Investigation of alkali elemental doping effects on solution processed Cu₂ZnSn(S,Se)₄ thin films for photovoltaics

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2016

Li, W. (2016). Investigation of alkali elemental doping effects on solution processed Cu₂ZnSn(S,Se)₄ thin films for photovoltaics. Master's thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/68830>

<https://doi.org/10.32657/10356/68830>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**INVESTIGATION OF ALKALI ELEMENTAL DOPING
EFFECTS ON SOLUTION PROCESSED $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ THIN
FILMS FOR PHOTOVOLTAICS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

**Investigation of Alkali Elemental Doping Effects on Solution
Processed $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ Thin Films for Photovoltaics**

School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Engineering

2016

Abstract

Due to the great potential for large scale and low cost production in photovoltaic industry, kesterite $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) based materials have been deemed as one of the most promising absorber materials for photovoltaic applications. Composed of relatively low toxic and earth abundant elements, this kesterite material could be used to avoid the limitation of elemental scarcity and relieve the environmental issues which are troubling the CdTe and $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$ (CIGS) based thin film technologies. Besides, CZTSSe also shows excellent electronic and optical properties, like high optical absorption coefficient ($>10^4 \text{ cm}^{-1}$) and direct tunable bandgap from 1.0 to 1.5 eV, making it good alternative to CIGS.

Similar to CIGS, both solution and vacuum based approaches could be adopted to fabricate CZTSSe thin film absorber. In order to reduce the manufacturing cost, there is urgent demand towards the usage of non-vacuum solution based approach. So in this thesis, a solution based sol-gel method for the synthesis of CZTS/CZTSSe thin film absorbers was presented. Generally, CZTS precursor films were successfully synthesized by a simple spin-coating process, followed by a preheating process at 280°C . Further high temperature annealing processes were required to enhance the grain growth and get high quality dense films for photovoltaic application. Therefore, the influence of annealing conditions such as annealing atmosphere and selenization temperature on both thin films and device performance has been investigated.

Alkali elemental doping such as sodium and potassium doping was employed into CZTSSe thin film solar cells by solution based method to improve the grain size and further enhance the device performance. It was found that the open circuit voltage (V_{oc}) and fill factor (FF) were improved due to the alkali elemental doping, thus leading to the improvement of solar cell power conversion efficiency (PCE). By tuning the doping concentration and selenization condition, the CZTSSe thin film solar cell with 1.5 mol% K doping under selenization at 560°C for 30 min exhibited the best efficiency of 7.78%. The alkali elemental doping

effects on the microstructure, chemical composition, electronic properties of CZTSSe thin films and solar cell performance were analyzed in details. It was revealed that the improvement of solar cell performance with K doping could be mainly attributed to the increase of carrier concentration. However, excess K together with non-ideal annealing condition may induce deep level states, high series resistance and low carrier mobility, thus quenching the performance. In order to compare the individual role of each alkali element (Li, Na, K), the CZTSSe absorbers were also deposited onto the substrates with alkali diffusion barrier (SLG/Al₂O₃/Mo). As a result, similar effects of increasing the carrier concentration and reducing depletion width were found. But the degree of improvement may be a little different, possibly due to different incorporation amount of each alkali element.

In summary, our solution based alkali elemental doping in CZTSSe offers some new insights into the improvement of thin film solar cell performance by alkali elemental doping. Our work also suggests a potential application of solution based alkali elemental doping in flexible solar cell devices.

Acknowledgement

First of all, I would like to express my huge gratitude to my supervisor Asst. Prof Lydia Helena Wong for giving me the opportunity to devote to this challenging but interesting research work. Her patience and enthusiasm on the guidance of my research work encouraged me to overcome any difficulties on my way of pursuing science and truth.

I would like to show my great respect and thanks to Dr Su Zhenghua as my mentor in my research work, who is always giving me valuable suggestions and sharing his experience with me when I'm faced with problems. The discussion with him benefits me a lot both in research and life.

I would like to thank Dr Sudip Batabyal for his help during my work, especially his innovative ideas, helpful suggestions and constant guidance.

I would like to thank Dr Li Zhen for giving me quite a lot support at the beginning of my work, helping me get familiar with everything new around me.

I would also like to thank Mr Wang Wei for teaching me the basic techniques and principal theory of related research filed during his short exchange time. His assisting in my experimental work helped me a lot.

I would like to thank all the other members of CIGS group (Shin Woei, Wang Hao, Xianglin, Joel, Guifang, Wan Lei, Kong Fai, Rajiv, Aamir, Xiaoyan, Zeng Xin, etc.) for sharing me with experience, giving me worthy advice during the research group meetings. Also special thanks to ERI@N technical staff for all the technical support in the lab.

Last but not least, I would also like to thank all my classmates, friends and my family giving me the support and encouragement when I feel depressed along my way of research.

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Abbreviations

CZTS	Copper Zinc Tin Sulfide, $\text{Cu}_2\text{ZnSnS}_4$
CZTSSe	Copper Zinc Tin Sulfur Selenide, $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$
CIGS	Copper Indium Gallium Selenide, $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$
CdS	Cadmium Sulfide
TCO	Transparent conductive oxide
E_g	Bandgap
PCE	Power conversion efficiency
PV	Photovoltaic
V_{oc}	Open circuit voltage
J_{sc}	Short circuit current density
FF	Fill factor
AM1.5	Air mass 1.5
J-V	Current density-Voltage
EQE	External quantum efficiency
EDX	Energy Dispersive X-ray Spectroscopy
SEM	Scanning Electron Microscopy
XRD	X-ray Diffraction
UV-Vis	Ultraviolet-visible/near infrared spectroscopy
VBM	Valence band maximum
SLG	Soda lime glass
GBs	Grain boundaries
PDT	Post deposition treatment

Chapter 1

Introduction

In this chapter, a brief introduction is summarized for this thesis. First of all, the background and motivation for the research of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin film solar cells are described. The objectives and scope of this thesis are presented next. Besides, the organization of this thesis is reviewed in sequence. In the end, the findings and outcomes are highlighted, which are the main contributions of this work.

1.1 Background and Motivation

Due to the fast growth of industrialization and population, along with the global warming and rise of oil price, the global energy demand has reached the apex in the 21st century, which makes energy crisis to be one of the most important issues urgent to be addressed. This crisis has led to the search for alternative energy sources, particularly those renewable, environmentally friendly ones. Compared to fossil fuels, renewable energy like solar, hydro, wind and geothermal energy meet the energy requirements in a more environmental-friendly way.

Among all these renewable energy sources, great progress in solar technologies is attracting worldwide attention. For example, worldwide solar cell production has rapidly increased to 11.5 GW in 2009 from about 300 MW in 2000, showing a growth of more than 30 times in only ten years (**Figure 1.1.1**). Simply inspired by light, solar cells could directly convert solar energy into electricity. With no moving parts, and can be operated near ambient temperature, solar cells are able to be assembled into any scale unlike wind turbines or thermal generators, which may lose efficiency with reduced scale.

Figure 1.1.1 World solar cell production from 2000 to 2009 [1].

In fact, photovoltaic technology is on the pathway to become more competitive, as the ongoing grid-parity events are throughout most of the regions in the world. For current PV production market, crystalline silicon solar cells make up around 90% of global PV

production capacity and are the most mature in industry compared to all the other technologies. Both single crystalline and multi-crystalline Si (c-Si) have reached rather high efficiencies nowadays, with record efficiencies of 25.6% and 20.8%, respectively [2]. But the limitation of c-Si solar cells is its indirect bandgap, which makes the absorber wafer to be at least several hundreds of microns to absorb enough light.

Figure 1.1.2 Evolution of thin film PV shares in global market [3].

To address these issues, thin film solar cells have developed as an alternative to the c-Si solar cells in recent years. With such thin film absorber incorporated into the cell, the device could absorb light 10-100 times more efficiently than using silicon wafer absorber. Therefore less amount of material is required, on the order of a few microns. Less material use and lower cost are the major advantages of these technologies. As shown in **Figure 1.1.2**, for the yearly PV production in the global range, the shares of thin film technologies increased from 5% in 2005, to 12% in 2010. Cadmium telluride (CdTe), Amorphous silicon (a-Si) and Cu(In,Ga)(S,Se)_2 (CIGS) are the three major commercial thin film PV technologies. Among all of them, CIGS solar cells reached the highest efficiency of 22.3% recently [4], and could easily be deposited by a variety of methods on flexible metal foils or polymer substrates, favorable for the integrating into the building and other large-scale applications.

As for CIGS solar cells, there still exist some problems to be solved in order to achieve the sustainable and low-cost goal. One challenge is that the Ga and In are rare elements in the earth, which could be used up in next few decades so that the price keeps rising rapidly nowadays. Hence searching for another material composed of earth-abundant elements while maintaining high solar cell efficiency is our urgent task. With higher abundance and lower price as shown in **Figure 1.1.3**, together with similar structure and electronic properties, Zn and Sn have been utilized to replace In or Ga, forming the quaternary compound $\text{Cu}_2\text{ZnSnS}_4$ (CZTS). Although CZTS is a relatively new material, the promising efficiency beyond 12% indicates that CZTS has great potential for further research as the alternative of CIGS [5].

Figure 1.1.3 Content and world trading price of the elements for thin film solar cells [6].

Like CIGS, CZTS could be fabricated by various approaches, among which solution-based deposition approach offers the advantages such as fast coating of wet layer with low wastage of precursor solution, high throughput and low cost. So in this work, a solution based sol-gel method was chosen to synthesize the CZTS/CZTSSe thin film absorber. Alkali elemental doping like sodium and potassium doping have been proved to show some positive effects on grain growth and reducing non-radiative recombination for CIGS solar cells, thus improving the cell performance. However, the mechanism and the

behaviors of these elements during the solution-based approach and annealing process of CZTSSe solar cells are not well understood. So more depth investigation into the alkali elemental doping for CZTSSe based thin film solar cells is essential and necessary for better understanding of material chemistry and developing high efficiency thin film photovoltaic devices.

1.2 Objectives and Scope

The aim of this work is to understand the effects of alkali elemental doping in CZTSSe thin film solar cells. CZTS and CZTSSe thin films were first synthesized by a simple and facile sol-gel spin coating method, followed by high temperature annealing in Se ambient. The high temperature annealing process plays a very important role in promoting the grain growth and crystallinity. So the effects of annealing process on the film quality and properties will be investigated. By tuning the annealing parameters, the phase purity, morphology and electrical properties of CZTS and CZTSSe thin films will be discussed. And the correlation between selenization temperature and film quality and final device performance was specifically examined. In order to further improve the grain growth and cell performance, extrinsic dopants like Na and K have been incorporated into CZTS precursor solution. The influence of alkali elemental doping on thin films and devices is the major focus of this work. For the solution based method, there are still few reports about alkali elemental doping and its precise control, which would possibly be the novelties of this work. The detailed sub-objectives of this thesis are summarized as below:

- I. Fabrication of photovoltaic-grade CZTS and CZTSSe thin films.
 - A. Synthesize CZTS precursor thin films by spin coating of sol-gel precursor solution.
 - B. Improve the grain size by sulfurization and selenization of CZTS precursor films.
 - C. Investigate the effects of different annealing atmospheres (Ar annealing, sulfurization, selenization) and temperature on the growth and formation of thin films.
 - D. Characterize the morphology and structure of CZTS and CZTSSe thin films by FE-SEM, XRD and Raman.

II. Fabrication and characterization of CZTSSe solar cells.

- A. Complete the whole thin film solar cell device with a configuration of SLG/Mo/CZTSSe/CdS/i-ZnO/AZO/Ag.
- B. Evaluate the solar cell performance from solar simulator.
- C. Evaluate the external quantum efficiency from IPCE.

III. Alkali elemental doping via solution based method.

- A. Investigate the influence of the sodium and potassium amount/gradient on the microstructure and electronic properties of CZTSSe thin films and device performance.
- B. Optimizing the selenization process (selenization duration) for K-doped CZTSSe thin films.
- C. Comparing the individual role of each alkali element (Li, Na, K) on CZTSSe thin films deposited on substrates with alkali diffusion barrier (SLG/Al₂O₃/Mo). The influence of each element on electronic properties was compared and analyzed by C-V, C-f measurement.

