Pure sulfide kesterite solar cells with cation substituted absorber and back contact intermediate layer

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**PURE SULFIDE KESTERITE SOLAR CELLS
WITH CATION SUBSTITUTED ABSORBER AND
BACK CONTACT INTERMEDIATE LAYER**

ZHUK SIARHEI

**SCHOOL OF ELECTRICAL & ELECTRONIC
ENGINEERING**

2019

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CATION SUBSTITUTED ABSORBER AND BACK
CONTACT INTERMEDIATE LAYER**

ZHUK SIARHEI

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

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

2019

Statement of Originality

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

31 July 2019

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Date

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Zhuk Siarhei

Supervisor Declaration Statement

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

31 July 2019

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Assoc. Prof. Wong Kin Shun Terence

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals where I was the first author.

Chapter 2 is partially based on the publication: S. Zhuk, A. Kushwaha, T.K.S. Wong, S. Masudy-Panah, A. Smirnov and G.K. Dalapati, Critical review on sputter-deposited $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) based thin film photovoltaic technology focusing on device architecture and absorber quality on the solar cells performance. *Solar Energy Materials and Solar Cells* **171**, 239 – 252 (2017).

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The contributions of the co-authors are as follows:

- Dr. G.K. Dalapati conceived the idea of this project. He and Prof. T.K.S. Wong supervised the research work.
- I searched and collected published results for the analysis.
- I and Prof. T.K.S. Wong summarized fundamental parameters of kesterite semiconductors.
- I, Prof. T.K.S. Wong and Dr. A. Kushwaha reviewed fabrication methods for CZTS thin films synthesis.
- I and Dr. S. Masudy-Panah analyzed methods for chemical etching of secondary phases.
- I, Prof. T.K.S. Wong and Prof A. Smirnov analyzed the effect of back interface passivation on CZTS solar cells performance.
- I and Dr. G.K. Dalapati analyzed and summarized photovoltaic properties of CZTS solar cells prepared by different sputter-deposited methods.
- I wrote the manuscript draft.
- Prof T.K.S. Wong and Dr. G.K. Dalapati revised the structure and content of the manuscript draft.
- All authors discussed the manuscript and provided comments on it.

Chapter 3 is published as S. Zhuk, T.K.S. Wong, E. Tyukalova, A. Guchhait, D.H.L. Seng, S. Tripathy, T.I. Wong, M. Sharma, H. Medina, M. Duchamp, L.H. Wong, G.K. Dalapati, Effect of TaN intermediate layer on the back contact reaction of sputter-deposited Cu poor $\text{Cu}_2\text{ZnSnS}_4$ and Mo. *Applied Surface Science* **471**, 277 – 288 (2019).

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The contributions of the co-authors are as follows:

- Prof. T.K.S. Wong conceived the idea of the project and supervised the research work.
- I deposited the thin films by sputtering
- I and Dr. H. Medina sulfurized samples.
- Dr. D.H.L Seng carried out SIMS analysis. I analyzed SIMS data.
- E. Tyukalova and Prof. M. Duchamp carried out STEM characterization and analyzed the data.
- T.I. Wong provided XRD characterization. I analyzed the data.
- Dr. S. Tripathy carried out Raman spectroscopy analysis. I analyzed the data.
- Dr. M. Sharma performed scratch hardness characterization and analyzed the data.
- I and Dr. A. Guchhait measured sheet resistance and film thickness.
- I, Prof. T.K.S. Wong, Dr. G.K. Dalapati and Prof. L.H. Wong analyzed the experimental data.
- I wrote the manuscript draft.
- Prof T.K.S. Wong and Dr. G.K. Dalapati revised the structure and content of the manuscript draft.
- All authors discussed the manuscript and provided comments on it.

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The contributions of the co-authors are as follows:

- I conceived the idea of the project and Prof. T.K.S. Wong and Dr. G.K. Dalapati supervised the research work.

- I and Dr. V. Tunuguntla synthesized sol-gel.
- I synthesized CZCTS thin films and carried out sulfurization.
- Dr. S. Tripathy performed Raman spectroscopy analysis. I analyzed the data.
- T.I. Wong carried out XRD characterization. I analyzed the data.
- I characterized cross-section morphology using FESEM.
- Dr. D.H.L. Seng carried out SIMS characterization.
- I fabricated and characterized CZCTS solar cells.
- I, Dr. A. Stsiapanau, Prof. A. Smirnov, Prof. L.H. Wong analyzed results.
- I and Prof. T.K.S. Wong prepared draft of the manuscript.
- All authors discussed the manuscript and provided comments on it.

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The contributions of the co-authors are as follows:

- Dr. G.K. Dalapati conceived the idea and Prof. T.K.S. Wong and Dr. G.K. Dalapati supervised the research work.
- I synthesized thin films, performed sulfurization and fabricated CZTS solar cells
- T.I. Wong carried out XRD characterization. I analyzed the data.
- I measured sheet resistance of the thin films.
- S. Lie and Dr. A. Guchhait characterized morphology of the solar cells using FESEM and EDX. I analyzed the data.
- I measured absorbance spectra of the films and analyzed the data.
- I carried out dark and light J-V characterization.
- A. Guchhait and S. Hadke performed EQE characterization of the solar cells. S. Hadke and I analyzed the results
- S. Hadke did C-V analysis. He and I analyzed the data.
- Dr. D.H.L. Seng carried out SIMS characterization.
- Y. Gao and Dr. X. Wang characterized cross-section morphology of the samples with STEM. They, Prof. T.K.S. Wong, Prof. S. Cheng and I analyzed the data.
- I wrote the draft manuscript.

- Prof. T.K.S. Wong and Dr. G.K. Dalapati revised the content of the manuscript.
- All authors discussed the manuscript and provided comments on it.

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Zhuk Siarhei

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Abstract

Chalcogenide Cu(In,Ga)Se₂ (CIGS) and CdTe thin film solar cells have the potential to reduce the cost of the photovoltaic (PV) technology. They showed high power conversion efficiency (PCE) of more than 20% shrinking the gap between them and champion crystalline Si solar cell. Despite of high efficiency and ease of fabrication, application of CdTe PV technology is limited on terawatt (TW) scale owing to scarcity of Te and because there is only one supplier. As for CIGS, a high demand for In from flat panel display industry along with its limited availability pushes the price of In up to several hundred USD/kg. Therefore, tremendous success of CIGS solar cells brought much attention to earth abundant, non-toxic and low cost kesterite Cu₂ZnSnS₄ (CZTS) where In and Ga are replaced with Zn and Sn. Similar electronic and optical properties of the materials enables CZTS solar cells to inherit the device structure of CIGS solar cells. CZTS is an intrinsic p-type semiconductor with a direct bandgap of about 1.5 eV and high absorption coefficient of $>10^4 \text{ cm}^{-1}$ for visible wavelengths. The bandgap of kesterite can be tuned from 1 eV to 1.5 eV by changing S/(S+Se) ratio from 0 to 1 which provides a degree of flexibility in device fabrication with the material.

There is still large gap in PCE between the best chalcogenide and kesterite solar cells. Firstly, solid state reaction occurs at the back interface between CZTS absorber layer and Mo back contact during high temperature sulfurization. S diffuses into Mo to form resistive MoS₂. In addition, as a result of the reaction, CZTS may decompose into secondary phases such as ZnS, Cu₂S and volatile SnS causing void formation. Secondly, large open-circuit voltage deficit limits performance of the kesterite solar cells. Similar size of cations in CZTS facilitates cation disordering and formation of detrimental defects causing charge recombination.

In this thesis, the effect of sputter of TaN, ZnS and CuO intermediate layers (IL) on the quality of the back interface, pure sulfide kesterite absorber layer and photovoltaic properties of the solar cells was studied in detail. The novel IL were used to slow down the back interface reaction and control crystal quality of kesterite absorber layer. It has been found

that interfacial MoS₂ thickness between sputtered Cu-poor CZTS and Mo can be effectively controlled using TaN IL. When 12 nm TaN IL is present, no continuous MoS₂ is observed using scanning transmission electron microscopy after sulfurization at 600°C for 10 min. Incorporation of 10 nm ZnS IL at the interface between solution-processed Cd-substituted CZTS (CZCTS) and Mo enhances CZCTS grain growth and suppresses void formation. Moreover, deposition of the ZnS IL does not cause increase of MoS₂ thickness. PCE of solution-processed CZCTS solar cells was enhanced from 9.5% to 10% as a result of 10 nm ZnS IL layer insertion. A higher PCE of 10.8% was achieved for solution processed CZCTS solar cells using CuO IL incorporation. Insertion of the optimized 4 nm CuO IL resulted in enhancement of short-circuit current density (J_{sc}) due to the increased width of depletion region while open-circuit voltage (V_{oc}) and fill factor (FF) were almost constant. Moreover, further increase of CuO IL thickness enables to get as high J_{sc} as 28.5 mA/cm². To the best of my knowledge, this is the highest reported J_{sc} for pure sulfide CZCTS solar cells.

To address the problem of the absorber layer quality, impact of Mo on sputtered CZTS thin films was studied. Mo was found to be a dopant for CZTS enabling to tune CZTS resistivity in a wide range. In addition, it has been revealed that Mo incorporation enables to enhance absorbance of CZTS thin films while not affecting bandgap of CZTS based on measured external quantum efficiency spectra. Furthermore, Mo incorporation in CZTS demonstrates a substantial effect on the photovoltaic performance of the solar cells prepared by sputtering of quaternary compound CZTS target. When optimized Mo co-sputtering power is applied, PCE of CZTS solar cell is increased from 1.6% to 5.5%. In addition, effect of carbon (C) incorporation in sputtered CZTS and Cu doped ZnS (ZnS:Cu) thin films was investigated. It has been found that optimized content of C facilitates growth of CZTS crystallites and reduces void formation. Furthermore, the addition of C in sputtered CZTS and ZnS:Cu thin films enables reduction of tail states through defects passivation, decrease resistivity and tune bandgap. Moreover, formation of copper sulfide phase is suppressed while formation of ZnS is enhanced with increase of C content in p-type ZnS:Cu thin films resulting in increase of its bandgap from 3.2 eV to 3.6 eV.

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Abbreviations

Abbreviations	Full expressions
CZTS	$\text{Cu}_2\text{ZnSnS}_4$
CZCTS	$\text{Cu}_2(\text{Zn}_x\text{Cd}_{1-x})\text{SnS}_4$
CMOS	Complementary metal oxide semiconductor
SLG	Soda-lime glass
Mo	Molybdenum
TaN	Tantalum nitride
ZnS	Zinc sulfide
CuO	Copper oxide
CdS	Cadmium sulfide
ZnO	Zinc oxide
ITO	Indium tin oxide
DIW	De-ionized water
NPs	Nanoparticles
PCE	Power conversion efficiency
V_{oc}	Open-circuit voltage
J_{sc}	Short circuit current
FF	Fill factor
R_s	Series resistance
R_{sh}	Shunt resistance
I-V	Current-voltage
J-V	Current density-voltage
AM1.5G	Air Mass 1.5 Global
EQE	External quantum efficiency
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
SEM	Scanning electron microscopy

FESEM	Field emission scanning electron microscopy
STEM	Scanning tunneling electron microscopy
EDS	Energy dispersive spectroscopy
EELS	Electron energy loss spectroscopy
TOF-SIMS	Time-of-flight secondary ion mass spectrometry
UV-Vis-NIR	Ultra-violet, visible, near infra-red
C-V	Capacitance-voltage
CBO	Conduction band offset
L_{diff}	Minority charge carrier diffusion length
IL	Intermediate layer
PV	Photovoltaic

Chapter 1 Introduction

1.1 Motivation

The increase of population and economic growth result in an increase in energy demand. It has been reported that global electricity demand will rise from 25000 terawatt-hours (TWh) in 2017 to 38700 TWh in 2050 [1]. Furthermore, most of the countries around the world still rely heavily on fossil fuels as a primary energy source for energy generation. For instance, 84% of global energy used in 2010 was produced using fossil fuels [2]. In addition, massive usage of coal for energy production in developing countries largely contributes to air particulate matter contamination causing various health problems. Moreover, 4-7 million premature deaths are reported annually around the globe owing to air pollution [3]. Furthermore, the usage of fossil fuels resulted in the emission of 33.3 billion tons of carbon dioxide (CO_2) in 2015 globally [4]. Thus, CO_2 concentration in the atmosphere has been growing constantly from 315 ppm in 1957 to 405 ppm in 2017 (see Fig. 1.1) [5]. The observed remarkable rise of CO_2 concentration is due to human activities causing global warming and climate change all over the world. Furthermore, the use of petrol and diesel contribute to the atmospheric concentration of gaseous pollutants such as NO_2 , O_3 , SO_2 [6].

Figure 1.1: CO_2 concentration in the atmosphere from 1958 to 2018 [5].

According to the Paris Climate Agreement in 2016, CO₂ emissions are to be reduced to ensure the expected average temperature rise around the globe to be limited to 1.5°C by 2100. To address this issue, the European Union (EU) plans to reduce CO₂ emissions by ~85% in 2050 with respect to that of 1990 [1]. This can be achieved by large scale application of clean energy technologies. The estimated total investments in renewable energy sources in 2017 were about USD 310 billion [7]. The report also reveals that the total investments in fossil fuel-based energy generation capacities were about one-third of that in renewables. The latter include solar energy (photovoltaic and thermal), wind energy, hydroelectric energy, biomass, geothermal energy and wave energy.

Solar photovoltaic (PV) has great potential to meet future large-scale electricity supply with low-carbon emission [8]. Unlike other types of renewable energy sources, e.g. hydropower, solar PV exhibits minimal environmental impact. In addition, solar energy is abundant as the total power output of the sun is about $3.8 \cdot 10^{26}$ W. Thus, by converting 0.1% of the sunlight directly incident on the earth surface using current PV technologies, humanity can generate enough renewable and clean energy to meet world power demand. It has been reported that global investments in solar power outweigh that of wind power by half and the difference continued to grow in 2017 [7]. In addition to the global installed PV power capacity of 500 GW in 2018, Haegel *et al.* predict the value will overcome 1 TW by 2023 [9].

Solar energy may be converted to thermal power using solar thermal power technologies and can generate power at night, however, it requires expensive optics. Furthermore, direct conversion of solar into electrical power is more promising as it provides ease of transmission of electrical energy over the distance from the place of generation to the end consumers. Moreover, usage of off-grid solar panels provides access to the electricity for people living in remote areas or islands with lack of electricity from grids.

The present multi-billion solar PV industry is made possible because of the PV effect discovery by Becquerel in 1839. Later, Hallwachs demonstrated the first copper oxide/copper semiconductor-junction solar cell in 1904. In the 1950s, a powerful momentum to photovoltaic research was enabled by space exploration. The first Si solar cell was fabricated in 1954 by Chapin, Fuller, and Pearson from Bell Laboratories at Murray Hill, New Jersey. The solar cell device exhibited PCE of 6% and was ready for

practical use. However, the very high cost of solar panels limited implementation of the technology to space applications. The record PCE of crystalline Si (c-Si) solar cell of 26.7% was reported in 2017 [10]. Advancement in research and manufacturing technology enabled a steady decrease of the cost of Si solar cells over the decades as can be seen in the Fig. 1.2. The average global price of solar PV module was below 0.25 \$/W in 2018 [9]. Nowadays, it is continuing to decrease making the technology a prevailing at the solar power panel market.

Figure 1.2: Swanson's law in photovoltaics [11].

c-Si PV technology dominates the solar power market with about 90% share. Si-based photovoltaic devices are widespread due to their durability, compatibility with the technology of microelectronics, and high PCE. However, this technology is material intensive owing to the low absorption of Si as it has an indirect band gap. For this reason, 50-200 μm thick Si wafer is to be used to absorb a sufficient amount of incident sunlight. In addition, 50% of the cost of a Si solar power module comes from the cost of the Si wafer. Therefore, it acts as a bottle-neck for further reduction in cost. Besides, the processing cost of c-Si solar cells is high, because it requires complex processes including high temperature treatment, ion implantation and high purity. Furthermore, c-Si is not suitable for the fabrication of flexible solar cells. Therefore, much attention has been devoted to the solar cells of the second generation, namely thin film solar cells. The latter is made of direct band gap photovoltaic materials with high absorption coefficient. This results in the decreased thickness of the absorber layer thickness down to a few μm and, hence, reduce materials usage. Furthermore, unlike c-Si solar cells, thin film solar cells

can be fabricated on a flexible polymer substrate and, hence, enable the substantial expansion of the application areas of photovoltaic devices.

Research on p-type CdTe thin films with a direct bandgap of 1.45 eV started in 1950s [12,13]. In 1993 Britt *et al.* reported soda-lime glass (SLG)/ F:SnO₂/CdS/CdTe/C solar cell with PCE of 15.8% with MgF₂ anti-reflection coating using a close-spaced sublimation deposition method [14]. In 2016 the champion CdTe solar cell showing PCE of 22.1% was reported by First Solar which is the major CdTe solar cells manufacturer [15].

In contrast to CdTe, chalcogenide p-type Cu(In,Ga)Se₂ (CIGS) does not contain toxic elements. High absorption coefficient ($>10^5 \text{ cm}^{-1}$) and bandgap tunable in the range from 1 eV to 1.7 eV by changing In/Ga ratio make the PV material suitable for solar cells application [16,17]. Co-evaporation and two-stage selenization processes are normally used to produce thin films of CIGS [18]. The typical structure of the device is indium tin oxide (ITO)/ZnO/CdS/CIGS/Mo/glass. However, toxic n-type CdS layer is also used to form a heterojunction. Furthermore, CIGS solar cells also have a long history of development as Fig. 1.3 shows. The Solar Frontier company reported champion CIGS solar cell exhibiting PCE of 23.35%, which is the highest value among other thin film solar cells [19].

Figure 1.3: History of the development of CdTe and CIGS solar cells [20].

Fig. 1.4 illustrates the PCE of the different champion solar cells developed worldwide showing a shrinking gap in terms of PCE between the best thin film and c-Si solar cells. However, in spite of the high efficiency, low cost and ease of fabrication, the application of CdTe PV technology is limited at TW range due scarcity of Te ($\sim 1 \cdot 10^{-7}$ % in the earth crust). In addition, high demand for In from the flat panel display industry along with its limited availability pushes the price of In up to several hundred USD/kg. Moreover, scarcity of In in the earth crust ($1.6 \cdot 10^{-5}$ %) limits application of the CIGS technology on TW production range [21]. Besides, the raw material cost of CIGS and CdTe is more expensive, and their annual electricity potential is lower compared to other promising alternative PV materials indicated in red in Fig. 1.5.

Figure 1.4: Reported power conversion efficiency of champion PV devices [10,19,22–25].

Figure 1.5: Four-quadrant plot of photovoltaic materials differentiated based on material extraction cost and annual electricity potential. Adapted with permission from [21]. Copyright (2009) American Chemical Society.

Sustainability limitation of CIGS solar cells brought much attention to earth abundant, non-toxic and low-cost kesterite CZTS where In and Ga are replaced with Zn and Sn. Moreover, the bandgap of sulfoselenide $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) semiconductor can be tuned from 1 eV for pure selenide $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) to 1.5 eV for pure sulfide CZTS by changing S/Se ratio [26]. Similar electronic and optical properties of the materials enabled CZTS solar cells to inherit the device structure of CIGS solar cells. Fig. 1.6 presents the typical structure of CZTS thin film solar cells. SLG is typically used as a substrate material and Mo thin film serves as back contact owing to its good conductivity and inertness. The n-type CdS buffer layer is typically deposited over p-type CZTS absorber layer by chemical bath deposition method to form a heterojunction. The buffer layer is followed by a window layer consisting of intrinsic ZnO and ITO films. History of CZTS solar cells will be presented in more detail in chapter 2.

Wang *et al.* demonstrated champion kesterite solar cell showing PCE of 12.6% based on sulfoselenide CZTSSe absorber layer prepared by hydrazine solution method in 2014

[22]. This is the highest efficiency reported certified kesterite solar cell to date. However, hydrazine is highly toxic and reactive which makes it challenging to industrialize the fabrication process. Although a high number of papers on kesterite solar cells was published recently, there is still a lack of PCE improvement owing to known limitations of kesterite such as open-circuit voltage deficit, defect intolerance nature and secondary phases. Low performance of kesterite solar cells mitigates commercialization of the PV technology. To the best of my knowledge, Crystalsol is the only company that produces kesterite based PV modules.

In order to provide a way for the technology commercialization, the PCE of CZTS solar cell devices needs to be increased beyond 15%. There are three main technological problems behind the inadequate performance of CZTS solar cells: (i) back interface reaction between Mo back electrode and CZTS absorber layer, (ii) CZTS absorber layer, and (iii) interface between the CdS buffer layer and CZTS. This thesis focuses on the first two. The experiments on the buffer layer were not carried out because our facilities for thin film growth were limited to sputtering, spin-coating and chemical bath deposition. First, CZTS/Mo back interface is characterized by the presence of resistive MoS₂ layer between Mo and CZTS. This is due to the diffusion of S into the Mo back electrode during high temperature sulfurization process. In addition, solid state reaction at the back interface causes the formation of voids and secondary phases in CZTS which also deteriorate device performance. Second, CZTS is characterized by short diffusion length of minority charge carriers (L_{diff}) owing to the secondary phases and defects in the film. This limits the optimal thickness of the CZTS absorber layer to $\sim 1.2 \mu\text{m}$, whereas it is 2-3 μm for CIGS solar cells [18,27]. This, in turn, leads to insufficient light absorption by CZTS layer causing a decrease of short-circuit current density (J_{sc}). On the other hand, recombination results in a decrease of open-circuit voltage (V_{oc}) of the solar cell devices which causes large V_{oc} deficit of CZTS solar cells [28]. Therefore, there is need to reduce point defects by cationic substitution.

Figure 1.6: Typical structure of CZTS solar cells [27]. Adapted with permission from Zhuk *et al.*, Sol. Energy Mater. Sol. Cells **171**, 239–252 (2017). Copyright 2017 Elsevier.

1.2 Objectives of the thesis

The overall goal is to improve the photovoltaic performance of pure sulfide CZTS devices (especially the V_{oc} deficit) by limiting the back contact reaction and enhancement of absorber properties.

Objectives:

- 1) Understand the effect of sputtered TaN IL in reducing solid state reaction between Mo and sputtered CZTS.
- 2) Understand the PV properties of solution-processed CZCTS and sputter-grown CZTS solar cells with ZnS IL and its effect on the quality of CZCTS/Mo interface.
- 3) Understand the effect of CuO IL thickness on photovoltaic properties of solution-processed CZCTS/CdS solar cells and the reasons for PCE enhancement.
- 4) Improve PV properties of CZTS solar cells deposited by using Mo co-sputtering and understand the PCE enhancement mechanism.

5) Develop a process of C incorporation into CZTS and Cu doped ZnS (ZnS:Cu) thin films deposited by sputtering approach. Investigate its impact on structural, optical and electrical properties of the CZTS and ZnS:Cu thin films

1.3 Major contributions of the thesis

The present work reports results on the novel intermediate layers (IL) for kesterite thin film solar cells. In addition, cationic substitution to improve quality of the CZTS absorber layer are presented. The major achievements can be summarized as follows.

1) Incorporation of TaN IL at sputtered CZTS/Mo back contact resulted in a remarkable reduction of interfacial MoS₂ layer. Furthermore, MoS₂ layer is not observed when continuous 12 nm TaN IL is deposited.

2) ZnS IL facilitates growth of CZCTS crystallites and reduces void formation in the absorber layer. In addition, it does not result in an increase of MoS₂ layer thickness. Thus, the PCE of solution-processed CZCTS solar cells is enhanced from 9.5% to 10% as a result of the insertion of 10 nm ZnS layer to the back contact. Efficiency improvement is associated with an increase in V_{oc} and J_{sc} .

3) PCE of 10.8% for solution-processed pure sulfide CZCTS solar cells was achieved using CuO IL. Insertion of the IL resulted in enhancement of J_{sc} while V_{oc} and FF were almost constant for the optimized 4 nm CuO layer. Moreover, further increase of CuO IL thickness enabled to get as high J_{sc} as 28.5 mA/cm². To the best of my knowledge, this is highest reported J_{sc} for pure sulfide CZCTS solar cells.

4) For the first time, Mo was found to be a dopant for CZTS. This enables to tune CZTS resistivity in a wide range. In addition, it has been found that Mo incorporation allows to enhance absorbance of CZTS thin films while not affecting bandgap of CZTS based on measured external quantum efficiency spectra. Finally, Mo incorporation in CZTS has a substantial impact on the photovoltaic performance of solar cells prepared by sputtering of quaternary compound CZTS target. When optimized Mo co-sputtering power is applied, PCE of CZTS solar cell is increased from 1.6% to 5.5%.

5) Incorporation of optimized amount of carbon was found to be useful to increase CZTS grains growth and reduce void formation. Furthermore, the addition of C in sputtered CZTS and ZnS:Cu thin films enabled to reduce tail states through defects passivation, decrease resistivity, tune bandgap.

1.4 Organization of the thesis

This thesis consists of 8 chapters as follows:

Chapter 1 shows the motivation for the application of renewable energy generation systems and, in particular, photovoltaic technologies. Following brief information on the historical development of solar cells, the current problems of crystalline Si and thin film CIGS, CdTe and CZTS solar cell technologies are discussed. This is followed by research objectives and major achievements of the study.

Chapter 2 discusses the structural, optical and electronic properties of kesterite semiconductors (CZTS, CZTSSe, CZTSe) and synthesis methods are reviewed. This is followed by a survey of key recent progress in single junction CZTS/CdS heterojunction devices made by sputtering and solution-based approaches. In addition, factors limiting PCE of the solar cells such as back contact and defects in CZTS are discussed.

Chapter 3 is about the effect of TaN IL on the sputtered back contact between Mo and CZTS. The morphology, chemical and structural properties of the samples were characterized by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), Raman spectroscopy, X-ray diffraction analysis (XRD), scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS) and scanning electron microscopy (SEM). Thin TaN IL show chemical reactivity towards sulfur (S) vapor at 600°C and the incorporation of S in TaN reduces the S concentration in Mo films at the sub-surface region and thus improves the electrical conductivity of sulfurized Mo. The use of a non-stoichiometric quaternary compound CZTS target along with TaN IL enables to minimize the thickness of MoS₂ layer and reduce void formation at the Mo/CZTS interface.

Chapter 4 describes the impact of ZnS IL incorporation into solution-processed CZCTS solar cells. Structural properties of the absorber layer were studied using XRD and Raman spectroscopy. Furthermore, elemental diffusion profile reveals that sputtered ZnS IL mitigates the diffusion of S into Mo, while SEM analysis confirms that ZnS IL does not contribute to the thickening of the MoS₂ interfacial layer. In addition, the IL serves as an effective seed layer to promote CZCTS crystallite growth and boost solar cell performance. Moreover, the impact of ZnS IL and sulfurization time on photovoltaic properties of sputtered CZTS solar cells is studied.

Chapter 5 investigates the effect of CuO IL thickness on the quality of CZCTS absorber layer and the photovoltaic properties of CZCTS solar cells. Structural properties of CZCTS thin films are studied using XRD and Raman spectroscopy. When 4 nm CuO IL of optimized thickness is incorporated, PCE increases from 10% to 10.8%, which is mostly due to the rise of J_{sc} . The fabricated solar cells are characterized in detail using IV, EQE and CV to explain the effect of the IL on device performance.

Chapter 6 shows the effect of Mo incorporation on the optical, structural, electrical properties and morphology of CZTS absorber layer. The study shows that Mo is incorporated into the CZTS unit cell by replacement of Sn. Moreover, it has been found that Mo enables to tune resistivity of CZTS films in a wide range.

Chapter 7 describes the effect of C incorporation in sputtered CZTS and ZnS:Cu thin films. Structural, optical and electronic properties of the thin films were studied in detail to reveal the effect of C addition in the films. The effect of Sn substitution by C on band structure of CZTS is studied using first-principle density functional theory (DFT) calculations.

Chapter 8 gives the conclusion and suggests possible ways to boost the performance of kesterite solar cells by addressing the problems of cation disordering in the absorber layer, back CZTS/Mo interface and CdS/CZTS hetero-interface.

Chapter 2 Literature review

2.1 Kesterite semiconductors

Kesterite is a type of mineral consisting of copper, zinc, tin, and sulfur and/or selenium which has received much attention as earth abundant non-toxic semiconducting material alternative to CdTe and CIGS. The first CZTS thin films were reported by Ito *et al.* in 1988 [29]. Ion beam sputtering of quaternary compound CZTS target was used to grow thin films of CZTS. Fig. 2.1 shows the growth of the number of publications on kesterite semiconductors since 2006.

Figure 2.1: Number of journal articles versus publication year for kesterite thin films (Thomson Reuters Web of Science database) [27]. Reproduced with permission from Zhuk *et al.*, Sol. Energy Mater. Sol. Cells **171**, 239–252 (2017). Copyright 2017 Elsevier.

