistry of Materials*. ACS Publications, 27(16), pp. 5755–5764.

Repins, I. L., Romero, M. J., Li, J. V., Wei, S. H., Kuciauskas, D., Jiang, C. S., Beall, C., DeHart, C., Mann, J. and Hsu, W. C. (2012) 'Kesterite successes, ongoing work, and challenges: a perspective from vacuum deposition', in *Photovoltaic Specialists Conference (PVSC), Volume 2, 2012 IEEE 38th*. IEEE, pp. 1–7.

Rey, G., Babbe, S., Weiss, T.P., Elanzeery, H., Melchiorre, M., Valle, N., El Adib, B. and Siebentritt, S. (2017) 'Post-deposition treatment of $Cu_2ZnSnSe_4$ with alkalis', *Thin Solid Films*. The Authors, 633, pp. 162–165.

Riha, S. C., Parkinson, B. A. and Prieto, A. L. (2009) 'Solution-based synthesis and characterization of Cu_2ZnSnS_4 nanocrystals', *Journal of the American Chemical Society*. ACS Publications, 131(34), pp. 12054–12055.

Rudmann, D., Bilger, G., Kaelin, M., Haug, F. J., Zogg, H. and Tiwari, A. N. (2003) ‘Effects of NaF coevaporation on structural properties of Cu(In,Ga)Se_2 thin films’, *Thin Solid Films*. Elsevier, 431, pp. 37–40.

Sarswat, P. K. and Free, M. L. (2015) ‘The effects of dopant impurities on Cu_2ZnSnS_4 system Raman properties’, *Journal of Materials Science*, 50(4), pp. 1613–1623.

Schnabel, T., Abzieher, T., Friedlmeier, T. M. and Ahlswede, E. (2015) ‘Solution-based preparation of $Cu_2ZnSn(S,Se)_4$ for solar cells—comparison of $SnSe_2$ and elemental Se as chalcogen source. IEEE J. Photovoltaics 2015, 5’, *IEEE Journal of Photovoltaics*. IEEE, 5(2), pp. 670–675.

Schorr, S. (2007) ‘Structural aspects of adamantine like multinary chalcogenides’, *Thin Solid Films*. Elsevier, 515(15), pp. 5985–5991.

Schorr, S. (2011) ‘The crystal structure of kesterite type compounds: A neutron and X-ray diffraction study’, *Solar Energy Materials and Solar Cells*. Elsevier, 95(6), pp. 1482–1488.

Scragg, J. J., Ericson, T., Kubart, T., Edoff, M. and Platzer-Björkman, C. (2011) ‘Chemical insights into the instability of Cu_2ZnSnS_4 films during annealing’, *Chemistry of Materials*. ACS Publications, 23(20), pp. 4625–4633.

Seboui, Z., Cuminal, Y. and Kamoun-Turki, N. (2013) ‘Physical properties of Cu_2ZnSnS_4 thin films deposited by spray pyrolysis technique’, *Journal of Renewable and Sustainable Energy 5*. AIP, 023113.

Shamardin, A. V., Opanasyuk, A. S., Kurbatov, D. I. and Istratov, M. E. (2017) ‘Cation Germanium Incorporation . New Direction Toward High-efficiency Kesterite Solar Cells’, pp. 11–14.

Shibuya, T., Goto, Y., Kamihara, Y., Matoba, M., Yasuoka, K., Burton, L. A. and Walsh, A. (2014) ‘From kesterite to stannite photovoltaics: Stability and band gaps of the $Cu_2(Zn, Fe)SnS_4$ alloy’, *Applied Physics Letters*. AIP, 104(2), p. 21912.

Shin, D., Saparov, B. and Mitzi, D. B. (2017) 'Defect Engineering in Multinary Earth-Abundant Chalcogenide Photovoltaic Materials', *Advanced Energy Materials*, 7(11).

Siebentritt, S. and Schorr, S. (2012) 'Kesterites—a challenging material for solar cells', *Progress in Photovoltaics: Research and Applications*. Wiley Online Library, 20(5), pp. 512–519.

Singh, M., Jiu, J., Suganuma, K. and Kim, J. H. (2015) 'Non-toxic precursor solution route for fabrication of CZTS solar cell based on all layers solution processed', *Journal of Alloys and Compounds*, 646, pp. 497–502.

Song, X., Ji, X., Li, M., Lin, W., Luo, X. and Zhang, H. (2014) 'A Review on Development Prospect of CZTS Based Thin Film Solar Cells', *International Journal of Photoenergy*, 2014, p. 11.