1.3 Dissertation Overview

The main objective of this thesis is to understand the selenization process and alkali elemental doping effects on the formation and grain growth of CZTSSe thin films and improve solar cell performance by tuning the annealing process and doping amount by a facile solution based sol-gel spin coating method. The thesis is organized as follows:

Chapter 1 provides a brief introduction of the development of solar energy and the photovoltaic technologies. The urgent search for environmentally friendly, earth abundant materials for thin film solar cells has been described and CZTS has proved to be one of the most promising photovoltaic materials as the alternative of conventional CIGS thin film solar cells.

Chapter 2 gives a wide range of literature review for better understanding of the basic knowledge and past research works about this material, including the structure and

properties of CZTS/CZTSSe compounds, fabrication approaches, working principles of thin film solar cells and recent alkali elemental doping studies.

Chapter 3 summarizes the experiments and characterization techniques conducted for the synthesis and study of CZTS/CZTSSe thin film absorbers and their application on thin film solar cells.

Chapter 4 focuses on the synthesis of CZTS/CZTSSe thin films by a facile solution based sol-gel method. The effects of different annealing conditions, such as annealing atmosphere, selenization temperature will be discussed.

Chapter 5 states the preparation of alkali elemental doping and its influence on CZTSSe thin films and devices. A range of doping levels for either sodium or potassium was introduced. The sodium was also doped evenly throughout the film and selectively doped at specific layer to investigate the effect of concentration gradient. The K doping in CZTSSe was optimized with different selenization duration as well. More specifically, the role of Li, Na, and K was studied individually by depositing thin film absorber onto substrates with alkali diffusion barrier.

Last but not least, Chapter 6 gives a summary of the overall research work and provides some recommendations for future research directions.

1.4 Findings and Outcomes

In brief, original findings and outcomes achieved by this Master thesis include:

- i. Investigated the effects of annealing atmosphere and annealing temperature on the microstructure and phase of thin films and device performance, CZTSSe device with high efficiency of 7.6% was achieved using a two-step selenization process in a half-sealed quartz tube.

ii. CZTSSe thin film solar cells were improved with alkali elemental doping by solution based method. The influence of alkali doping concentration and gradient on thin films and solar cells was studied. Especially the solution processed K doping effects on the electrical properties of CZTSSe thin film solar cells and accordingly V_{oc} enhancement was reported for the first time with an improved efficiency up to 7.78% after optimizing selenization time.

iii. Identified the similarity among alkali elemental doping (Li, Na, K) effects on CZTSSe devices, that is, increasing the carrier concentration and decreasing the junction depletion width to different extent.

iv. The key problem of alkali elemental doping was also described. Excess alkali elements may remain in the absorber layer and could act as impurities, which would deteriorate J_{sc} , V_{oc} and FF. Combining optimized selenization process with suitable alkali elemental doping concentration would be helpful for reducing deep defects and developing high efficient devices.

Chapter 2

Literature Review

Cu₂ZnSnS₄ (CZTS) related kesterite compounds have been developed rapidly as a promising candidate for PV application in recent years. Therefore, the background, application and current research progress for CZTS are introduced in this chapter. The fundamental aspects of this material are reviewed at the beginning. Next, the fabrication approaches for CZTS/CZTSSe absorber layers and their application in solar cell device are presented. Finally, some recent research progress about the incorporation methods and effects of alkali elemental doping on either chalcopyrite or kesterite are briefly reviewed.

2.1 Fundamentals of CZTS Kesterite Material

2.1.1 Structures and properties of CZTS kesterite

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a p-type $\text{I}_2\text{-II-IV-VI}_4$ quaternary compound. By substituting of In or Ga with Zn and Sn atom, CZTS normally adopts a kesterite crystal structure which is the most stable (**Figure 2.1.1.1**, left). But CZTS also has other less stable structures, like stannite, according to the different locations of Cu and Zn (**Figure 2.1.1.1**, right). The stannite structure evolves from (001) oriented CuAu structure while kesterite derives from (201) oriented chalcopyrite structure. And the evolutionary path from binary II–VI compounds to $\text{I}_2\text{-II-IV-VI}_4$ quaternary compounds is depicted in **Figure 2.1.1.2** [7].

Figure 2.1.1.1 Kesterite (left) and stannite (right) structure; large yellow spheres: S and Se; small spheres: blue, Cu; yellow, Zn; red, Sn [8].

Figure 2.1.1.2 Relationship between binary, ternary, quaternary semiconductors from II–VI parent compound.

With a direct bandgap nature, CZTS shows the absorption coefficient beyond 10^4 , much higher than that of Si. By tuning the S/Se ratio, the bandgap could be varied from 1.0 to 1.5 eV, which is required for high efficiency solar cells. The band alignments for CZTS and CZTSe are shown in **Figure 2.1.1.3** as below, along with the CISE and CdS as reference [7].

Figure 2.1.1.3 Band alignment of CdS, CuInSe₂, Cu₂ZnSnS₄ and Cu₂ZnSnSe₄.

2.1.2 Defects and secondary phases

Although CZTS has so many advantages, defects and secondary phases within this material are limiting the performance. For quaternary compounds, it is usually difficult to get pure homogeneous single phase samples, and secondary phases always unintentionally form during the synthesis. As with CZTS, binary and ternary secondary phases such as ZnS(Se) , Cu_xS , SnS , SnS_2 , Cu_2SnS_3 will present if the composition of certain element shows higher or the growth condition changes due to the narrow area of single phase kesterite CZTS in the phase diagram. Additionally, the tolerability of component deviation was only 1%-2% below 550 °C, far less than that of Cu-poor chalcopyrite CIGS (**Figure 2.1.2.1**). Similarly for CZTS, the phase stability could also be described by atomic chemical potential space as shown in **Figure 2.1.2.2** as below. The stable region is only 1.0 eV long and 0.1 eV wide.

Figure 2.1.2.1 Ternary phase diagram of $\text{Cu}_2\text{ZnSnS}_4$ [6].

Figure 2.1.2.2 Chemical potential stability diagram of $\text{Cu}_2\text{ZnSnS}_4$ [7].

In kesterite CZTS solar cells, defects affect both the band bending and the recombination properties of carriers. Kesterite CZTS are intrinsically p-type largely due to the effects of acceptor defects like Cu_{Zn} , Cu_{Sn} , V_{Cu} , which have lower formation energy compared to the donor defects like V_{S} , Zn_{Cu} . Therefore, there are no reports about n-type CZTS so far. According to recent density function theory calculation, the distribution of intrinsic defects in the bandgap of CZTS is shown in **Figure 2.1.2.3**.

Figure 2.1.2.3 Schematic intrinsic defects in the bandgap of $\text{Cu}_2\text{ZnSnS}_4$ [7].

It is important to notice that Cu_{Zn} is the major defect in CZTS unlike chalcopyrite CIGS, in which shallower level of V_{Cu} is more common. This dominant acceptor level is 0.12 eV above the valence band maximum (VBM), about 0.1 eV deeper than that of V_{Cu} . For CZTS solar cells, this kind of deep level Cu_{Zn} antisite defect is harmful to the V_{oc} . So reducing the quantity of the deeper Cu_{Zn} while increasing the shallow V_{Cu} would be beneficial to the device performance. Therefore, a Cu-poor and Zn-rich condition has been employed for the fabrication of CZTS materials. And experimental results from this condition show high solar cell efficiency at present [9-12].

2.1.3 Interface and grain boundaries

Apart from the defects and secondary phases, front and back interfaces of CZTS solar cells also have to be optimized to minimize the interfacial recombination, parasitic absorption and resistive losses. Generally, CdS front interface is used to reduce recombination, in which there is a “spike” band alignment for CZTS/CdS, similar to the band alignment of CIGS (**Figure 2.1.3.1**). The CBM of CdS is a slightly higher than the absorber, promoting the charge inversion at the surface. So there has been a large number of works focusing on engineering suitable alternative buffer layers to adjust band offsets. Back contact Mo layer is considered to be another place where secondary phases like MoS_2 or MoSe_2 grow. Thick MoS_2 or MoSe_2 layer will exhibit high series resistance and affect the film growth and stability.

Figure 2.1.3.1 Schematic band alignment of CIGSe solar cell [13].

Besides, the detrimental defects in the bulk interface and grain boundaries (GBs) are strongly limiting the efficiency and performance of current thin film solar cells. And among all these defects, the study of defects at grain boundaries in CZTS is still in the early stage. For high efficiency CIGS solar cells, grain boundaries are supposed to eliminate deep defect states and act as neutral hole barriers, promoting charge separation. While in the case of CZTS, there still exist some debates. Wei and his group investigated the electronic properties at CZTS GBs using DFT calculations [14]. They found that intrinsic GBs are harmful and Fermi level is pinned at the defect states. But through the segregation of defects such as Zn_{Sn} , O_{Se} and Na_{i} into the GBs, the GBs could be fully passivated. This phenomenon leads to the elimination of deep states and creation of hole barrier and electron attracter, beneficial for enhancing V_{oc} and boosting charge carrier collection in CZTS solar cells. As a result, engineering suitable grain boundaries for CZTS based photovoltaic devices should be carefully studied in the long run.

2.2 Fabrication of CZTS/CZTSSe Absorber Layer

2.2.1 Vacuum based deposition approach

Basically, vacuum based deposition techniques could provide high uniformity for the device fabrication. By employing these vacuum deposition techniques, CZTS compounds are deposited on the substrates from target sources by controlling the temperature and pressure in the vacuum chamber. What's more, the chemical composition can be easily controlled in thin films and good reproducibility may be achieved. These vacuum based approaches could be specifically classified into PLD, thermal evaporation/co-evaporation and sputtering, etc.

Among all the vacuum based techniques, co-evaporation is the most widely used one. Due to the capacity for precisely control of elemental fluxes, it shows great advantages for growing high quality, small-scale materials. Thermal evaporation of CZTS yielded 8.4% and CZTSe yielded 11.6% recently [15-16].

Another successfully used vacuum method is sequential sputtering, based on the thermal treatments of different arrangement of chalcogen and metal related stacked precursor

layers. And selenization of sputtered Cu, Zn and Cu₁₀Sn₉₀ multilayers achieved 10.4% efficiency [17].

Due to the advantages such as enhancing the crystallinity of films and flexibility in clean deposition, pulsed laser deposition technique is suitable for the deposition of films with complex compositions. But during the PLD deposition process, a lot of parameters like substrate temperature, pulse rate and length will strongly affect the final film quality.

2.2.2 Non-Vacuum based approach

Although vacuum based techniques have shown great advantages in low-cost, mass production, non-vacuum based techniques such as spray-pyrolysis, electrodeposition and direct liquid coating, are expected to show the potential for higher throughput and lower cost of the equipment in use, compositional uniformity and higher utilization in materials production over large scale.

Spray-pyrolysis is generally a simple spraying process on the preheated substrate. The substrate is heated to around 300 °C before the deposition of precursor. During the spray process, solvent droplet could be evaporated upon contact with the hot surface of substrate while the decomposition and film growth would also take place at the same time. The evaporation and decomposition would cause the cooling effect on the substrate surface; therefore it's quite important to continuously maintain the high substrate temperature in the spray process to achieve uniform films. Various results have been reported to yield 5-8% CZTSSe solar cells using spray-pyrolysis [18-20].

Different from spray-pyrolysis, which is severely influenced by the substrate temperature fluctuation, electrodeposition overcomes this problem and could be used for the fabrication of thin films from small scale in the lab to large industrial scale applications, making it another low-cost, attractive technique. And 8.2% pure selenide CZTSe solar cell was fabricated by this large-area electrodeposition method [21].

The direct liquid coating method includes all the methods by which a layer of either true molecular precursor or nanoparticle-formed ink is directly coated on the substrates followed by thermal annealing (**Figure 2.2.2.1**). This method consists of a variety of techniques, such as ink-jet printing; spin coating, doctor blading and so on. For the direct liquid coating method, each specific technique doesn't have too much difference on the film quality if a uniform and enough thick film could be achieved. Using different precursor solution system may have different influence on the film quality and final device performance. IBM group used hydrazine as solvent for the CZTSSe fabrication, capable of making quite homogeneous precursor solution and getting the record efficiency of 12.6% (**Figure 2.2.2.2**). And less-toxic solvents such as DMSO, 2-metholethanol, ethanol have been successfully used to gain high quality devices from 7% to 11% so far [23-26].