Diamond, zincblende ZnS, chalcopyrite CuInS₂ (CIS) and CZTS belong to adamantine family based on their atomic structure [26]. These binary, ternary and quaternary compounds are crystallized according to the tetrahedral coordination of atoms as in diamond where C atoms are bonded to four neighboring atoms. Two most common forms of CZTS are stannite and kesterite [26]. These two forms of CZTS differs by site occupancies of Zn and Cu in the unit cell as it can be seen in Fig. 2.2.

Figure 2.2: Two most common structures of CZTS (a) kesterite, (b) stannite [30]. Adapted with permission from J. Appl. Phys. **111**, 083707 (2012). Copyright 2012 AIP Publishing.

Kesterite crystal exhibits I-4 symmetry while stannite is characterized by I-42m symmetry. Slice view of both kesterite and stannite unit cells is given in Fig. 2.3. In stannite crystal Cu sites are limited to $4d$ Wyckoff positions whereas in kesterite Cu atoms are located at $2a$ and $2c$ Wyckoff positions [26]. In contrast, in stannite crystal, $2a$ Wyckoff position is occupied by Zn while Zn in ideal kesterite crystal is present at Wyckoff position of $2d$. Note, kesterite CZTS is more useful owing to its enhanced stability compared to stannite CZTS [31]. The unit cell of kesterite CZTS is characterized by lattice parameters a of 0.543 nm and c of 1.0845 nm [26]. Since $a \neq 2a$ in CZTS, this results in peaks splitting of CZTS XRD pattern which can be only observed with high-resolution scan.

Figure 2.3: Slice view of kesterite and stannite unit cells (anions are not shown).

CZTS is a p-type semiconductor owing to intrinsic defects such as copper vacancies (V_{Cu}) and copper-on-zinc (Cu_{Zn}) anti-site defects [32] which act as a shallow acceptors level. As the acceptor level of the V_{Cu} defect is only 0.02 eV above the valence band edge (E_v), it is more preferable for the device performance compared to Cu_{Zn} . The latter defect forms acceptor level 0.2 eV above E_v . All other defects such as vacancies, anti-sites, and interstitials are unfavorable for the device performance because they form shallow donor levels, deep and midgap states [33]. Defects tend to form a variety of defect complexes to compensate its charge which, in turn, affect the position of valence and conductance bands in CZTS as it can be seen in Fig. 2.4 [34]. Anti-site point defects and defect complexes associated with Sn such as Sn_{Cu} , Sn_{Zn} and Cu_{Sn} are particularly detrimental as they cause a significant shift of the band edges. Moreover, CZTS has a narrow thermodynamic stability range (see Fig. 2.5). This may lead to the formation of secondary phases such as Cu_2S , ZnS , Cu_2SnS_3 and SnS_2 in CZTS during the material synthesize [33]. The inherent defects in CZTS result in a short L_{diff} of $\sim 0.35 \mu m$ in pure sulfide CZTS solar cells [35].

Figure 2.4: Energy diagram showing the effect of defect complexes on the position of conduction and valence bands in CZTS and CZTSe. Figure reproduced with permission from [34]. Copyright WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

CZTS shows direct bandgap of about 1.5 eV and high absorption coefficient of $>10^4 \text{ cm}^{-1}$ for visible wavelengths [32,33,36–38]. At 1.5eV CZTS thin film demonstrates a refractive index of 2.858, while real and imaginary parts of complex dielectric function are 8.129 and 1.093, respectively [26]. The tunability of kesterite bandgap provides a degree of flexibility in device fabrication with the material. Similar to CIGS, the grain boundaries of CZTS provide an enhanced minority carrier collection [39]. In addition, the carrier concentration in CZTS is similar to CIGS and is about 10^{15} - 10^{17} cm^{-3} while carrier mobility of CZTS thin films is $0.1 - 35 \text{ cm}^2/\text{V}\cdot\text{s}$ [26]. According to the Shockley-Queisser limit, single junction CZTS solar cells have the potential to reach a PCE of 28% [40].

Figure 2.5: Phase diagram of CZTS and its associated secondary phases [41]. Reproduced with permission from J. Appl. Phys. **115**, 173502 (2014). Copyright 2014 AIP Publishing.

2.2 Synthesis methods

2.2.1. Vacuum approaches

Kesterite thin films have been prepared using various vacuum-based techniques including sputtering [42–45], thermal evaporation [46–48], pulsed laser deposition [49,50].

2.2.1.1. Evaporation

Since evaporation approach is used in commercial production of CIGS solar panels, it has also been studied for the preparation of kesterite thin films. The evaporation process is performed in a high vacuum to prevent oxidation. The flux of the evaporated material is produced by the heating of wire or crucible that contains the material. Moreover, heating and subsequent evaporation can be carried out either by means of electrical current or by using electron-beam. Then evaporated species travel from the source to the substrate where they are adsorbed forming a thin film. Furthermore, a substrate is rotated to ensure uniformity of the growing film. In addition, heating of a substrate is often applied to improve crystal quality of thin film. However, re-evaporation of Sn from the growing film may occur during the deposition process when deposited on a heated substrate [51]. Shin *et al.* fabricated pure sulfide CZTS thin films by co-evaporating Cu, Zn and Sn in the presence of cracked flux of sulfur [47]. The temperature of the substrate was maintained at 150°C to minimize evaporation of volatile elements. This was followed by annealing for 5 min at 570°C to facilitate grain growth. Robles *et al.* demonstrated a way to reduce Sn loss while keeping substrate temperature relatively high by subsequent evaporating of Cu_2SnS_3 (CTS) and ZnS [52]. During evaporation of CTS film, the temperature of the substrate was kept at 350°C while for ZnS evaporation it was decreased to 200°C. Finally, the as-grown samples were sulfurized at 500°C for 60 min to produce CZTS phase.

2.2.1.2. Sputtering

When compared with other physical vapor deposition based methods such as thermal evaporation and pulsed laser deposition, a sputtering approach typically enables to produce pure sulfide CZTS solar cells of higher PCE [23,32,47]. In addition, sputtering is a suitable method for high volume manufacturing owing to the following advantages: uniformity of deposited films on a large scale, high deposition rate and reproducibility of the process [53–56]. Besides, sputtering enables interface engineering, tuning of crystallinity and composition of the films [57–60].

Sputtering is a widely used technique for depositing metallic, oxide and sulfide thin films on various substrates. A high vacuum deposition chamber and high purity sputtering targets are required to produce thin films of high quality. Typically, Ar is used as a working gas in a sputtering system equipped with DC and/or RF power supplies to ignite on Ar plasma near the surface of a sputtering target. When the Ar plasma is ignited, high energy plasma particles bombard the surface of the target causing ejection of the target material by momentum transfer. Thereafter, sputtered particles reach a substrate and form a thin film. Rotation of the substrate ensures adequate uniformity of the grown film. Furthermore, the sputter deposition rate is controlled by the sputtering power while crystal quality of the thin film is tuned by the flow rate of the working gas. Fig. 2.6 gives a schematic representation of most common sputter-based methods used for CZTS thin film fabrication which are discussed in detail below.

Sequential deposition of precursors followed by sulfurization is an early method to fabricate CZTS thin films [61–63]. Metallic (Cu, Zn, Sn) and binary sulfide (Cu_2S , ZnS , SnS and etc.) thin films may be deposited in a sequence to form a stack of precursor thin films as shown in Fig. 2.6a. The composition of the CZTS absorber layer is controlled by the thickness of the precursor films. Furthermore, as high efficiency CZTS solar cells have a Cu-poor and Zn-rich composition of the absorber [64], careful control of precursor films thickness is critical. The as-deposited stack of precursor thin films is subjected to high temperature sulfurization to facilitate elemental inter-diffusion and CZTS phase formation. Sulfurization is crucial processing step to convert the stacked precursor to the single-phase CZTS film. Sulfurization time, temperature, pressure, source of sulfur, thickness of precursor layers, their content and sequence have a significant impact on properties of the CZTS films [65–67].

Optimization of the composition is crucial because it enables to reduce defect density and improve the L_{diff} [33]. Furthermore, prolonged sulfurization (30 min at 570–580°C) of stacked precursor films was required to fabricate CZTS-based solar cells showing PCE higher than 7% [68–70]. However, loss of volatile Sn occurs during high temperature treatment [71]. Abusnina *et al.* revealed that Sn deficit caused the formation of Cu_{2-x}S secondary phase at the surface of the film [72]. Wang *et al.* reported that Sn loss deteriorated stoichiometry of CZTS absorber which in turn led to the formation of cracks

and small voids between grain boundaries [67]. Thus, prevention of Sn loss seems to be crucial to suppress secondary phase during fabrication of CZTS thin films by the precursor method.

Figure 2.6: Schematic representation of sputter-based methods to fabricate CZTS thin films for PV application [27]. Reproduced with permission from Zhuk *et al.*, Sol. Energy Mater. Sol. Cells **171**, 239–252 (2017). Copyright 2017 Elsevier.

The co-sputtering technique can also be used to produce CZTS films [73–76] (see Fig. 2.6b). This method provides an effective way to uniformly mix elements from several targets [77] which in turn enables faster solid state reaction during the thermal treatment process. Reduction of high temperature sulfurization time results in minimizing of elemental loss during the sulfurization [78]. Besides, record efficiency pure sulfide

kesterite solar cell of 11.5% was fabricated based on co-sputtering of ZnS, SnS and Cu targets followed by CdS deposition and sulfurization at 560°C for several minutes using rapid thermal processing system to form $\text{Cu}_2\text{Zn}_{0.6}\text{Cd}_{0.4}\text{SnS}_4$ (CZCTS) alloy [23]. Although sulfurization was carried out for a short time, as it can be seen in Fig. 2.7 the CZCTS thin films exhibit large grains of about 2 μm .

Figure 2.7: Top view SEM images of CZTS (left) and CZCTS thin film (right) deposited on Mo-coated SLG. Reprinted with permission from [23]. Copyright (2017) American Chemical Society.

In addition, CZTS thin films can be prepared using the reactive co-sputtering technique [79]. Scragg *et al.* deposited fully sulfurized film by co-sputtering of Cu/Sn alloy and Zn targets on a heated substrate in H_2S atmosphere while carrier gas was not mentioned [80]. This is followed by rapid thermal annealing treatment for 3 min to enhance crystallinity of the as-deposited thin films.

Single target sputtering of quaternary compound CZTS target is suitable for the large scale manufacturing of the CZTS-based PV devices due to many advantages. This approach is relatively simple and cost-effective since it requires only one target and one RF power source. Furthermore, it provides uniform element distribution within deposited films [81]. As with the co-sputtering technique, implementation of single target sputtering allows reduction of sulfurization temperature and time because the as-deposited film is of CZTS phase.

Nakamura *et al.* compared properties of CZTS thin films obtained using co-sputtering of Cu/ZnS/SnS targets and single target CZTS sputtering methods [82]. It has been found

that samples sulfurized at 500°C exhibited similar chemical composition, optical and crystalline properties. However, scanning electron microscopy (SEM) study of co-sputtered CZTS thin films revealed the presence of voids while CZTS thin films made by single target sputtering were void free. CZTS PV device fabricated by single target sputtering demonstrated PCE of 4.4%. Its performance was better compared with the device based on the absorber deposited using the co-sputtering method and showing PCE of 2.06%.

Lin *et al.* prepared CZTS sputtering target from CuS, ZnS, and SnS₂ raw powders with a molar ratio of Cu:Zn:Sn:S = 1.6:1:1:4 [83]. After intermixing of the powders, the precursor pellets were fabricated by pressing. This was followed by sintering at 600°C for 8 hours in a vacuum furnace. Furthermore, a significant effect of the working pressure (WP) during sputtering on the grain structure of the sulfurized CZTS films was shown. Deposition at low WP of 1 mTorr resulted in the formation of CZTS thin film with a larger grain size of about 1µm. In contrast, CZTS thin film deposited at WP of 10 mTorr exhibited ~0.2-0.5 µm grains. Fig. 2.8 shows Raman spectra of CZTS thin films grown at different WP. It can be seen that full width at half maximum of the major CZTS peak decreases with the reduction of WP from 10 mTorr to 1 mTorr. This points to the reduced structural disorder in the films grown at low WP. The positive effect of a low WP was explained by the higher kinetic energy of sputtered CZTS atoms due to the larger mean free path. The higher energy leads to better rearrangement the during deposition process and, hence, better film quality.

Figure 2.8: Raman spectroscopy analysis of sputtered CZTS thin films deposited at WP of 1 mTorr, 5 mTorr and 10 mTorr [83]. Reproduced with permission from Lin *et al.*, J. Alloy. Compd. **654**, 498–508 (2016). Copyright 2016 Elsevier.

Jheng *et al.* reported a one-stage fabrication method of CZTS thin films using single target sputtering approach [84]. The substrate temperature was kept at 50°C, 100°C, 150°C and 200°C during the deposition processes. It has been found that the increase of substrate temperature caused a significant reduction of sulfur content and increment of Cu content in the as-grown films. The study also showed that increase of substrate temperature resulted in a decrease of strain and dislocation density in the deposited films. A substrate temperature of 150°C was found to be optimal in terms of carrier concentration, carrier mobility, and resistivity in the CZTS thin films.

A still higher PCE was achieved by Jheng *et al.* in a subsequent study in which the absorber layer was prepared by co-sputtering of CZTS and ZnS target onto heated substrate [85]. Cu-poor/Zn-rich CZTS film was prepared without sulfurization since the substrate temperature was maintained at 500°C during the deposition. Cu/(Zn+Sn) and Zn/Sn ratios of the best device were 0.87 and 1.26, respectively. This one-stage fabrication process resulted in a CZTS solar cell with a PCE of 5.5%. Moreover, a higher PCE of 6% was achieved by the implementation of conical ZnO nanorods as an anti-

reflection coating (ARC). To the best of my knowledge, PCE of 6% is the highest reported efficiency for pure sulfide CZTS solar cells prepared using quaternary compound CZTS sputtering target.

Kusano *et al.* proposed a way to minimize composition deviation for CZTS thin films prepared by one-stage approach using CZTS target [86]. The space between cathode and substrate was confined by the temperature-controlled reflector wall to enhance the probability of re-deposition of the sputtered or evaporated particles back to the growing film. Composition control of CZTS target can be critical to fabricate CZTS thin films of higher quality. Besides, Cu content in the as-deposited film can be adjusted by variation of WP [83] which may be useful in the fabrication of CZTS absorber films with charge carriers gradient.

2.2.2. Non-vacuum approaches

A number of non-vacuum based deposition methods has been employed to synthesize kesterite thin films. These methods are associated with low fabrication cost and high scalability that are required to commercialize thin film photovoltaic technologies. These include electrodeposition, spray pyrolysis, ink-based methods and etc.

2.2.2.1. Electrodeposition

Electrodeposition is a widely used method in the microelectronics industry to grow thin films of Cu over a large area for multilevel interconnects. The process is based on Faraday's law of electrolysis and is typically carried out at room temperature. Therefore, the approach is energy efficient. Furthermore, materials usage can be close to 100% if stable electrolytes are employed [87]. This approach enables to deposit a stack of metallic thin film, metallic alloys and quaternary compound sulfide and/or selenide precursor thin films [88]. Electrodeposition is carried out in electrolyte bath containing precursor(s) dissolved in an aqueous or non-aqueous solvent. Moreover, conductive substrate and electrical bias are required [89].

F. Jiang *et al.* [90] reported fabrication of CZTS thin films by sulfurization of a sequentially deposited stack of metallic thin films Zn/Sn/Cu/Mo. Prior to sulfurization stack of precursor thin films was annealed at 310°C which was found to improve device performance. This is because low temperature treatment facilitates inter-diffusion of elements and suppress Sn loss during high temperature sulfurization. In contrast, the co-electrodeposition approach does not allow to effectively control the content of the films and uniformity of elemental distribution [88].

2.2.2.2. Spray pyrolysis

Spray pyrolysis is known as a simple and cheap method to grow thin films over a large area at a high deposition rate. The precursor solution is sprayed over a heated substrate at normal pressure in the air. The temperature of the substrate along with properties of the solution such as precursor concentration and pH are critical process parameters [91]. Furthermore, heating of the substrate is required to evaporate the solvent and organic components it contains and facilitate crystal growth. However, spraying of precursor solution lowers the actual temperature of the substrate compared with one measured by thermocouple near the surface of a hot plate [91]. In a recent review Pal *et al.* reported that the highest PCE for pure sulfide CZTS and sulfoselenide CZTSSe solar cells prepared using the spray pyrolysis method were 5% and 5.1% respectively [92–94]. This indicates a lack of progress in PCE improvement since 2014. Unlike the spin coating method, in the spray-pyrolysis approach, un-dissolved salt particles are not removed from the surface of the sample resulting in degradation of the device performance [92].

2.2.2.3. Methods based on inks

A number of industries adopted deposition methods such as printing, spin coating and casting which can be employed to successfully growth thin films of CZTS using ink. These methods are low-energy, high-throughput and scalable. Ink is synthesized using 3 widely used approaches: pure solution, nanoparticles and hybrid (a combination of pure

solution and nanoparticles). Pure solution approach implies intermixing of precursors on the molecular level.

Figure 2.9: Schematic representation of CZTS thin films synthesis using spin-coating and thermal decomposition of CZTS sol-gel precursors. Republished with permission of the Royal Society of Chemistry, from [95], Copyright 2014.

Z. Su *et al.* reported fabrication of CZTS thin films using sol-gel method by dissolving copper acetate monohydrate, zinc acetate dihydrate, tin chloride and thiourea in 2-methoxyethanol [95]. The schematic representation of the process is given in Fig. 2.9. Furthermore, additives were added to prevent crack formation during subsequent thermal treatment. Spin-coating of the sol-gel was followed by drying at 200°C in air. The drying step is used to evaporate organic components, dense the precursor film through the formation of a 3-dimensional network of nanoparticles. Spin-coating and drying steps were repeated several times to form a film of required thickness. In addition, high temperature annealing in S rich atmosphere was carried out at 560°C for 60 min to convert residual oxide phases in sulfide, form CZTS phase and facilitate grain growth. Furthermore, monoethanolamine is used as a stabilizer to facilitate the dissolving of metal precursors in the solvent and solution of high concentration [26]. The champion pure sulfide CZTS solar cell of 10.8% was fabricated using this sol-gel approach [24].

CZTS thin films can be also prepared by sintering of nanoparticle ink. In contrast to the sol-gel method, nanocrystals of CZTS phase are present in nanoparticles based ink. Preliminary colloidal synthesis of CZTS nanocrystals allows facile control over

composition and phase of CZTS thin films [96]. Furthermore, the synthesis process is often carried out at a temperature higher than 200°C to prevent secondary phase formation [97]. After deposition high temperature sulfurization is used to facilitate grain growth. In addition, the method enables deposition of the thin films over a large area compatible with roll-to-roll technology. First CZTS colloidal nanoparticles were reported in 2009 by Q. Guo and co-workers using hot injection method [98]. In a recent study X. Zhang and co-authors demonstrated CZTS solar cell prepared using nanoparticles ink [99]. The spin-coating method was used to deposit the ink over Mo back electrode. This is followed by sulfurization at 600°C for 20 min to form CZTS thin films. The measured PCE of CZTS/CdS solar cell was 6.2% with V_{oc} of 633 mV, J_{sc} of 17.6 mA/cm² and FF of 55.8%.

Addition of organic agents to prevent particles aggregation and cracks formation in the film is typically required for both pure-solution and particle-based approaches to synthesize CZTS thin films [100]. However, these agents also cause contamination of CZTS thin films with C.

Figure 2.10: SEM cross-sectional image of CZTSe solar cells. Figure reproduced with permission from [100]. Copyright WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

A hybrid pure solution-nanoparticles based approach to fabricate kesterite thin films was reported by Todorov *et al.* in 2010 making a breakthrough in kesterite photovoltaics [100]. Use of hydrazine solvent allows a straightforward way to dissolve Cu₂S, SnS/SnSe,

S and Se in the solvent [101]. Although Zn-chalcogenides are not readily dissolved in hydrazine, $\text{ZnS}(\text{Se})\text{N}_2\text{H}_4$ nanocrystallites were formed in place by adding Zn nanoparticles into the solution. Furthermore, the method does not require the addition of organic binding agents to the ink [101]. Then it was spin-coated over Mo-coated SLG substrates which was followed by thermal treatment at a temperature higher than 500°C . This resulted in the formation of large grain size sulfoselenide CZTSSe thin film. Fig. 2.10 demonstrates a cross-section image of the fabricated solar cell with large grains size fabricated using the hybrid hydrazine-based method.

2.3 CZTS/CdS devices

The first CZTS solar cell was reported by H. Katagiri *et al.* in 1997 [36]. Thin films of Zn, Sn and Cu of 160 nm, 230 nm and 180 nm were subsequently deposited by electron-beam evaporation on Mo-coated SLG. Then Cu/Sn/Zn/Mo/SLG samples were sulfurized in flow of N_2 (95%)/ H_2S (5%) at 500°C for 1-3 hours to convert the stack of precursor films into CZTS. As a result, 1.9 μm thick CZTS films were prepared whereas cross-sectional SEM analysis revealed the formation of $\sim 3 \mu\text{m}$ grains. It has been found that long sulfurization time results in loss of volatile Zn. In addition, the direct bandgap of 1.45 eV and absorption coefficient of 10^4 cm^{-1} were measured. In order to fabricate CZTS/CdS heterojunction solar cells, 20 nm thick CdS layer was grown by chemical bath deposition. This is followed by sputter deposition of AZO layer. Finally, Al grids were evaporated to form top contact. The measured photovoltaic parameters of the first fabricated CZTS solar cells were V_{oc} of 400 mV, J_{sc} of 6 mA/cm^2 , FF of 27.7% resulting in PCE of 0.66% (see Fig. 2.11). However, adhesion of CZTS thin films was found to be an issue.

Figure 2.11: Light J-V curve of the first CZTS solar cell [36]. Reproduced with permission from Katagiri *et al.*, Sol. Energy Mater. Sol. Cells 49, 407–414 (1997). Copyright 1997 Elsevier.

To address the adhesion problem identified in the previous work, Zn precursor thin film was replaced by ZnS in evaporated Cu/Sn/ZnS/Mo/SLG structure. Thickness of ZnS, Sn and Cu thin films were 220 nm, 115 nm and 80 nm, respectively. Then, sulfurization was carried out at 530°C in an atmosphere of N₂ (95%)/H₂S (5%). Composition analysis revealed the content of the film was very close to stoichiometric where Cu/(Zn+Sn) ratio was 0.988, Zn/Sn – 1.01, and S/(Cu+Zn+Sn) – 1.07. CZTS solar cell demonstrated PCE of 1.08% with V_{oc} of 372 mV, J_{sc} of 8.36 mA/cm² and FF of 34.7%. However, it has also been found that the change of CZTS composition from stoichiometric to Cu-poor resulted in significantly improved photovoltaic performance. Synthesis of CZTS absorber with Cu/(Zn+Sn) ratio of 0.893 resulted in improvement of PCE from 1.08% to 2.49%. Furthermore, the Cu-poor CZTS solar cell demonstrated a high V_{oc} of 735 mV.

In addition to the optimization of CZTS absorber fabrication process, Katagiri and co-authors addressed the problems associated with CdS buffer layer [102]. It has been found that chemical bath deposition of CdS thin films using CdI₂ as a Cd source is beneficial for the device performance than CdSO₄. The reported PCE improved from 3.46% to 4.25% when CdI₂ was used. The performance enhancement is due to the marked increase

of FF from 46% to 63% and V_{oc} from 530 mV to 659 mV. This was associated with a decrease of leak current density when higher quality CdS layer was employed.

In contrast to the evaporation approach used in the previous works to synthesize CZTS thin film, K. Jimbo *et al.* report use of a co-sputtering approach [103]. ZnS, SnS and Cu sputtering targets were co-sputtered at RF powers of 160 W, 100 W and 95 W, respectively. This is followed by sulfurization of the samples at 580°C for 3 hours in a mix of N₂ (80%)/H₂S (20%). The sputter deposition and sulfurization were carried out in-line without breaking a vacuum. H. Katagiri *et al.* demonstrated a way to further improve the performance of the co-sputtered CZTS solar cells by soaking of sulfurized CZTS thin films in de-ionized water [104]. Soaking of the sulfurized CZTS thin films in de-ionized water (DIW) for 10 min resulted in selective etching of metal oxide phase at the surface of the film. The measured PCE of AZO/CdS/CZTS/Mo/SLG solar cell was 6.77%. The observed improvement was due to an increase of J_{sc} to 17.9 mA/cm² and FF to 62%. The enhancement of FF is associated with a marked decrease of series resistance from 9.04 Ω to 4.25 Ω as surface oxide is removed. On the other hand, the decrease of V_{oc} from 662 mV to 610 mV was revealed as a result of the treatment.

Thus, PCE of CZTS solar cells increased from 0.66% to 6.77% in 2008 thanks to the pioneering works of H. Katagiri and co-workers. These promising results stimulated research and caused a rapid growth of publications on kesterite thin films in the next years.

In 2011 V. Chawla *et al.* reported sulfoselenide based AZO/ZnO/CdS/CZTSSe/Mo/SLG solar cell showing PCE of 9.3% [105]. The absorber layer containing both sulfur and selenium was prepared by co-sputtering of binary copper sulfur-selenide, zinc sulfur-selenide and tin sulfur-selenide targets and subsequent sulfurization at 580°C in an atmosphere of S and SnS. It has been found that ratio of Se/S was not critical to the overall performance of the fabricated solar cells as long as Se is incorporated into the absorber (see Fig. 2.12). However, the study revealed a decrease of V_{oc} and increase of J_{sc} with the rise of Se content in the sulfoselenide CZTSSe absorber layer. Furthermore, charge carrier density was found to decrease with the increase of Se content.

In 2013, PCE of 7.9% was reported by Scragg *et al.* for pure sulfide CZTS solar cell grown by reactive co-sputtering of Zn and alloy of Sn/Cu (35/65) in an atmosphere of

H₂S [106]. This was followed by sulfurization at 560-570°C for 10 min in a graphite box containing high purity S. The measured photovoltaic parameters of AZO/ZnO/CdS/CZTS/Mo/SLG device were as follows: $V_{oc} = 667$ mV, $J_{sc} = 19.6$ mA/cm², FF = 60%.

Figure 2.12: Light J-V characteristics of the sputter deposited CZTS solar cell with various Se/S ratio [105]. Copyright 2011 IEEE.

Progress in PCE improvement of kesterite solar cells inspired companies such as Solar Frontier, Avancis, Toyota, AQT solar to work on sputtered kesterite solar cells shown by the brief technological status review published in 2013 by C.M. Fella and co-authors [107]. Hiroi *et al.* reported sulfoselenide CZTSSe PV submodule with an active area of 14 cm² with measured PCE of 10.8% [108]. The deposited stack of precursors was subjected to sulfurization and subsequent selenization to synthesize sulfoselenide CZTSSe thin film. The device showed J_{sc} of 33.5 mA/cm², FF of 64% and V_{oc} of 502 mV per cell. On the other hand, pure sulfide CZTS submodule demonstrated lower PCE of 9.19% with J_{sc} of 21.6 mA/cm², FF of 60.1% and V_{oc} of 708 mV per cell.

Spin-coating of hydrazine based precursor solution was also intensively used to produce high efficiency kesterite solar cells [109–111]. The record efficiency certified kesterite solar cell showing PCE of 12.6% was reported by Wang *et al.* in 2014 [22]. The hydrazine-based pure solution approach was used to synthesize kesterite thin films. The spin deposition was followed by annealing in temperature above 500°C to prepare 2 μ m

thick absorber layer. 25 nm thick CdS buffer layer was deposited by CBD. Then 10 nm ZnO and 50 nm ITO thin films were grown subsequently to form a window layer. After depositing Ni/Al metal grid, 110 nm MgF₂ anti-reflection coating was deposited. The champion solar cell demonstrated FF of 69.8%, J_{sc} of 35.2 mA/cm² and V_{oc} of 513.4 mV (see Fig. 2.13). However, V_{oc} deficit for the record efficiency PV device was found to be 617 mV pointing out to the bottleneck of the PV technology. Furthermore, calculated minority carrier diffusion length was about 0.75 μ m which is almost 3 times lower than that of high performance CIGS solar cells.

Figure 2.13: Light J-V characteristics of record efficiency kesterite solar cell. Figure reproduced with permission from [22]. Copyright WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Recently sputter-deposited sulfoselenide CZTSSe solar cell showing high PCE of 12.5% was reported by Kim *et al.* [25]. Thin films of Zn, Cu and Sn with thickness of 188 nm, 160 nm and 275 nm were deposited by sputtering to form a stack of Sn/Cu/Zn/Mo. Thereafter it was subjected double stage sulfo-selenization in a mixed atmosphere of Se, H₂S and Ar to synthesize sulfoselenide CZTSSe absorber layer. During the low temperature processing stage the samples were annealed at 300°C for 15 min. This was followed slow ramping up the processing temperature to 480°C and subsequent annealing for 10 min. Although many voids and secondary phases were observed in the bottom sub-portion of the sulfoselenide CZTSSe absorber layer, the

AZO/ZnO/CdS/CZTSSe/Mo/SLG solar cell with MgF₂ anti-reflection coating demonstrated V_{oc} of 516 mV, J_{sc} of 36.13 mA/cm² and FF of 66.89%. This promising result shows a possibility to significantly boost PCE of the kesterite solar cell if problems of void, secondary phase formation and solid-state reaction at the back interface can be mitigated by using of an effective intermediate layer.