Steinhagen, C., Panthani, M. G., Akhavan, V., Goodfellow, B., Koo, B. and Korgel, B. A. (2009) 'Synthesis of Cu_2ZnSnS_4 nanocrystals for use in low-cost photovoltaics', *Journal of the American Chemical Society*. ACS Publications, 131(35), pp. 12554–12555.

Su, Z., Li, W., Asim, G., Fan, T. Y. and Wong, L. H. (2016) 'Cation substitution of CZTS solar cell with > 10% efficiency', *Conference Record of the IEEE Photovoltaic Specialists Conference*, 2016-Novem, pp. 534–538.

Suman, R., Revathy, M. S., Priyal, V. M., Chitravel, T. and Kumar, T. P. (2015) 'Fabrication and Characterization of SLG / Mo / CZTS / CdS / i- ZnO / Al : ZnO / Al Thin Film Solar Cell Device', *Journal of Ovonic Research.* 11(5), pp. 243–248.

Sun, L., Shen, H., Huang, H. and Lin, A. (2019) 'The effect of Ge content on photovoltaic property of flexible - $Cu_2ZnSn(S,Se)_4$ thin film solar cells', *Applied Physics A*. Springer Berlin Heidelberg, 125(5), pp. 1–6.

Suryawanshi, M. P., Agawane, G. L., Bhosale, S. M., Shin, S. W., Patil, P. S., Kim, J. H. and Moholkar, A. V. (2013) 'CZTS based thin film solar cells: a status review', *Materials Technology*, 28(1–2), pp. 98–109.

Suryawanshi, M. P., Shin, S. W., Ghorpade, U. V., Gurav, K. V., Hong, C. W., Patil, P. S., Moholkar, A. V. and Kim, J. H. (2016) 'Improved solar cell performance of Cu_2ZnSnS_4 (CZTS) thin films prepared by sulfurizing stacked precursor thin films via SILAR method', *Journal of Alloys and Compounds*. Elsevier B.V, 671, pp. 509–516.

Sutter-Fella, C. M., Stückelberger, J. A., Hagendorfer, H., La Mattina, F., Kranz, L., Nishiwaki, S., Uhl, A. R., Romanyuk, Y. E. and Tiwari, A. N. (2014) 'Sodium assisted sintering of chalcogenides and its application to solution processed $Cu_2ZnSn(S,Se)_4$ thin film solar cells', *Chemistry of Materials*. ACS Publications, 26(3), pp. 1420–1425.

Teichler, A., Perelaer, J. and Schubert, U. S. (2013) 'Inkjet printing of organic electronics – comparison of deposition techniques and state-of-the-art developments', *Journal of Materials Chemistry C*, 1(10), p. 1910.

Tiong, V. T., Zhang, Y., Bell, J. and Wang, H. (2015) 'Carbon concentration dependent grain growth of Cu_2ZnSnS_4 thin films', *RSC Advances*. Royal Society of Chemistry, 5(26), pp. 20178–20185.

Todorov, T., Gunawan, O., Chey, S. J., De Monsabert, T. G., Prabhakar, A. and Mitzi, D. B. (2011) 'Progress towards marketable earth-abundant chalcogenide solar cells', *Thin Solid Films*. Elsevier B.V., 519(21), pp. 7378–7381.

Tong, Z., Yan, C., Su, Z., Zeng, F., Yang, J., Li, Y., Jiang, L., Lai, Y. and Liu, F. (2014) 'Effects of potassium doping on solution processed kesterite Cu_2ZnSnS_4 thin film solar cells', *Applied Physics Letters*, 105(22).

Tse, K., Wong, M., Zhang, Y., Zhang, J., Scarpulla, M. and Zhu, J. (2017) 'Defect Properties of Na and K in Cu_2ZnSnS_4 from Hybrid Functional Calculation', pp. 1–13.

Wallace, S. K., Mitzi, D. B. and Walsh, A. (2017) 'The Steady Rise of Kesterite Solar Cells', *ACS Energy Letters*, 2(4), pp. 776–779.

Wang, W., Winkler, M. T., Gunawan, O., Gokmen, T., Todorov, T. K., Zhu, Y. and Mitzi, D. B. (2014) 'Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency', *Advanced Energy Materials*, 4(7).

Wang, W., Shen, H., Yao, H., Shang, H., Tang, Z. X. and Li, Y. (2017) 'Effect of sulfurization temperature on the property of Cu_2ZnSnS_4 thin film by eco-friendly nanoparticle ink method', *Applied Physics A*. Springer Berlin Heidelberg, 123(9), p. 599.

Wei, S.-H., Zhang, S. B. and Zunger, A. (1999) 'Effects of Na on the electrical and structural properties of $CuInSe_2$', *Journal of Applied Physics*. AIP, 85(10), pp. 7214–7218.