Figure 2.2.2.1 Processing steps in direct solution coating of a kesterite layer [22].

Figure 2.2.2.2 (a) Top view, (b) cross-section and (c) J-V curve of the record 12.6% CZTSSe device [5].

2.3 Application of CZTS/CZTSSe in Solar Cells

2.3.1 Device structure and basic working principles

The configuration of CZTS thin film solar cells usually consist of six parts, that is, substrate, metal back contact (e.g. Mo), p-type CZTS absorber, n-type buffer layer, transparent conductive window layer (TCO), front contact grid (**Figure 2.3.1.1**). As a passive portion, the substrate should be both mechanically and chemically stable during the whole fabrication processes. Besides, the thermal expansion coefficients of the substrate are required to match other layers in case of film peel off during the high temperature annealing process. The TCO window layer is optically transparent together with good electrical conductivity, typically 300 nm thick. And for the metal front grid, Ni-Al grids are the most often used. For the sake of prevent the formation of a resistive Al_2O_3 barrier, a 50nm Ni layer followed by a 1 μm Al layer is used as metal grids. The

most important part for the solar cell is the CZTS absorber, where most of the electron-pairs are generated. After absorbing photons with higher energies than the bandgap, the electron-pairs could be produced. To better separate and transport these carriers, a very thin n-type buffer layer is utilized, normally 50-70 nm CdS. The lattice mismatch between the window layer and absorber could be relieved by the buffer layer, and the band alignments could also be affected. The back contact is deposited on the glass substrate and forms ohmic contact with absorber. Mo is the most common choice for the back contact since it does not diffuse into the absorber layer and forms a low-resistivity contact with the absorber.

Figure 2.3.1.1 The configuration of CZTS solar cell.

Generally, the p-n junction is formed at the interface between p-type CZTS and n-type CdS buffer layer due to the diffusion of holes and electrons along concentration gradient. And depletion region will be formed with electric field within this region. When sunlight is illuminated onto the solar cell, most of the photons could be absorbed by the CZTS thin film absorber and electron-hole pair would be formed. Then the electron-hole pair will be separated by the electric field; the electrons will be transported to the n-side while the holes will be transported to the p-side. As a consequence, holes are collected by the back contact, and electrons are collected by the TCO layer.

2.3.2 Factors limiting solar cell performance

As the solar cell efficiency is mainly determined by V_{oc} , J_{sc} and FF, as shown in the below equation [27]:

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

where η is the solar cell efficiency and P_{in} is the total input power to the cell. Therefore the factors affecting these parameters will largely limit the solar cell performance. As for CZTS devices, one of the biggest challenges is the huge V_{oc} deficit compared with high efficiency CIGS devices [28]. V_{oc} is highly dependent on the interface qualities, in which the dominant recombination process could greatly influence V_{oc} value. J_{sc} is dependent on the light absorption efficiency and carrier recombination within the cell, indicating effective collected amount of photo-generated carriers. FF is generally limited by the quality of all the individual layers and the interfaces between all these layers. Briefly speaking, high defect density, band tail states, non-radiative recombination, high series resistance, non-ohmic back contact could be the main reasons killing the V_{oc} , J_{sc} , FF and solar cell efficiency, which should be carefully identified and avoided in order for further optimization of CZTS based thin film solar cells [29-30].

2.4 Alkali Elemental Doping

Since the importance of sodium on the electrical properties of CIGS was discovered [31], more and more research work has been done on the sodium doping by different kinds of methods. Soda lime glass (SLG) was usually applied as the substrate for it could provide sodium during the annealing process. Some groups incorporated Na by means of thermal evaporation of NaF before or after the annealing process (**Figure 2.4.1**), which both show the improvement of structure and performance [32].

Figure 2.4.1 Schematic representation of the effect of a NaF precursor layer deposited on Mo before the growth of the absorber layer (left) and a post-deposition treatment where NaF is evaporated after the absorber is fully grown (right).

Generally for CIGS solar cells, Na helps to reduce the number of electrically active donors, thus increasing free carrier concentration. On the case of CZTS, similar phenomena was reported, the presence of Na increases the grain size, (112) texturing and effective hole concentration. Mitzi's group also found that Na would segregate along surface and grain boundaries (GBs) and the amount of Na at surface is correlated with the oxygen [33].

Besides Na doping, it was also shown that K doping was helpful for the improvement of efficiency, which significantly enhances the V_{oc} and FF. Using post-deposition of KF, Tiwari's group gained 20.4% flexible CIGSe solar cell on polyide (PI) substrate [34]. Future studies for alkali metal doping should focus on the best strategies to incorporate dopants and potential cross-effects of K together with Na.

Chapter 3

Experimental Methodologies

In this chapter, the detailed experimental methods for the synthesis of CZTS/CZTSSe thin films and fabrication of thin film solar cells are described. The characterization methods for both the thin films and CZTSSe devices are also introduced in sequence.

3.1 Synthesis and Characterization of CZTSSe Thin Film Absorber

Experimental Chemicals

Copper (II) acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, 99%), zinc (II) acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99%), tin (II) chloride dihydrate ($\text{SnCl}_2 \cdot \text{H}_2\text{O}$, 99%), thiourea ($\text{SC}(\text{NH}_2)_2$), 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$, 99%), monoethanolamine ($\text{C}_2\text{H}_7\text{NO}$, 99%) and triethanolamine ($\text{C}_6\text{H}_{15}\text{NO}_3$, 99%), sodium chloride (NaCl , 99.99%), potassium chloride (KCl , 99.99%), lithium chloride (LiCl , 99.99%), selenium pellets (Se , 99.99%), ethanol and acetone were purchased from Sigma Aldrich Company and used as received, without any further purification.

Experimental Procedures

3.1.1 Spin coating of CZTS precursor film

The sol-gel precursor solution was first prepared by dissolving $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (1.55 mol/L), $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (1.0 mol/L), $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ (0.8 mol/L) and thiourea (6.6 mol/L) directly into the 2-methoxyethanol organic solvent. Then the precursor solution was stirred at 50 °C for two hours till the solution turned to be dark yellow. The $\text{Cu}/(\text{Zn}+\text{Sn})$ and Zn/Sn ratios are around 0.86 and 1.25, respectively. After homogeneously mixed and aging for hours, the sol-gel precursor solution was diluted to 1/3 and proper monoethanolamine and triethanolamine was added into the solution to stabilize the solution, improve the adhesion and avoid the cracks during spin-coating process. After that, this diluted solution was spin coated on molybdenum coated soda-lime glass (SLG/Mo) at 3000 rpm for 30 s, followed by preheating at 280 °C for 2 min on a hot plate in air (**Figure 3.1.1.1**). This spin coating and heating step was repeated 12 times to get enough thick film.

Figure 3.1.1.1 Schematic diagram of spin-coating setup and formation of CZTS [87].

3.1.2 Annealing of CZTS precursor thin film

Sulfurization

The CZTS precursor thin films were annealed at 600 °C (heating rate 20 °C/min) in sulphur/Ar atmosphere in a two-zone tube furnace for 40 min. As shown in **Figure 3.1.2.1**, precursor films were placed at the left high temperature zone of the furnace where the temperature was maintained at 600 °C and solid sulfur sulphur powder (0.5 g) was placed in a boat at the right low temperature zone of the furnace at 200 °C. During the whole annealing process, the total pressure was controlled at around 400 mbar.

Figure 3.1.2.1 Schematic diagram of sulfurization set-up.

Selenization

The spin-coated CZTS precursor thin films were annealed in Se vapor at 520-560 °C to form $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) films. Selenization process was conducted in a quartz tube furnace as shown in **Figure 3.1.2.2**. The tube was first pumped to vacuum and refilled with N_2 gas for three times to exhaust the oxygen inside the tube before annealing.

Se pellets (40 mg) were placed in the both sides of the tube to ensure sufficient Se vapor pressure when evaporated during heating. As for this room pressure selenization, a two-step annealing process was used. That is, the films were firstly annealed at 200 °C for pre-alloying for 10 min, then the temperature was quickly ramped beyond 500 °C, at which the selenization process lasted for 30 minutes. After finishing selenization, the tube was cooled to room temperature naturally. The tube was vacuumed and refilled with N₂ again to remove the residual Se vapor before taking out of the samples.

Figure 3.1.2.2 Schematic diagram of selenization set-up with flowing N₂ gas.

Ar annealing

To compare the different annealing atmosphere on the grain growth and microstructure of CZTS thin films, CZTS precursor films were also annealed in Ar atmosphere at 560 °C for 30 min and 1 h using the two-zone furnace, respectively. The annealing process was conducted in the left zone of furnace, with same heating rate to sulfurization process, and the total pressure was also maintained at 400 mbar during the annealing process.

3.1.3 Alkali elemental doping preparation

After the CZTS precursor solution was prepared as stated above, alkali elemental dopants were dissolved into the precursor solution. The doping percentages of alkali elements were based on Cu ion concentration in the solution. First of all, the effects of sodium concentration and gradient were investigated. The solution with 0.5 mol%, 1.0 mol% and 2.5 mol% sodium doping was spin-coated on molybdenum coated soda-lime glass with a 200 nm Al₂O₃ blocking layer (SLG/Al₂O₃/Mo). While the solution with 0.5 mol%, 1.0 mol% and 1.5 mol% potassium doping was simply spin-coated on the molybdenum coated soda-lime glass to study the effects of external potassium doping as well as its

cross effects with sodium diffusing from soda-lime glass. Finally, to further compare and distinguish the role of each alkali elemental plays in our solution processed CZTSSe system, the as-prepared precursor solution was divided into four parts. And 2 mol% of lithium, sodium and potassium dopants were added into each part, respectively. The last part of solution was left blank as the control. The solution with and without alkali elemental doping was then spin-coated on the glass substrates with Al_2O_3 barrier layer, as mentioned before. In order to compare the alkali doping effects more efficiently under the same selenization condition, the thin films were then selenized in the big two-zone furnace at 400 mbar, and under 560 °C for 10 to 40 min.

3.1.4 Characterization

Field Emission Scanning Electron Microscopy (FE-SEM)

Surface structure and morphology of CZTS precursor films and sulfurized or selenized films were imaged by FESEM (JEOL JSM-7600F, 5 KV) and FESEM (JEOL JSM-6340F, 5 KV). Cross-section images of full CZTS and CZTSSe solar cells were also obtained by FESEM (JEOL JSM-7600F, 5 KV). Thin Au or Pt was deposited for cross-section samples before imaging. The stoichiometry of annealed-film and elemental distribution at surface was investigated by Energy dispersive x-ray spectroscopy (EDX) and EDX mapping attached to FESEM.

X-Ray Diffraction (XRD)

X-ray Diffraction (XRD) was used to investigate the crystal structure, crystallinity and phase purity of CZTS and CZTSSe films by Bruker D8 Advance. The spectrum was recorded in the 2θ range from 10°-80° using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

Raman spectroscopy

Raman spectroscopy was performed to analyze the surface structure and secondary phases of selenized samples. It was conducted by a Renishaw Raman system using 532 nm excitation wavelength.

DC Hall effect measurement

Electrical properties (carrier density, carrier mobility, and resistivity) of CZTSSe thin films with and without potassium doping were characterized by Hall Effect measurement using MMR Variable Temperature Hall System (VTHS) in a four-probe configuration. The CZTSSe thin films were spin-coated on glass slides and 4 square electrodes (1.6 mm x 1.6 mm) of aluminum were thermally evaporated in square geometry onto the films. The measurement was conducted at room temperature at atmosphere pressure.

X-ray photoelectron spectroscopy (XPS)

Surface sensitive X-ray photoelectron spectroscopy (XPS, Omicron) was performed on K doped-CZTSSe and undoped thin films in ultrahigh vacuum chamber. To further look into the bulk elemental composition and chemical environment, depth profile was obtained by Ar^+ sputtering with ion energy of 1 KeV for 30 min followed by XPS scans again.