As shown in Fig. 1.4, the highest reported PCE of pure sulfide sputtered and solution-processed kesterite solar cells are 11.5% and 10.8% respectively. From a number of published review works on kesterite solar cells [28,33,34,101,112–116] it can be inferred that reasons limiting performance of kesterite solar cells are (i) solid state reaction at the back interface between the absorber layer and Mo, (ii) defects intolerance nature of kesterite, (iii) unfavorable cliff-like band alignment and high density of defects at the hetero-interface. These issues are discussed in detail in 2.4-2.6 subsections.

2.4 Back interface reaction

One important reason for the low PCE of kesterite solar cells is the instability of the kesterite semiconductors upon heat treatment at high temperatures [117]. A thermal annealing step is usually required after deposition to facilitate grain growth and improve absorber properties. However, as explained in a detailed study of the kesterite absorber CZTS by Scragg *et al.* [117], this semiconductor can undergo reversible decomposition into ZnS, SnS and Cu₂S according to the reaction:

The decomposition of CZTS is due to the weakness of the Sn-S bond [117]. In order to prevent this from occurring at high temperature, the heat treatment or sulfurization step is carried out in an atmosphere with an excess of S vapor. This vapor and S present in the deposited CZTS film can undergo diffusion and result in further reactions between CZTS and Mo back contact [47,118]:

The MoS_2 formed from these reactions is a semiconductor with a band gap of 1.23 eV and resistivity of 829.54 Ωcm and thus can increase the parasitic series resistance of a CZTS solar cell [119]. In recent report [120], the effect of sulfurization temperature on the inter-diffusion of S and Mo and how the resulting interfacial layer affects the properties of CZTS thin film solar cells deposited by radio frequency (RF) sputtering from a stoichiometric CZTS compound target was systematically studied. In general, the interfacial region between RF sputtered CZTS and Mo comprises a Mo-rich CZTS layer and a MoS_2 layer [120]. Fig. 2.14 shows MoS_2 interfacial layer between CZTS and Mo. The Mo-rich layer is due to the diffusion of Mo into CZTS during sulfurization. In addition, due to the presence of S in CZTS sputtering target, a MoS_2 layer is grown while deposited the CZTS layer.

Figure 2.14: Cross-sectional SEM and TEM images of CZTS PV devices with 550 nm absorber layer sulfurized at (a) 500°C and (b) 600°C showing interfacial MoS_2 layer [120]. Reproduced with permission from Dalapati *et al.* Sci. Rep. **7**, 1350 (2017). Copyright 2017 licensed under a Creative Commons Attribution (CC BY) license.

The undesirable effects of the MoS₂ layer on CZTS/CdS solar cells can be mitigated by introducing diffusion barrier layers. As shown in Table 2.1, TiN, TiB₂, ZnO, Ag, C, Al₂O₃, Bi, MoO₃ and Ti have been studied thus far for their S blocking properties. Scragg *et al.* investigated the insertion of TiN barrier layer between sputter deposited CZTS and Mo back contact layer [121]. Although the diffusion of S was found to be reduced after sulfurization, the PCE of the device with the 20 nm TiN barrier layer was not improved relative to the control device. Insertion of the barrier layer caused significant decrease in FF from 60% to 47.1%. This drop in FF was associated with marked increase in R_s from 2 Ωcm² to 6.9 Ωcm². Furthermore, it has been observed that both V_{oc} and J_{sc} also decreased with incorporation of 20 nm TiN layer resulting in drop of PCE from 7.9% to 5.5%. The addition of the TiN barrier layer did not affect diffusion of Na from SLG to CZTS absorber layer. The decrease in PCE was explained by formation of energy barrier at the back interface owing to TiN layer addition which affected transport of majority carriers and enhanced recombination rate. TiN is more effective for pure selenide CZTSe devices. As reported by Shin *et al.* [122], the PCE of the solution processed CZTSe/CdS devices was improved from 2.95% to 8.9% due to the incorporation of 20 nm TiN layer between CZTSe and Mo.

Lopez-Marino *et al.* [123] investigated the effect of sputter deposited intrinsic ZnO nanolayer on the formation of MoSe₂. Although the ZnO intermediate nanolayer reduces the voids between the pure selenide CZTSe and MoSe₂ layers, the formation of MoSe₂ is not inhibited by ZnO. The effect of ZnO intermediate layer (IL) was also reported for sputtered CZTS solar cells by Liu *et al.* [124]. 10 nm ZnO IL was deposited by sputtering whereas CZTS thin film was synthesized by sulfurization of sputtered Cu/Sn/Zn stack at 570°C for 30 min. It has been found that this IL mitigates S diffusion into Mo and reduce MoS₂ thickness from 384 nm to 270 nm. Furthermore, voids are reduced when ZnO IL is incorporated at the back interface. The reduced voids are associated with suppressed formation of SnS₂ secondary phase owing to the addition of 10 nm ZnO IL. Moreover, this IL caused increase in PCE from 1.13% to 4.3%. A marked improvement in V_{oc} from 324 mV to 641 mV was observed while J_{sc} increased from 10.8 mA/cm² to 16 mA/cm². Both R_s and R_{sh} were improved as a result of the IL incorporation causing increase in FF from 32% to 42%. The significant improvement of the solar cell performance was

attributed to the reduced thickness of MoS₂, suppression of SnS₂ formation and less voids. Some of the observed voids in the absorber layer of the control sample extended from CZTS/Mo interface to near CdS/CZTS interface making shunt issue of critical importance.

Sputter deposited TiB₂ was found to inhibit the formation of MoS₂ interfacial layer for CZTS deposited by sol-gel synthesis [125] as it can be seen in Fig. 2.15. However, the diffusion of S cannot be eliminated entirely. Furthermore, it has been found that voids are reduced with the addition of TiB₂ IL. Although no secondary phases were detected in the CZTS absorber deposited on TiB₂, the CZTS crystallite size was reduced with more grain boundaries present in the CZTS. Incorporation of 30 nm TiB₂ IL resulted in increase of J_{sc} from 9.56 mA/cm² to 11.35 mA/cm², FF from 49% to 56% and reduction of R_s from 22 Ω cm² to 10.3 Ω cm². This was explained by reduction of MoS₂ thickness and voids. However, V_{oc} was found to decrease with insertion of this IL from 658 mV to 598 mV due to degradation of CZTS crystal quality. These authors also suggested that careful control of the diffusion barrier layer thickness is critical to enhancing the performance of CZTS based photovoltaic devices [125].

Figure 2.15: TEM cross-sectional images of CZTS solar cells (a) without and (b) with TiB₂ layer of 30 nm [125]. Reproduced with permission from Appl. Phys. Lett. **104**, 051105 (2014). Copyright 2014 AIP Publishing.

Cui *et al.* [126] investigated the use of 20 nm thick Ag IL on sputter deposited CZTS. As with TiB_2 , voids at the bottom of the absorber and MoS_2 were reduced in comparison with the control sample. However, partial substitution of Cu by Ag in the kesterite lattice occurs and this alters the bandgap of the absorber. The use of thin evaporated carbon IL for both sol-gel and sputter deposited CZTS was reported by Zhou *et al.* [127]. Unlike TiB_2 IL, incorporation of 25 nm carbon IL did not degrade crystallinity of CZTS absorber layer. Furthermore, secondary phases were not formed owing to the addition of this IL. It has been revealed that thickness of MoS_2 and voids are not reduced as a result of the back interface engineering. PCE of both sputtered and sol-gel derived CZTS solar cells improved with the addition of carbon IL. The major driver for the improvement of the device performance was found to be J_{sc} while change in V_{oc} and FF was negligible (see Fig. 2.16a). With the increase of J_{sc} from 13.6 mA/cm^2 to 16.96 mA/cm^2 , PCE of solution-processed solar cells was enhanced from 4.47% to 5.52%. The observed improvement in PCE was explained by the improved charge carrier transport at the back contact which resulted in overall enhancement of EQE as shown in Fig. 2.16b. Carbon forms a conductive coating in the inner walls of voids at the bottom of the absorber and improves the contact resistance of the device back contact.

Figure 2.16: (a) Light J-V characteristics and (b) EQE spectra of sol-gel derived CZTS solar cells without and with carbon IL. Adapted with permission from [127]. Copyright (2015) American Chemical Society.

Table 2.1: Intermediate layers for SLG/Mo/CZTS/CdS and SLG/Mo/CZTSe/CdS solar cells.

Intermediate layer	Absorber (deposition method)	Effect of intermediate layer on the absorber.	Reference
TiN	CZTS (sputtered)	Reduces S diffusion into Mo. Adds to R_s of the CZTS/CdS devices	[121]
TiN	Evaporation	Reduces MoSe ₂ thickness. Improves PCE of CZTSe/CdS solar cells	[122]
ZnO	CZTSe (sputtered)	Reduces voids between CZTSe and MoSe ₂ interface. Does not inhibit MoSe ₂ formation.	[123]
TiB ₂	CZTS (sol-gel)	Inhibit MoS ₂ formation; reduces roughness and voids at MoS ₂ /CZTS interface; affects grain size of CZTS	[125]
Ag	CZTS (sputtered)	Inhibit MoS ₂ formation; reduces voids between MoS ₂ and CZTS and SnS ₂ secondary phase.	[126]
C	CZTS (sol-gel)	C adheres to the inner wall of voids and improves contact resistance of Mo back contact. No effect on crystallinity of CZTS	[127]
Al ₂ O ₃	CZTS (sputtered)	Prevents the interaction between CZTS and Mo to form secondary phases and voids	[128]
Bi	CZTS (sol-gel)	Inhibits MoS ₂ formation. Improves crystallinity of CZTS absorber layer. Reduce ZnS secondary phase	[129]
MoO ₃	CZTS (sputtered)	Enhances Na diffusion and increase the grain size of CZTS crystallites	[130]
Ti	CZTS (sputtered)	Reduces MoS ₂ thickness. Inhibits voids formation. Increases Hall mobility	[131]

Most recently, Al_2O_3 has been used as an IL in ultrathin sputtered CZTS solar cells with high efficiency [128]. In the initial stage of sulfurization, the Al_2O_3 dielectric layer prevents the interaction between CZTS and Mo to form secondary phases. The subsequent breakup of the Al_2O_3 layer into discontinuous aggregates with a self-organized pattern results in openings between the Al_2O_3 that facilitate charge transport at the back contact. Tong *et al.* studied the effect of Bi IL on solution-process CZTS thin film [129]. It has been found that the IL facilitate crystallization of CZTS and reduce grain boundaries (see Fig. 2.17). Furthermore, S diffusion into Mo and, hence, MoS_2 thickness is reduced while the formation of ZnS phase formation is suppressed. When Bi IL layer of optimized thickness (20 nm) was present at the back interface, PCE of CZTS solar cells increased from 3.59% to 4.75%. Increase of V_{oc} from 555 mV to 590 mV and J_{sc} from 12.5 mA/cm^2 to 15.7 mA/cm^2 was explained by the reduced recombination as a result of improved crystallization of CZTS absorber layer and reduced thickness of MoS_2 layer. MoO_3 IL was also reported to improve the size of CZTS crystallites through enhancement of Na diffusion [130]. The study of Guo *et al.* shows that insertion of Ti IL not only mitigates solid state reaction at the back interface but also improves Hall mobility of charge carriers [131]. This is realized by the reduction of hole concentration in CZTS as the thickness of Ti IL increases.

Figure 2.17: SEM cross-sectional images of CZTS solar cells (a) without IL and with (b) 10 nm, (c) 20 nm, (d) 30 nm thick Bi IL [129]. Reproduced with permission from Tong *et al.*, Sol. Energy Mater. Sol. Cells **144**, 537 - 543 (2016). Copyright 2016 Elsevier.

From the above discussion, it is evident that despite considerable research in the past few years, a satisfactory barrier layer remains to be found for the pure sulfide CZTS/Mo and pure selenide CZTSe/Mo back contact. The key requirements for the barrier layer or IL can be summarized as: (i) suppression of the solid state reaction between S and Mo; (ii) no adverse secondary phase formation; (iii) no effect on the crystallinity of the kesterite absorber after sulfurization and (iv) reduction of device series resistance.

2.5 Defects intolerance nature of kesterite

The complex CZTS crystalline structure is defect intolerant [132]. Due to the similarity in ionic radii of the Cu^+ and Zn^{2+} ions, the enthalpy of formation of Cu_{Zn} and Zn_{Cu} anti-site point defects is low and these defects and the associated defect complexes can form readily in large numbers in CZTS [33]. As a result, a high density of Cu_{Zn} and Zn_{Cu} anti-site defects can form in the CZTS lattice which leads to the random occupation of the 2c and 2d Wyckoff sites for Cu^+ and Zn^{2+} respectively at the $z=1/4$ and $z=3/4$ cationic planes of the unit cell [133]. The fully randomized occupation of these sites changes the symmetry of the CZTS crystal from the ordered I-4 to the disordered I-42m unit cell [134]. This cation disordering can cause local band fluctuations [28]. Furthermore, the localized states resulting from this cationic disorder leads to the formation of band tails that increase sub-gap absorption and recombination and degrades the CZTS solar cell open circuit voltage [133]. These are now recognized to be a major contributor to the V_{oc} deficit [133].

Using resonant Raman scattering, Scragg *et al.* found that the cationic disorder phenomenon can be avoided by annealing the pure sulfide CZTS film below an order-disorder threshold temperature of 533 K [135]. Furthermore, the study found a positive effect of slow cooling on the structural properties of CZTS thin films (see Fig. 2.18). In addition, Grossberg *et al.* reported a large increase in cationic disorder when cooling rates after sulfurization is greater than 10-24 K/min [136]. Since process engineering appears to be difficult to manage defect generation in stoichiometric CZTS, it has become common practice to use Cu poor Zn rich CZTS as the absorber in high performance CZTS solar cells [24,137]. Nevertheless, various intrinsic defects are readily formed in CZTS

due to the complexity of its quaternary compound system. However, these defects can be compensated to some extent by extrinsic doping [138].

Figure 2.18: Raman spectra of CZTS thin films exposed to slow (VS) and fast (VF) cooling after sulfurization recorded at the laser wavelength of 532nm and 785nm [135]. Reproduced with permission from Appl. Phys. Lett. 104, 041911 (2014). Copyright 2014 AIP Publishing.

Incorporation of isoelectronic and non-isoelectronic cations into CZTS has also been extensively studied [139–141]. Doping of kesterite with alkali metal ions such as K^+ and Na^+ can increase charge carrier density and increase carrier lifetime respectively [142–144]. Furthermore, Li doping reduces charge carriers recombination at grain boundaries by inverting the polarity of the electric field there [145]. Doping of solution processed kesterite by Bi was found to increase the absorber grain size [146] while the incorporation of Sb enabled to passivate defects and, hence, reduce V_{oc} deficit of sulfoselenide CZTSSe/CdS solar cells [147].

Since the critical temperature for ordered CZTS is only 533 K [133], much attention has been given to the effects of cationic substitution on the performance of CZTS thin film solar cells [148]. Here, cationic substitution refers to the partial or complete replacement

of a cation in CZTS by an isoelectronic cation of different size. Such ions can reduce the formation of anti-site defects by increasing the enthalpy of formation for these defects so that the amount of these defects can be reduced.

In a recent review, Li *et al.* have described the progress in cationic substitution on kesterite solar cells in considerable detail [149]. Partial substitution of Cu, Zn and Sn in CZTS thin films by Ag [24,150,151], Cd [23,152,153] and Ge [154], respectively were reported to enhance the performance of CZTS thin film solar cells substantially.

A. Guchhait *et al.* studied the effect of partial Cu substitution by Ag in solution-processed CZTS thin film [151]. Ag/Cu ratio was maintained at 7/93. Incorporation of Ag into the crystal lattice of CZTS was proved by XRD owing to a shift of (112) kesterite CZTS peak position to a lower 2 Theta angle. Furthermore, it has been revealed that Ag substitution facilitates grain growth of kesterite. Moreover, the density of anti-site defects was found to be reduced with Ag substitution as Urbach tail energy reduced from 48 meV to 38 meV. In addition, Ag incorporation caused an increase of depletion width from 190 nm to 290 nm. This is associated with a boost of J_{sc} from 15 mA/cm² to 18.1 mA/cm² owing to more effective separation of charge carriers at the heterointerface when Ag is incorporated. The analysis of photovoltaic performance showed the increase of PCE from 4.88% to 7.24% due to a significant increase of FF from 52% to 59.7% and J_{sc} .

Z. Su *et al.* investigated the impact of Cd incorporation in solution-processed CZTS thin films through partial substitution of Zn by Cd (see Fig. 2.19) [152]. The study showed transformation of kesterite crystal structure of CZTS into stannite when Cd/(Zn+Cd) ration is in the range from 0.6 to 1. In addition, the grain size of kesterite crystallite was found to increase with the increase of Cd/(Zn+Cd) ratio from 0 to 0.5. Moreover, the bandgap of Cd incorporated CZTS thin films decreased from 1.54 eV to 1.36 eV as Cd/(Zn+Cd) increased from 0 to 0.6. Further increase of Cd content resulted in an increase of E_g to 1.41 eV. The study showed that the optimal composition of the absorber layer is Cu₂Zn_{0.6}Cd_{0.4}SnS₄ (CZCTS) due to the increase of PCE from 5.3% to 9.24% when compared to the reference device. The device performance improvement was associated with the boost of J_{sc} from 14.7 mA/cm² to 24.1 mA/cm² and FF from 56% to 66%.

Figure 2.19: (a) Plot of bandgap and lattice parameter a as a function of Cd/(Zn+Cd) ratio, (b-c) EQE spectra of solar cells with different Cd/(Zn+Cd) ratio. Figure reproduced with permission from [152]. Copyright WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In particular, sputter grown Cd-rich pure sulfide CZTS solar cell with a record PCE of 11.5% was demonstrated by Yan *et al.* [23]. The absorber of the solar cell was prepared by alloying of co-sputtered CZTS precursors stack with CdS film deposited over it by chemical bath deposition (CBD). The incorporation of Cd resulted in a reduction of the band gap from 1.53 eV to 1.38 eV and a decrease of the V_{oc} deficit from 847 mV to 730 mV.

In a recent study, S. Hadke proposed double cation substitution [24]. Both Cu and Zn are partially substituted by Ag and Cd in solution-processed CZTS thin films. It has been found that Cd substitution reduces the density of defects that form shallow acceptor states. On the other hand, Ag substitution resulted in a decrease of non-radiative recombination. The combined effect of the double cation substitution resulted in an increase of PCE from 6.7% for CZTS to 10.8% for $Ag_{0.05}Cu_{0.95}Zn_{0.75}Cd_{0.25}SnS_4$ (ACZCTS), which is the record efficiency for pure sulfide solution processed kesterite solar cells. The measured V_{oc} of the record solar cell is 650 mV, while J_{sc} and FF are 25 mA/cm² and 66.2%, respectively.

It has been reported the bandgap of kesterite thin films increased linearly from 0.99 eV to 1.35 eV with the increase of Ge/(Sn+Ge) ratio from 0 to 1 [155]. However, Ge loss also occurs via evaporation of volatile GeSe₂ phase. A high PCE of 12.3% was demonstrated for Ge-substituted kesterite solar cell by S. Kim [156]. CZTGSe thin films were fabricated by co-evaporation of elemental sources on a substrate at 200°C followed by selenization at 500-550°C. In addition, SnSe₂ and GeSe₂ pellets were introduced to suppress the loss of volatile Sn and Ge compounds. Ge/(Sn+Ge) ratio was 0.22 in the

absorber layer resulting in the bandgap of 1.11 eV. Furthermore, measured V_{oc} of 527 mV resulted in V_{oc} deficit of 583 mV. In addition, high FF of 72.7% and J_{sc} of 32.2 mA/cm² were observed for the solar cell. Enhancement of the device performance was explained by decreased band tailing and reduced non-radiative recombination both at the CdS/CZTGe interface and in the bulk.

2.6 Effect of buffer layer in device architecture

CdS thin films are widely used as a buffer layer in CZTS-based solar cells to form a heterojunction [84,157]. However, the carrier recombination at the interface between CZTS absorber and CdS buffer results in a decrease of V_{oc} . The recombination at the interface can be caused by the 7% lattice misfit between CZTS and CdS which favors the formation of defects that deteriorate device performance [158]. Besides, cliff-like conduction band offset (CBO) of about 0.3 eV leads to the carrier recombination at the interface [73,113] while favorable band alignment is associated with spike-like CBO ranging from 0 to 0.4 eV [159]. Furthermore, implementation of CdS buffer with an optical bandgap of 2.42 eV results in parasitic light absorption of a short wavelength which limits J_{sc} of the solar cell [108].

Passivation of the interface is needed to reduce defect density there and improve the PCE of the CZTS solar cells. Li *et al.* studied the influence of ZnS secondary phase segregation near the absorber/buffer interface [160]. It has been suggested that ZnS could effectively passivate the interface owing to small misfit of about 0.5% between CZTS and ZnS. This could reduce interface recombination thus increasing V_{oc} . However, the presence of ZnS increased series resistance (R_s) of the device due to spike-like CBO of 0.86 eV at CZTS/ZnS interface. CZTS PV device with ZnS buffer was fabricated by Kim *et al.* [161]. ZnS buffer layer was deposited on top of CZTS absorber by RF sputtering technique. It has been reported that the optimized sputtering power and thickness of the buffer were 95 W and 30 nm respectively. CZTS/ZnS-based PV device with a PCE of 2.11% was reported while PCE of the reference device with CdS buffer prepared by chemical bath deposition (CBD) technique was 4.97%. The low PCE of the CZTS/ZnS-

based solar cell can be attributed to the large spike-like CBO at the interface between CZTS and ZnS which limits electron transport through the heterojunction. In addition, defects at the hetero-interface caused by sputter damage may also add to the low performance of the solar cell.

Ericson *et al.* prepared a CZTS solar cell with Zn(O,S) alternative buffer having a PCE of 4.6% [162]. Taking into account the large positive CBO between CZTS and ZnS, large negative CBO between CZTS and ZnO, it has been supposed that implementation of Zn(O,S) alternative buffer could result in optimal band alignment. It has also been shown that CBO between buffer and absorber could be varied by adjusting the O/S ratio. The buffer layer was grown by atomic layer deposition (ALD) at 120°C to minimize the damage to the hetero-interface. The best Zn(O,S)-based PV device showing PCE of 4.6% had 6:1 Zn(O,S) buffer layer composition while the reference solar cell with CdS buffer had a measured PCE of 7.3%. The possible reason for the higher PCE of the reference device is a positive effect of etching that occurs at the early stage of CBD process that may remove surficial oxide and secondary phases from the surface of the absorber layer [163].

An alternative $\text{Zn}_{0.35}\text{Cd}_{0.65}\text{S}$ buffer layer was used to fabricate a CZTS PV device by Sun *et al.* [73]. The buffer layer was grown by successive ionic layer adsorption and reaction (SILAR) method. The SILAR deposition cycle consists of 4 steps: (i) dipping of a substrate into a cation precursor, (ii) rinsing in DIW, (iii) dipping into anion precursor solution, and (iv) rinsing in DIW to grow few monolayers of the film [164]. As shown in Fig. 2.20, the composition of the buffer was adjusted to get optimum CBO which was directly measured by XPS technique [73]. CZTS solar cell based on this alternative buffer layer had a measured PCE of 9.2% while a PCE of 7.8% was obtained for the reference solar cell with CdS buffer. Furthermore, implementation of the alternative buffer layer with a bandgap of 2.7 eV enabled to enhance V_{oc} and FF compared to the reference device. Increase of V_{oc} from 665 mV to 748 mV points to the reduced recombination at the surface of the device owing to improved band alignment and reduced defect density at the hetero-interface.

Figure 2.20: Schematic band diagrams showing the effect of buffer layer composition on the band alignment at the buffer/CZTS hetero-junction. Figure reproduced with permission from [73]. Copyright WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Bras *et al.* reported a CZTS solar cell with sputter-grown In_2S_3 buffer [157]. Flexible stainless steel substrates were used instead of soda-lime glass (SLG) to withstand fast temperature changes. Sodium precursor (MoNa) layer was deposited prior to Mo back contact deposition to enhance re-crystallization of the CZTS absorber. Single quaternary target of Cu-poor Zn-rich composition was used to fabricate the absorbers. The device fabrication process was performed without breaking the vacuum and took less than 40 minutes. This approach prevented contamination of the CZTS absorber. The solar cell with In_2S_3 buffer had a measured PCE of 4.2% while the PCE of the solar cell with CdS buffer was only 2%. This improvement was attributed to better heterojunction quality of CZTS/ In_2S_3 . Hiroi *et al.* used a hybrid buffer based on a combination of CdS and In_2S_3 layers to suppress carrier recombination at the interface [108]. As a result, a V_{oc} of 758 mV was achieved, and the solar cell showed a PCE of 9.19%. In addition, the reduction of recombination at both absorber/buffer and buffer/i-ZnO interfaces was obtained. Moreover, it has been suggested that small CBO at absorber/buffer layer interface (0 – 0.1 eV) could cause a decrease of shunt resistance (R_{sh}). Yan *et al.* also

investigated the effect of hybrid $\text{In}_2\text{S}_3/\text{CdS}$ on the performance of CZTS solar cells [165]. V_{oc} of 714 mV and PCE of 6.62% were achieved for the best device. Improvement in V_{oc} compared to CdS reference device was explained by higher carrier concentration in CZTS due to In doping (In diffuses from buffer layer to CZTS absorber layer) and more favorable band alignment at buffer/absorber interface.

Platzer-Bjorkman *et al.* implemented $\text{Zn}_{1-x}\text{Sn}_x\text{O}_y$ (ZTO) buffer layer instead of CdS to reduce the interface recombination [166]. ZTO buffer was formed using the ALD technique. The device with ZTO buffer exhibited activation energy of 1.36 eV while the activation energy of the CZTS device with CdS buffer was only 1 eV. Such an increase in activation energy was explained by the reduction of recombination at the buffer/absorber interface as a result of improved band alignment at the interface between CZTS and ZTO. It has been shown that the implementation of ZTO buffer caused an increase of V_{oc} from 607 mV to 682 mV compared to CdS reference devices. As a result, a PCE of 7.4% was achieved. Table 2.2 summarizes reported information regarding the impact of the buffer layers on the photovoltaic properties of sputter-grown CZTS solar cells.

Tajima *et al.* fabricated solar cell based on two-layered CZTS absorber with world record V_{oc} of 780 mV [68]. CZTS layer near Mo electrode was stoichiometric while CZTS layer near the absorber/buffer interface was Cu-poor. It has been suggested that Cu content gradient caused an increase of carrier concentration gradient within the absorber, which in turn could lead to an increase of inner potential between the absorber and buffer layers. The best solar cell showed V_{oc} of 710 mV and had a PCE of 8.8%. However, the extrapolated V_{oc} to 0 K was only about 1.2 V which is significantly less than the bandgap of CZTS. This result was attributed to the recombination at the CZTS/CdS interface.

Table 2.2: Reported photovoltaic properties of sputter-deposited CZTS solar cells with and without buffer layer.

Type of buffer layer	Buffer layer growth method	J_{sc} , mA/cm ²	V_{oc} , V	FF	PCE, %	Ref.
Zn _{0.35} Cd _{0.65} S	SILAR	19.5	0.7478	0.632	9.2	[73]
CdS ref.device	CBD	20.4	0.665	0.574	7.8	[73]
In ₂ S ₃ /CdS	CBD	21.6	0.708	0.601	9.19	[108]
In ₂ S ₃	Sputtering	13.9	0.531	0.508	4.2	[157]
CdS ref.device	CBD	11.2	0.423	0.38	2	[157]
ZnS	Sputtering	12.16	0.311	0.5573	2.11	[161]
CdS ref. device	CBD	18.4	0.561	0.482	4.97	[161]
Zn(O,S)	ALD	17.2	0.482	0.555	4.6	[162]
CdS ref. device	CBD	17.5	0.652	0.638	7.3	[162]
In ₂ S ₃ /CdS	CBD	17.6	0.714	0.527	6.62	[165]
CdS ref. device	CBD	15.9	0.641	0.537	5.47	[165]
Zn _{1-x} Sn _x O _y	ALD	17.9	0.682	0.602	7.4	[166]
CdS ref. device	CBD	17.1	0.607	0.559	5.8	[166]

2.7 Electrical characteristics of solar cells

The ideal solar cell equivalent circuit is composed of current source connected in parallel with diode. However, a real solar cell J-V characteristic is affected by R_s and R_{sh} . The equivalent circuit of the real solar cell is presented in Fig. 2.21. Presence of the resistances causes decrease in FF. In order to minimize the negative impact of the parasitic resistances, solar cells are to be designed in a way to minimize R_s and maximize R_{sh} .