Wild, J. D., Babbe, F., Robert, E. V. C., Redinger, A. and Dale, P. J. (2017) 'Silver-doped Cu_2SnS_3 absorber layers for solar cells application', *IEEE Journal of Photovoltaics*, 4(1), pp. 1–6.

Xin, H., Vorpahl, S. M., Collord, A. D., Braly, I. L., Uhl, A. R., Krueger, B. W., Ginger, D. S. and Hillhouse, H. W. (2015) 'Lithium-doping inverts the nanoscale electric field at the grain boundaries in $Cu_2ZnSn(S,Se)_4$ and increases photovoltaic efficiency', *Phys. Chem. Chem. Phys.* Royal Society of Chemistry, 17(37), pp. 23859–23866.

Yang, R., Mazalan, E., Chaudhary, K. T., Haider, Z. and Ali, J. (2017) 'Non-vacuum deposition methods for thin film solar cell: Review', *AIP Conference Proceedings*, 1824, p. 030018.

Yang, Y., Huang, L. and Pan, D. (2017) 'New Insight of Li-Doped $Cu_2ZnSn(S,Se)_4$ Thin Films: Li-Induced Na Diffusion from Soda Lime Glass by a Cation-Exchange Reaction', *ACS Applied Materials and Interfaces*, 9(28), pp. 23878–23883.

Yang, Z., Chueh, C. C., Zuo, F., Kim, J. H., Liang, P. W. and Jen, A. K. (2015) 'High-Performance Fully Printable Perovskite Solar Cells via Blade-Coating Technique under the Ambient Condition', *Advanced. Energy Materials.* Wiley Online Library, pp. 1–6.

Yuan, M., Mitzi, D. B., Liu, W., Kellock, A. J., Chey, S. J. and Deline, V. R. (2009) ‘Optimization of CIGS-based PV device through antimony doping’, *Chemistry of Materials*. ACS Publications, 22(2), pp. 285–287.

Yuan, M., Mitzi, D. B., Gunawan, O., Kellock, A. J., Chey, S. J. and Deline, V. R. (2010) ‘Antimony assisted low-temperature processing of $CuIn_{1-x}Ga_xSe_{2-y}S_y$ solar cells’, *Thin Solid Films*. Elsevier, 519(2), pp. 852–856.

Yuan, Z., Chen, S., Xiang, H., Gong, X. G., Walsh, A., Park, J. S., Repins, I. and Wei, S. H. (2015) ‘Engineering solar cell absorbers by exploring the band alignment and defect disparity: the case of Cu-and Ag-based kesterite compounds’, *Advanced Functional Materials*. Wiley Online Library, 25(43), pp. 6733–6743.

Zakutayev, A. (2017) ‘Brief review of emerging photovoltaic absorbers’, *Current Opinion in Green and Sustainable Chemistry*. Elsevier B.V., 4, pp. 8–15.

Zhang, C., Ren, Z., Yin, Z., Jiang, L. and Fang, S. (2011) ‘Experimental FTIR and simulation studies on H-bonds of model polyurethane in solutions . I : In dimethylformamide (DMF)’, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. Elsevier B.V., 81(1), pp. 598–603.

Zhang, S., Wu, L., Yue, R., Yan, Z., Zhan, H. and Xiang, Y. (2013) ‘Effects of Sb-doping on the grain growth of $Cu(In,Ga)Se_2$ thin films fabricated by means of single-target sputtering’, *Thin Solid Films*. Elsevier, 527, pp. 137–140.

Zhou, H., Hsu, W. C., Duan, H. S., Bob, B., Yang, W., Song, T. B., Hsu, C. J. and Yang, Y. (2013) ‘CZTS nanocrystals: a promising approach for next generation thin film photovoltaics’, *Energy & Environmental Science*, 6(10), p. 2822.

Zhou, H., Song, T. B., Hsu, W. C., Luo, S., Ye, S., Duan, H. S., Hsu, C. J., Yang, W. and Yang, Y. (2013) ‘Rational defect passivation of $Cu_2ZnSn(S,Se)_4$ photovoltaics with solution-processed Cu_2ZnSnS_4: Na nanocrystals’, *Journal of the American Chemical Society*. ACS Publications, 135(43), pp. 15998–16001.

LIST OF PUBLICATIONS

Indexed Conference Proceedings

1. **Mohd Shahril Salleh**, Kashif Chaudhary, Elham Mazalan, Jalil Ali. (2019). Potassium Doping Effect on $Cu_2ZnSn(S,Se)_4$ Thin Film Absorber Layer Deposited via Spray Pyrolysis. In *30th Regional Conference of Solid State Science and Technology 2018 (RCSSST18).* **(Indexed by SCOPUS)**