3.2 Fabrication and Characterization of CZTSSe Thin Film Solar Cells

Experimental Chemicals

Cadmium sulfate hydrate ($\text{CdSO}_4 \cdot \text{H}_2\text{O}$, 99%), ammonium hydroxide solution (NH_4OH , 99.99%), hydrochloric acid (HCl , 99%), thiourea ($\text{SC}(\text{NH}_2)_2$, 99.99%), silver glue and 2-methoxyethanol were purchased from Sigma Aldrich.

Experimental Procedures

3.2.1 Solar cell device fabrication

In this work, a basic solar cell configuration of SLG/Mo/CZTS/CdS/i-ZnO/AZO/Ag was adopted for the fabrication of whole device. The detailed fabrication steps are as below: Firstly, a 3 mm thick soda lime glass (SLG) was applied as the substrate for the device. After carefully cleaned by the detergent and mixed ethanol-acetone solution, the glass was dried in the N_2 gas. A high resistant Mo layer was firstly deposited on the glass by DC sputtering at 1.4 Pa for favorable adhesion between the Mo layer and glass. Then another layer of Mo was deposited at 0.4 Pa. The total thickness of Mo back contact

would be around 1 μm and the sheet resistance would be 1 $\Omega/\square$.

Secondly, CdS buffer layer (60 nm) was deposited onto the prepared SLG/Mo/CZTS by chemical bath deposition (CBD) method (**Figure 3.2.1.1**). The CBD solution was prepared with deionized H_2O (140 mL), NH_4OH (25%, 20 mL), CdSO_4 (0.015 M, 20 mL) and thiourea (0.75 M, 20 mL). The substrates were immersed in the solution for 8 minutes at 80 $^\circ\text{C}$ and the thickness of buffer layer was around 60 nm.

Figure 3.2.1.1 Schematic diagram of CBD set-up.

Next, i-ZnO/AZO window layers were deposited for lateral current collection. Intrinsic ZnO (i-ZnO) was deposited by RF sputtering at 1 Pa for 15 minutes to get a thickness of 50 nm. Then 600 nm Al:ZnO (AZO, TCO layer) was sputtered on top at 0.4 Pa for 35 minutes by DC sputtering. After deposition, the sheet resistance of these two layers was measured to be 20-50 $\Omega/\square$, which is good enough for solar cell device.

Finally, front contact fingers were formed by silver glue printing onto the AZO layer. The total device was scribed into several cells (0.16 cm^2) mechanically.

3.2.2 Device characterization

Capacitance-voltage (C-V) and Capacitance-frequency (C-f) measurement

The C-V measurement was achieved using HP 4284A and Keithley 4200 analyzers. The C-f measurement was conducted using Autolab 302N Potentiostat. More specifically, the C-V measurement was performed using 50 mV and 100 kHz AC signal with DC bias from 0 to -5 V at 300 K and the C-f measurement was performed under zero bias at room temperature, and the frequency was tuned from 100 Hz to 1 MHz.

Current density-voltage (J-V) characterization

Current density-voltage curves for solar cells were performed in ambient condition under simulated 1 Sun AM 1.5 G illumination (100 mW/cm²) using Xe-based light source solar simulator (San-Ei Electric, XEC-301S). The current response and J-V characteristics (J_{sc} , V_{oc} , fill factor and efficiency) were measured by Keithley 2612A sourcemeter and the light intensity was calibrated with a standard Si reference cell.

Color J-V test

Color J-V test was performed under white light (no filter), blue light (600 nm short pass filter) and red light illumination (600 nm long pass filter).

External quantum efficiency (EQE)

The incident photon to current conversion efficiency (IPCE) of the solar cells was measured by the PVE300 (Bentham) IPCE Instrument equipped with dual xenon/quartz halogen light source. Standard certified Si and Ge cells were used as calibration reference before measurement. The EQE curve for CZTS solar cells was recorded from 300 nm to 1000 nm, while the range extended to 1400 nm for CZTSSe solar cells.

Chapter 4

Preparation of CZTSSe Absorber by Sol-gel Method

In this chapter, the as-synthesized CZTS precursor film was characterized and the effects of different annealing atmospheres (Ar annealing, sulfurization, selenization) on the film qualities and device performance were investigated. The selenization was optimized with different annealing temperature at room pressure with flowing N₂ gas. The correlation between selenization temperature and properties of thin films, device performance was also explored.

4.1 Introduction

CZTS precursor films were fabricated by solution based sol-gel method and formed after low temperature preheating at 280 °C, therefore, the as-synthesized precursor films always consist of very small grains around several or tens of nanometers and the crystallinity of thin films is also quite poor. However, it is unfavorable to have such large amount of small fine grains within the films for solar cell fabrication, which will lead to a high density of grain boundaries. As intrinsic grain boundaries in CZTS were reported to create deep traps, which may act as non-radiative recombination centers and affect solar cell performance [14, 35], so it is necessary to avoid small grains and reduce grain boundaries as much as possible. Besides, the ideal grains should be columnar grains, whose thickness is close to the film thickness, as revealed by several high efficiency CZTS/CZTSSe solar cells from either co-evaporation technique or hydrazine based solution method [5, 15, 16, 36]. So in this chapter, we are trying to investigate the influence of annealing conditions on the film formation and grain growth. The annealing atmosphere and annealing temperature were studied carefully in sequence.

4.2 Results and Discussion

4.2.1 Effects of annealing atmosphere

As mentioned before, annealing process plays a vital role in the grain growth and final device performance of solar cells, this section will cover the basic study of the effects of annealing process on the microstructure of annealed CZTS and CZTSSe thin films. The effects of different annealing atmospheres (Ar annealing, sulfurization, and selenization) were compared. The detailed evaluation of selenization temperature was conducted to improve device performance.

Figure 4.2.1.1 XRD pattern of CZTS precursor film.

The precursor film was deposited on Mo coated soda lime glass (SLG) by spin-coating and preheated at 280 °C in air. Then precursor film was annealed in either sulfur or selenium atmosphere. The spin-coated precursor film showed bright color, which turned into dark brown and grey after sulfurization and selenization, respectively. The sulfurization was conducted at 600 °C for 40 minutes and selenization was at 560 °C for 10 minutes. For further comparison, additional Ar annealing was performed at 560 °C for 30 min and 1 h. The XRD pattern of precursor film is shown in **Figure 4.2.1.1**. From the XRD pattern, three major peaks at 28.5°, 47.3°, and 56.1° reflect the existence of CZTS phase in the precursor film [37]. However, the width of the main peak is rather low, which means the crystallinity of the precursor film is still poor. There are also some small peaks shown in the background, which could be caused by the remaining sulphur. According to the Scherrer equation $D = K\lambda / B \cos\theta$, the crystalline size was estimated to be around 50 nm. **Figure 4.2.1.2** shows the XRD patterns of Ar-annealed CZTS thin films. After annealing at 560 °C for 30 min, the grain size and crystallinity have been improved greatly, while the improvement becomes more evident with further annealing for 1 hour.

Some previous study demonstrated that CZTS nanocrystals could grow into several microns in size, when annealed at high temperature (above 600 °C) for enough time (1-2 hours), in which the formation of large grains is driven by the abnormal grain growth [38]. However, a large number of secondary phases such as Cu_xS , ZnS , Sn_xS were found on the XRD patterns of Ar-annealed thin films. This could be ascribed to the unstable nature of CZTS and volatile components in the precursor films like SnS . It is likely that CZTS could decompose into Cu_2S , SnS , ZnS , as described in below reaction equation [39-40]:

Therefore, in order to increase the grain size while avoid the formation of large amount of secondary phases; it is required to anneal at high temperature under sulphur or selenium atmosphere to prevent the decomposition of CZTS/CZTSSe and reduce the loss of volatile components.

Figure 4.2.1.2 XRD patterns of CZTS precursor film and Ar-annealed thin films.

As shown in **Figure 4.2.1.3**, the crystallinity and crystal size are also improved greatly after sulfurization or selenization compared to the precursor film. The present peaks of sulfurized-CZTS thin film matches well with those of CZTS (PDF#26-0575), indicating the formation of kesterite CZTS. As for the CZTSSe thin film, three major sharp peaks at 27.48° , 45.68° , and 54.18° correspond to the characteristic peaks of CZTS (PDF#26-0575) and CZTSe (PDF#52-0868), which proves the presence of CZTSSe [30, 37]. The three main peaks of CZTSSe thin film are found to shift towards lower 2θ angles, suggesting that the enlargement of lattice constants, as most of the S in the precursor film has been replaced by Se during the selenization process [30].

Figure 4.2.1.3 XRD patterns of CZTS precursor film, sulfurized-CZTS and selenized-CZTSSe thin film.

The Mo peak intensity also increases after annealing as the high temperature annealing process may lead to the grain growth and improve the crystallinity of Mo layer as well. There is also a shift to the lower angles for Mo peaks of CZTSSe thin film, which may be caused by the secondary phase like MoSe_2 . Besides, as the existence regions of pure

phase CZTS and CZTSe in the phase diagrams are rather narrow, it becomes quite difficult to avoid the formation of secondary phases such as Cu_xSe , ZnSe , Cu_xS , ZnS , Sn_xS , Cu_2SnS_3 , etc [41]. However, these secondary phases have similar XRD peaks to that of CZTS and CZTSe, which may not be effectively distinguished by XRD. So Raman spectroscopy is required for further investigation of the phase purity [30, 42]. The Raman spectroscopy pattern of CZTSSe thin film with 532 nm excitation wavelength is shown in **Figure 4.2.1.4**.

Figure 4.2.1.4 The Raman spectroscopy pattern of CZTSSe thin film.

As shown in **Figure 4.2.1.4**, the Raman spectra of CZTSSe show both characteristic peaks of CZTS and CZTS. The A1 vibration mode peaks at 199 and 235 cm^{-1} are caused by the partial replacement of S by Se atoms. Besides, for pure sulphide CZTS, the major peak appears at 338 cm^{-1} , while it will shift to lower wavenumbers (325 cm^{-1}) due to the incorporation of Se, in agreement with reported literature [30]. This shift for CZTS peak is larger, which means a higher Se to S ratio, also confirmed by XRD pattern. By

combining the Raman data with XRD pattern, no secondary phases have been identified for the selenized-CZTSSe thin film.

Figure 4.2.1.5 shows plan view SEM images of CZTS precursor film, Ar-annealed, sulfurized and selenized thin films. The precursor film has a relatively porous structure and its average grain size is also very small, in accordance with the XRD results. After Ar annealing for 30 min, some bigger grains ranging from tens of nanometers to a few hundred nanometers were observed. The sulfurized-film has an average grain size of several hundred of nanometers, and even some bigger grains could reach nearly 1 μm . For the selenized sample, the surface of film is relatively dense and the grain size is in the range of 1-2 μm , while some smaller grains can also be detected.

Figure 4.2.1.5 Plan view SEM images of (a) CZTS precursor film, (b) Ar-annealed CZTS (c) sulfurized-CZTS and (d) selenized-CZTSSe thin film.

EDX data and EDX mapping image of CZTSSe thin films are shown in **Table 4.2.1.1** and **Figure 4.2.1.6**. As shown in the below figure, each element of CZTSSe thin film

distributes uniformly at the surface, and no secondary phases are found. **Table 4.2.1.1** shows the chemical composition of the CZTSSe thin film. There is a little deviation from the initial composition in the precursor solution, since there may be Sn and Zn loss during the selenization process. In addition, most of the sulphur in the film has been substituted by the selenium, which is also confirmed by the XRD and Raman data.

Figure 4.2.1.6 The EDX element mapping images of CZTSSe thin film.

Table 4.2.1.1 EDX data and chemical composition of CZTSSe thin film.