Figure 2.21: Schematic representation of equivalent circuit of non-ideal solar cell.

The output J-V relation of the solar cell with parasitic R_s and R_{sh} can be described as follows [167]:

$$J = J_0 \left[\exp \frac{q}{Ak_B T} (V - JR_s) - 1 \right] + \left(\frac{V - JR_s}{R_{sh}} \right) - J_L \quad (2.1)$$

J_0 is reverse saturation current density, q is elemental charge, A is diode ideality factor, k_B is Boltzmann constant, T is temperature (in Kelvin). The relation between J_0 and activation energy of recombination rate (E_a) is given below [167]:

$$J_0 = J_{00} \exp \left(-\frac{E_a}{Ak_B T} \right) \quad (2.2)$$

where J_{00} is prefactor of reverse saturation current density.

V_{oc} can be extracted from (2.1)-(2.2) by assuming $J = 0$ and $J_L = J_{sc}$ [167].

$$V_{oc} = \frac{E_a}{q} - \frac{Ak_B T}{q} \ln \left(\frac{J_{00}}{J_{sc}} \right) \quad (2.3)$$

Thus, taking into account that $V_{oc \text{ deficit}} = E_g/q - V_{oc}$ [168], the equation for V_{oc} deficit can be expressed in the following form:

$$V_{oc \text{ deficit}} = \frac{E_g - E_a}{q} + \frac{Ak_B T}{q} \ln \left(\frac{J_{00}}{J_{sc}} \right) \quad (2.4)$$

E_a can be determined from the slope of the fitted line by plotting $A \ln(J_0)$ as a function of $1/T$ [101] (see Fig. 2.22a). For the solar cells with dominant recombination mechanism at

space charge region, E_a is equal to E_g . On the other hand, if $E_a < E_g$, interface recombination is considered as a dominant recombination mechanism [101]. Alternative approach to reveal the major recombination mechanism is to plot V_{oc} as a function of T , as shown in Fig. 2.22b. If intersection of the interpolated line to $T = 0$ gives V_{oc} lower than E_g/q than interface recombination is the main bottleneck limiting V_{oc} .

Figure 2.22: (a) Plot used to extract E_a from the slope of $A \ln(J_0)$ as a function of $1/T$, (b) temperature dependent data of V_{oc} and its interpolation to $T = 0 \text{ K}$ [101]. Reproduced with permission Mitzi *et al.*, Sol. Energy Mater. Sol. Cells 95, 1421–1436 (2011). Copyright 2011 Elsevier.

The determination approach of A and J_0 from light and dark J-V data is described in detail in work of Hegedus *et al.* [169]. Fig. 2.23 shows 4 plots used to extract the parameters of CIGS solar cell by the co-authors. Use of dark J-V data is preferable to minimize noise. Shunt conductance of the solar cells is extracted from the reverse bias region where first derivative of current density against voltage (dJ/dV) becomes insignificant. R_s and A can be determined by plotting dV/dJ as a function of inverse $(J+J_{sc})$. Slope of the linear fit to the data is used to extract the diode ideality factor A while intersect of the line with ordinate gives R_s . This approach can also be used for a not well-behaved solar cells where blocking effect at the back contact [169]. Intersection of $(J+J_{sc}-GV)$ versus $(V-RJ)$ plot is used to extract J_0 while slope of the linear fit gives A .

Figure 2.23: (a) Dark and light J-V plot, (b) plot of dJ/dV versus V , (c) plot of dV/dJ as a function of $(J+J_{sc})^{-1}$, (d) plot of $(J+J_{sc}-GV)$ versus $(V-RJ)$ [169].

2.8 Summary

In summary, large V_{oc} deficit of kesterite solar cells remains to be a great challenge hindering photovoltaic performance of the devices. This results in short minority carrier diffusion length in pure sulfide CZTS solar cells. Presence of secondary phases, cation disorder, recombination at front and back interfaces of the absorber layer are known to be factors causing decrease of V_{oc} . The issue of secondary phases is rarely reported for state of the art kesterite solar cells due to extensive optimization of precursor composition and sulfurization/selenization conditions performed. On the other hand, cation disorder is still a critical issue attributing to low V_{oc} of the solar cells. The effect of Na and K incorporation which are reported to passivate defects in CZTS has been well studied. In

addition, DFT simulation studies demonstrated importance of cation disordering in kesterite semiconductors revealing energy levels of various anti-site defects within the band gap. Density of Cu_{Zn} and Zn_{Cu} defects is high owing to a similar radii of Cu and Zn atoms. Therefore, effect of cation substitution for Cu and Zn by Ag and Cd respectively was reported in many studies. In contrast, Sn-related anti-site defects such as Sn_{Cu} , Cu_{Sn} , Sn_{Zn} introduce deep defects and mid-gap states which significantly deteriorate device performance. Although there are reports on substitution of Sn by isovalent Ge, however more research on this is required. Therefore, this work studies the effect of incorporation of Mo and C into sputtered CZTS absorber layer. There are few reasons for this. First, Mo and C having oxidation state of +4 may substitute Sn which, in turn, may reduce V_{oc} deficit of the solar cell devices. Second, residual C is normally present in solution processed kesterite thin film due to organic solvents and various additives used. In addition, Mo diffuses into kesterite from Mo back contact during sulfurization process. In this study Mo and C are intentionally introduced into sputter-grown CZTS to study its effect.

From the discussion in section 2.4, it is evident that despite considerable research in the past few years, a satisfactory barrier layer remains to be found for the CZTS/Mo and CZTSe/Mo back contact. The key requirements for the barrier layer or IL can be summarized as: (i) suppression of the solid state reaction between S and Mo; (ii) no adverse secondary phase formation; (iii) no effect on the crystallinity of the kesterite absorber after sulfurization and (iv) reduction of device series resistance. With the aim to find the satisfactory barrier layer, TaN, ZnS and CuO IL were studied. TaN may be a suitable candidate for S blocking layer as it has been used as an ultrathin barrier layer to block Cu diffusion into low-k dielectrics in multilevel Cu interconnects in CMOS related processes [170,171]. As CZTS, ZnS is crystallized based on tetrahedral coordination of atoms resulting in similar crystal structure. Therefore, this IL may not only mitigate S diffusion into Mo but also serves as a seed layer for kesterite. Finally, CuO is employed as IL because it may react with S and slow down S diffusion into Mo.

Chapter 3 Sputtered TaN IL on back contact reaction of sputtered CZTS

3.1 Introduction

In the present chapter, the impact of the Cu-poor CZTS and TaN IL on the formation of MoS_2 and secondary phases is studied. TaN is used as a barrier material to prevent Cu diffusion into Si wafers in CMOS processes. It is a dense refractory material and thus may be suitable for blocking S diffusion in the back contact of CZTS devices. Furthermore, it is characterized by a low bulk resistivity of $200 \mu\Omega\text{cm}$ and thermal stability up to 700°C [172]. The effect of sputtered TaN IL on the inter-diffusion and interfacial layer formation between sputter deposited Cu-poor CZTS and Mo is discussed in detail. After reporting the basic electrical properties of sputter deposited TaN layers, the effect of TaN IL thickness on the CZTS/Mo back contact reaction is investigated.

3.2 Experimental details

Thin films preparation

SLG substrates were ultrasonicated in isopropyl alcohol (IPA) for 10 min followed by drying using nitrogen gas flow. The substrates were then loaded into the chamber of a Denton Discovery-18 sputtering system for Mo back electrode deposition. The sputtering system can accommodate up to three 76.2 mm diameter targets and is equipped with two direct current (DC) and one radio frequency (RF) power supplies. After deposition of ~ 900 nm thick Mo film, TaN films with a thickness of 3 nm, 7 nm and 12 nm were deposited at DC sputtering power of 40 W. Thereafter, 860 nm thick CZTS films were deposited by RF sputtering from a non-stoichiometric Cu poor $\text{Cu}_{1.69}\text{ZnSnS}_4$ quaternary target (ALB Inc.). Prior to the deposition, the base pressure in the sputtering chamber was $\sim 1.33 \times 10^{-4}$ Pa. The sputtering was carried out at RF sputtering power of 100 W and Ar working pressure of 0.52 Pa. All depositions were performed without intentional heating of the SLG substrate. After sputter deposition, the CZTS/Mo/SLG and Mo/SLG stacks

without and with TaN IL were sulfurized in the presence of elemental S vapor provided by melted 99.99% purity S powder and Ar in a two zone furnace at a temperature of 600°C for 10 min. The ramping rate in the main section was 19.2°C/min while sulfur powder was subjected to the temperature of 200°C during the thermal treatment.

Thin film characterization

A Raman measurement system equipped with a 514 nm laser was used to investigate structural and bonding properties of the samples in backscattering mode. Crystal quality of the samples was characterized using a Bruker D8 general area detector XRD system by θ -2 θ scan at a source wavelength of 0.15418 nm. Elemental depth profile was measured with a TOF-SIMS system. Bi⁺ ions were employed for the analysis. Masses of the analyzed ions were as follows: Na (22.9901), S (31.9721), Cu (62.9299), Zn (63.9282), Mo (91.9059), Sn (119.9017), Ta (180.9503). XPS system (VG ESCALAB 220i-XL) equipped with monochromatic AlK α source (1486.6 eV) was used to study the surface composition of the samples. Surface of the samples was not sputter etched prior to the XPS analysis. Sheet resistance (R_{sheet}) was measured using MicroxAct A4P-200 four-point probe automated resistivity mapping system. The thickness of the films was measured using a surface profiler system.

An FEI dual-beam focused ion beam (FIB) Helios workstation equipped with an *in-situ* micromanipulator and Pt gas injection system was used to prepare the TEM lamellae for scanning transmission electron microscopy (STEM) imaging, energy-dispersive X-ray spectroscopy and electron energy loss spectroscopy analysis. The final FIB milling was performed at 3 kV. STEM investigations were conducted using JEOL ARM200F TEM equipped with a spherical aberration corrector at the condenser plane at 200 kV. A semi-convergence angle of 32 mrad was used. High-angle annual dark field (HAADF) STEM images were recorded with collection angles in the 68-280 mrad range. The EDX STEM data were collected using the Oxford X-MaxN 100TLE EDX detector. In addition, JEOL GrandARM300F TEM with the ability to perform EDX and EELS at the same time were used for the elemental analysis at 300 kV. Surface morphology was studied using a field emission scanning electron microscope (JEOL FESEM JSM 6700F).

Scratch hardness of the samples was measured with diamond indenter using ASTM G171-03 standard. The samples were polished to enable the scratch width (w) measurement. A constant z-directional load was applied by the diamond indenter and scratch mark was appeared due to reciprocating motion of the sliding stylus. The average scratch width is calculated using an optical microscope.

3.3. Results and discussion

3.3.1. TaN/Mo/SLG

The effect of TaN IL thickness on R_{sheet} of sulfurized Mo films was studied first to evaluate the ability of TaN film to limit the diffusion of S into Mo. Table 3.1 shows measured R_{sheet} of the samples before and after the sulfurization. The deposition of ultrathin TaN films causes a slight increase in R_{sheet} before sulfurization from $0.18 \Omega/\square$ to $0.24 \Omega/\square$ due to the higher resistivity of TaN ($\sim 200 \mu\Omega\text{cm}$) relative to Mo ($6\text{-}10 \mu\Omega\text{cm}$) [173]. On the other hand, the R_{sheet} decreases with the addition of a TaN IL when measured after sulfurization. As a result of the sulfurization, R_{sheet} of the control sample increases from $0.18 \Omega/\square$ to $3.2 \Omega/\square$. This can be explained by the formation of resistive MoS_2 layer at the surface of Mo film. The deposition of 3 nm TaN film causes a decrease of R_{sheet} after sulfurization from $3.2 \Omega/\square$ to $0.71 \Omega/\square$. Besides, the increase of TaN thickness from 3 nm to 12 nm results in a further reduction of R_{sheet} down to $0.46 \Omega/\square$ which is only 1.9 times higher than the R_{sheet} before sulfurization. Thus, insertion of TaN IL can limit the negative effect of sulfurization on the parasitic series resistance of Mo back contact for CZTS solar cells. Note: only qualitative approach was used to analyze the changes in the sheet resistance of Mo samples without and with TaN IL. The reason for this is that absence of CZTS absorber layer on top of TaN/Mo/SLG sample may cause more intense sulfurization and deeper penetration of S into the sample because of its direct contact with S-rich atmosphere. This, in turn, may lead to the change of the nature and thickness of the IL and multilayers. The change in morphology, as seen in TaN IL, render the thickness of the IL after sulfurization. Thus, its thickness is difficult to be determined accurately which in turn makes the determination of the resistivity difficult.

Table 3.1: Effect of TaN thickness on sheet resistance (R_{sheet}) of as-deposited and sulfurized Mo thin films.

	Sheet resistance (R_{sheet}), $\Omega/\square$			
	w/o TaN	3 nm TaN	7 nm TaN	12 nm TaN
Before sulfurization	0.18	0.24	0.24	0.24
After sulfurization at 600°C for 10 min	3.2	0.71	0.53	0.46

SIMS study was carried out to investigate the ability of the ultrathin TaN films to inhibit S diffusion into Mo during the high temperature treatment in S-rich atmosphere. Fig. 3.1 shows elemental S diffusion profile for the Mo samples with and without TaN IL after sulfurization. For the Mo sample without TaN IL, there is a significant diffusion of S into the Mo. The thickness of the MoS_x is proportional to the shoulder in the intensity profile of S. For the samples with TaN IL, there is a higher concentration of S at the surface compared to the control sample. Deposition of ultrathin TaN films enables remarkable reduction of S-rich region in the Mo layer since TaN acts as a barrier layer. Although the S profile for 3 nm, 7 nm and 12 nm TaN are comparable, the S concentration is highest at the surface for 7 nm TaN. A possible explanation for the reduction of S-rich region in Mo layer upon the incorporation of TaN IL is that the S in the TaN intermediate layer reduces the amount of S that can diffuse into the Mo. The penetration of S into Mo observed for these samples with TaN intermediate layer may be due to discontinuities in the TaN layer and a different concentration profile of S in these samples compared with the control sample.

Figure 3.1: SIMS depth elemental profile of S for the sulfurized Mo samples with and without TaN ILs.

XPS analysis was employed to investigate the effect of sulfurization on the surface composition of 7 nm TaN/Mo sample (see Fig. 3.2). Fig. 3.2a shows the Ta 4f signal before and after sulfurization. The Ta 4f spectra of the as-deposited sample show three clear peaks located at a binding energy of 23.5 eV, 25.9 eV and 27.8 eV which are associated with Ta 4f_{5/2} and Ta 4f_{7/2} of Ta⁺ in TaN, respectively [174]. A reduction of the intensity for Ta-related peaks after the sulfurization is observed. Since XPS is a surface sensitive technique, this suggests diffusion of elemental Ta into the bulk of the Mo film. In Fig. 3.2b, N 1s core level scan reveals presence of a single peak attributed to Ta 4p_{3/2} at the binding energy of 404.6 eV as well as N 1s peak at 398.1 eV [174] (see Fig. 3.2b). After the sulfurization, N 1s peak shifts to 395.1 eV while no obvious peak is observed for Ta 4p_{3/2}. This suggests a change in the local chemical bonding of N due to the chemical reaction between TaN and S. Similarly, in Fig. 3.2c and 3.2d, sharp peaks for the Mo 3d and S 2p signals appear after sulfurization. The core-level Mo 3d scan of the sulfurized sample reveals the presence of two major peaks at a binding energy of 232.3 eV and 229.1 eV which are attributed to Mo 3d_{3/2} and Mo 3d_{5/2} [175]. S 2p scan shows two clear peaks at a binding energy of 162 eV and 163.1 eV which are associated with S 2p_{3/2} and S 2p_{1/2} in MoS₂ [175]. This substantial increase of Mo related peaks supposes

intermixing of TaN and MoS₂ at the surface of the sample. Intermixing between MoS₂ and IL was also reported in the study of Liu *et al.* [125].

Figure 3.2: XPS analysis of as-deposited and sulfurized 7 nm TaN films deposited over Mo films.

Top view SEM images of Mo films without and with TaN IL before and after sulfurization are presented in Fig. 3.3. Before sulfurization, the Mo has a morphology consisting of short filaments (see Fig. 3.3a), whereas after the sulfurization the surface becomes more granular (see Fig. 3.3b). This may be due to the chemical transformation of Mo to MoS₂. Surface morphology of as-deposited TaN/Mo samples is similar to that of Mo owing to the low thickness of TaN IL (see Fig. 3.3c,e,g). The morphology analysis of the sulfurized samples indicates that TaN passivation enables to mitigate surface modification and MoS₂ formation (see Fig. 3.3d,f). The possible explanation for this is S diffusion blocking properties of TaN ILs. In addition, the surface morphology of the sulfurized sample passivated with 12 nm TaN is apparently different from the rest of the samples (see Fig. 3.3h). This may be associated with the chemical reaction between TaN and S. Moreover, the figure shows a number of discontinuities in the IL which may cause penetration of S and, hence, the reaction between S and underlying Mo.

In order to better understand why TaN IL enables improving electrical conductivity of sulfurized Mo films, ultrathin TaN layers with a thickness of 3 nm, 7 nm and 12 nm were deposited by DC sputtering onto plain SLG substrates. The measured R_{sheet} of the films before and after sulfurization is tabulated in Table 3.2. High R_{sheet} of as-deposited 3 nm TaN film indicates that the film is not continuous. Further increase of the sputtering time caused coalescence of separated TaN islands and a substantial reduction of R_{sheet} to 1.88 k $\Omega/\square$ and 0.638 k $\Omega/\square$ for the 7 nm and 12 nm TaN films, respectively. After sulfurization, the R_{sheet} for the two latter samples increases by four orders of magnitude. Since Mo is not involved in this experiment, the formation of MoS₂ can be ruled out. Instead, this may be explained by the modification of the film composition owing to the incorporation of S and formation of TaN_xS_y.

Table 3.2: Sheet resistance of TaN on glass before and after sulfurization.

	$R_{\text{sheet}}, \Omega/\square$		
	3 nm TaN	7 nm TaN	12 nm TaN
Before sulfurization	$1.1 \cdot 10^8$	1880.4	638.1
After sulfurization at 600°C for 10 min	$1.1 \cdot 10^8$	$1.29 \cdot 10^8$	$5.83 \cdot 10^7$

The above characterization results from the sulfurization of TaN/Mo/SLG samples suggest the following mechanism for partial S blocking by ultrathin TaN (3-12 nm). Depending on the sputtered film thickness, the as-deposited TaN on Mo before sulfurization may be discontinuous. During sulfurization at 600°C, a chemical reaction occurs between the S vapor and TaN. This results in the synthesis of TaN_xS_y and regardless of the initial morphology, the sulfurized TaN becomes discontinuous and consists of islands of TaN_xS_y as a result of this reaction. The formed islands can be clearly observed in Fig. 3.3h. The size of the islands is ranging from few tens of nm to about 100 nm. It can also be seen that these islands are relatively densely packed. The areas of Mo film that are directly underneath the TaN_xS_y are thereby deprived of S and the formation of MoS₂ is inhibited. This can explain why the TOF SIMS S profiles for 3 nm, 7 nm and 12 nm TaN show higher S intensity than the control sample near the surface.

For the exposed Mo between the TaN_xS_y islands, the formation of MoS_2 can occur by the reaction between Mo and S. The diffusion of S into Mo between the TaN_xS_y islands can account for the broad tail in the TOFSIMS S profile and the appearance of sharp peaks in the XPS spectrum for Mo 3d. The pronounced change in the Ta 4f XPS spectrum after sulfurization is also consistent with this chemical reaction interpretation. The surface of TaN/Mo/SLG after sulfurization at 600°C thus consists of TaN_xS_y and MoS_2 phases.

Figure 3.3: Top view SEM images of control Mo films (a) before and (b) after sulfurization, and Mo films coated with (c), (d) 3 nm TaN, (e), (f) 7 nm TaN, (g), (h) 12 nm TaN before and after sulfurization, respectively.

3.3.2 CZTS/TaN/Mo/SLG

Structural properties of sulfurized CZTS film were characterized by a Raman spectroscopy system equipped with 514 nm laser. The penetration depth of the laser beam in the CZTS film is ~ 100 nm [26]. The Raman spectra of CZTS films with TaN IL of different thickness are presented in Fig. 3.4. The major peaks located at 284 cm^{-1} and 335 cm^{-1} are attributed to A vibrational mode of CZTS while the broad peak at 367 cm^{-1} is assigned to the E mode of CZTS [176,177]. Position of the minor peak observed at 345 cm^{-1} is attributed to ZnS secondary phase [178]. Furthermore, an additional peak located at 312 cm^{-1} was observed for the 3 nm TaN sample. This peak can be attributed to SnS_2 secondary phase [179,180]. Wang *et al.* recently reported growth of SnS_2 secondary phase during cooling down process after sulfurization at the surface of CZTS thin films [181]. Both the Raman active ZnS and SnS_2 secondary phases should be situated near the surface of the CZTS layer.

Figure 3.4: Raman spectra of sulfurized CZTS thin films with and without TaN ILs of 3 nm, 7 nm and 12 nm.

X-ray diffraction analysis was carried out to further study the structural properties of the sulfurized CZTS thin films without and with TaN IL (see Fig. 3.5a). Two major peaks located at 28.5° and 47.4° are associated with the (112) and (220) CZTS kesterite planes respectively (JCPDS PDF card # 00-026-0575). In addition, minor peaks observed at 18.3° , 33° and 56.2° are attributed to the (101), (200) and (312) diffractive planes of CZTS, respectively. Crystallites size corresponding to the planes was calculated using Scherrer's equation [84] and presented in Fig. 3.5b.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (3.1)$$

In the above equation, D is the average crystallite size; λ is the X-ray wavelength of 0.15418 nm used for the analysis; β is the full width at its half maximum (FWHM) in radians and θ is the diffraction angle in degrees. In Fig. 3.5b, the crystallite size associated with the (220) planes decreases from 180 nm to 130 nm when TaN thickness is increased from zero to 12 nm. On the other hand, the crystallite size associated with the (112) planes is quite constant at 80 nm. This shows that TaN IL can reduce the crystallite size of CZTS and may increase the amount of grain boundaries in the absorber layer.

Figure 3.5: (a) XRD spectra of sulfurized CZTS thin films with and without TaN ILs of 3 nm, 7 nm and 12 nm (peak associated with (110) diffractive plane of Mo was excluded). (b) Effect of TaN IL thickness on the crystallite size corresponding to (112) and (220) diffractive planes of CZTS.

A broad peak at 15.2° is observed for the control sample. The position of this peak is close to (001) diffractive plane of SnS_2 (JCPDS PDF card # 00-022-0951). Moreover, peaks located at 15° and 30.3° are associated with the (001) and (002) diffractive planes of SnS_2 secondary phase. These peaks are observed only for the samples with 3 nm and 7 nm thick TaN IL while the sample with 12 nm TaN IL does not exhibit SnS_2 peak. The possible explanation for this is suppression of the CZTS decomposition into secondary phases at the back interface owing to the incorporation of thick TaN IL which excludes direct contact between Mo and CZTS. In addition, the peak located at 26.7° is observed for all TaN-based samples. The intensity of this peak increases with TaN thickness. This peak may be attributed to the (002) diffractive plane of Cu_2S (JCPDS PDF card # 01-078-4793). The presence of these secondary phases in CZTS samples deposited on TaN IL is undesirable for photovoltaic device applications because they can lead to reduced FF and PCE. Lattice parameters a and c of CZTS kesterite unit cell derived using (112) and (220) peaks are shown in Table 3.3.

Table 3.3: Lattice parameters of kesterite CZTS unit cell.

Sample	a (nm)	c (nm)	$c/2a$
Control	0.54197	1.08244	0.9986
3 nm TaN	0.54219	1.08156	0.9974
7 nm TaN	0.54219	1.08384	0.9995
12 nm TaN	0.54219	1.08156	0.9974

The effect of TaN IL on the elemental out diffusion at the CZTS/Mo interface was studied using TOF-SIMS system. Fig. 3.6 and 3.7 depict elemental depth profile of Cu, Zn, Sn, S, Mo, Ta, MoS and Na for the as-deposited and sulfurized samples respectively. In Fig. 3.6, as-deposited CZTS thin film exhibit uniform distribution of Cu, Zn, Sn, S and Na. The Ta SIMS profile overlaps with that for MoS in Fig. 3.6b-d and there is an apparent correlation between the thickness of the MoS layer and the TaN thickness. Furthermore, the deposition of TaN IL does not limit Na diffusion into as-grown CZTS film.

Figure 3.6: TOF-SIMS depth elemental profile of Cu, Zn, Sn, S, Mo, Ta, MoS and Na for as-deposited CZTS/Mo/SLG (a) reference sample and samples with TaN ILs of (b) 3 nm, (c) 7 nm, (d) 12 nm.

Fig. 3.7a-d shows that introduction of TaN IL films results in reduced Cu, Zn, Sn and S out diffusion into Mo after sulfurization. Similarly, the TaN IL limits Mo diffusion into CZTS. The Ta and MoS profiles of sulfurized samples confirm the ability of ultrathin TaN films to reduce the thickness of the MoS₂ layer at the interface between CZTS and Mo. The beneficial effect of TaN IL can be seen more clearly from the superposed MoS profiles in Fig. 3.7e. An increase of TaN IL thickness results in a decrease of signal intensity associated with the MoS₂ layer. Thus, 12 nm TaN IL exhibits the best MoS₂ blocking performance. Hence, the sample with 12 nm TaN IL along with the control sample were chosen for STEM-EDX analysis.

Figure 3.7: TOF-SIMS depth elemental profile of Cu, Zn, Sn, S, Mo, Ta, MoS and Na for sulfurized Mo/CZTS (a) reference sample and samples with TaN ILs of (b) 3 nm, (c) 7 nm, (d) 12 nm, (e) enlarged plot of MoS profile and (f) superposed Na diffusion profile for all four samples.

Another important observation from the TOF-SIMS analysis is the loss of uniform distribution of the metallic elements in the CZTS layer after sulfurization when TaN IL is present (see Fig. 3.7b-d). There is a lower concentration of Cu, Zn and S at the surface of the CZTS film and increased concentration of Sn. There are two possible reasons for this. The first is the formation of Sn-related or other secondary phases within CZTS due to the reactivity of TaN towards S as demonstrated in the Raman and XRD characterization. In addition, enhancement of Na diffusion to the surface of CZTS was observed. This can be seen from the superposed profiles in Fig. 3.7f. Since Na easily diffuses, another plausible explanation is that the crystallinity of the CZTS is slightly affected by the TaN IL with more fast diffusion paths such as grain boundaries formed within CZTS. This then leads to the diffusion of Cu, Zn, Sn and S.

STEM-EDX and EELS characterization of the samples was carried out to reveal the effect of TaN IL on the diffusion of S and Mo as well as on the composition of the CZTS layer. The HAADF-STEM images show the overall structure of the control CZTS sample (see Fig. 3.8a) and the sample with a nominal 12 nm thick TaN IL (see Fig. 3.8c). HAADF-STEM contrast of the CZTS layer of the control sample is homogeneous, but there are significant amount of small voids on the whole layer and bigger ones at the interface between CZTS and Mo (see Fig. 3.8a). The average size of the grains is around 200 nm, which can be observed with better contrast from STEM-ABF image (see Fig. 3.8b). Moreover, there is an additional contrast between CZTS and Mo layer. With the introduction of TaN layer (see Fig. 3.8c,d) significant reduction of voids in CZTS as well as at the interface can be seen. Furthermore, the contrast due to the formation of the additional phase with bright contrast, which is not observed for the control sample, can be seen. In order to understand better the chemical composition of the samples, STEM-EELS analysis was implemented.

Figure 3.8: (a,c) High-angle annular dark-field (HAADF) and (b,d) annual bright field (ABF) scanning transmission electron microscopy (STEM) images of sulfurized samples without (a), (b) and with (c), (d) 12 nm TaN IL.

For the control sample, STEM-EELS signal of S L-edge (164 eV) and Mo M-edge (227 eV) were recorded from three different areas: CZTS layer (see Fig. 3.9b, area 1), interface between CZTS and Mo (see Fig. 3.9b, area 2), and Mo layer (see Fig. 3.9b, area 3). Fig. 3.9 (a-b) show the area used for acquisition of the EELS spectral image (SI) and the corresponding Mo and S maps (see Fig. 3.9 c-d). The EELS spectra from the area 2 (see Fig. 3.9b) show the signal of both Mo M-edge and S L-edge. Even though the M₄-edge of Mo overlaps with L₂-edge of S, it is possible to map Mo using two characteristic minor edges at 392 eV and 410 eV (see Fig. 3.9e). Therefore, the area between CZTS and

Mo can be attributed to the formation of ~ 40 nm MoS_2 interfacial layer at the back interface of the control sample. In our earlier study in which a stoichiometric CZTS sputtering target was used [120], a ~ 240 nm and ~ 142 nm thick MoS_2 layer were measured for 650 nm and 550 nm CZTS absorber layer, respectively, at the same sulfurization conditions. This demonstrates the positive effect of the implementation of non-stoichiometric CZTS target on MoS_2 layer formation compared to the stoichiometric one.

Figure 3.9: (a-e) STEM analysis of the control sample. a) Overall HAADF STEM survey image used for acquisition of (b) the HAADF STEM image acquired simultaneously with EELS SI dataset. (c-d) - EELS maps from Mo M-edge and S L-edge respectively. (e) EELS spectra from three different areas specified on the image (b): 1 - CZTS layer, 2 - interface between CZTS and Mo, and 3 - Mo layer. (f-j) STEM analysis of CZTS with a 12 nm TaN IL. (f) Overall HAADF STEM survey image used for acquisition of EELS SI dataset. (g-i) - EELS maps from Mo M-edge, S L-edge and Ta M-edge respectively, (j) - EELS spectra from two different areas specified on the image (f): 1 - CZTS layer, 2 - interface between the CZTS and the Mo layer.

Passivation of the interface with the 12 nm TaN film results in a remarkable reduction of voids at the interface (see Fig. 3.8c-d) which are reported to cause low R_{sh} and high R_s of CZTS solar cells [182,183]. However, deposition of the TaN IL also results in composition change in CZTS film. The HAADF-STEM image of the CZTS/Mo back contact with 12 nm TaN IL after sulfurization is shown in Fig. 3.9f. Next to the image are the elemental composition maps for Mo, S and Ta obtained from the STEM-EELS SI recorded simultaneously with a HAADF-STEM image. In Fig. 3.9f, the Mo layer is shown in white at the bottom of the figure. The region being imaged for the EELS mapping is indicated by the red area. It can be seen that S is not diffused into the Mo layer when TaN IL is continuous. However, the discontinuity of the TaN layer allows the diffusion of S in the Mo layer and results in MoS_2 formation, as shown in Fig. 3.9h. Note that this is consistent with the TaN blocking mechanism discussed in the previous section. In contrast, for the control sample, the layer of MoS_2 is clearly observed. Ta is mainly present at the interface between CZTS and Mo (see Fig. 3.9i). The overall image of CZTS with TaN IL (see Fig. 3.8c) shows the secondary phase with a white contrast present through all CZTS layer. The presence of this phase correlates with the Cu and S EELS maps (see Fig. 3.10f,h,i), indicating that the white contrast in the CZTS layer seen in Fig. 3.8c and 3.8d are secondary phases inside the CZTS. Fig. 3.10 shows the HAADF-STEM images and associated EELS elemental maps for the CZTS surface region for the control sample and the sample with 12nm TaN. Fig. 3.11 shows the HAADF-STEM image and EDX elemental map for the CZTS/Mo control sample. In general, the elemental distribution of Cu, Zn, Sn and S for the control sample is uniform (see Fig. 3.10a-e, Fig. 3.11a-f). However, the analysis also reveals aggregation of Zn for both CZTS/Mo samples without and with TaN IL (see Fig. 3.11, Fig. 3.10j). These observations are consistent with TOFSIMS data on Fig. 3.7.

Figure 3.10: HAADF-STEM images and EELS elemental maps obtained from STEM-SI analysis of the top surface region of sulfurized CZTS for (a-e) the control sample and (f-l) the CZTS solar cell with 12 nm TaN IL. Elemental EELS maps of the regions marked in red in a) and f) are given in b-e and g-l for the CZTS/Mo samples without and with 12 nm TaN IL respectively.

Figure 3.11: HAADF-STEM image (a) and EDX elemental maps of the control CZTS/Mo sample after sulfurization. EDX maps were taken from the full region of the image (a).

For fabrication of large area CZTS/CdS thin film solar cells, it is important to have good adhesion between the CZTS, Mo and SLG. In order to demonstrate the effect of TaN IL on the adhesion of sputter-deposited CZTS/Mo to SLG, a scratch hardness test was performed. The scratch hardness number HS_p was calculated using equation [184]:

$$HS_p = \frac{8P}{\pi w^2} \quad (3.2)$$

where HS_p is the scratch hardness number in GPa, P is the normal force in N, and w is the scratch width in mm. The measured data is tabulated in Table 3.4. Deposition of ultrathin TaN film causes an increase of scratch hardness of sulfurized Mo/CZTS samples from 0.15 GPa to 0.32 GPa when 12 nm TaN IL is inserted. The highest scratch hardness of 2.86 GPa and 1.59 GPa was calculated for 3 nm and 7 nm TaN based samples respectively. Increase of the scratch hardness with the introduction of 3 nm TaN IL can be explained by the suppressed solid state reaction at the interface which may result in less voids. Reduced number of voids may enable an increase of the scratch hardness. However, owing to the incorporation of S into TaN and formation of TaN_xS_y , thickness of the IL is expected to increase significantly as size of S and N atoms is different. This may result in additional stress between Mo and CZTS layers which causes decrease of scratch hardness when 7 nm and 12 nm TaN IL are present. The conversion of TaN into discontinuous TaN_xS_y with island morphology will weaken the adhesion of the IL to the Mo. More TaN_xS_y will be formed with increasing thickness of TaN. Hence the scratch hardness will decrease with increasing TaN thickness. The increased scratch hardness for the samples with TaN suggests that the TaN IL can be beneficial to improve adhesion of CZTS/Mo which will help fabricate large area CZTS solar cells.

Table 3.4: Scratch hardness of sulfurized sputter-deposited CZTS/Mo thin films with TaN IL of different thickness.

TaN thickness, nm	0 (control sample)	3	7	12
Scratch hardness, GPa	0.15	2.86	1.59	0.32

3.4 Summary

The effect of TaN IL on the quality of Mo/CZTS interface and CZTS absorber layer has been studied in detail. Thickness of resistive interfacial MoS₂ layer and secondary phases at the Mo/CZTS interface can be tuned using the non-stoichiometric CZTS target and TaN interfacial engineering. By using the CZTS target, thickness of the MoS₂ can be reduced below 40 nm, whereas incorporation of TaN IL also suppresses MoS₂ formation remarkably.

Sputter deposited TaN films react chemically with S vapor at 600°C to form TaN_xS_{1-x}, thus, suppresses the diffusion of S into Mo significantly. The effect of S diffusion suppression increases with the thickness of TaN IL. Furthermore, the voids in the bulk CZTS and at Mo/CZTS interface are significantly reduced as a result of TaN IL deposition. Moreover, undesirable secondary phase of SnS₂ is also inhibited with the increase of TaN thickness, whereas, the intensity of Cu₂S slightly increases and crystallite size of CZTS is reduced. In addition, enhancement of CZTS/Mo films scratch hardness to SLG substrate as a result of TaN IL deposition is observed.

By integrating TaN passivation and Cu-poor CZTS prepared by sputtering of the quaternary compound target, interfacial reaction at CZTS/Mo interface can be minimized. However, sputtered CZTS solar cell devices with TaN IL were not successfully fabricated. This may be due to detrimental effect of conductive Cu₂S secondary effect causing device shunting. Hence, there is need to use a different IL.

Chapter 4 Sputtered ZnS IL on back contact reaction of sputtered CZTS and solution processed CZCTS

4.1 Introduction

In this chapter, solution-based and co-sputtering approaches are used to synthesize CZCTS and CZTS thin films respectively. Furthermore, interface engineering is applied to improve the back interface of kesterite thin film solar cells. The IL material incorporated into the Mo/kesterite contact is ZnS. As both ZnS and kesterite belong to adamantine family due to tetrahedral coordination of atoms, they exhibit similar crystal structure. Therefore, ZnS may act as a seed layer facilitating growth of kesterite absorber layer. In addition, since Zn and S are both constituents of CZTS, they may be consumed during the formation of CZTS phase. Moreover, large band gap ZnS may be an interesting candidate for formation of kesterite thin film solar cells with back surface field because ZnS can be doped p-type. The main objectives are to understand the effect of this IL on the MoS₂ formation during sulfurization, crystallinity of the absorber layer and photovoltaic properties of kesterite solar cells.

4.2 Experimental details

IL deposition and device fabrication

ZnS IL film (~10 nm) was deposited over ~900 nm Mo coated SLG by RF magnetron sputtering of 99.99% purity 76.2 mm diameter ZnS target. The base pressure and working pressure were $\sim 1 \cdot 10^{-6}$ Torr and $4.2 \cdot 10^{-3}$ Torr, respectively whereas the applied RF sputtering power was 100 W. Some samples were used for solar cell fabrication to study the impact of the IL on structural properties of the CZCTS absorber layer. The remaining samples were subjected to sulfurization in a tube furnace to study the ability of the IL to inhibit MoS₂ formation.

Synthesize method #1

The precursor solution for CZCTS thin films deposition was synthesized by dissolving copper acetate monohydrate (0.38 mol L^{-1}), zinc acetate dihydrate (0.15 mol L^{-1}), cadmium acetate dihydrate (0.1 mol L^{-1}), tin chloride dihydrate (0.2 mol L^{-1}) and thiourea (1.6 mol L^{-1}) in 2-methoxyethanol under continuous stirring for 2 hours at 50°C . Then a few drops of MEA and TEA were added into the solution. The Cd/(Zn+Cd) ratio was 0.4. After sputter deposition of ZnS IL, $\sim 1 \text{ }\mu\text{m}$ thick CZCTS absorber layer was deposited by spin-coating of the precursor solution at 4000 revolutions per minute (rpm) for 20 s followed by drying at 280°C for 2 min. Thereafter, the samples were sulfurized at 600°C for 40 min in mixed atmosphere of elemental S and Ar. After sulfurization, the tube furnace was allowed to cool naturally to room temperature.

Synthesize method #2

Co-sputtering of 76.2 mm diameter ZnS, SnS and Cu targets was used to deposit precursor film for the synthesize of CZTS absorber layer. Sputtering power of 100 W (RF), 33 W (DC) and 16 W (DC) was applied to ZnS, SnS and Cu target for 20 min. Thereafter, the samples were sulfurized at 550°C for 10 min and 40 min in the atmosphere of S and Ar. The furnace was cooled down to the room temperature naturally.

Solar cells fabrication

A CdS buffer layer ($\sim 50 \text{ nm}$) was deposited over the CZCTS and CZTS thin films by chemical bath deposition (CBD) method. The precursor solution is a mixture of 140 ml distilled water, 20 ml water solution of CdSO_4 (0.015 M), 20 ml of 28-30% ammonium hydroxide, 20 ml water solution of thiourea (0.75 M). The deposition process was carried out at 80°C for 8 min under continuous stirring. For sputtered CZTS solar cells 40 nm ZnO layer was deposited over CdS by RF sputtering at 50 W. Transparent conductive 300 nm thick ITO film was deposited at room temperature by RF sputtering of 76.2 mm diameter ITO target at 50 W. This was followed by annealing in Ar at 300°C for 10 min. Individual solar cells were defined by mechanical scratching. Thereafter, front and top contacts were printed using a Ag paste. Active area of solar cell was 0.15 cm^2 . Photo of a typical fabricated solar cell is presented in Fig. 4.1.

Figure 4.1: Photo of typical kesterite solar cells showing Ag back and front contact and scratches. Dimensions of the individual cell are 4 mm x 4 mm.

Characterization methods

Cross sectional SEM analysis was carried out using a JEOL JSM7600F field emission SEM system. XRD, TOF-SIMS, XPS, Raman, four point probe measurement systems used in this study were described in section 3.2. Keithley 2612A source meter and VS-0852 solar simulator based on Xe-lamp was used to measure light current density-voltage characteristics under AM1.5 spectrum and standard light intensity of 100 mW/cm^2 . Prior to the measurement, the solar simulator was calibrated with a certified Si reference solar cell. Bentham PVE 300 system, calibrated using reference Si photodetector, was implemented to record external quantum efficiency spectra of the solar cells. Photovoltaic parameters were calculated using IV Tracer software.

4.3. Results and discussion

4.3.1. ZnS/Mo/SLG

XRD was used to analyze the crystalline structure of the sulfurized samples with and without the IL (Fig. 4.2). The diffraction scan of the control sample revealed the presence of MoS₂ phase owing to the peak located at 29.07° (Fig. 4.2a). This peak is attributed to the (004) diffraction planes of MoS₂ according to JCPDS #00-037-1492. In addition, there is a prominent peak at 40.52° due to the (110) planes of Mo and a minor peak at 73.69° due to the (211) planes of Mo (JCPDS #00-004-0809). In Fig. 4.2b, a peak associated with (111) ZnS diffractive plane was observed at 28.62° (JCPDS #01-071-4763) along with MoS₂ related peak. In addition, the XRD scan revealed a peak located at 21.7° which may be due to the presence of Zn(O,S) phase as a result of oxidation. The XRD data of Fig. 4.2 shows that the ZnS IL is does not suppress the formation of MoS₂ during sulfurization.

Figure 4.2: XRD patterns of sulfurized Mo films (a) without IL, with (b) ZnS IL.

Fig. 4.3 shows measured Raman spectra of the sulfurized Mo sample without and with ZnS IL. Raman peaks located at 380 cm⁻¹ and 406 cm⁻¹ attributable to the E_{2g}¹ and A_{1g} vibrational modes of MoS₂ phase are observed for all samples [11,12]. This indicates that MoS₂ formation has occurred and is consistent with the XRD data. The intensity of the MoS₂ peaks for the ZnS/Mo sample (Fig. 4.3b) was higher compared to the control one. The obtained result may suggest formation of more ordered MoS₂ layer.

Figure 4.3: Raman spectra of Mo thin films without and with ZnS IL after sulfurization.

R_{sheet} of the samples was measured before and after sulfurization. The measured data is presented in Table 4.1. The measured R_{sheet} of the as-deposited samples without and with ZnS IL are $0.76 \, \Omega/\square$ and $1.17 \, \Omega/\square$, respectively. This can be due to the much higher resistivity of ZnS compared to that of Mo. After sulfurization, R_{sheet} of all samples increased owing to the formation of the resistive MoS_2 layer. The measured R_{sheet} of the control sample is $1.62 \, \Omega/\square$. On the other hand, R_{sheet} of the sulfurized ZnS/Mo sample is slightly higher ($1.75 \, \Omega/\square$) than that of control one. The R_{sheet} data in Table 4.1 demonstrate that ZnS IL will add additional series resistance to kesterite solar cell.

Table 4.1: Effect of the ILs on sheet resistance of Mo thin films before and after the sulfurization.

	$R_{\text{sheet}}, \, \Omega/\square$	
	Without IL	ZnS
Before sulfurization	0.76	1.17
After sulfurization at 600°C for 40 min	1.62	1.75

4.3.2. Effect of ZnS IL on CZCTS

SEM was used to examine the cross section morphology of CZCTS/CdS solar cells. Fig. 4.4a presents cross section morphology image of the control CZCTS solar cell. $\sim 0.2 \mu\text{m}$ thick MoS_2 layer at the interface between CZCTS absorber layer and Mo back electrode can be clearly seen. The cross sectional SEM image also shows some voids present at the back interface and between CZCTS crystallites. This can be explained by the evaporation of volatile secondary phases during the sulfurization. On the other hand, no voids are observed for the ZnS IL based sample indicating adequate adhesion of the absorber layer to the back contact (see Fig. 4.4b). Thus, it can be concluded that deployment of ZnS IL can be used to slow down void formation in CZCTS absorber layer. In addition, it can be seen that the CZCTS absorber layer grown on Mo-coated SLG with ZnS IL exhibits crystallites of larger size. This may suggest that ZnS IL facilitates CZCTS grain growth. The possible explanation for this is a similar crystal structure of ZnS and kesterite CZCTS. Therefore, ZnS IL also acts as a seed layer for CZCTS. Moreover, as can be seen in Fig. 4.4b, MoS_2 layer of similar thickness is present at the back interface. Thus, it can be concluded that incorporation of ZnS IL does not cause increase interfacial MoS_2 thickness.

Figure 4.4: Cross sectional SEM images of fabricated CZCTS/CdS solar cells: a) control sample, b) with ZnS IL (voids are marked in red).

The impact of IL on the crystalline structure of CZCTS absorber was studied using XRD.

Fig. 4.5 shows that for the control sample and the sample with IL, the diffraction patterns consist of peaks corresponding to the (002), (101), (110), (112), (200), (220) and (312) planes of CZCTS (PDF card # 00-026-0575) and the (110) planes of Mo (PDF card # 00-004-0809). The peak observed at 27.76° for the sample with ZnS IL may be attributed to the (111) diffraction plane of cubic Cu_2S secondary phase (PDF card # 00-053-0522). The average crystallite size (D) was calculated using the Scherrer formula (equation 3.1). Fig. 4.6 reveals that the crystallite size of CZCTS absorber layer increases for both (112) and (220) related kesterite CZCTS peaks as ZnS IL is inserted.

Figure 4.5: XRD patterns of sulfurized CZCTS thin films without and with ZnS IL.

Figure 4.6: The calculated average size of crystallites related to (112) and (220) diffractive planes of CZCTS.

4.3.3. Characterization of sputtered CdS/CZTS solar cell

Photovoltaic parameters of CZTS/CdS solar cells prepared using synthesis method #2 were studied. In this subsection, the effect of sulfurization time and ZnS IL on the measured PV parameters is investigated. It has been found that the increase of sulfurization time from 10 min to 40 min while maintaining the sulfurization temperature at 550°C significantly improves performance of CZTS/CdS solar cells. The study shows that PCE of solar cells without and with ZnS IL is doubled with the increase of the annealing time (see Table 4.2). The measured light and dark J-V characteristics of the solar cells are given in Fig. 4.7. Light J-V characteristics of CZTS/CdS solar cells prepared at sulfurization time of 10 min demonstrate kink. This can be due to diode ideality factor (A) > 2 [185,186]. Furthermore, all measured PV parameters (V_{oc} , J_{sc} , FF, R_s and R_{sh}) demonstrate improvement as a result of the longer sulfurization time. V_{oc} of the control solar cell increases from 545 mV to 690 mV. Furthermore, it is worth mentioning that standard deviation of V_{oc} is also significantly reduced from 49.8 mV to only 4.9 mV owing to the increase of sulfurization time. The study reveals that the major driver for the PCE improvement is FF. It increases from 25% to over 40% with the increase of sulfurization time for the solar cells without and with ZnS IL. Moreover, the solar cells sulfurized for 10 min show significantly higher R_s and lower R_{sh} relative to the devices sulfurized for 40 min. The possible reasons for this are better crystal quality of CZTS absorber layer, reduced density of defects and reduction of secondary phases in CZTS.

Figure 4.7: (a) Light and (b) dark J-V characteristics of sputtered CZTS/CdS thin film solar cells without and with ZnS IL sulfurized at 550°C for 10 min and 40 min.

Incorporation of ZnS IL at the back interface of CZTS solar cells sulfurized for 10 min causes negligible effect on the overall device performance as PCE increases slightly from 1.4% to 1.43%. Although a slight drop in PCE from 3.02% to 2.91% is observed for CZTS solar cells sulfurized for 40 min, the average PCE of the 10 best control solar cells is slightly higher relative to the devices with ZnS IL. However, it has been found that ZnS IL deposition results in a marked enhancement of V_{oc} from 544.8 mV to 651.3 mV. Furthermore, improvement in V_{oc} from 690.5 mV to 703.8 mV was observed for the devices after 40 min sulfurization. These results suggest that ZnS IL improves the crystallization of CZTS absorber layer where it is more significant for the case of short sulfurization time. On the other hand, measured J_{sc} was lower for the solar cells with ZnS IL. A possible reason for this is a hole blocking effect of a large bandgap ZnS IL at the back interface. Moreover, drop in J_{sc} is much lower for the case of prolonged sulfurization which may suggest that ZnS IL layer is partially consumed during CZTS phase formation.

Table 4.2: Photovoltaic parameters of sputtered CZTS/CdS solar cells without and with ZnS IL.

		V_{oc} , mV	J_{sc} , mAcm^{-2}	FF, %	R_s , Ωcm^2	R_{sh} , Ωcm^2	PCE, %
10 min sulfur.	Ref.	544.8 (568±49.8)	10.25 (8.83±0.81)	25.10 (24.1±1.38)	108.9 (141.7±47.2)	69.4 (80.3±12.4)	1.4 (1.21±0.15)
	ZnS IL	651.3 (646.1±13.2)	8.76 (7.83±0.76)	25.13 (24.39±1.93)	154 (191.9±56.4)	102 (106.4±10.6)	1.43 (1.25±0.22)
40 min sulfur.	Ref.	690.5 (687.4±4.4)	10.62 (10.22±0.59)	41.16 (40.16±1.63)	31.8 (34.5±2.2)	234.1 (235.2±33.3)	3.02 (2.82±0.16)
	ZnS IL	703.8 (698.9±4.9)	10.2 (9.16±0.75)	40.54 (38±1.97)	25.9 (34.2±7.3)	220.5 (224±13.8)	2.91 (2.45±0.33)

4.3.4. Characterization of solution-processed CdS/CZCTS solar cell

Fig. 4.8 shows the TOF-SIMS elemental profile for fabricated CZCTS/CdS solar cells with and without IL. For ease of reference, the approximate location of the various interfaces is annotated at the top of each profile. It can be seen that for Fig. 4.8a,b, the

profile for the metallic elements Cu, Zn, and Sn is quite uniform within the CZCTS layer. For Cd, there is an increase in the SIMS signal intensity near the heterojunction due to the CdS buffer layer. These profiles show that the incorporation of ZnS IL does not have an adverse effect on the composition profile of the absorber. By superposing the extracted Mo and S profiles (see Fig. 4.8c,d), it is found that the peak of the Mo profile is the highest for the reference device compared to the device with ZnS IL. For the S diffusion profile, there is more S in the Mo for the reference device than for the device with the ZnS IL. Therefore, it can be concluded that the ZnS IL enables blocking S diffusion into Mo.

Fig. 4.9 shows representative J-V characteristics of solution-processed CZCTS/CdS solar cells with and without ZnS IL under AM1.5 illumination. The extracted V_{oc} , J_{sc} , FF, R_s , R_{sh} and PCE of the top 10 solar cells without and with ZnS IL are presented in Table 4.3. The reference device has a baseline efficiency of 9.47% with $V_{oc} = 612.6$ mV; $J_{sc} = 24.28$ mAcm⁻² and FF = 63.64%. It can be seen that the incorporation of ZnS IL results in enhancement of device PCE. The CZCTS/CdS device PCE increased from 9.47% to 10.02% due to improvements in V_{oc} , J_{sc} and R_{sh} . The increase in V_{oc} from 612.6 mV to 638.3 mV can be attributed to the improved crystal quality of CZCTS absorber layer shown in subsection 4.3.2. Furthermore, reduced grain boundaries (see Fig. 4.4) and defect density may be a reason for the enhanced J_{sc} from 24.28 mA/cm² to 25 mA/cm². However, the FF decreases due to an increase in R_s . This increase is consistent with the higher R_{sheet} found for ZnS/Mo films after sulfurization shown earlier. Introduction of a energy barrier blocking the charge transfer at the back interface due to the large bandgap of ZnS may be a reason for higher R_s . Thus, by tuning a bandgap, electronic properties and thickness of ZnS IL it may be possible to mitigate the increase in R_s .

Figure 4.8: TOF-SIMS depth elemental profile for (a) control solar cell and device with (b) ZnS IL. Superposition of (c) S and (d) Mo diffusion profiles for the samples without and with ZnS IL.

Figure 4.9: J-V curves for (a) control CZCTS device, solar cell with (b) ZnS IL.

During the light J-V measurement probe contacting the top contact introduces shading which affects the measured J_{sc} . Moreover, deviation in its placing may add to the measurement error of J_{sc} . Therefore, in addition to the data from the best solar cells, table 4.3 also gives the average value and its standard deviation for each measured photovoltaic parameter. Thus, it is useful to analyze the measured data of top 10 solar cells to evaluate the impact of this experimental uncertainty. It can be seen that the difference in PCE and J_{sc} between the best solar cell device with ZnS IL and best reference device is similar to that of the mean values. In addition, the standard deviation for both PCE and J_{sc} is less than this difference. This is also true for other measured photovoltaic parameters demonstrating that the claimed improvement in performance of CZCTS solar cells due to the incorporation of ZnS IL is valid.

Fig. 4.10 presents EQE characteristics of the solar cells without and with ZnS IL. The spectra of the best and second best solar cell devices with ZnS IL are shown to avoid confusion caused by short wavelength detector issue which resulted in upward shift (device #3) and downward shift (device #7) of the recorded spectra at wavelength shorter than 700 nm. On the other hand, the detector used to measure spectral response of the solar cells in the range from 700 nm to 1100 nm did not have this issue. This study shows improvement in overall EQE spectra of the CZCTS solar cells when ZnS IL is present. Moreover, the positive effect of ZnS IL incorporation on the carrier transport in the long wavelength region of the spectra is clearly seen. This can be explained by the improved back interface quality owing to the addition of ZnS IL.

Figure 4.10: EQE spectra of CZCTS solar cells without and with ZnS IL.

Table 4.3: Photovoltaic parameters of solution processed CZCTS/CdS solar cells without and with ZnS IL.

	V_{oc} , mV	J_{sc} , mAcm^{-2}	FF, %	R_s , Ωcm^2	R_{sh} , Ωcm^2	PCE, %
Ref.	612.6 (615.9±3.1)	24.28 (24.06±0.37)	63.64 (61.88±1.24)	1.9 (2.5±0.4)	504 (446±31)	9.47 (9.17±0.2)
ZnS IL	638.3 (631.3±6.1)	25.00 (25.17±0.47)	62.79 (60.69±1.5)	4.9 (5.1±1.3)	799 (619±141)	10.02 (9.64±0.15)

4.4 Summary

Back interface engineering by incorporation of ZnS ultrathin IL has been demonstrated for solution-processed CZCTS/CdS and sputter-deposited CZTS/CdS thin film solar cells. ZnS IL deposited on Mo films resulted in an increase of sheet resistance for the samples measured before and after the sulfurization. Unlike TaN IL, ZnS IL was found to increase the crystallite size of CZCTS absorber layer. In addition, in contrast to TaN IL, incorporation of ZnS IL did not inhibit MoS₂ formation. However, it also did not lead to an increase of MoS₂ thickness. Furthermore, TOF-SIMS study revealed that ZnS IL mitigates S diffusion from CZCTS absorber layer into Mo as TaN IL. Solution-processed CZCTS/CdS solar cells with ZnS IL have demonstrated PCE of 10.02% compared 9.47% of the control device. A negligible effect of ZnS IL on sputtered CZTS/CdS solar cells of lower PCE was observed. ZnS IL caused increase in V_{oc} for both sputtered and solution-processed kesterite solar cells. In addition, the study revealed a significant positive effect of sulfurization time increase from 10 min to 40 min on photovoltaic properties of sputtered CZTS solar cells. It can also be concluded that ZnS IL thickness has to be carefully controlled to reduce its negative impact on series resistance of the solar cells. Furthermore, decrease of the IL bandgap and resistivity may be also beneficial to improve the device performance.

Chapter 5 Sputtered CuO IL on back contact of solution processed CZCTS

5.1 Introduction

In this chapter, the effect of CuO IL thickness on the photovoltaic characteristics of sol-gel derived CZCTS/CdS thin film solar cells is investigated. This IL may react with S and, hence, reduce diffusion of S into Mo. In addition, similar to S in ZnS IL, CuO may also affect diffusion profile of Cu which can cause change in electronic properties of kesterite absorber layer. CuO IL is used to eliminate direct contact between Mo and CZCTS. To the best of our knowledge, Cu based IL were not examined for the application in kesterite solar cells. As an IL material, CuO is interesting because like CZTS it is sustainable and non-toxic. The earth abundance per unit atom of raw element for CuO can be calculated to be 23.05% which is comparable to Si (28.2%). In our previous report [187], a detailed review of CuO as a PV material was carried out. Previously studied IL by this and other groups only block S diffusion and so it is interesting to know if an IL can be found that also serves as a supplementary absorber.

5.2 Experimental details

Device fabrication

Mo-coated SLG substrates were ultrasonically cleaned in soap water, acetone, ethanol and DIW followed by drying in N₂ flow prior to CuO IL sputter-deposition. RF sputtering power of 100 W was applied to 99.99% purity 76.2 mm diameter CuO target to grown 4 nm, 18 nm and 32 nm thick CuO films.

The precursor solution for CZCTS thin film deposition was prepared as described in chapter 4. Furthermore, the experimental details on spin-coating and sulfurization can also be found in section 4.2. This is followed by chemical bath deposition of 60 nm CdS buffer layer. The precursor solution is a mixture of 140 ml distilled water, 20 ml water

solution of CdSO_4 (0.015 M), 23 ml of 28-30% ammonium hydroxide, 20 ml water solution of thiourea (0.75 M). The deposition process was carried out at 80°C for 9 min under continuous stirring. Then RF sputtering power of 50 W was used to deposit 40 nm ZnO and 300 nm ITO layers using the 76.2 mm diameter targets at room temperature. Note, RF sputtering power was increased slowly to reduce the damage to the CdS buffer layer during ZnO deposition. Finally, the samples were subjected to annealing in Ar atmosphere at 300°C for 10 min. Thereafter, solar cells with the active device area of 0.15 cm^2 were defined by mechanical scribing followed by Ag paste printing to make contacts.