Element	Cu (%)	Zn (%)	Sn (%)	Se (%)	S (%)	Cu/(Zn+Sn)	Zn/Sn	S/(S+Se)
Atomic (%)	22.80	13.31	12.48	36.93	14.48	0.88	1.07	0.28

As shown in the **Figure 4.2.1.7**, the current-voltage (J-V) curves of CZTS and CZTSSe solar cells under air mass 1.5 illumination are displayed. The efficiency of obtained CZTS solar cell is 2.7% while the CZTSSe solar cell is 5.9%. The device parameters are calculated based on the active area (0.15 cm^2), which doesn't include the area shaded by silver grids. For the sulfurized sample, the J_{sc} , V_{oc} , and FF are 14.77 mA/cm^2 , 0.52 V and 36.7%, respectively. While after selenization, the performance has improved greatly with

J_{sc} and fill factor values of 28.68 mA/cm² and 58.4%. The decrease of V_{oc} to 0.39 V is due to the variation of bandgap for selenized sample.

Figure 4.2.1.7 J-V curves of the CZTS and CZTSSe solar cells under AM 1.5 illumination.

Figure 4.2.1.8 (a) EQE spectra of CZTS and CZTSSe solar cells and (b) bandgap of CZTS and CZTSSe thin films calculated from EQE spectra.

In order to analyze the photoresponse of CZTS and CZTSSe devices under different wavelength of light, the EQE spectrums for both devices are measured and shown in **Figure 4.2.1.8 (a)**. First of all, the photoresponse ranges of CZTS devices are narrower than that of the CZTSSe devices, mainly due to the considerable difference in the bandgaps (**Figure 4.2.1.8 (b)**) in the near-infrared region, which accordingly lead to the J_{sc} of CZTSSe twice higher than that of CZTS cells. Also, a less steep decay in the blue light region from 400 nm to 500 nm for CZTSSe cells indicates less light loss caused by the absorption of CdS buffer layer. While in the red light region beyond 600 nm, both EQE curves drop rapidly, which could be ascribed to the high recombination loss in the interface and bulk regions [43].

4.2.2 Effects of selenization process

The selenization process was achieved in a small half-sealed quartz tube at room pressure with constant N_2 gas flowing through, which has already been described in previous chapter. The selenization temperature was adjusted from 520 °C to 580 °C. The exact selenization process is shown in **Figure 4.2.2.1** as below.

Figure 4.2.2.1 Scheme of the entire selenization process.

Figure 4.2.2.2 shows the XRD patterns of CZTSSe films selenized at different temperature ranging from 520 °C to 580 °C. It reveals that CZTSSe phase will form without any Cu or Sn related secondary phases above 500 °C. The (112) peak intensity will increase gradually with the increase of selenization temperature. Minor peaks such as (101) and (110) were also observed in the patterns, implying good crystallinity of CZTSSe thin films. The cross-section SEM images of CZTSSe devices fabricated under different selenization temperature are displayed in **Figure 4.2.2.3**. From the cross-section images, it is demonstrated that two layers (large grain layer and fine grain layer) of CZTSSe grains are observed under all the selenization processes, which is often reported in solution processed CZTSSe [26, 44]. After increasing the selenization temperature to 560 °C, the bottom small grains become much larger, probably due to the incorporation of more selenium into the bottom layers. And when the temperature rises even higher to 580 °C, the grain size of bottom layer is close to that of large grain layer. Therefore, it is beneficial to reduce bulk recombination and help carrier transport by properly controlling the selenization temperature.

Figure 4.2.2.2 XRD patterns of CZTSSe thin films selenized at 520-580 °C.

Figure 4.2.2.3 Cross-section images of CZTSSe devices selenized at (a) 520 °C, (b) 540 °C, (c) 560 °C and (d) 580 °C for 30 min.

The electrical characteristics of the best CZTSSe devices selenized at different temperature are shown in **Figure 4.2.2.4** and the device parameters are listed in **Table 4.2.2.1** as below. It is clear that remarkably high J_{sc} , moderate V_{oc} and relatively low FF have been obtained for the devices. The V_{oc} values increase with the rising of selenization temperature, while the J_{sc} and FF decrease. The series resistance also increases with the increase of temperature, which in turn leads to the drop of J_{sc} and FF. The best cell was achieved at 560 °C, with J_{sc} of 39.69 mA/cm², V_{oc} of 432.8 mV and FF of 44.26%. Both V_{oc} and J_{sc} values are comparable to high efficiency CZTSSe devices [23-25]. From the EQE curves of these devices, 560 °C selenized-CZTSSe device shows the highest value up to 80% in the visible range. However, with regards to the device selenized at 580 °C, EQE value is quite low and decays rapidly in the infrared region, which may be correlated with narrower depletion region and shorter minority carrier lifetime [43, 45].

Figure 4.2.2.4 (a) J-V characteristics and (b) EQE spectra of CZTSSe thin film solar cells selenized under 520-580 °C for 30 min.

Table 4.2.2.1 Device performance of the best CZTSSe devices under different selenization temperature.

Selenization temperature (°C)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)	Efficiency (%)
520	339.2	37.07	51.96	10.26	852.06	6.53
540	384.1	38.73	49.15	15.20	1056.51	7.31
560	432.8	39.69	44.26	19.48	550.61	7.60
580	468.4	32.86	34.85	21.20	249.16	5.36

4.3 Conclusions

In this chapter, CZTS/CZTSSe thin film absorbers were synthesized by solution based sol-gel method, followed by high temperature annealing process. A deeper investigation of annealing atmosphere and selenization temperature was conducted. The CZTS precursor thin films were annealed under Ar, S, Se atmosphere, respectively. Increasing annealing temperature would improve the grain size and crystallinity and further sulfurization or selenization could even promote grain growth to micron-level large grains. While annealing in Ar at 560 °C, the CZTS may decompose and some secondary phases were found. Therefore, it is required to enhance grain growth in either sulfur or selenium atmosphere. By tuning the selenization temperature, the best CZTSSe solar cell

with 7.6% efficiency was obtained under 560 °C for 30 min. Further increasing selenization temperature could deteriorate device performance.

Chapter 5

Alkali Elemental Doping in CZTSSe via Solution Based Method

In this chapter, the effects of alkali elemental doping on the properties of CZTSSe thin films and solar cell device performance were investigated in details. Sodium and potassium doping by solution based method were adopted to enhance the performance of the solar cell and their effects on both electronic properties of CZTSSe and device parameters were investigated. Different selenization holding time was optimized to achieve better efficiency. Last but not least, individual roles of alkali elements (Li, Na, and K) in CZTSSe were compared by fabricating thin films and devices on SLG/Al₂O₃/Mo substrates and possible alkali doping mechanism was proposed.

5.1 Introduction

Alkali elemental doping, such as Na and K doping, has been proposed to exert beneficial effects on both CIGS and CZTS devices. For Na doping in CIGS and CZTS solar cells, its positive effects like promoting grain growth, increasing hole concentration, passivating non-radiative defects and GBs, have been investigated thoroughly in recent years [46, 47-51]. While in the case of potassium, some different positive effects were found on CIGS, facilitating higher Ga content at CIGS/CdS interface and boosting the efficiency of CIGS up to 20.8% [52]. Further optical and buffer layer optimization has pushed it into the record efficiency of 21.7% [4]. However, in regards to the effects of sodium or potassium even lithium on CZTSSe, only few reports have been published [33, 53-54]. Besides, there still lack systematic study of alkali elemental doping by solution based approach, as most reported doping method are based on alkali diffusion from different substrates or NaF/KF post deposition treatment (PDT) method. For these reasons, we are trying to focus on the alkali elemental doping by simply adding alkali source directly into the solution, which provides more precise control on alkali doping concentration compared with vacuum based methods. We demonstrate that the solar cell performance could be improved with optimized alkali elemental doping, mainly attributed to the enhancement of V_{oc} and FF.

5.2 Results and Discussion

5.2.1 Sodium doping in CZTSSe with various concentration and gradient

In order to further improve thin film quality such as grain size and enhance device performance, sodium chloride (NaCl) was chosen as sodium source here, which was mixed in the precursor solution directly for solution based sodium doping instead of conventional vacuum based NaF post deposition treatment (PDT). In this section, we investigated both the effects of sodium doping concentration and gradient on the grain growth and surface morphology of CZTSSe thin films. Na was added into CZTS precursor solution at various low doping concentrations from 0.5 mol% to 2.5 mol% with respect to Cu concentration, as Na is likely to mainly occupy the Cu sublattice sites and act as substitutional defects [55]. The selenization for the Na-doped thin films was performed under 560 °C for 10 min. With more sodium incorporated into the film, the

crystallinity of CZTSSe is improved, which is reflected in the XRD patterns (**Figure 5.2.1.1**). Both Na-doped and undoped-samples are identified as kesterite CZTSSe with preferred (112) orientation and no any secondary phases are found. Since the Na doping concentration was quite small, the quantity of secondary phases might be below the detection limits of instrument. Besides, XRD patterns of all the Na-doped CZTSSe thin films show a main peak left shift tendency to smaller 2θ values compared with undoped samples, while this trend is less obvious with further increasing Na doping concentration from 0.5 mol% to 2.5 mol%. This phenomenon could be due to the slightly variation of stress and enlargement of lattice parameters or the formation of some secondary phases. It is likely that Na could assist reactive selenization and form Na_2Se_x liquid phases, thus leading to the increase in Se incorporation in the thin films [46].

Figure 5.2.1.1 (a) XRD patterns of the Na-doped CZTSSe thin films and magnified view of (b) (112) peak and (c) (220/204) peak.

The plan view images of selenized CZTSSe thin films with different Na doping concentration are shown in **Figure 5.2.1.2**. It is clear that rather uniform thin films are achieved for all the Na-doped samples. Micron-size grains are present at the surface of Na-doped films, while some smaller grains still exist. However, with the increase of Na doping concentration, the change of surface morphology and average grain size is very small. The quantity of sodium required to promote large grains is different from that needed to passivate grain boundaries (GBs), as previously reported in the case of CZTS [33]. Therefore, we propose that even 2.5 mol% Na doping concentration is still below the required quantity for large scale grain growth and further increasing of concentration will decrease the performance, which may be related to rather high defect density. And for the 2.5 mol% Na-doped thin film, a few white shiny spots and pinholes are observed. As reported, these white shiny spots might be ZnS or ZnSe secondary phases, due to the charging effects for their conductive nature [56]. However, these phases still require to be confirmed by further characterization with Raman and EDX mapping.

Figure 5.2.1.2 Plan view SEM images of CZTSSe thin films with (a) 0 mol%, (b) 0.5 mol%, (c) 1.0 mol% and (d) 2.5 mol% Na doping.

The effect of Na doping concentration on the device performance was studied and the relationship between the average device performance and sodium concentration is shown in **Figure 5.2.1.3**. The best device parameters are listed in **Table 5.2.1.1**. The photovoltaic parameters were based on 10 best cells with standard deviation. The 2.5% Na-doped device shows the best efficiency around 6%, while higher doping level will deteriorate the efficiency. The behaviors of fill factor (FF) and open circuit voltage (V_{oc}) are in accordance with that of cell efficiency. Sodium has been known to help increase the effective hole density, passivate defects at interface and grain boundaries and reduce non-radiative recombination, therefore both the fill factor and V_{oc} are improved. Nonetheless, short circuit current (J_{sc}) keeps dropping with higher Na concentration and the 2.5 mol% Na-doped device shows the lowest J_{sc} . The defect physics of these devices should be further examined to explain the reasons for less-efficient carrier collection with more sodium doping.

Figure 5.2.1.3 Device parameters for CZTSSe solar cells with Na doping concentration from 0.5% to 4.0%.

Table 5.2.1.1 Solar cell performance of best CZTSSe devices with Na concentration from 0.5% to 4.0%.

Na conc. (mol %)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (%)
0.5	334.6	32.18	48.38	5.30
1.0	334.1	29.73	51.82	5.27
2.5	381.4	27.43	58.87	6.12
4.0	326.7	30.58	46.56	4.58

Figure 5.2.1.4 Schematic of sodium gradient doping experimental design.

To investigate the influence of sodium gradient on the CZTSSe solar cells, the precursor solution with 2% Na was spin-coated on the bottom, middle and top five layers, respectively, which is shown in **Figure 5.2.1.4**. Also an undoped sample was used as a control. In order to prevent the sodium diffusion from the soda lime glass substrate during the annealing process, a 200 nm Al_2O_3 barrier layer was deposited prior to Mo deposition by sputtering. The plan view images of undoped and Na-doped samples are shown in **Figure 5.2.1.5**. The Na-doped sample shows more homogeneous grain size distribution at the surface and the average grain size becomes a bit larger than undoped samples. Compared to the bottom and top layer doping, the middle layer-doped sample shows a slightly more large grains and less fine grains at the surface.