Thin film characterization

Absorbance spectra of thin films were measured using Shimadzu UV-3600 spectrophotometer. XRD and XPS characterization systems used in this study were described in section 3.2 whereas the details of SEM system were presented in section 4.2. Raman spectroscopy measurement system equipped with 488 nm laser was used to characterize structural properties of the samples.

Device characterization

Experimental details used for measurement of light and dark J-V characteristics and EQE spectra of solar cells were described in section 4.2. Capacitance-voltage measurements were carried out using Keithley 4200 source meter and HP 4284A system. The short-circuit current/open-circuit voltage method was used to determine carrier lifetime. Transient photovoltage (TPV) characterization of the solar cells was performed at open-circuit voltage conditions under $1\text{ M}\Omega$ resistance with fast LED (480 nm) in the small perturbation regime with the amplitude always $<10\%$ of background voltage. The analysis was carried out under white light bias to produce photovoltage. The exposure to the short LED pulse causes increase in photovoltage while oscilloscope is used to record decay of the signal. Transient photocurrent (TPC) measurement was performed in large perturbation mode at a bias current of 0.8 mA. First, the devices were charged for 25 μs , then the charge was extracted through the external circuit for the next 25 μs . More details

on the characterization methods and schematic diagrams of TPV and TPC measurement setup can be found in [188].

5.3 Results and discussion

5.3.1. CZCTS/CuO/Mo/SLG

X-ray photoelectron spectroscopy was employed to study the surface of as-deposited 32 nm CuO film. As shown in Fig. 5.1a, peaks located at binding energies of 934 eV and 954.4 eV are ascribed to $\text{Cu}2p_{3/2}$ and $\text{Cu}2p_{5/2}$ [189,190]. In addition, two strong Cu^{2+} satellite peaks are present further confirming that Cu is present in an oxidation state of +2. Moreover, the presence of oxygen in the film was confirmed using O1s core-shell by detecting peak located at 531.1 eV [191] (Fig. 5.1b). Thus, it can be concluded that as-deposited IL is CuO.

Figure 5.1: High resolution XPS scan of (a) Cu2p and (b) O1s for as-deposited 32 nm thick CuO film.

The surface of samples without and with CuO IL was investigated after peeling off CZCTS absorber layer. Fig. 5.2a demonstrates presence of S in the control sample owing to the peaks observed at 161.9 eV and 163.1 eV peaks attributed to $\text{S}2p_{3/2}$ and $\text{S}2p_{1/2}$ respectively [85]. Furthermore, S related peaks of comparable intensity are also observed for samples with CuO IL (see Fig. 5.2a). This clearly points to the S blocking effect of

CuO IL layer. Since the diffusion of S into Mo causes formation of resistive MoS₂, presence of CuO IL at the back interface may allow mitigating the negative effect of S diffusion on conductivity of Mo back electrode. Tauc plot of as-deposited 340 nm thick CuO film is given in Fig. 5.2b. It shows that measured direct bandgap of the film is 2 eV.

Figure 5.2: (a) High resolution S2p core-shell scan of the samples without and with CuO IL after peeling off CZCTS absorber layer (C1 means sample with 4 nm CuO IL, C5 – 18 nm CuO IL, C9 – 32 nm CuO IL), (b) Tauc plot for 340 nm thick CuO film deposited on SLG.

Structural properties of the CZCTS thin films deposited on Mo-coated SLG without and with CuO IL after sulfurization were studied using X-ray diffraction (see Fig. 5.3a). Major CZCTS peaks are observed at 28.33° and 47.1° and, hence, ascribed to (112) and (220) diffractive planes of kesterite CZTS (JCPDS PDF card # 00-026-0575). As Cd/(Zn+Cd) ration in CZCTS film is 0.4, there is ~0.2° shift to lower 2θ degree for CZCTS film compared to Cd-free CZTS mentioned in the PDF card. This is explained by the expansion of CZCTS unit cell owing to the substitution of Zn by Cd of larger size [24]. In addition, a number of minor peaks attributed to CZCTS are observed. These are peaks related to (002), (101), (110), (103), (220), (221) and (312) diffractive planes of kesterite CZCTS. On the other hand, no peaks associated with Cu₂S, SnS₂ and ZnS secondary phases were detected using the technique for the samples without and with CuO IL.

Fig. 5.3b presents an enlarged view of (112) kesterite CZCTS peak. In addition to the main peak, there is a side peak which is due to the tetragonal peak splitting effect [26].

This effect is caused by a structure-superstructure relationship of the tetragonal unit cell of the kesterite and more symmetrical cubic spharelite unit cell of ZnS. The peaks shift to higher 2θ angles slightly when 4 nm and 18 nm thick CuO is incorporated. In contrast, when 32 nm thick CuO IL is present at the interface between CZCTS absorber layer and Mo back contact, the peak demonstrates a slight shift to the lower 2θ angle. The possible explanation for the observed effects is that CuO IL affects elemental diffusion profiles of Zn and Cd in CZCTS absorber layer and, hence, affects cation substitution there. Moreover, this explanation is supported by our earlier study [192]. Furthermore, Scherrer equation was applied to calculate crystallite size of CZCTS and the obtained data is tabulated in Table 5.1. It has been found that the size of CZCTS crystallites reduces when CuO IL is present. The control sample is characterized by the crystallite size of 107 nm, whereas C1 and C9 samples exhibit crystallite size of 81 nm and 78 nm, respectively. In addition, for a tetragonal crystalline material such as CZTS, the Bragg equation can be written in terms of the Miller indices (hkl) as [193]:

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2) + \frac{\lambda^2}{4c^2} l^2 \quad (5.1)$$

In the above equation, a and c are the lattice parameters and λ is the wavelength of the X-ray source. For the ($hk0$) planes, equation 1 simplifies to:

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2) \quad (5.2)$$

Hence for the present devices, the (220) peak can be used to determine the lattice parameter a . Once a is determined, c can be determined from the Bragg angle for the (112) plane and back substitution by using:

$$\frac{\lambda^2}{4c^2} l^2 = \sin^2 \theta - \frac{\lambda^2}{4a^2} (h^2 + k^2) \quad (5.3)$$

By using this method, the lattice parameters a and c derived from the (112) peak at $2\theta \sim 28.33^\circ$ for samples without and with CuO IL are calculated and shown in Table 5.1. The observed change in size of the unit is an evidence of the cation substitution which could be caused by the modification of elemental diffusion profile as mentioned earlier.

Figure 5.3: (a) XRD analysis of CZCTS/Mo thin films without and with CuO IL, (b) high resolution scan of (112) kesterite CZCTS peak.

Table 5.1: Calculated crystallite size of CZCTS and unit cell parameters a and c .

	Ref.	C1	C5	C9
Crystallite size (nm)	107.12	80.76	106.46	77.63
a (nm)	0.5457	0.5457	0.5453	0.546
c (nm)	1.09	1.088	1.087	1.09

Raman spectroscopy analysis was also carried out to characterize crystal quality of the CZCTS films and to confirm phase purity. In Fig. 5.4 Raman spectrum of the control sample and sample C1 shows three optically active Raman modes. These includes a major peak located at 336 cm^{-1} which is attributed to A vibrational mode and minor peaks at 287 cm^{-1} and 368 cm^{-1} related to A and E vibrational modes. These observed Raman shift of these peaks are very similar to the reported values for CZTS [101]. Although change in FWHM of the major A peak for the control and C1 samples is negligible, there is a marked increase of it for the 18 nm and 32 nm thick CuO IL. This clearly points at the increased structural disorder of CZCTS layer when thick CuO IL is present at the interface between CZCTS and Mo. Furthermore, it has been noticed the peak shifts to lower wavenumber when CuO IL is incorporated. One possible reason for this is the

incorporation of CuO IL at the back interface affects stress in CZCTS absorber layer. This is also supported by the change of CZCTS unit cell parameters (see Table 5.1).

Figure 5.4: Raman spectroscopy characterization of CZCTS/Mo thin films without and with CuO IL.

5.3.2. CdS/CZCTS solar cell characterization

Cross-section of CZCTS thin film solar cells without and with CuO ILs was studied with FESEM. The study of the control sample reveals that voids are present at the interface between CZCTS absorber layer and Mo back electrode. Furthermore, the voids can also be observed between CZCTS crystallites at the bottom portion of the absorber layer. It is explained by the evaporation of volatile secondary phases which are the product of a solid state reaction at the back interface between Mo and CZCTS. On the other hand, Fig. 5.5b-d demonstrate that incorporation of CuO IL reduces voids at the interface and between CZCTS crystallites in the bottom part of the absorber layer. The observed effect is more pronounced for samples with 18 nm and 32 nm CuO ILs. This suggests that the CuO IL effectively mitigates the reaction at the back interface as CuO thickness increases. There are two explanations for this effect. First, CuO IL eliminates direct contact between CZCTS and Mo. Second, CuO IL limits S diffusion into Mo causing suppression of the undesirable solid state reaction at the interface.

Figure 5.5: Cross-section SEM image of CZCTS solar cells of (a) control device and with (b) 4 nm CuO IL, (c) 18 nm CuO IL, (d) 32 nm CuO IL.

Light J-V characteristics of CZCTS solar cells without and with CuO IL were recorded to study the effect of CuO IL incorporation on photovoltaic properties of the devices. The dark and light J-V characteristics measured under the standard illumination conditions of 1 sun AM1.5 are presented in Fig. 5.6a. The photovoltaic parameters of the solar cells are given in table 5.2. 10 solar cells from each batch of different CuO IL thickness were tested. The photovoltaic parameters of solar cell with the highest PCE from each batch are shown together with the the average value and standard deviation. The best reference device exhibits V_{oc} of 613 mV, J_{sc} of 25.28 mA/cm², FF of 64.69% resulting in PCE of 10.03%. On the other hand, CZCTS solar cell with 4 nm CuO IL demonstrates the improvement of the photovoltaic performance and reaches PCE of 10.77%. This is close to PCE of the record certified efficiency for pure sulfide CZTS solar cell (11%) [19]. The enhancement of the device performance is mostly associated with the boost of J_{sc} by 7% from 25.28 mA/cm² to 27.11 mA/cm² whereas the change of V_{oc} and FF is almost negligible.

Figure 5.6: (a) Light and dark J-V characteristics, (b) EQE spectra, (c) normalized EQE spectra, (d) plot of the first derivative of EQE versus photon energy for CZCTS solar cells without and with CuO IL.

Table 5.2: Summarized photovoltaic parameters of CZCTS solar cells without and with CuO IL (average value and standard deviation of the measured parameters are mentioned in parentheses).

	V_{oc} , mV	J_{sc} , mA/cm ²	FF, %	R_s , Ω .cm ²	R_{sh} , Ω .cm ²	PCE, %
Ref.	613 (609.1±11.1)	25.28 (25.21±0.29)	64.69 (59±4.9)	2.5 (3.5 ± 1.4)	562.2 (359.8±134.4)	10.03 (9.07±0.87)
C1	615.7 (606.6±10)	27.11 (26.57±0.6)	64.52 (58.48±5.3 8)	2.6 (4.1 ± 1.9)	460.1 (382.4±118.7)	10.77 (9.42±0.91)
C5	592.3 (597.2±17.5)	28.46 (28.16±0.68)	61.59 (55.81±3.6 2)	3 (4.1 ± 0.9)	425.4 (323±115.5)	10.38 (9.39±0.67)
C9	561.5 (564.6±24.5)	28.05 (28.22±1.18)	58.7 (55.6±2.8)	2.4 (3.7 ± 2)	273.96 (248±70.6)	9.25 (8.84±0.27)

J_{sc} is further increased to its maximum value of 28.46 mA/cm^2 when 18 nm CuO IL is present at the back interface. Note that the solar cell with the highest PCE in a batch may not have the highest J_{sc} . Thus, the device shows ~13% increment in J_{sc} compared to the reference solar cell. However, deposition of 18 nm CuO IL also results in a decrease of PCE to 10.4% as both V_{oc} and FF drop to 592.3 mV and 61.59% respectively. The decrease in FF is due to reduction in shunt resistance. Further increase of CuO IL thickness up to 32 nm leads not only to lower V_{oc} and FF of 561.5 mV and 58.7% respectively but also to a slight decrease in J_{sc} . The decrease in J_{sc} may be due to the back contact blocking effect to be shown below. This results in a significant drop of PCE to 9.25%.

Increase of CuO IL thickness was found to decrease R_{sh} of the solar cells. The possible reason for this is reduction of CZCTS absorber layer crystallinity with the increase of CuO IL thickness as shown in table 5.1. On the other hand, incorporation of CuO IL showed negligible effect on R_s in contrast to ZnS IL (see Chapter 4). Therefore, it may be concluded that CuO IL does not introduce an additional energy barrier limiting carrier transport at the back interface unlike ZnS IL.

As discussed previously in Chapter 4, probe contact shading may affect the measured J_{sc} . Therefore, the photovoltaic parameters of 10 solar cells from each batch were measured. It has been found that the mean PCE values of all solar cells are consistent with the measured results of the best devices. In addition, the standard deviation of PCE value decrease with increasing CuO IL thickness. Moreover, it has been noted that the PCE standard deviation of the reference CZCTS solar cells is larger compared with the solution-processed CZCTS solar cells without ZnS IL presented in Chapter 4. This is due to the increased standard deviation in V_{oc} and FF. The observed effects can be due to the more contaminated surface of the Mo coated SLG substrates purchased from the vendor, Note: prior to CZCTS thin film deposition, the substrates were ultrasonically cleaned. In contrast, in Chapter 4 Mo thin films were deposited by DC sputtering over ultrasonically cleaned plain SLG substrates and quickly transferred for CZCTS thin film deposition without any additional cleaning.

Method of Hegedus and Shafarman [169] was used to extract the single diode equivalent circuit parameters of CZCTS solar cells. By plotting dJ/dV vs V , shunt conductance (G)

was determined while diode ideality factor (A) and R_s were extracted from a plot of dV/dJ vs $1/(J+J_{sc})$. In addition, using plot of $(J+J_{sc}-GV)$ vs $(V-RJ)$ diode reverse saturation current density (J_0) was determined. Fig. 5.7 presents results for C9 solar cell. From the dark data ($J_{sc}=0$), $G = 0.086 \text{ mS.cm}^{-2}$, $R_s = 4.1 \text{ } \Omega.\text{cm}^2$, $A = 1.99$ and $J_0 = 2 \cdot 10^{-5} \text{ mA/cm}^2$. Dark J-V characteristics were used for the parameters extraction to avoid noise signal.

The values of R_s deduced using this method from dark J-V and calculated using IV Tracer software from light J-V (see Table 5.2) are relatively similar compared with difference between G and R_{sh} . R_s of $2.4 \text{ } \Omega.\text{cm}^2$ extracted from light J-V characteristic is lower compared to R_s of $4.1 \text{ } \Omega.\text{cm}^2$ deduced from the dark J-V curve. Similarly, R_{sh} of the C9 solar cell derived from light J-V curve ($274 \text{ } \Omega.\text{cm}^2$) is lower relative to G of 0.086 mS.cm^{-2} (R_s of $11628 \text{ } \Omega.\text{cm}^2$) extracted from dark J-V curve. The observed decrease of the dark resistances can be explained by the increased density of charge carriers in CZCTS absorber layer due to the illumination.

Nevertheless, the study shows that there is voltage dependence for both photocurrent and the device conductance. This can be due to two reasons: (i) bias voltage dependent device quantum efficiency and (ii) presence of a blocking contact that limit majority charge collection. The cross-over of dark and light J-V curves (see Fig. 5.6a) for CZCTS solar cells points to the presence of blocking contact. The latter can be due to the energy barrier at the back contact according to the model of Niemegeers and Burgelman [194]. Moreover, the back contact energy barrier is larger for the solar cells with the crossover located closer to the voltage axis [101]. By analyzing the data presented in Fig. 5.6a, it can be concluded that performance of reference and C1 devices is more affected by the back contact blocking energy barrier. The back contact is improved for C5 solar cell. However, degradation is observed for the sample with the thickest CuO IL as back contact barrier again increases. Thus, it can be concluded that collection efficiency of majority charge carriers can be improved when CuO IL of optimized thickness is present at back interface through reduction of the back contact blocking energy barrier.

Since J_{sc} is a major driver for the PCE improvement, external quantum efficiency spectra were measured to study the impact of CuO IL thickness on spectral response and carrier transport of the CZCTS solar cells (see Fig. 5.6b,c). Fig. 5.6b shows that the recorded spectra correlate with measured J_{sc} for the analyzed solar cells. In addition, it has been

found that absorption edge shifts slightly to the longer wavelength with the increase of CuO thickness. It can be attributed to the reduction of the bandgap from 1.39 eV to 1.37 eV when the thickness of CuO IL increases from 0 to 32 nm (see Fig. 5.6d and table 5.3).

Table 5.3: Bandgap of the absorber layers extracted from EQE spectra and V_{oc} deficit of the solar cells.

	Ref.	C1	C5	C9
Bandgap, eV	1.39	1.39	1.38	1.37
V_{oc} deficit, mV	0.777	0.774	0.788	0.809

Figure 5.7: Characterization of C9 solar cell: (a) light and dark J-V curves, (b) shunt conductance, (c) series resistance and diode ideality factor (dark J-V data were used to calculate the parameters), (d) $\log(J+J_{sc}-GV)$ (dark J-V data were used to calculate reverse saturation current density).

Fig. 5.6c presents normalized EQE spectra for the solar cells without and with CuO IL of different thickness. The measured data reveal that charge carrier collection in the wavelength range from 550 nm to 900 nm improves steadily with CuO incorporation till the IL reaches a thickness of 18 nm. This may be due to fewer voids and better back interface quality, as CuO IL is inserted. For C9 sample, however, there is a distinct degradation of the carrier collection in the above mentioned wavelength range. The explanation for this is the existence of a blocking back contact as demonstrated earlier by the crossover study of the dark and light J-V curves. Moreover, insertion of CuO IL at the back interface cause change in spectra response in the range from 380 nm to 530 nm. This spectral range is mostly associated with the absorption by CdS buffer layer. It can be seen that spectral response of the solar cells in the range improves with CuO IL thickness (see Fig. 5.6c). Thus, it may be suggested that incorporation of CuO IL affects top surface morphology of the absorber layer and, hence, impacts CdS growth during the chemical bath deposition process. Nevertheless, improvement in overall EQE is more significant than due to better charge collection (see Fig. 5.6b).

TPV and TPC measurements were carried out to study the effect of CuO IL thickness on the charge transport and recombination in CZCTS solar cells (see Fig. 5.8a,b). The fastest TPV decay time of 22.72 μs at a bias of 0.3 V was recorded for the reference solar cell. It increases slightly to 24.32 μs and 34.58 μs for C1 and C5 devices. Moreover, there is a significant improvement in TPV decay time for C9 solar cell, as it demonstrate the longest decay time of 66.95 μs . As can be seen in Fig. 5.8b, the TPV results correlate well with TPC characteristics. Therefore, increase of CuO IL thickness enables to enhance decay time. The longer decay time can be explained by the reduced recombination of the charge carriers in solar cell. Possible reasons for the improved quality of the back interface are (i) reduced density of defects, (ii) suppressed solid state reaction, (iii) suppressed formation of secondary phases at the interface.

Figure 5.8: Comparison of (a) lifetime decay recorded at bias of 0.3V using transient photovoltage, (b) lifetime decay recorded at bias of 0.8mA using transient photocurrent.

In order to better understand the nature of overall EQE improvement, capacitance-voltage analysis was carried out. The study reveals a drop in space charge density (N_{cv}) and increases of depletion width when the thickness of CuO IL is increased (see Fig. 5.9a). The calculated width of depletion region for the control samples is 60 nm, whereas it increases to 87 nm, 105 nm and 125 nm for C1, C5 and C9 samples respectively. A possible explanation for the effect is the modification of Cu diffusion profile owing to the presence of CuO ILs. Cu-based IL may mitigate the diffusion of elemental Cu in Mo and, hence, reduce the density of copper vacancies (V_{Cu}) within CZCTS absorber layer. Since V_{Cu} are the shallow acceptors with the lowest formation energy of 0.02 eV in CZTS [33], the density of these defects may be crucial for the major carrier density in p-type CZCTS. Moreover, Fig. 5.9b shows that built-in voltage (V_{bi}) tends to decrease with the increase of CuO thickness. This may be due to reduced N_{cv} .

Light J-V characteristics of CZCTS/CdS solar cells without and with CuO IL were measured under illumination intensities ranging from 0.12 Sun to 2.3 Sun 5 months after the device fabrication (see Fig. 5.10a,c,e,g). The solar cells were stored in a laboratory dry box in dark. All solar cells demonstrate increase in V_{oc} and J_{sc} with the illumination intensity (See Fig. 5.10b,d,f,h). FF of the control device increases in the range from 0.12 to 1 Sun, then saturates and later decreases slightly. The maximum FF for C1 and C5 solar

cells is observed in the range from 0.25 Sun to 0.75 Sun. In contrast, FF of C9 solar cell decreases from its initial maximum at low illumination intensity of 0.12 Sun.

Figure 5.9: C-V characterization of CZCTS solar cells without and with CuO IL (a) estimation of depletion width, (b) extraction of built-in voltage.

Figure 5.11 presents the PCE of these CZCTS solar cells vs illumination intensity. It can be seen that PCE of the control device increases with illumination intensity and approaches a limiting value of 7.25% at 2.3 Sun. Furthermore, PCE of the control device measured under the illumination of 1 Sun drops from 10% to 7.06%. This can be attributed to the effect of aging. The device performance degrades due to the drop in FF from 64.69% to only 53.1% and decrease in V_{oc} from 613 mV to 543 mV. On the other hand, change of J_{sc} from 25.28 mA/cm² to 24.49 mA/cm² is less significant than that of FF and V_{oc} . A possible explanation for the drop in V_{oc} and FF is a modification of the back and front interfaces due to the solid state reaction as a result of aging.

Figure 5.10: Light J-V characteristics and photovoltaic parameters measured under various illumination intensity of (a, b) control device, (c, d) C1, (e, f) C5, (g, h) C9 solar cells (the measurements were carried out 5 months after the device fabrication).

Figure 5.11: PCE of CZCTS solar cells measured under various illumination (the measurements were carried out 5 months after the device fabrication).

In addition, the study reveals the positive effect of CuO IL incorporation on long term stability of CZCTS solar cells. As the thickness of CuO IL increases, CZCTS solar cells demonstrate less drop in PCE with time at 1 Sun. Moreover, C9 solar cell even shows increase in PCE from 9.25% to 9.88% as a result of the aging. This can be seen by comparing Fig. 5.11 and table 5.2. It is worth mentioning that C9 solar cell is the only device which does not show a drop in FF with time. Furthermore, the solar cell with 32 nm CuO IL shows the smallest drop in V_{oc} from 561.5 mV to 529 mV with time. Thus, it may be concluded that the incorporation of the CuO IL helps to slow down changes at back interface of CZCTS solar cells.

5.4 Summary

Insertion of nanoscale CuO IL at the Mo back interface of CZCTS/CdS devices enabled tuning of the crystal quality of CZCTS thin films. In contrast to TaN IL, incorporation of CuO IL did not cause secondary phases formation. Like both TaN IL and ZnS IL, CuO IL was found to reduce voids at the interface and in the bottom portion of the absorber layer. The effect of CuO IL thickness on photovoltaic properties of CZCTS solar cells

was studied in detail. Incorporation of 4 nm thick CuO IL enabled to improve device performance from 10 to 10.8% due to increase in J_{sc} whereas ZnS IL resulted in increase of V_{oc} and J_{sc} . In addition, incorporation of CuO IL resulted in a marked enhancement of J_{sc} when 18 nm CuO IL is present. When the CuO IL thickness is optimized, carrier transport is enhanced in the long wavelength region. The similar effect was also observed for CZCTS solar cells with ZnS IL. Besides, it has been found that space charge density (N_{cv}) decreases as the thickness of CuO IL increases. This enabled to expand depletion width and facilitate charge collection. In addition, it has been found that incorporation of CuO IL allows to boost long term stability of CZCTS solar cells. Although PCE of the control devices degraded with time owing to decrease in FF and V_{oc} , insertion of CuO IL helped to slow down the negative effect of aging on the device performance. Insertion of 32 nm CuO even allowed to boost PCE of the solar cell from 9.25% to 9.88% over a period of 5 months.

Chapter 6 Effect of Mo incorporation on sputtered CZTS/CdS devices

6.1 Introduction

The use of quaternary compound CZTS target and a target containing dopant cations may provide a facile control over composition and distribution of the dopants. Sapeli *et al.* investigated the effect of Cr doping on the properties of CZTS thin films prepared by co-sputtering of CZTS and Cr targets [195]. However, Cr was found to adversely affect the crystallization of CZTS and cubic ZnCr_2S_4 secondary phase was formed instead.

In our previous work [120], the effect of Mo out diffusion from Mo back contact into sputtered CZTS absorber layer during high temperature sulfurization was studied. It has been found that Mo out diffusion has a significant impact on the solar cell performance improving both R_s and R_{sh} . To further study the effect of Mo, fabrication of Mo incorporated CZTS thin film solar cells prepared by co-sputtering of Mo and Cu-poor CZTS targets is demonstrated. Mo is also considered because it has oxidation state +4. Therefore, it is possible that Mo substitute Sn in CZTS and reduce V_{oc} deficit. Moreover, effective ionic radii of Mo in halides and chalcogenides range from 0.041-0.073 nm depending on oxidation state and coordination number [198]. When incorporated into the CZTS lattice, Mo may also be effective as a dopant for CZTS. This chapter reports a comprehensive study of the effect of Mo incorporation on the photovoltaic properties of CZTS thin film solar cells.

6.2 Experimental details

Mo-incorporated CZTS solar cell fabrication

SLG substrates (20 mm x 20 mm x 1.1 mm) were cleaned using soapy water and ultrasonication in acetone, ethanol and deionized water prior to Mo sputter deposition. The SLG substrates were dried in a high purity N_2 flow before loading into the sputtering

chamber. Mo thin films were deposited using a Denton Discovery 18 magnetron sputtering system. A 99.95% purity 76.2 mm Mo target (ALB Materials) was used to deposit ~900 nm thick Mo films. Thereafter, Mo-rich CZTS absorber layer was deposited by co-sputtering of a 99.95% purity 76.2 mm Cu-poor CZTS target ($\text{Cu}_{1.69}\text{ZnSnS}_4$, ALB Materials) and the Mo target. The sputtering chamber was evacuated using a turbomolecular pump to a base pressure of about 8×10^{-5} Pa. Then, high purity Ar gas was introduced into the chamber to maintain a working pressure of 0.48 Pa during the deposition process. A sputtering power of 100 W was applied to the RF cathode for the Cu poor CZTS target whereas Mo target was sputtered at a DC power of 5 W, 10 W and 15 W to vary the Mo content in the CZTS thin films. A list of all four samples (B1-B4) and the associated sputter deposition parameters is tabulated in Table 6.1. The typical thickness of the co-sputtered as-deposited absorber layer before sulfurization is ~900 nm. Note that all samples do not have any intermediate layer inserted between CZTS and Mo. Sulfurization of the Mo-incorporated CZTS samples was carried out in a two-zone tube furnace. The CZTS samples were sulfurized at 600°C for 10 min while sulfur powder was heated at 200°C during the processing. The temperature ramping up rate was 19.2°C/min whereas, after sulfurization, the samples were cooled down naturally. Thereafter the sulfurization, a 50 nm CdS film was grown using CBD method over the CZTS absorber layer to form the CdS/CZTS heterojunction. This is followed by sputter deposition of 300 nm thick ITO film using 76.2 mm ITO target. After thermal annealing treatment in Ar ambient was carried out at 300°C for 10 min, individual devices were defined by mechanical scratching. Finally, top contacts were prepared by the printing of Ag paste. Thus, solar cell devices with an active area of 0.15 cm² were formed.

Table 6.1: Sputter deposition parameters of Mo incorporated CZTS thin films.

Sample	CZTS RF sputtering	Mo DC sputtering
	power (W)	power (W)
B1	100	0
B2	100	5
B3	100	10
B4	100	15

Device characterization

Experimental details used for measurement of light/dark J-V characteristics and EQE spectra of solar cells were described in section 4.2 whereas the details for C-V measurements were given in section 5.2.

CZTS film characterization

Cross-section scanning electron microscopy images were obtained using a JEOL JSM7600F FESEM equipped with EDS system. Excitation voltage of 20 KV was used for the EDS analysis. In addition, JEOL JEM-2100F STEM was used to study cross-section of the solar cells. XRD, TOF-SIMS, XPS and four point probe measurement systems used in this study were described in section 3.2 whereas details about spectrophotometry measurement system were presented in section 5.2. Masses of the analyzed ions in TOF-SIMS analysis were as follows: Na (22.9901), S (31.9721), Cu (62.9299), Zn (63.9282), Mo (91.9059), Sn (119.9017), In (112.9505), O (15.9948), Cd (113.9018). The thickness of the CZTS films was measured using a surface profiler.

6.3. Results and discussion

Fig. 6.1a shows the cross sectional FESEM images of sample B1 deposited on SLG substrate after sulfurization. As shown, sample B1 (Fig. 6.1a) is polycrystalline with a thickness of ~ 800 nm and there is significant surface roughness. This morphology is different from the co-sputtered samples B2-B4 for which the cross sectional images after sulfurization show two distinct polycrystalline sub-layers (see Fig. 6.1b for sample B2). The upper sub-layer of B2-B4 exhibits a larger grain size and is slightly thinner than the lower sub-layer with finer grains. Fig. 6.1c and 6.1d show the cross sectional FESEM images of sample B4 before and after sulfurization. It can be seen clearly that immediately after sputtering, there is only one homogeneous layer. This shows that co-sputtering of CZTS and Mo cannot result in a uniform Mo doped CZTS layer after sulfurization. Instead, the co-sputtered Mo seems to inhibit the grain growth of CZTS causing a reduction in grain size and an increase in grain boundaries. The grain boundaries provide fast diffusion pathways for Mo either during sputtering or sulfurization so that more Mo

is present in the lower part of the film. This should be especially significant for samples B3 and B4 where higher DC sputtering power results in more energetic Mo ions. As shown in the next section, the lower concentration of Mo in the upper sub-layer of B2-B4 then results in larger grain size.

Figure 6.1: Cross-section SEM images of Mo-incorporated CZTS thin films deposited on SLG for (a) B1 after sulfurization, (b) B2 after sulfurization, (c) B4 before sulfurization and (d) B4 after sulfurization.

In order to verify this hypothesis, EDS was carried out for samples B1-B4. The compositional data for Cu, Zn, Sn and S in at% are tabulated in Table 6.2. For samples B2-B4, two points at the upper and lower sub-layers are measured by EDS. (The EDS system is not capable of performing line scans.) Since the EDS detector of the FESEM is not capable of detecting the Mo K edge signal (17.44 keV) and the Mo L edge overlaps

with the S K edge signal [125], the S concentration as shown in Table 6.2 for samples B2-B4 is actually a combined concentration of S and Mo. The EDS data for the CZTS sample B1 shows that the composition is not uniform with the upper part of the film having a lower concentration of S than the lower part. On the other hand, the $[\text{Cu}]/([\text{Zn}]+[\text{Sn}])$ ratio for the upper part of the film is higher than the lower part. For comparison, the $[\text{Cu}]/([\text{Zn}]+[\text{Sn}])$ ratio for the sputtering target is 0.845. This non-uniform composition may be due to the sulfurization process and possible loss of S in the form of volatile sulfides. For the co-sputtered samples B2, B3 and B4, the S composition measured at both the lower and upper part of the film is significantly higher than the corresponding part of B1. This is indirect evidence that Mo should have been incorporated into CZTS because the same compound sputtering target and sulfurization conditions have been used to prepare these two samples. It is also probable that more Mo is present in the lower part of the film than at the upper part. However, this can only be confirmed by SIMS profiling as will be discussed later. As with sample B1, the $[\text{Cu}]/([\text{Zn}]+[\text{Sn}])$ ratio for the upper part of sample B2 is higher than the lower part. However, for sample B3, the $[\text{Cu}]/([\text{Zn}]+[\text{Sn}])$ ratio is almost the same for the upper and lower part. This suggests that the Cu distribution becomes more uniform as the amount of Mo incorporated increases. For sample B4, there is more variation in the $[\text{Cu}]/([\text{Zn}]+[\text{Sn}])$ for both the upper and lower part of the sample. Table 6.2 also shows the $[\text{Sn}]/[\text{Zn}]$ ratio for these samples. For samples B2 and B3, the $[\text{Sn}]/[\text{Zn}]$ ratio are higher than that of B1 in both the upper and lower part of the film. This indicates loss of Zn as Mo is incorporated into CZTS. For sample B4, the $[\text{Sn}]/[\text{Zn}]$ ratio again shows greater variation than B2 and B3.

Cross-sectional FESEM images of CZTS/CdS thin film solar cells (B1-B4) are shown in Fig. 6.2. For the control device B1 (Fig. 6.2a), the CZTS layer shows some small grains near the CZTS/CdS interface. The morphology of the absorber layer of Mo-incorporated CZTS solar cells (B2, B3 and B4) resembles that shown in Fig. 6.2b-d and consists of 2 sub-layers with different degree of crystallinity. The upper sub-layer of the absorber (~500 nm) consists of larger CZTS crystallites whereas the bottom sub-layer is made up of smaller grain CZTS. The measured thickness of the bottom layer increases with Mo

Table 6.2: EDS compositional analysis of sulfurized Mo incorporated CZTS deposited on the SLG substrate.

Sample	Probed area	Elements					
		Cu at. %	Zn at. %	Sn at. %	S at. %	[Cu]/ ([Zn]+[Sn])	[Sn]/[Zn]
B1	Center	17.05	13.94	16.15	52.87	0.57	1.16
B2	Large grain	24	9.61	13.5	52.89	1.04	1.4
	sub-layer						
	Fine grain	12.94	9.46	17.63	60.42	0.48	1.86
	sub-layer						
B3	Large grain	19.5	7.24	12.96	60.3	0.97	1.79
	sub-layer						
	Fine grain	18.78	7.19	13.17	60.86	0.92	1.83
	sub-layer						
B4	Large grain	23.71	10.87	11.01	54.41	1.08	1.01
	sub-layer						
	Fine grain	15.07	8.14	11.58	65.21	0.76	1.42
	sub-layer						

content from ~630 nm for B2 to ~680 nm and ~725 nm for B3 and B4 samples respectively (Fig. 6.2b-d). This shows that co-sputtering of Mo and CZTS onto Mo-coated SLG results in a similar film morphology. Interestingly, this morphology has also been reported for CZTS films deposited by solution processed nanocrystal ink [196]. By using scanning Kelvin probe microscopy and conductive atomic force microscopy, J.B. Li *et al.* have shown that grain boundaries in CZTS have similar electrical effects as in the chalcopyrite semiconductors [197]. Grain boundaries are beneficial to photovoltaic performance because the positive surface potential at the grain boundaries attracts electrons and the network of grain boundaries facilitates minority carrier collection [197].

Figure 6.2: Cross-section SEM images of CZTS solar cells (a) B1, (b) B2, (c) B3, (d) B4.

X-ray diffraction was used to characterize the crystal quality of CZTS thin films deposited on Mo-coated SLG after Mo incorporation and sulfurization (Fig. 6.3a). The two major peaks observed are attributed to the (112) and (220) diffractive planes of CZTS (JCPDS PDF card # 00-026-0575). In addition, the diffraction scans revealed the presence of three minor peaks related to kesterite CZTS which are the (101), (200) and (312) diffractive planes. Fig. 6.3b shows the fitted data for a high resolution θ - 2θ scan of the (112) peak. It can be seen that this peak, in fact, comprises two adjacent peaks in close proximity. A similar pair of peaks can also be observed for the (220) diffractive plane. This so called tetragonal peak splitting is due to the fact that the kesterite crystal unit cell is essentially the superstructure of two cubic sphalerite (zinc blende) structure [26]. However, since the lattice parameter c is not exactly equal to $2a$, the kesterite unit cell has lower symmetry and the Bragg peak of the parent sphalerite structure appears as a split peak. The changes in the peak position and full width at half maximum (FWHM) for the same crystallographic index plane of samples B1-B4 are a consequence of the CZTS film

microstructure and composition. This is because the direction of the diffracted beam is determined solely by the shape and size of the crystallographic unit cell [193].

By using the method described in Chapter 5, the lattice parameters a and c derived from the (112) peak at $2\theta \sim 28.56^\circ$ for samples B1-B4 are calculated and shown in Table 6.3. It can be seen that there is an overall decreasing trend for both a and c in samples B1-B4. The ratio $c/2a < 1$ decreases monotonically from 0.998 for B1 to 0.9946 for B4. Since the atomic radius of Mo is smaller than Sn and greater than Cu and Zn, this suggests Mo incorporation into the CZTS lattice by Sn substitution. By using the Scherrer equation, the typical crystallite size associated with (112) peak is found to decrease monotonically from 155.4 nm for B1 to 49.1 nm for B4.

Figure 6.3: (a) XRD analysis of the samples, (b) high resolution scan of (112) peak.

Table 6.3: Lattice parameters of kesterite CZTS unit cell and crystallite size.

Sample	a (nm)	c (nm)	$c/2a$	Crystallite size (nm)
B1	0.54206	1.08200	0.9980	155.43
B2	0.54175	1.07867	0.9955	131.67
B3	0.54219	1.07892	0.9949	92.98
B4	0.54164	1.07745	0.9946	49.09

The relatively broad peak observed for B1 sample at 15.2° in Fig. 6.3a can be associated with (001) diffractive plane of SnS₂ (JCPDS PDF card # 00-022-0951). The analysis also

reveals the presence of SnS₂ secondary phase for B2 sample. However, the peak attributed to (001) plane of SnS₂ is not observed for B3-B4 samples. This shows that Mo incorporation does not lead to new secondary phase formation.

The effect of Mo incorporation on the chemical environment of Sn in CZTS films was studied by high resolution Sn 3d core-level XPS scan (Fig. 6.4c). For B1 sample, the separation of 8.3 eV between the Sn 3d_{5/2} and Sn 3d_{3/2} peaks located at binding energies of 486.7 eV and 495 eV respectively indicates the presence of Sn(IV) ions [65,75,84]. As Mo co-sputtering power increases, a marked change of the Sn 3d_{3/2} peak shape is observed. There are two possible reasons for this effect. First, the Sn 3d_{3/2} peak broadening may be due to the Zn Auger peak L₃M₄₅M₄₅ [153] which is associated with the loss of Sn and increase of Zn content at the surface of these two samples. The second reason is substitution of some Sn ions by Mo since no such modifications were observed for the Cu 2p and Zn 2p related peaks (see Fig. 6.4a and 6.4b). The extra peak observed for B3 sample is likely due to contamination.

Figure 6.4: XPS Cu 2p (a) Zn 2p (b) and Sn 3d (c) core-shell scan.

Fig. 6.5a shows the absorbance spectra for samples B1-B4 deposited on SLG. In order for the optical properties to be measurable, the layer thickness has to be limited to ~300 nm. For all samples, the absorbance increases with decreasing wavelength. For the reference sample B1, the increase is gradual. However, as the amount of Mo incorporated in CZTS increases, there is a marked increase in absorbance for wavelengths below ~650 nm. By measuring the film thickness of B1-B4 using a surface profiler, the Tauc plots of these samples on SLG are obtained and shown in Fig. 6.5b. All four samples are direct band gap semiconductors. The band gap of Mo incorporated CZTS increases from 1.63 eV to 1.71 eV with Mo sputtering power while the band gap of sample B1 is only 1.38 eV. There is significant sub-band gap absorption for all samples and the absorption coefficient α ranges from $5.6 \times 10^4 \text{ cm}^{-1}$ to $1.87 \times 10^5 \text{ cm}^{-1}$.

Figure 6.5: UV-Vis (a) absorbance and (b) Tauc plot of ~300 nm Mo-incorporated CZTS thin films (B1-B4) deposited on SLG after sulfurization.

Sheet resistance of the sulfurized CZTS thin films deposited on plain SLG substrates was measured to study the effect of Mo incorporation on the electrical properties of these films. The calculated room temperature resistivity data is tabulated in Table 6.4. There is a considerable reduction of the resistivity for samples B2, B3 and B4 relative to B1. Incorporation of Mo causes reduction of resistivity from $2.70 \times 10^3 \Omega\text{cm}$ to $8.35 \times 10^1 \Omega\text{cm}$ for B1 and B2 samples, respectively. The lowest resistivity of $3.08 \times 10^1 \Omega\text{cm}$ was measured for B4 sample. Since the sheet resistance of this set of samples may be affected by Na^+ diffusion into CZTS from SLG, a further experiment using B1-B4 sputter deposited on quartz substrates and sulfurized at the same conditions was carried out. As

shown in Table 6.4, there is a decrease in resistivity from $3.13 \times 10^4 \Omega\text{cm}$ for B1 to $2.14 \times 10^1 \Omega\text{cm}$ for B3 followed by an increase to $1.42 \times 10^2 \Omega\text{cm}$ for B4. Except for sample B3, the resistivity of samples deposited on quartz is higher than those samples deposited on SLG. The resistivity of CZTS thin films can thus be tuned using Mo incorporation and Mo acts as a p-type dopant in CZTS.

Table 6.4: Resistivity of sulfurized CZTS thin films deposited on SLG and quartz substrates.

	B1	B2	B3	B4
CZTS/SLG (Ωcm)	2.70×10^3	8.35×10^1	1.18×10^2	3.08×10^1
CZTS/quartz (Ωcm)	3.13×10^4	8.09×10^2	2.14×10^1	1.42×10^2

TOF-SIMS analysis was carried out to characterize the elemental depth profile of CZTS/CdS solar cells. Fig. 6.6a-d show elemental distribution of all constituents related to Mo, CZTS, CdS and ITO films. In addition, the Na profile is shown for all samples. The TOF-SIMS profiles reveal the non-uniform distribution of elemental Mo within the CZTS absorber layer consistent with the EDS data discussed above. As shown in Fig. 6.6a, Mo can diffuse into CZTS during sulfurization to form MoS_2 . Mo incorporated into the absorber layer by co-sputtering can further facilitate the diffusion of Mo from the Mo/CZTS interface by reducing the crystallite size of CZTS near the Mo back contact (see SEM of Fig. 6.2b-d). As a result, the content of Mo is considerably higher at the CZTS/Mo interface than at the front interface. Therefore, it can be concluded that the concentration gradient of Mo is enhanced by co-sputtering of Mo in the CZTS layer. The profiles for Cu, Zn and Sn show diffusion of these metallic elements into Mo. In addition, the upper portion of the CZTS is richer in Cu similar to the results of EDS analysis. No obvious variation in the S elemental profile within the CZTS absorber layer is observed in Fig. 6.6b-d.

Figure 6.6: TOF-SIMS depth elemental distribution study of (a) B1, (b) B2, (c) B3, (d) B4 samples.

The SIMS profiles of Na for co-sputtered samples B2-B4 show an increase in the amount of Na in the bottom portion of the CZTS compared with the upper portion (Fig. 6.6b-d). This is likely due to the reduced crystallinity of the Mo-rich portion of the absorber. The increased grain boundaries allow the Na^+ ions to diffuse readily into the lower portion of the CZTS. Since Na is known to enhance the hole concentration in CZTS and passivate defects [139,143], Mo may enhance the photovoltaic properties of the CZTS by this mechanism. In contrast, the Na profile for sample B1 is different from samples B2-B4. There is more Na at the upper portion of the CZTS and this may be due to the different crystallinity of B1. Further investigation will need to be carried out. Diffusion of In from the ITO film into CZTS for Mo-incorporated solar cells is more substantial compared with the control sample. The enhanced diffusivity of In may be related to the reduction of absorber layer crystallinity owing to the increase of Mo content. Diffusion of In in CZTS and formation of shallow In_{Sn} anti-site defect was reported to enhance V_{oc} of sulfoselenide

CZTSSe solar cells through mitigating deep states and increase of hole density and mobility [198]. In addition, the formation of favorable In_{Sn} defects is facilitated by Sn loss in CZTS film [67].

Figure 6.7: (a) Current density-voltage curves of the illuminated solar cells, (b) normalized EQE of the solar cells, (c) estimation of absorber band gap from EQE data, (d) C-V analysis of Mo-incorporated CZTS solar cells at room temperature measured at 10 KHz.

The effect of Mo incorporation on the photovoltaic properties of CZTS thin film solar cells was studied. Current density-voltage (J-V) curves of the solar cells measured under 1 Sun AM1.5 illumination are shown in Fig. 6.7a. Table 6.5 summarizes the extracted photovoltaic parameters of the devices. For each Mo co-sputtering power, typically 12 devices were fabricated and the device parameters of the best device together with statistics for working devices are listed. The measured PCE of the control device B1 is only 1.63%. As shown by the dark field STEM cross sectional image of Fig. 6.8a, this may be due to voids inside the absorber. There could also be void formation at the Mo/CZTS interface as reported previously in [45]. On the other hand, there is a

remarkable boost in PCE as a result of Mo incorporation into the CZTS absorber layer. For sample B2, the PCE increases to 4.69% due to V_{oc} of 621.9 mV, J_{sc} of 14.14 mA/cm² and FF of 53.39%. All the measured V_{oc} , J_{sc} and FF of B2 are significantly higher than sample B1. The PCE for sample B3 increases to a maximum of 5.49% for this set of devices because of the increase in V_{oc} , J_{sc} and FF. The increase in J_{sc} and FF can be attributed to the reduced sheet resistance and increased carrier concentration in Mo incorporated CZTS (Table 6.4). As for V_{oc} , the increase may be due to increased Na⁺ ion passivation of grain boundary defects which increases the shunt resistance. Further increase of Mo co-sputtering power to 15 W (B4 sample) however, results in the decrement of the photovoltaic parameters. Solar cell B4 exhibits a PCE of 3.99%. The V_{oc} of 585.6 mV, J_{sc} of 13.38 mA/cm² and FF of 50.93% for B4 are all lower than B3. Thus the optimum co-sputtering power for Mo incorporation should be 10 W.

Although the highest reported PCE of pure sulfide CZTS solar cell prepared by co-sputtering of precursor materials is 11.5% [23], to the best of our knowledge, the highest PCE of pure sulfide CZTS solar cells deposited by sputtering of quaternary compound CZTS target is only 5.5% (without anti-reflection coating) [85]. Therefore, it can be seen that although performance of the sputter-deposited CZTS solar cells given in table 6.5 is small compared to the solution-processed CZCTS devices presented in Chapters 4 and 5, the best Mo incorporated CZTS solar cell demonstrate as high PCE as champion device.

Figure 6.8: Dark field STEM image of (a) sample B1 and (b) sample B3.

Table 6.5: Measured photovoltaic parameters of CZTS based solar cells (the mean values and associated standard deviation are given in parentheses).

	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)	PCE (%)
B1	389.5 (383.4±34.2)	11.51 (10.62±0.72)	36.3 (35±1.2)	35 (37.7±6)	72.8 (71.8±6.1)	1.63 (1.42±0.17)
B2	621.9 (573.4±61.4)	14.14 (13.74±0.52)	53.39 (44.6±9.1)	12.9 (10.8±1.2)	425.9 (253±190.7)	4.69 (3.6±1.17)
B3	638.9 (616±16.2)	15.51 (14.84±0.57)	55.4 (52.2±3.4)	7.9 (7.3±0.4)	416.1 (337.5±98)	5.49 (4.8±0.5)
B4	585.6 (555.6±59.7)	13.38 (12.54±0.95)	50.93 (47.14±6.1)	6.4 (6.5±1)	259.1 (215.9±83)	3.99 (3.29±0.63)

Deposition of a thin film absorber layer with gradient doping can result in an internal electric field that enhances the performance of a solar cell [46,47]. Tajima *et al.* demonstrated a remarkable boost in V_{oc} from 660 mV to 780 mV by using a two-layered CZTS absorber [48]. The top part of the CZTS film was Cu-poor resulting in low hole concentration while the bottom part consisted of stoichiometric CZTS having high hole concentration. The authors explained the enhancement of V_{oc} by the existence of an inner potential in the absorber layer due to the charge carrier gradient. In a similar way, the concentration gradient of Mo in co-sputtered CZTS thin films revealed by the TOF-SIMS profiles (Fig. 6.6) and the effect of Mo on CZTS sheet resistance may give rise to an effective two-layered absorber with an internal field directed from the upper sub-layer to the lower sub-layer. The boost in performance of Mo-incorporated solar cell devices may be attributed to this back surface field (BSF) which repels photo-generated minority charge carriers (electrons) from the defective back interface and reduces recombination there. The reduced recombination results in higher V_{oc} for samples B2 and B3.

As discussed in the study by Scragg *et al.* [49], a solid state chemical reaction between Mo and CZTS can occur at the Mo/CZTS interface resulting in the formation of ZnS, Cu₂S, MoS₂ and volatile SnS. The loss of Sn may cause the formation of Sn vacancies (V_{Sn}), copper-on-tin (Cu_{Sn}) and zinc-on-tin (Zn_{Sn}) anti-sites. A comparison of the Sn composition data in Table 6.2 shows that this may have occurred in the present samples. Additional evidence for this can be seen from cross sectional STEM images discussed

later. Kumar *et al.* reported that these defects form deep levels and mid-gap states in CZTS [33]. The increased defect density enhances bulk recombination in CZTS and, hence, deteriorates the performance of the solar cells mainly through the reduction of V_{oc} . At high levels of Mo incorporation, Mo related surface recombination may thus lead to lower V_{oc} and FF for sample B4.

The normalized EQE spectra for solar cells B1-B4 are shown in Fig. 6.7b. The normalized EQE is plotted here in order to eliminate the possible effect of the top contact line width variation on the device EQE. Interestingly, the normalized EQE curves for B2-B4 almost coincide whereas an obvious difference in slope for wavelengths shorter and longer than 550 nm is observed for B1. The slight difference observed from 700 nm to 900 nm for B2-B4 can be due to a modification of the charge transport properties in the absorber layer or a change in the bandgap of absorber layer upon Mo incorporation. Fig. 6.7c shows the plot of the first derivative of the EQE as a function of energy for all four devices. The energy band gap can be found from the maximum of this $d(EQE)/dE$ plot. The extracted bandgap for the devices (Table 6.6) varies within a tight range from 1.59 eV to 1.61 eV which can be ascribed to device-to-device variation. Note that these band gap values are different from those shown in Fig. 6.5b because the CZTS absorber is deposited onto Mo-coated SLG instead of SLG. It can be seen that the band tailing in CZTS has been improved slightly by Mo incorporation for sample B3. The small improvement is reasonable given that in the CZTS unit cell, the Sn^{4+} ions are not located at the same planes as the Zn^{2+} ions. Furthermore, by using the data of Table 6.5, the V_{oc} deficit for the optimized device B3 is determined to be about 250 mV smaller than B1. The better EQE response for solar cell B1 for the long wavelengths relative to B2-B4 may be due to the presence of thick bottom CZTS sub-layer of lower crystal quality for Mo-incorporated solar cells. Thus, further improvement of the device performance may be realized through the reduction of small grain CZTS sub-layer thickness.

Table 6.6: Extracted band gap from EQE measurements.

Sample	B1	B2	B3	B4
Band gap (eV)	1.60	1.59	1.61	1.60

For the spectral range from 300 nm to 500 nm, the normalized EQE plots for devices B2-B4 show more variation. There are two reasons for this. First, there may be small variations in the thickness of the CBD CdS layer which leads to slightly different absorption below 517 nm. The second reason is that the incorporation of Mo in CZTS results in increased absorption at short wavelengths as shown in Fig. 6.5a. In order to understand the mechanism of increased absorption at the short wavelength region in Mo incorporated CZTS devices, STEM was used to analyze sample B3 in more detail. As shown in the dark field image of Fig. 6.8b, the lower sub-layer of the absorber with smaller grain size appears to have higher porosity. It thus has a lower effective refractive index than the upper sub-layer. This lower index layer can enhance absorption by increasing the optical path length through multiple reflections at its interfaces. A possible explanation for the lower absorbance of sample B4 in the range from 680 nm to 1000 nm is the property of a metal to reflect near infra-red wavelength [50]. Thus, a further increase of Mo co-sputtering power reduces absorption in the long wavelength region of the spectra and hence causes a decrease of J_{sc} for B4 solar cell.

In order to further understand the effect of Mo on carrier concentration in CZTS, the fabricated CZTS solar cells were characterized by a C-V profiling method at 10 kHz (see Fig. 6.7d). The analysis revealed that the depletion charge density N_{CV} is similar for all Mo-incorporated CZTS solar cells whereas it is about one order of magnitude lower for the control device. This causes shrinkage of the depletion width from 335 nm for the control CZTS solar cell to a minimum of 69 nm for B3 sample owing to its N_{cv} . The increased carrier concentration can reduce parasitic series resistance and is conducive to a higher J_{sc} .

6.4 Summary

Mo incorporation into CZTS by co-sputtering results in the formation of a CZTS absorber with bimodal grain structure. The bottom CZTS sub-layer is Mo-rich while the upper sub-layer is Mo-poor. There is a reduction in both lattice parameters of CZTS as Mo substitutes Sn in the lattice. Mo in CZTS acts as a p-type dopant and was found to reduce sheet resistance and increase N_{CV} . The higher conductivity of the bottom CZTS sub-layer

favors the formation of a higher quality ohmic contact between CZTS and the Mo back electrode. For deposition on Mo back contact, incorporation of Mo into CZTS films results in increased light absorption at short wavelengths while not affecting the band gap of CZTS (~ 1.6 eV). Mo incorporation in CZTS does not cause significant secondary phase formation. Moreover, it facilitates diffusion of In from ITO into CZTS where In can passivate deep states due to Sn loss at the interface and hence reduces recombination.

Mo incorporation has a significant impact on the photovoltaic performance of CZTS thin film solar cells. PCE of CZTS solar cell was enhanced from 1.63% to 5.49% as a result of optimization of Mo co-sputtering power. V_{oc} and FF were found to be major factors contributing to the device performance enhancement owing to the Mo addition. In particular, Mo incorporation in CZTS results in reduced V_{oc} deficit. The present study demonstrates a promising approach to further enhance photovoltaic performance of CZTS solar cell by Mo incorporation.

Chapter 7 Effect of C incorporation on properties of CZTS and Cu doped ZnS thin films

7.1 Introduction

A number of attempts to substitute Sn in CZTS were reported [149,203]. Aside of reducing cation disorder, another reason for this is the loss of Sn during high temperature sulfurization [28]. Evaporation of volatile SnS during the processing may result in formation of Sn vacancies (V_{Sn}) and anti-sites such as Zn_{Sn} and Cu_{Sn} . These defects are highly detrimental because they form deep levels deteriorating solar cells performance [33]. It has been found that Ge incorporation facilitates grain growth, enables to increase kesterite bandgap, and improves photovoltaic performance of the solar cells when present in low content [204]. However, Ge loss also occurs through evaporation of volatile GeS_2 secondary phase [203]. An interesting candidate for Sn substitution is carbon. C thin films were successfully used as ILs to suppress $MoSe_2$ and void formation at the back interface for kesterite solar cells [127,205]. Furthermore, accumulation of C at the inner surface of the voids enabled to provide a better electrical contact between absorber layer and Mo back contact.

In the present study, the effect of C incorporation on structural, optical and electrical properties of sputtered Cu doped ZnS and CZTS thin films is investigated. The objective of C incorporation into Cu doped ZnS thin films is to synthesize Sn free Cu_2ZnCS_4 by using a co-sputtered bi-layer precursor. The approach is similar to a conventional method to deposit CZTS. Moreover the potential role of carbon in enhancing performance of solution-processed CZTS absorber layers has thus far not been reported. As C has oxidation state of +4, it may be related to partial substitution or passivation of Sn-related defects or vacancies in CZTS. In addition, since solution-processed CZTS solar cells demonstrate lower R_s relative to sputtered CZTS devices in this study, the effect of C incorporation in sputtered CZTS thin films needs to be studied. Moreover, as demonstrated in Chapter 6, the Mo incorporated devices showed enhancement of PCE relative to the reference devices. However, the absolute efficiencies are still low. An

alternative dopant is therefore needed. Therefore, in the second process, C was sputtered onto CZTS deposited from a quaternary compound Cu-poor CZTS sputtering target. Both sets of samples were subjected to the same sulfurization conditions.

7.2 Experimental details

Thin films preparation

Mo coated and plain SLG substrates were ultrasonically cleaned in soapy water, acetone, ethanol and DIW consequently. Then, the samples were dried in a flow of N₂ gas before loading into chamber of Denton Discovery-18 system for sputter deposition. The chamber was evacuated with turbo molecular pump to the pressure below $1.33 \cdot 10^{-4}$ Pa, then Ar gas was introduced (25 sccm). Sputter deposition was carried out without intentional heating of the substrate.

Deposition method 1: 99.99% 76.2 mm ZnS and Cu sputtering targets were co-sputtered at RF and DC power of 100 W and 24 W respectively to deposit ~190 nm Cu doped ZnS film (ZnS:Cu). Thereafter, 25 nm, 36 nm and 45 nm C thin films were grown by sputtering of the C target at RF power of 100 W.

Table 7.1: Thickness of incorporated C thin films into ZnS:Cu layer.

Sample	B	B25	B36	B45
C thickness, nm	0	25	36	45

Deposition method 2: Quaternary compound 99.95% purity 76.2 mm Cu-poor CZTS sputtering target was employed to grow ~280 nm CZTS thin films at RF power of 100 W. This is followed by deposition of 3 nm, 11 nm, 25 nm, 36 nm, 45 nm C thin films by sputtering of 99.99% purity 76.2 mm C target at the RF power of 100 W. The data on the prepared samples are presented in table 7.2.