Figure 5.2.1.5 Plan view SEM image of CZTSSe thin films with (a) no Na doping, 2 mol% Na on the (b) bottom layers, (c) middle layers and (d) top layers.

As for the sodium gradient doping, the J-V curves of best doped and undoped devices are shown in **Figure 5.2.1.6** and the average cell performance of best 7 cells are shown in **Table 5.2.1.2**. Compared to the undoped sample, there is a big increase of V_{oc} for uniform doped sample. And the V_{oc} of top-doped and bottom-doped samples outperforms the uniform doped one significantly. All the non-uniform doped samples have better fill factor than the uniform doped ones. The power conversion efficiency has been improved from 5.1% to 6.1% with sodium doping on the bottom layers.

Figure 5.2.1.6 J-V curves of best doped and undoped CZTSSe devices selenized at 560°C for 10 min under AM 1.5 light illumination. (Black) undoped device; (red) uniform doped 2% Na; (blue) bottom layers doped 2% Na; (purple) middle layers doped 2% Na; (green) top layers doped 2% Na.

Table 5.2.1.2 Solar cell characteristics of Na-doped and undoped CZTSSe devices from the best 7 cells.

Doping Position	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	η (%)	R_{sh} (Ω)	R_s (Ω)
Undoped	341.2	30.05	46.40	4.74	212.3	8.5
Uniform doped	350.0	31.62	49.71	5.49	407.4	11.4
Bottom layers	361.3	29.06	54.14	5.67	678.2	11.2
Middle layers	340.1	29.55	53.87	5.40	734.7	11.2
Top layers	363.7	29.29	53.42	5.68	792.6	13.0

5.2.2 Potassium doping in CZTSSe with different selenization duration

For CIGS solar cells, potassium doped device has achieved 15-20% efficiency on both SLG and flexible polyimide substrates [4, 34, 57]. Since the effects of potassium doping on the CZTSSe thin film solar cells still lack enough theoretical and experimental study, we carefully explore the potassium doping effects on CZTSSe. K doping concentration was optimized together with different selenization duration from 10 to 40 min while keeping the temperature at 560 °C.

Figure 5.2.2.1 shows plan-view SEM images for both CZTS precursor thin films and selenized-CZTSSe thin films. The CZTSSe thin films were selenized at 560 °C for 10 min. All the CZTS precursor films remain porous structure. Some cracks were noticed in the undoped precursor film due to the relatively small grain size and poor crystallinity. There is an obvious increase of grain size in precursor films with the incorporation of K. The 1.5% K doped precursor film consists of larger grains in the order of hundred nanometers. After selenization for 10 min, the average grain size of 1.5% K doped film could reach 1.5-2 μm , while the majority grains are less than 1 μm for the undoped CZTSSe thin film.

Figure 5.2.2.1 Plane-view SEM images of CZTS precursor films with (a) 0%, (b) 0.5%, (c) 1.0%, (d) 1.5% K doping and CZTSSe thin films selenized at 560 °C for 10 min with (e) 0%, (f) 0.5%, (g) 1.0%, (h) 1.5% K doping.

The XRD patterns and Raman spectra of as-selenized CZTSSe thin films are shown in **Figure 5.2.2.2**. After selenization for 10 min, a well crystallized single phase is obtained. EDX composition analysis of the films selenized at 560 °C for 10 min (**Table 5.2.2.1**) confirms that the S/(S+Se) ratio is around 0.28, and this value hardly changes for the K-doped films. All the films display a Cu-poor (0.88-0.9) and Zn-rich (1.02-1.10) ratio, which is suitable for high efficiency solar cells as reported before [5, 19, 23, 26]. Compared with the Raman spectra of undoped samples, the K-doped films show a slight peak shift towards higher wavenumbers. This phenomenon could be explained by the introduction of potassium into the crystal lattice, leading to the minor bond force variation [42].

Table 5.2.2.1 Chemical composition of CZTSSe thin films with different K doping concentration.

K conc. (mol %)	Cu (%)	Zn (%)	Sn (%)	Se (%)	S (%)	Cu/(Zn+Sn)	Zn/Sn
0	22.80	13.31	12.48	36.93	14.48	0.88	1.07
0.5	22.89	13.67	12.47	36.78	14.12	0.88	1.10
1.0	22.59	12.69	12.39	38.05	14.15	0.90	1.02
1.5	22.51	13.11	12.33	38.24	13.65	0.88	1.06

Figure 5.2.2.2 (a) XRD patterns and (b) Raman spectra of the undoped and K-doped CZTSSe thin films selenized at 560 °C for 10 min. The Raman spectra were taken using 532 nm laser excitation wavelength.

The selenization temperature and duration, as reported before, would affect the sodium diffusion behavior and the grain growth, which could have a huge impact on the formation of thin film and final device quality [31, 58-59]. Therefore, here the selenization duration has been extended from 10 min to 20, 30 and 40 min, respectively.

Figure 5.2.2.3 shows the solar cell efficiencies of K-doped CZTSSe devices under 560 °C for different selenization durations. The solar cell efficiency shows a tendency of improvement with the increase of K doping concentration when the selenization duration is 20 or 30 min, which is the optimum selenization condition for our K-doped system. When the selenization time is either shorter (10 min) or longer (30 min), the cell efficiency could be slightly improved with 0.5% K doping, and then it would drop rapidly with further increase of K doping concentration.

Figure 5.2.2.3 Solar cell efficiencies of K-doped devices fabricated with different selenization duration.

Table 5.2.2.2 Summary of device parameters for K-doped CZTSSe devices prepared with different annealing conditions. (The data shown are the average values obtained from 7 devices with standard deviation)

Annealing condition	K conc. (mol %)	V_{oc} (mV)	J_{sc} (mA/cm ²)	Fill factor (%)	Efficiency (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
560 °C for 10 min	0	375.5±16.6	29.7±1.6	48.0±3.0	5.3±0.3	0.8±0.4	43.3±7.7
	0.5	375.1±7.3	29.4±1.7	57.1±4.3	6.3±0.3	1.1±0.3	161.3±12.7
	1.0	353.8±10.0	30.6±2.1	48.6±3.0	5.2±0.1	1.6±0.7	53.1±18.0
	1.5	326.6±27.9	23.9±2.2	33.5±2.5	2.6±0.4	1.3±0.8	23.1±4.5
560 °C for 20 min	0	356.0±25.6	30.2±2.0	60.7±1.5	6.5±0.3	0.6±0.1	124.3±40.1
	0.5	372.0±19.2	31.6±2.3	58.8±1.2	6.9±0.2	0.6±0.1	119.2±28.1
	1.0	367.7±16.9	30.0±1.6	61.9±1.9	6.8±0.4	0.6±0.2	146.4±32.1
	1.5	358.0±15.2	30.9±1.5	60.6±1.2	6.7±0.4	0.7±0.1	122.3±24.6
560 °C for 30 min	0	369.7±11.7	27.9±1.7	60.4±4.4	6.2±0.6	0.8±0.3	165.0±44.5
	0.5	377.4±15.7	30.3±1.5	61.3±2.3	7.0±0.3	0.7±0.3	169.9±39.7
	1.0	401.8±11.9	29.5±1.0	58.7±2.8	7.0±0.4	0.8±0.5	140.0±27.0
	1.5	396.3±6.1	30.3±0.9	61.0±1.6	7.3±0.2	0.6±0.1	159.8±13.5
560 °C for 40 min	0	381.0±7.0	30.2±0.9	46.7±2.7	5.4±0.3	1.3±0.4	59.4±9.9
	0.5	403.3±9.7	32.5±1.8	58.8±1.2	5.9±0.3	0.7±0.2	52.7±9.0
	1.0	392.2±21.0	30.3±2.2	32.8±3.2	3.9±0.3	0.9±0.7	29.0±5.5
	1.5	397.0±6.4	25.1±1.0	28.9±2.3	2.9±0.2	0.6±0.3	25.9±2.8

The exact device parameters were further extracted to show this trend, as listed in **Table 5.2.2.2**. The device parameters were calculated based on the active device area (0.15 cm²); series resistance (R_s) and shunt resistance (R_{sh}) were determined from light J-V data [60]. The short circuit current (J_{sc}) values are almost constant regardless of the K doping concentration and selenization time in the cases of 20 and 30 min, when considering the standard deviations. But for selenization time of 10 or 40 min, excess K doping could lead to the large decrease of J_{sc} and fill factor, which may be attributed to the relatively high defect density which leads to higher series resistance and lower shunt resistance. With the same annealing time, the series resistance was found to be more affected by the doped K concentration. For the low annealing time of 10 min, the R_s tend to increase with

higher K ratio; while the R_s could decrease for the high annealing time of 40 min. When annealed under the optimum condition, the devices exhibited good fill factor of 60% and J_{sc} beyond 30 mA/cm^2 . As shown in the table, the most beneficial role that K doping plays in CZTSSe is the improvement for V_{oc} . The average V_{oc} has been improved from 370 mV to 400 mV for the best 30 min selenization condition. And the 1.5% K-doped CZTSSe device yielded the best efficiency of 7.78% with a V_{oc} of 405 mV, a J_{sc} of 30.90 mA/cm^2 and a FF of 62.2% (**Figure 5.2.2.4**), which is comparable to other non-hydrazine solution processed CZTSSe thin film solar cells [19, 23-25]. In summary, suitable K doping concentration and optimized annealing treatment is beneficial to the solar cell performance mainly due to the V_{oc} and fill factor enhancement. However, the longer or shorter annealing time at high temperature could cause higher series resistance, lower shunt resistance and fill factor, probably due to the higher defect densities.

Figure 5.2.2.4 J-V characteristics of 7.78% CZTSSe solar cell with 1.5 mol% K doping.

Figure 5.2.2.5 Plan-view SEM images of CZTSSe thin films with (a) 0%, (c) 0.5%, (e) 1.0%, (g) 1.5% K doping and cross-section images of CZTSSe devices with (b) 0%, (d) 0.5%, (f) 1.0%, (h) 1.5% K doping. All the thin films and devices were selenized at 560 °C for 30 min.

The surface morphology of CZTSSe thin films and cross-section images of CZTSSe devices selenized for 30 min are shown in **Figure 5.2.2.5**. The undoped-CZTSSe films grown at 560 °C for 30 min show large planar grains around 2 μm in size, while there are also a few smaller grains that are even less than half a micron. This could be attributed to the inhomogeneous diffusion of sodium and the abnormal grain growth due to the increased annealing time [38, 61]. However, contrary our earlier hypothesis, the external addition of potassium does not further promote to the grain growth as sodium usually does. In the plan-view images, the K-doped films show the uniformly distributed grains close to 1 μm in size. For the cross-section images, there also exist two grain layers for all the devices. The top large grain layers consist of columnar grains in micron size, while the bottom fine layers consist of much smaller grains may be due to rather carbon-rich and selenium-deficit. Although the large grain layers don't change too much in the K-doped devices, the increase in the thickness of fine grain layers with the increase of potassium doping is observed. Meanwhile, some voids are also found in the fine grain layers for all the devices, indicating the selenization process is still required further improvement. Many groups have shown that it's advantageous to grow single large grain layer CZTSSe with high preheating temperature above 500 °C and annealed in a highly sealed graphite box with sufficient Se vapor pressure [24]. The larger grains could be

helpful to reduce recombination at the grain boundaries and maximize the minority carrier diffusion length.

Figure 5.2.2.6 XPS spectra of undoped and 1.5% K-doped CZTSSe absorbers before and after Ar^+ sputtering for 30 min.

Figure 5.2.2.7 XPS wide scan on undoped and 1.5% K-doped CZTSSe absorbers before and after Ar^+ sputtering for 30 min.

To further identify the chemical composition and the possible elemental migration behaviors, X-ray photoelectron spectroscopy (XPS) was applied to CZTSSe absorber with and without potassium doping. **Figure 5.2.2.6 (a) to (f)** shows the XPS spectra for elements like Cu, Zn, Sn, Se, K and Na at the surface of CZTSSe absorber. For comparison, all the films were also sputtered by Ar^+ for 30 min to approximately 20 nm in depth. Similar to the hydrazine processed CZTSSe [62], we note that the surface of both undoped and K-doped CZTSSe films are Cu-depleted and Se-deficit relative to the bulk, and the Cu and Se peaks are clearly observed after sputtering. After sputtering, the Cu peaks and Zn peaks of 1.5% K-doped films decrease by a factor of about 1.3 and 1.7 as compared with the undoped samples, respectively. The K doping leads to a slightly reduction of Cu and Zn peak intensities, but has little influence on Sn and Se peak intensities. As shown in **Figure 5.2.2.6 (e)**, K is obviously detected at the surface only in the surface of 1.5% K-doped CZTSSe films, whereas no K has been detected after the depth reaches 20 nm from the surface. Similar to the K, strong Na peaks are detected at the surface and nearly no Na detected after sputtering. As far as we know, sodium is most likely to locate at the surface and along the grain boundaries in CZTS [33]. Therefore we proposed that the uniformly doped potassium in CZTSSe could also likely diffuse into the near surface (below 20 nm) together with sodium diffusion from SLG substrate during the annealing process, which is similar to the results of KF PDT in CIGS [34]. The presence of both sodium and potassium in large concentration at the surface could relate to the high concentration of oxygen, as an oxide covering on surface could facilitate the alkali elemental diffusion as reported before [63]. This was also confirmed by the oxygen detected only on the surface as suggested in **Figure 5.2.2.7**. In conclusion, K would accumulate at the near surface (below 20 nm) along with Na, and induce a modification of surface composition, enhancing the depletion of Cu at the surface, and even a slightly Cu and Zn poor at the depth of 20 nm with respect to the samples without doping.

To further understand the effects of K doping on the p-n junction quality and electronic transport properties of CZTSSe solar cells, capacitance-voltage (C-V) and capacitance-frequency (C-f) measurements were performed for both undoped and K-doped devices selenized with different duration from 10 to 40 min. The C-V sweep was performed

under reverse bias voltage condition to make the junction capacitance more dominant, in the range from 0 to -5V. **Figure 5.2.2.8** displays the C-V sweep and space charge density profiling as a function of the distance to the p-n junction interface. The charge density N_{C-V} and distance $\langle x \rangle$ can be calculated as below according to the previous reports [60, 64].

$$N_{C-V} = \frac{C^3}{q\epsilon_0\epsilon_r A^2} \left(\frac{dC}{dV}\right)^{-1} \dots\dots\dots (3)$$

$$\langle x \rangle = \frac{A\epsilon_0\epsilon_r}{C} \dots\dots\dots (4)$$

C is the measured capacitance for each DC bias. And ϵ_0 , ϵ_r , q, A stands for the vacuum dielectric constant, dielectric constant for CZTSSe devices, elementary charge and device area, respectively.

As the charge density includes both the contributions from shallow and deep defects, it offers more insight into the concentration and nature of the defects at the heterojunction. It is clearly noted that the capacitance for all the CZTSSe devices decrease monotonously with the increase of reverse bias voltage, meaning that increased reverse bias could widen the depletion width. The capacitance values of doped-devices are higher than undoped devices in the full sweep range and the variation of capacitance value with reverse bias is much bigger for the K-doped solar cells. Furthermore, there are also some differences among the devices under different selenization durations. For the CZTSSe devices selenized for 20 or 30 min, the capacitance values are relatively lower at zero bias, while these values become almost two times higher when the selenization duration is 10 or 40 min. The influence of K doping on the depletion width and charge density of CZTSSe devices are shown in **Figure 5.2.2.8**, **Figure 5.2.2.9** and **Table 5.2.2.3**. With the increase of K doping concentration, the depletion width decreases from 128 nm to 113 nm and 173 nm to 102 nm for the selenization duration of 20 and 30 min. And the charge density increases by several orders in both two cases. The higher charge density is always

accompanied with shorter depletion width in CZTSSe, in accordance with a few reports before [5, 64].

In order to confirm the K doping effects on the change of carrier concentration, the Hall measurement was also conducted for CZTSSe thin films selenized at 560 °C for 30 min, as shown in **Table 5.2.2.4**. It shows the hole concentration of 5.24×10^{15} and hole mobility of $12.84 \text{ cm}^2/\text{Vs}$ for CZTSSe thin films without K doping, which are comparable to the electronic properties of other reported CZTSSe thin films [30, 51]. The hole concentration has been increased while carrier mobility has been decreased with the increase of K doping level, as the film becomes more resistive with K doping. According to the first principle study in CZTS and CZTSe, it has been demonstrated that Cu_{Zn} and V_{Cu} are the dominant acceptor defects that lead to the p-type conductivity [84-85]. Therefore we propose that the K doping could influence the formation of these dominant acceptors as revealed by C-V and Hall measurement. This trend is also observed for other selenization conditions. However, the depletion width becomes quite short and the defect density is much higher when the selenization time is either too short (10 min) or too long (40 min). Accordingly, the solar cells obtained by 10 or 40 min selenization show the poor performance as stated above.

As discussed previously, one of the most dominant effects for Na doping in CIGS solar cells is the increase of p-type hole concentration. Similarly, the effects of K doping on the variation of charge density would be helpful for the V_{oc} improvement, in which the increase in V_{oc} caused by higher hole concentration could be estimated approximately as below [65, 88]:

$$\Delta V_{\text{oc}} = \frac{kT}{q} \ln\left(\frac{N_{\text{K doping}}}{N_{\text{No doping}}}\right) \dots \dots \dots (5)$$

Where k , T , q stands for the Boltzmann constant, temperature and elementary charge, respectively. For the devices selenized at 560 °C for 30 min, the estimated increase in V_{oc} for 1.5% K-doped device is around 50 mV with $N_{1.5\% \text{ K doping}} = 6.65 \times 10^{16} \text{ cm}^{-3}$ and N_{No}

$n_{\text{doping}} = 1.01 \times 10^{16} \text{ cm}^{-3}$. It is in agreement with the V_{oc} values shown in **Table 5.2.2.2** to some extent, where the maximum V_{oc} increment is around 40 mV. The corresponding lower actual increment of V_{oc} demonstrates that except from increasing hole concentration, our solution processed K doping may have some negative effect on some other electronic properties of CZTSSe solar cells. For example, it was reported that post deposition treatment of KF on CIGS growth has been proposed to lead to the formation of deep defect levels [66]. Therefore, it is also likely that our solution based K doping could also lead to the formation of deep defect levels, which causes higher recombination rate, lower carrier mobility and shorter carrier lifetime, and consequently reduces the V_{oc} below the expected value. Furthermore, the selenization process could also strongly influence the defect density, as the charge densities of K-doped devices annealed in 10 or 40 min are as high as $2\text{-}9 \times 10^{17} \text{ cm}^{-3}$, indicating the defect density are rather high for the K-doped CZTSSe absorber. As a result, both K doping and selenization process need to be optimized together.

Table 5.2.2.3 Space charge density (at 0 bias) and depletion width for CZTSSe devices with and without K doping under different selenization duration.

Annealing condition	K conc. (mol %)	Charge density ($\times 10^{16} \text{ cm}^{-3}$)	Depletion width (nm)
560 °C for 10 min	0	9.68	57.60
	0.5	22.69	50.62
	1.0	69.01	45.53
	1.5	88.98	33.54
560 °C for 20 min	0	2.58	128.72
	0.5	3.67	129.03
	1.0	6.05	123.47
	1.5	5.10	113.07
560 °C for 30 min	0	1.01	173.48
	0.5	1.20	192.67
	1.0	2.84	119.42
	1.5	6.65	102.2
560 °C for 40 min	0	2.39	81.79
	0.5	2.32	88.62
	1.0	22.25	42.45
	1.5	46.26	38.28

Table 5.2.2.4 Hall effect measurement of CZTSSe thin films with different K concentration selenized at 560 °C for 30 min.

K conc. (mol %)	0	0.5	1.0	1.5
Resistivity ($\Omega \text{ cm}$)	92.8	304.8	222.2	130.03
Mobility (cm^2/Vs)	12.84	1.20	0.92	0.87
Carrier Density (cm^{-3})	5.24×10^{15}	1.71×10^{16}	3.08×10^{16}	5.53×10^{16}
Sheet Resistance (Ω/cm^2)	5.16×10^5	1.69×10^6	1.23×10^6	7.22×10^5

Figure 5.2.2.8 C-V curves and standard C-V profiles of undoped and K-doped CZTSSe devices taken at 560 °C for 10-40 min: (a) + (b) 10 min, (c) + (d) 20 min, (e) + (f) 30 min, (g) + (h) 40 min. The C-V is performed using 50 mV and 100 kHz AC signal with DC bias from 0 to -5 V at 300 K.

Figure 5.2.2.9 (a) Space charge density and (b) depletion width vs K doping concentration for CZTSSe devices under different selenization time.

Figure 5.2.2.10 shows the C-f curves of CZTSSe devices. The C-f measurement was performed under zero bias at room temperature, and the frequency was tuned from 100 Hz to 1 MHz. The applied frequency determines the thermally emitted defects within the bandgap and gives an idea on their contributions to the recorded profile. The higher capacitance value in low frequency region (below 10^4 Hz) means relatively higher density of deep traps, while the response in high frequency region (10^4 Hz to 1MHz) reflects the free carrier density within the absorber.

All the K-doped devices processed with different selenization time consistently show a higher capacitance value in low frequency region and more rapidly drop of capacitance values to almost zero in high frequency region. This phenomenon becomes more obvious with the increase of K doping concentration. When comparing the devices processed with different selenization time, it is found that when selenization time was 10 or 40 min, the capacitance values in the low frequency region were several times larger than those samples selenized for 20 or 30 min. In summary, we conclude that deep states within the depletion region would increase with higher K doping concentration no matter what selenization duration was. What's more, it is likely that non-ideal selenization process would also induce large amount of deep defects, which is in agreement with our device performance as shown previously.

Figure 5.2.2.10 C-f curves of undoped and K-doped CZTSSe devices taken at 560 °C for 10-40 min: (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min.

Figure 5.2.2.11 (a) displays the external quantum efficiency (EQE) spectra of the corresponding undoped and K-doped CZTSSe solar cells. The quantum efficiency has been improved in a wide range from 400 to 1100 nm, indicating the enhancement of light absorption for the absorber layer. And the maximum quantum efficiency exceeding 80 % is obtained for a photon wavelength of 580 nm. The bandgap values of CZTSSe devices annealed at 560 °C for 30 min are shown in **Figure 5.2.2.11 (b)**, determined by fitting a plot of $[E \ln(1-EQE)]^2$ vs. photon energy graph near the band edge. The external K doping from 0.5% and 1.5% hardly change the bandgap of as-selenized CZTSSe. The bandgap values for all the CZTSSe thin films are around 1.05 eV.

Figure 5.2.2.11 (a) EQE spectra and (b) bandgap of undoped and K-doped CZTSSe device selenized at 560 °C for 30 min.

Figure 5.2.2.12 J-V characteristics of (a) undoped and (b) 1.5% K-doped CZTSSe solar cell under white, red and blue light illumination.

The influence of K doping on the diode characteristics of CZTSSe solar cells was checked by the color J-V measurement, which is shown in **Figure 5.2.2.12**. The diode characteristics of thin film solar cells can be distorted by a front interface (CdS/CZTSSe) secondary barrier if the conduction band offset (CBO) is large with a “spike like” CBO beyond 0.5 eV, as minority carrier transport could be blocked by this large barrier. Therefore, the investigation of J-V distortion of our K-doped CZTSSe devices as well as the distortion magnitude on the light wavelength could be achieved by color J-V measurement.

By making use of different optical band pass filters with a cut off wavelength at 600 nm, the location of photon absorption into either the absorber layer or n-type top layers could be controlled, which is usually used to investigate the absorption behaviours of ZnO and CdS layers. When using the blue light band pass filter (<600 nm), the light will not only be absorbed by the absorber layer, but also by ZnO window layer ($E_g=3.2$ eV) and CdS buffer layer ($E_g=2.4$ eV); while the light can only be absorbed by the absorber if the red light band pass filter is used (>600 nm).