Table 7.2: Thickness of incorporated C thin films into CZTS layer.

Sample	A	A3	A11	A25	A36	A45
C thickness, nm	0	3	11	25	36	45

Then all the samples were sulfurized at 570°C for 30 min in two-zone furnace in mixed atmosphere of elemental S and Ar. The temperature in sulfur zone was maintained at 200°C during the processing. The sulfurization process was followed by natural cooling down of the furnace.

Thin film characterization

Description of XRD and four point probe measurement system used in this study was presented in section 3.2 while description of the Raman and spectrophotometry measurement system were given in section 5.2. Surface profiler was used to measure thickness of the films. Hall effect measurement system (Bio-Rad HL5550) was employed to measure carrier concentration and Hall mobility.

Density functional theory modelling

The density functional theory (DFT) based first-principles calculations were performed by using the plane-wave Vienna ab initio simulation package (VASP) [206]. The hybrid Heyd–Scuseria–Ernzerhof (HSE) functional was used for the simulations. All the structures are fully relaxed until the atomic forces and total energy were smaller than 0.01 eV/Å and 10^{-5} eV, respectively. The kinetic energy cutoff of 400 eV was adopted. Periodic boundary conditions were applied in all three directions. The first Brillouin zone was sampled with a $15 \times 15 \times 8$ k-mesh grid. Stoichiometric CZTS and fully C substituted Cu_2ZnCS_4 (CZCS) were simulated in this study.

7.3 Results and discussion

7.3.1 First-principles density functional theory calculations

DFT simulations were carried out to study effect of Sn substitution by C in CZTS. First, stoichiometric CZTS unit cell was simulated. It has been found that material is characterized by direct bandgap of 1.38 eV (see Fig. 7.1a) which is similar to the measured using Tauc plot. The study shows the kesterite where all Sn atoms are replaced by C is a p-type semiconductor with indirect bandgap of 1.19 eV (shown as solid line) (see Fig. 7.1b). On the other hand, there is also direct bandgap of 1.24 eV (shown as dash

line) which makes the material attractive for photovoltaic applications. Moreover, the direct bandgap can be tuned by applying stress. As presented in Fig. 7.2, the direct bandgap of CZCS can be increased up to 1.85 eV when 5% compressive stress is applied. The latter may be realized through back interface engineering by inserting appropriate intermediate layer between kesterite film and Mo back electrode. Thus, tunability of CZCS bandgap makes it an interesting candidate for the application in tandem solar cells.

Figure 7.1: Simulated band structure of (a) CZTS and (b) CZCS. The horizontal dash red line represents Fermi level.

To estimate stability of the new kesterite, average binding energy (E_b) of CZTS and CZCS systems were calculated using the formula below.

$$E_b = (n_{Cu} \cdot E_{Cu} + n_{Zn} \cdot E_{Zn} + n_{Sn} \cdot E_{Sn/C} + n_S \cdot E_S - E_{tot}) / n_{tot}, \quad (7.1)$$

where E_{tot} is the total energy of the system, E_{Cu} , E_{Zn} , $E_{Sn/C}$ and E_S are the energies of a single Cu, Zn, Sn and S atom, n_{Cu} , n_{Zn} , n_{Sn} and n_S are the total number of Cu, Zn, Sn and S atoms, and n_{tot} is the total number of atoms in the system. The calculated E_b of CZTS is 10.16 eV whereas CZCS exhibits the higher energy of 10.47 eV. This points out to the higher stability of CZCS compared to CZTS. Higher stability of the system along with absence of Sn which can form volatile secondary phases during sulfurization may be useful to mitigate secondary phases formation and composition change owing to evaporation of volatile compounds out of kesterite thin film. Furthermore, it may help to

reduce density of defects which are not favorable for the device performance. In addition, the ability of C atoms to readily substitute Sn in CZTS can be useful to suppress formation of various deep defects and mid-gap states formed due to Sn loss. These includes Cu_{Sn} and Zn_{Sn} anti-sites and Sn vacancies (V_{Sn}).

Figure 7.2: (a) simulated band structure and (b) atomic structure of CZCS under 5% compressive stress (Cu is shown in pink, Zn in blue, C in grey, S in yellow).

7.3.2 C incorporated Cu doped ZnS thin films

Structural properties of sulfurized ZnS:Cu thin films without and with C grown on Mo-coated SLG substrate were studied with X-ray diffraction analysis. As Fig. 7.3a shows the control sample B consists of ZnS and CuS phases. The major peak observed at 28.64° is ascribed to (111) diffractive plane of ZnS (PDF card # 00-005-0566). In addition, minor ZnS related peaks observed at 47.59° and 56.44° are attributed to (220) and (311) diffractive planes respectively. Furthermore, peaks located at 29.38° , 31.88° and 32.92° are ascribed to (102), (103) and (006) diffractive planes of CuS respectively (PDF card # 00-006-0464). As C is incorporated into ZnS:Cu thin films, the dominant ZnS peak shifts from 28.64° to 28.68° . It indicates change of the unit cell size as a result of C incorporation. Table 7.3 presents calculated a and c unit cell parameters for ZnS:Cu thin film without and with C incorporation. It can be seen that size of the ZnS unit cell decreases as a result of C introduction. The possible reason for this is substitution of Zn or S by C. In addition, grain size for the samples was calculated (see Table 7.3). The study

shows that grain size of B25-B45 samples are larger than that of the control sample. As a result of 45 nm C film deposition, grain size increases from 34.3 nm to 51.9 nm compared to sample B. The effect of C incorporation on the ZnS crystallite size can be seen clearly from SEM images in Fig. 7.4. For the sample B45 (see Fig. 7.4d), large grains with well-developed crystallographic facets can be seen. In contrast, (006) CuS peak does not show any significant shift as thickness of C film increases. Fig. 7.3c also shows decrease in peak intensity suggesting that the amount of CuS in samples B25-B45 decreases compared to the control sample B.

Figure 7.3: XRD analysis of the samples (a) full scan, (b) enlarged view of (111) ZnS peak, (c) enlarged view of (006) CuS peak.

Table 7.3: Calculated a and c lattice parameters and grain size of ZnS:Cu without and with C incorporation.

Sample	a (nm)	c (nm)	Grain size (nm)
B	0.54043	0.53861	34.3
B25	0.54065	0.53590	48.5
B36	0.53999	0.53723	48.8
B45	0.54021	0.53792	51.9

Figure 7.4: Top view SEM image of sulfurized (a) B, (b) B25, (c) B36 and (d) B45 samples deposited on Mo-coated SLG.

Fig. 7.5a demonstrates absorbance spectra of sulfurized ZnS:Cu thin films without and with C. It can be seen that overall absorbance of C incorporated thin films is lower compared to ZnS:Cu thin film. This can be attributed to the larger bandgap of C incorporated ZnS:Cu thin films as shown by the Tauc plot in Fig. 7.5b. For the control ZnS:Cu sample, two direct bandgaps of 3.2 eV and ~1.9 eV can be extracted from the Tauc plot. They are attributed to cubic ZnS and hexagonal CuS respectively. In contrast, for C-incorporated ZnS:Cu samples, only direct bandgap of 3.6 eV can be extracted. This can be explained by the increased amount of ZnS phase due to C incorporation. The bandgap value of 3.6 eV is greater than that for the wide bandgap semiconductors such as 4H-SiC (3.2 eV) and GaN (3.4 eV) [207]. However, it is smaller than the bandgap of cubic ZnS (3.76 eV) [208]. The increase of bandgap can be related to the shrinkage of ZnS lattice unit cell owing to incorporation of C as shown by XRD study. In addition, Fig. 7.5a reveals significant band tailing for the control ZnS:Cu sample. This can be due to Cu doping. On the other hand, Fig. 7.5a demonstrates sharper absorption edge of C-incorporated Cu:ZnS thin films compared with the control sample B. This indicates reduction of band tailing in ZnS:(Cu,C). Therefore, C incorporation may result in

passivation of defects in ZnS thin films. The absence of significant band tailing in C incorporated ZnS:Cu suggests possible applications in semitransparent solar cells.

Figure 7.5: (a) Absorbance spectra of sulfurized ZnS:Cu thin films without and with C and (b) Tauc plot.

Sheet resistance of the films was measured to study the effect of C incorporation on the electrical properties of ZnS:Cu thin films. Table 7.4 shows that the sheet resistance of the control ZnS:Cu sample decreases from $164 \text{ k}\Omega/\square$ to $\sim 12.5 \text{ k}\Omega/\square$ for samples B36 and B45. The corresponding resistivity decreases by an order of magnitude from $3.08 \text{ }\Omega\text{cm}$ for sample B to $\sim 0.29 \text{ }\Omega\text{cm}$ for C incorporated samples. An increase of C thickness demonstrates negligible effect on reduction of sheet resistance. The possible reasons for the reduced sheet resistance are: (i) decreased density of defects due to C incorporation, (ii) C may act as a dopant in ZnS thin films. Due to the resistive nature, carrier mobility and carrier concentration of sample B cannot be measured by Hall effect measurement system. However, the Hall effect study shows high carrier concentration density in the range from 10^{19} cm^{-3} to 10^{20} cm^{-3} for the C incorporated ZnS:Cu thin films. The carrier Hall mobility was found to be in the range from $0.252 \text{ cm}^2/\text{Vs}$ to $1.95 \text{ cm}^2/\text{Vs}$ for B25-B45 samples. The sign of the Hall coefficient revealed the majority charge carriers were holes. The high hole concentration and low resistivity for the C incorporated ZnS:Cu samples supports that C acts as a dopant in ZnS:Cu. It is also worth mentioning that presence of CuS phase in the layer also contribute to the conductivity of the film.

Table 7.4: Resistivity, Hall mobility and carrier concentration of ZnS:Cu thin films without and with C incorporation.

Sample	B	B25	B36	B45
Sheet resistance ($k\Omega/\square$)	164	13.9	12.5	12.4
Resistivity (Ωcm)	3.08	0.297	0.28	0.289
Hall mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)	-	0.252	1.95	0.979
Carrier concentration (cm^{-3})	-	$1 \cdot 10^{20}$	$1.5 \cdot 10^{19}$	$3.45 \cdot 10^{19}$

7.3.3 C incorporated CZTS thin films

Fig. 7.6 show high magnification top view FESEM images of the control and C incorporated CZTS thin films after sulfurization. All the samples are polycrystalline. Fig. 7.6a shows that CZTS layer consists of large grains with a maximum size of $\sim 1 \mu\text{m}$ and smaller grains. Furthermore, a number of voids are observed at the surface. Their presence may be explained by the solid state reaction and loss of volatile SnS secondary phase during the sulfurization process. Fig. 7.6b shows densely packed grains of the A3 (3 nm C) sample and reduced density of voids. This clearly demonstrates the positive effect of C addition on the grain growth in CZTS thin films. Fig. 7.6c-f show that as thickness of the C deposited on CZTS is increased from 11 nm to 45 nm, fewer voids and smaller grains in the CZTS are observed compared with A and A3 samples. This shows the importance of C incorporation on crystallization of CZTS thin films. Since larger grain size and absence of voids are preferable, only an ultrathin layer of C ($\sim 3 \text{ nm}$) should be deposited over CZTS.

Particles that strongly scatter electrons are observed at the surface of A36 sample as can be seen in Fig. 7.6e. In addition, similar features are observed at the surface of the sample at lower magnification (see Fig. 7.7). The similar features are also observed at low magnification for A25 and A45 samples. Since these features are not present for samples with thinner layers of C, they may be related to metal or sulfur containing residual C on the surface of the samples.

Figure 7.6: Top view SEM images at the x30000 magnification of sulfurized (a) A, (b) A3, (c) A11, (d) A25, (e) A36, (f) A45 samples.

Figure 7.7: Top view SEM image of A36 sample after sulfurization at a low magnification of X400.

The effect of C incorporation on structural properties of CZTS thin films was studied using XRD. Fig. 7.8a presents XRD patterns of sulfurized CZTS thin films deposited on Mo-coated SLG substrate. As it can be seen, major peak located at 28.58° is attributed to (112) diffractive plane of kesterite CZTS (PDF card # 00-026-0575). Moreover, a number of minor peaks related to (002), (101), (200), (220), (312) and (008) diffractive planes of

CZTS were detected. In addition, presence of thick Mo film beneath CZTS layer gives rise to Mo peak ascribed to (110) plane (PDF card # 00-004-0809). The peak observed at 31.8° may be related to (211) diffractive planes of Sn_2S_3 secondary phase (PDF card #01-075-2183). This secondary phase could appear due to the solid state reaction at the interface between Mo and CZTS during high temperature sulfurization. It is worth mentioning that for samples A25-A45 the peak associated with Sn_2S_3 secondary phase is absent. Thus, it may be concluded that C incorporation mitigates secondary phase formation. Furthermore, Fig. 7.8b,c demonstrate a high resolution scan of (112) and (200) CZTS peaks respectively. It can be seen that the peaks are comprised of two closely placed peaks: major peak is on the left side and side one is on the right side. The observed peak splitting arises as a result of non-ideal symmetry of CZTS where $c \neq 2a$ CZTS [26]. As C is incorporated into CZTS, (112) peak shifts to the lower 2 Theta angles in the range from 28.54° to 28.56° . The similar shift is also observed for (200) CZTS peak (see Fig. 7.8c). The possible explanation for this is increase of volume of CZTS unit cell due to C incorporation into CZTS lattice. To verify this, a and c unit cell parameters were calculated using method described in chapter 6. The obtained data is presented in table 7.5. The study shows that incorporation of C causes increase of both a and c whereas change of c is more significant. Furthermore, as size of C atom is smaller than that of Cu, Zn, Sn and S, it may be concluded that C atom forms interstitial within CZTS unit cell rather than substitute cations or anions constituting CZTS. This may also mitigate crystallization of CZTS and reduce grain growth as shown in Fig. 7.6.

Figure 7.8: (a) High resolution XRD scan of sulfurized CZTS thin film without and with C incorporation, enlarged view of (b) (112) and (c) (200) peaks of kesterite CZTS.

Table 7.5: Calculated a and c lattice parameters of kesterite CZTS without and with C incorporation.

Sample	a (nm)	c (nm)
A	0.54175	1.07878
A3	0.54197	1.0800
A11	0.54175	1.08104
A25	0.54197	1.08244
A36	0.54197	1.08017
A45	0.54197	1.08017

Raman spectroscopy analysis was also employed to characterize structural properties of the samples (see Fig. 7.9). The dominant peak observed at 336 cm^{-1} is attributed to A vibrational mode of CZTS [176]. In addition, the peaks related to A and E vibrational modes of CZTS are located at 285 cm^{-1} and 372 cm^{-1} respectively [176,209,210]. The intensity and shape of the major peak of A3 and A11 samples is similar to that of control sample. In contrast, a drop in the intensity of the peak attributed to A vibrational mode is observed for samples A25-A45 with the increase of C film thickness. It is worth mentioning that solubility of C in CZTS thin films is low because residual C is present at the surface of the samples with thick C film (A25-A45) shown by SEM earlier. Therefore, the residual C at the surface blocks Raman signal resulting in drastic change of the major peak shape. The peaks attributed to E and A vibrational mode of MoS_2 are observed at 383 cm^{-1} and 407 cm^{-1} respectively [211]. This may point to the enhanced formation of voids in CZTS film for A25-A45 samples due to increase of C content. This is because penetration depth of 488 nm wavelength into the film is in the range from 46 nm to 63 nm which is much lower compared to the total thickness of the film. Moreover, no significant amount of secondary phases was detected.

Figure 7.9: Raman spectroscopy analysis of (a) CZTS thin films and (b) enlarged image of major CZTS related peak.

The effect of C incorporation on absorbance spectra of the films was studied using UV-Vis-NIR spectroscopy. As fig. 7.10a shows samples A3 and A11 demonstrate lower absorbance over the all recorded spectra compared with the control sample. On the other hand, incorporation of 36 nm and 45 nm C film in CZTS results in significant enhancement of the absorbance in the measured range of wavelengths. In order to investigate more on this, optical bandgaps of the films were extracted using Tauc plots. Fig. 7.10b shows that the change in absorbance of the films correlates with the extracted bandgaps. The measured bandgap of the control sample is 1.46 eV which is well match to the data reported in the literature [27,29,36]. As thickness of deposited C film increases from 3 nm to 11 nm, the bandgap increases to 1.57 eV and 1.6 eV respectively. In addition, both samples demonstrate sharper absorbance edge relative to other C incorporated CZTS samples. The observed decrease of sub-bandgap absorption for A3 and A11 sample may be due to reduced defect density as a result of C incorporation. In contrast, the extracted bandgap of A25-A45 samples are within the tight range from 1.37 eV to 1.42 eV. This may be due to shrinking of CZTS bandgap as content of C in the CZTS is increased. This also may be due to residual C at the surface of the samples as shown in Fig. 7.7 which modify the optical properties of CZTS.

Figure 7.10: (a) Absorbance spectra of CZTS films, (b) Tauc plot used to extract bandgap of the films.

Four point probe method was used to study effect of C incorporation on sheet resistance (R_{sheet}) of CZTS thin films (see Table 7.6). The measured R_{sheet} of the control sample is $2.02 \cdot 10^7 \Omega/\square$. Both R_{sheet} and resistivity of the films decrease significantly as a result of C incorporation and tend to a minimum. R_{sheet} decreases from $4.53 \cdot 10^6 \Omega/\square$ for A3 sample (3 nm C) to $1.85 \cdot 10^5 \Omega/\square$ and $2.11 \cdot 10^4 \Omega/\square$ for A11 and A25 samples respectively. For A36 and A45 sample, R_{sheet} is saturated at $2.08 \cdot 10^4 \Omega/\square$ and $1.59 \cdot 10^4 \Omega/\square$ respectively. This can be due to aggregation of C at the surface of the films. Thus, it can be concluded that resistivity of CZTS thin films can be tuned in a wide range (3 orders of magnitude) by C incorporation. Marked decrease of the film resistivity for A3 and A11 samples may be explained by dopant nature of C in CZTS. This is also supported by the observed change in bandgap and size of the unit cell.

Table 7.6: Sheet resistance and resistivity of CZTS thin films without and with C incorporation.

Sample	A	A3	A11	A25	A36	A45
Sheet resistance ($\Omega/\square$)	$2.02 \cdot 10^7$	$4.53 \cdot 10^6$	$1.85 \cdot 10^5$	$2.11 \cdot 10^4$	$2.08 \cdot 10^4$	$1.59 \cdot 10^4$
Resistivity (Ωcm)	565.6	128.2	5.38	0.64	0.66	0.52

In contrast to ~280 nm CZTS films used in the materials study, much thicker CZTS absorber layer was sputtered to fabricate solar cell devices in Chapter 6. In turn, use of a thicker CZTS layer would also require a proportionally thicker C film deposited on top. However, as it was shown earlier, C tends to agglomerate at the surface of the sulfurized CZTS film if it is thick enough. The latter may cause formation of defective hetero-interface and result in low performance of CZTS/CdS solar cells. To avoid this issue, co-sputtering of CZTS and C may be used. However, this approach was not feasible as the sputtering system available was equipped with only 1 RF and 2 DC cathodes. The reason for this is a very low deposition rate of C even at RF sputtering power of 100 W while the maximum DC power that was achieved for C target was only ~35 W. Thus, C incorporated CZTS solar cells were not fabricated.

7.4 Summary

First-principles DFT calculations predict formation of p-type Cu_2ZnCS_4 kesterite with a direct bandgap of 1.24 eV. Moreover, the new kesterite demonstrates higher binding energy (10.47 eV) compared to CZTS (10.16 eV) which indicates its higher stability. It has been revealed that bandgap of Cu_2ZnCS_4 can be increased from 1.24 eV to 1.85 eV by applying 5% compression stress. Sulfurization of sputtered ZnS:Cu/C bi-layer results in mix of doped ZnS and CuS with a wide bandgap, high charge carrier concentration and low resistivity. On the other hand, Cu_2ZnCS_4 phase has not been synthesized. To synthesize Cu_2ZnCS_4 thin films sulfurization temperature higher than 600°C may be required. Furthermore, co-sputtering of ZnS, Cu and C targets would be beneficial to intermix the elements in order to facilitate the solid state reaction to form the new quaternary compound kesterite semiconductor. It has been found that increase of C content mitigates formation of CuS phase while enhances formation of ZnS phase. Incorporation of C into wide bandgap p-type ZnS:Cu results in increase of the bandgap from 3.2 eV to 3.6 eV. Moreover, tail states in ZnS:Cu are significantly reduced as C incorporation results in more sharp absorbance edge of the thin films. C substitutes Zn or S in ZnS and acts as a dopant since resistivity of C incorporated ZnS:Cu films decreases by 1 order of magnitude relative to the control sample.

Crystal quality of sputter-grown CZTS is enhanced as optimized amount of C is incorporated whereas Mo incorporation results in decrease of CZTS grain size. In contrast to Mo substituting Sn in CZTS, C atoms were found to form interstitials in CZTS as size of CZTS unit cell increases owing to C incorporation. The interface reaction and secondary phases formation are suppressed with the increase of C content as in the case of Mo incorporation. Moreover, bandgap of CZTS thin films can be tuned by C incorporation. Resistivity of C incorporated CZTS thin films decreases by 1 – 3 orders of magnitude compared to the control sample. Thus, both C and Mo incorporation result in decreased resistivity of CZTS thin films.

Chapter 8 Conclusions and recommendations

8.1. Concluding remarks

The effect of TaN IL thickness on the quality of absorber layer prepared by RF sputtering of quaternary Cu-poor CZTS target and properties of CZTS/Mo interface was studied in detail in chapter 3. It has been found that S diffusion into the Mo layer can be reduced by inserting TaN IL. This is due to the property of TaN IL to block S diffusion into Mo and ability of TaN to chemically react with S at 600°C to form tantalum sulfo-nitride. In addition, it has been shown that use of non-stoichiometric CZTS target along with TaN IL enables to minimize the thickness of MoS₂ layer and reduce void formation at the Mo/CZTS interface. When 12 nm TaN layer was present, no continuous interfacial MoS₂ layer was observed at the interface, whereas ~40 nm thick MoS₂ was observed for the control sample. However, discontinuities in TaN layer allow S to diffuse into Mo layer. Moreover, it has been found that incorporation of TaN IL does not limit Na diffusion from SLG substrate into CZTS absorber layer. Nevertheless, TaN was found to cause formation of detrimental Cu₂S secondary phase in sputtered CZTS thin films.

The effect of ZnS IL which demonstrates a similar crystal structure to CZTS was studied in chapter 4. The sputtered 10 nm ZnS IL incorporated at the interface between solution-processed CZCTS and Mo facilitates growth of CZCTS grains. On the other hand, the negligible effect of the sulfide-based IL on the thickness of interfacial MoS₂ layer was observed. Moreover, diffusion of S in Mo is reduced as ZnS is present at the interface. In addition, void formation is suppressed as a result of ZnS IL deposition. The measured photovoltaic performance of the CZCTS solar cell with ZnS IL increased from 9.5% to 10% due to the enhancement of both V_{oc} and J_{sc} . This suggests that ZnS IL is more suitable for solution-processed CZCTS solar cells relative to sputtered CZTS/CdS devices where effect of the IL on PCE is negligible.

The highest PCE of 10.8% was achieved for solution processed CZCTS solar cells employing CuO IL. Chapter 5 has studied the effect of CuO IL thickness on the absorber layer, back interface and properties of CZCTS solar cells in detail. It has been found that

sputtered CuO IL reacts with S to and, hence, mitigates the diffusion of S into Mo back electrode. Furthermore, it does not add to secondary phases formation and reduces voids at the back interface and in the bottom portion of the absorber layer. The increase in PCE from 10% to 10.8% is mainly attributed to the boost of J_{sc} . The study reveals that the depletion width in CZCTS solar cells increases with the increase of CuO thickness. Moreover, recombination at the back interface is reduced when the optimum thickness of CuO IL is deposited. In addition, it has also been found that deposition of CuO IL allows to significantly improve long term stability of CZCTS/CdS solar cells.

Effect of co-sputtering of the CZTS and Mo targets was investigated in detail in chapter 6. The study found the Mo incorporation results in the formation of bi-layer CZTS absorber layer where Mo-rich bottom layer consists of small grains while the Mo-poor upper layer is made of large grains. Furthermore, it has been found that Mo substitutes Sn in the CZTS unit cell. Mo acts as a p-type dopant in CZTS and allows to decrease resistivity of the thin films. Incorporation of Mo results in improved light absorption of CZTS thin films while not affecting its bandgap. In addition, the study shows that Mo incorporation facilitates In diffusion from ITO which is known to be useful to passivate deep defects formed owing to Sn loss. PCE of sputter deposited CZTS solar cell is enhanced from 1.63% to 5.49% when optimized Mo co-sputtering power is applied. The boost of the device performance is mainly associated with the increase of V_{oc} and FF. Furthermore, Mo incorporation provides a promising way to decrease V_{oc} deficit of CZTS solar cells.

Effect of C incorporation in sputter-grown CZTS and Cu doped ZnS thin films was investigated in chapter 7. The first-principles DFT simulation study predicts the formation of Cu_2ZnCS_4 kesterite with a direct bandgap of 1.24 eV. Furthermore, the substitution of Sn by C in kesterite was found to increase the average calculated binding energy of the compound from 10.16 eV to 10.47 eV which indicates higher stability of the new kesterite. Sulfurization of sputtered ZnS:Cu/C bi-layer results in blend of doped ZnS and CuS with a wide bandgap, high charge carrier concentration and low resistivity. However, Cu_2ZnCS_4 phase has not been synthesized. C incorporation was found to facilitate formation of ZnS phase and suppress formation of CuS phase. It also has been found that addition of C into p-type ZnS:Cu wide bandgap semiconductor allows to increase bandgap from 3.2 eV to 3.6 eV, reduce tail states, and decrease resistivity by 1 order of magnitude from 3 Ωcm to 0.29 Ωcm . The addition of optimized amount of C facilitates

CZTS grains growth and reduces void formation. In addition, formation of Sn_2S_3 secondary phase is suppressed with increase of C content. Resistivity of CZTS thin film can be reduced by few orders of magnitude by C introduction. Besides, C incorporation allows to tune CZTS bandgap in the range from 1.39 eV to 1.6 eV.

8.2 Recommendations for further research

Further research is required to enhance PCE of kesterite solar cells beyond 15%. As low V_{oc} is considered as a major factor limiting the device performance, more research has to be done on the hetero-interface of kesterite solar cells. It is also worth mentioning that alternative buffer material with a bandgap larger than 2.42 eV is required to reduce parasitic absorption in the CdS. Fabrication of kesterite solar cells using sputtering only approach without breaking a vacuum would be beneficial to reduce solar cells fabrication time and cost. On the other hand, treatment of the CZTS thin films in the water solution of ammonia hydroxide was reported to remove surficial oxide and secondary phases at the top of the absorber layer [163].

Although ZnS buffer layer would be an interesting candidate to replace toxic CdS in CZTS solar cell owing to small lattice mismatch between CZTS and ZnS, a carrier transport at the hetero-interface is limited. The possible reasons for lack of photovoltaic performance is a high CBO offset limit carrier transport at the heterojunction. Furthermore, the sputter deposition of ZnS buffer layer causes damage of CZTS film. Therefore, deposition methods such as chemical bath deposition (CBD), successive ion layer adsorption and reaction (SILAR) and atomic layer deposition (ALD) are more suitable for buffer layer deposition. A thin film of $\text{Zn}(\text{O},\text{S})$ with a tunable bandgap and CBO is a possible candidate for the buffer layer application. Thus, careful control of the film composition is needed to realize the required spike like band alignment in the range from 0 to 0.4 eV [28].

Double cation substitution by Ag and Cd in CZTS absorber layer was reported to be an effective approach to suppress the cation disorder and reduce V_{oc} deficit [24]. However, anti-site defects related to Sn form a midgap and deep levels significantly affect device performance [33]. Partial substitution of Zn and Sn by isovalent cations in CZTS may be

an effective solution to simultaneously address the problem of Cu/Zn disorder and Sn related anti-site defects.

The ideal IL should (i) suppress solid state reaction at the back interface, (ii) avoid secondary phases formation within the absorber layer, (iii) improve crystallinity of CZTS absorber layer, (iv) introduce back surface field repelling minority carriers from the back interface and (v) reduce device series resistance through minimizing thickness of MoS₂ layer. It can be seen that a single IL can hardly meet all criteria. Therefore, a combination of ILs can be used to make the high quality back interface and, hence, improve the performance of a kesterite solar cell.

Finally, an abundance of Cu, Zn, Sn and S in the earth crust along with the potential low cost of CZTS thin film solar cells make this technology a promising candidate for building integrated photovoltaics (BIPV). On the other hand, lightweight and flexibility of the solar panels are highly required to reduce installation cost and expand application areas for the panels in BIPV. Therefore, more research needs to be performed to study kesterite solar cells grown on flexible substrates such as foils or polymer substrates.

List of publications

Journal:

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