Here the color J-V characteristics of the best 1.5% K-doped CZTSSe and undoped devices were measured under dark conditions, white light conditions, filtered red light and blue light conditions. For the undoped CZTSSe device, an efficiency of 6.5% under white light conditions with a V_{oc} of 371.6 mV, a J_{sc} of 30.1 mA/cm² and a fill factor of 58.3%. This solar cell exhibits a cross-over effect between the white light and dark light J-V curves at a voltage around 396 mV. After incorporation of K, the best CZTSSe solar cell shows a higher V_{oc} of 405 mV, a higher J_{sc} of 30.5 mA/cm² and a higher fill factor of 62.2%. For this K-doped device, there is no obvious cross-over effect between white and dark J-V curves even beyond 500 mV. Since the distortion of J-V curves could be caused by non-Ohmic back contact, deep level defects at the absorber, buffer layers or buffer/absorber interface [67-68], the disappearance of cross-over phenomenon possibly indicates that the front interface has been passivated with 1.5% K doping under optimum selenization condition and the front interface secondary barriers may be relieved [69].

Due to the reduced light intensity under these conditions, both devices for all these measurements exhibited lower V_{oc} and J_{sc} values compared with those under white light illumination. At both low energy and high energy illumination conditions, there is no visible kink on the J-V curves for all the devices. And the J-V curves have similar shapes to the ones measured under white light. When using red light band pass, a slight decrease of fill factor for all the devices could be observed while the fill factor values are higher when the high energy blue light illumination condition is utilized. The decrease of FF is correlated with the absence of photons absorbed in CdS buffer layer and increased series resistance. And the cross-over effect is observed for both devices under blue light

illumination, whereas it's more severe for the undoped one. Therefore we assume that the K doping in CZTSSe solar cells could relieve the cross-over effects due to the improvement of carrier collection and passivation of front contact [69-70].

5.2.3 Comparison among Li, Na, K doping and proposed doping mechanism

As reported, a 300 nm Al_2O_3 layer was proved to be effective in preventing the sodium diffusion from SLG [86]. So in this chapter, Al_2O_3 was also chosen as a blocking layer to prevent alkali elemental diffusion (mostly Na) from SLG during the annealing process to better investigate the effect of external addition of each alkali element (Li, Na, K). The cross-section images for CZTSSe devices with alkali elemental doping are shown in **Figure 5.2.3.1**. From the following images, the Al_2O_3 blocking layer with a thickness around 300 nm was clearly observed, and there is still little variation of grain size and morphology with alkali elemental doping.

Figure 5.2.3.1 SEM cross-section images for CZTSSe devices (a) without doping, (b) with 2% Li doping, (c) with 2% Na doping and (d) with 2% K doping.

The J-V characteristics and device performance of CZTSSe solar cells with and without alkali elemental doping fabricated under optimum 560 °C for 30 min are shown in **Figure 5.2.3.2** and **Table 5.2.3.1**. For the undoped device, an efficiency of 5.61% was achieved with V_{oc} of 336.8 mV, J_{sc} of 30.79 mA/cm², FF of 44.69%. We noticed similar effects like previous study of Na and K doping. All the alkali elemental doped CZTSSe devices show more obvious V_{oc} and FF improvement. The devices with LiCl and NaCl doping show the V_{oc} values close to 400 mV, with an increase of 30 mV. After measuring the device parameters of the best 13 CZTSSe solar cells from two batches, the average V_{oc} values were calculated to further improve the accuracy of V_{oc} improvement. It is found that average V_{oc} has been promoted from 340 mV to nearly 390 mV, with a great increase of 50 mV (**Figure 5.2.3.4**).

The EQE spectra and bandgap of these devices are shown in **Figure 5.2.3.3**. The undoped device shows the highest value in the wavelength beyond 600 nm; while the K-doped device has the worst EQE performance. There is also little variation of bandgap for the devices with alkali elemental doping (1.05 eV) except for the K-doped device which shows a slightly higher bandgap of 1.1 eV. It is likely that excess alkali elements may segregate at the surface and GBs and form some minority secondary phases, thus changing the bandgap a bit [71].

Figure 5.2.3.2 J-V characteristics of best CZTSSe devices with and without alkali elemental doping.

Table 5.2.3.1 Device performance of best CZTSSe solar cells with and without alkali elemental doping.

Doping conc. (mol %)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (%)
0	366.8	30.79	49.69	5.61
2% LiCl	396.6	29.64	55.62	6.54
2% NaCl	389.8	32.16	52.10	6.53
2% KCl	370.9	31.36	53.11	6.18

Figure 5.2.3.3 (a) EQE spectra and (b) bandgap of CZTSSe device with and without alkali elemental doping.

Figure 5.2.3.4 V_{oc} data of CZTSSe devices with and without alkali elemental doping (each from 14 cells).

Figure 5.2.3.5 shows the C-f and C-V curves of CZTSSe devices with and without alkali elemental doping. In the C-f curves, all the devices with alkali elemental doping reflect higher capacitance values in low frequency region ranging from 100 Hz to 100 KHz. This phenomenon agrees well with what we speculate before. Higher density of deep traps is indicated in the devices with alkali elemental doping, which should be carefully checked and avoided by controlling the selenization process and doping concentration. In high frequency region, the undoped device shows a steep decrease of capacitance value, which means that the free carrier within the absorber will be decreased if Na diffusion is restricted. When under negative bias in the range from 0 to -5V, the capacitance values of all the devices with alkali elemental doping are higher than that of undoped cell. It demonstrates that the depletion width has been also reduced. The detailed data of depletion width and charge concentration is displayed in **Figure 5.3.3.6** and **Table 5.2.3.2**. The Na-doped cell shows the highest carrier concentration and the shortest depletion width. Therefore from this perspective, Na still proves to be the most helpful in

V_{oc} enhancement among these three alkali elements due to the increase of carrier concentration, while all the alkali elements are effective in pushing forwards the device performance if processed with optimum amount.

Figure 5.2.3.5 (a) C-f and (b) C-V curves of CZTSSe devices with and without alkali elemental doping.

Figure 5.2.3.6 Standard C-V profiles of CZTSSe devices with and without alkali elemental doping.

Table 5.2.3.2 Space charge density (at 0 bias) and depletion width for CZTSSe devices with and without alkali elemental doping.

Doping conc. (mol %)	Charge density ($\times 10^{16} \text{ cm}^{-3}$)	Depletion width (nm)
0	2.52	154.20
2% LiCl	5.76	129.07
2% NaCl	8.95	117.61
2% KCl	6.12	118.45

5.3 Conclusions

In this chapter, the effects of solution processed Na and K doping on CZTSSe thin films and solar cells were investigated in details. V_{oc} and FF improvement is clearly shown in devices with both Na and K doping. The doping concentration and doping gradient of Na was studied. The 2.5% Na-doped device shows the best PCE of 6.12%, and the top layer and bottom layer Na doping is better than the middle layer doping. As for K doping, the best PCE of 7.78% was obtained for the 1.5% K-doped device by optimizing the selenization duration to 30 min. The exact K doping effects on different selenization time was investigated. The enhancement of solar cell efficiency has been found for all the selenization time from 10 to 40 min, whereas the optimum K doping concentration is varied. The increase of solar cell efficiency could mostly attribute to the V_{oc} or the FF improvement with K doping.

Individual alkali doping effects were also explored by depositing thin film absorbers onto substrates with Al_2O_3 blocking layers. Similar V_{oc} and FF enhancement is observed for the devices with alkali elemental doping. It further confirms that this enhancement is caused by the increase of carrier concentration, while large amount of deep level states may form within bandgap with alkali elemental doping as well if the doping level is too high or the selenization condition is not optimum. Among the three alkali elements (Li, Na and K), Na proves to be most effective, possibly because it helps to increase the most carrier density while decreasing depletion width a little.

Chapter 6

Discussion and Future Work

In this chapter, the overall contents of results and discussion will be briefly summarized. The future research directions for solution based alkali elemental doping and its potential application in the field of thin film solar cells have been proposed. Investigation of defect physics of dopants in CZTS/CZTSSe may greatly contribute to a deeper understanding of the material chemistry and precise control of doping effects for the improvement of cell performance, which would also promote the development of flexible electronics accordingly.

6.1 Overall Summary

CZTSSe currently is one of the most promising candidates as an alternative to conventional CIGS in application of next generation thin film photovoltaics. Solution processed approach has been regarded as an efficient and economical way for large scale manufacturing of solar cells in the near future. Therefore here in this thesis, the main objectives are fabricating CZTSSe thin film solar cells by non-hydrazine environmental friendly solution based approach and solar cell performance by alkali elemental doping.

CZTS/CZTSSe thin films were first prepared a simple facile spin-coating method followed by high temperature annealing process. The annealing conditions were varied to promote grain size and improve film quality and device performance. The influence of different annealing atmosphere on the grain growth of CZTS was investigated. Both sulfurization and selenization could greatly promote grain growth, while increasing annealing time under Ar atmosphere also shows positive effects. However, some secondary phases could exist due to the decomposition of absorber at high temperature. Besides, the influence of selenization temperature was also studied. There is an obvious increase of fine grain layers with the increase of selenization time, thus reducing GBs. As a result, 7.6% PCE was obtained for the absorber fabricated with 560 °C selenization. Further increasing selenization temperature could deteriorate the performance, which is related with higher R_s , resulted from thicker MoSe_2 layer.

In order to further enhance device performance, CZTSSe absorbers were prepared with alkali elemental doping. The doping level and gradient of Na or K was tuned. Top and bottom Na-doping shows better results than middle layer doping, and 2.5% Na-doped device shows the best PCE of 6.12%. As for K doping, 7.78% CZTSSe cell was obtained after optimized selenization duration to 30 min. The improvement of device performance is attributed to the V_{oc} and FF enhancement. The C-V and C-f measurement were performed to investigate the cross-effect of external K doping together with Na diffused from SLG. It reveals that the increase of V_{oc} and FF is mainly caused by the increase of carrier concentration. However, excess K doping or non-ideal selenization conditions

could lead to large amount of deep traps within the bandgap, which will reduce the solar cell performance.

Additionally, the comparison of alkali elemental doping effects was also performed. Similar V_{oc} and FF enhancement has been found in all the cases to some extent, whereas this impact may be a little different for different elements possibly ascribed to the different incorporated amount of each element. Among the three alkali elements (Li, Na and K), Na proves to be most effective, possibly because it helps to increase the carrier density most while decreasing depletion width a little, when compared with Li and K. K doping may not be as helpful as the other two, due to the difficulties to be incorporated into the lattice.

In conclusion, further precise control of alkali elemental doping concentration and optimization of selenization conditions is required to avoid high density of defects while maintaining the advantages of V_{oc} enhancement, providing a path for further pushing cell efficiency of CZTSSe solar cells.

6.2 Future Directions

6.2.1 Investigation of defect physics of alkali elemental doping

In order to get deep insight into the mechanism of alkali elemental doping effects on CZTSSe devices, the defect physics and device properties should be carefully examined. Therefore, temperature-dependent photoluminescence (PL) and J-V measurement could be applied to investigate the device physics of CZTSSe solar cells with alkali elemental doping. As shown in **Figure 6.2.1.1**, the samples doped with less Na shows a reduced luminescence signal, which confirms that sodium could play a role in reducing non-radiative recombination in CZTS [33, 72]. Also the temperature dependent solar cell parameters could be measured to calculate the activation energy of the recombination process as shown in **Figure 6.2.1.2** [33, 73-74]. Time-resolved photoluminescence (TR-PL) could also be used to calculate the lifetime of minority carriers [45, 75-76]. These characterization methods would be very useful to figure out the defect physics and the role of alkali elements in performance enhancement. What's more, KPFM and C-AFM

are proved to be useful tools for the deep investigation of the band alignment and properties of grain boundaries [35, 54, 77-79], which are quite helpful to clearly distinguish and further control the roles of these elements in CZTS based device for further device improvement.

Figure 6.2.1.1 Temperature-dependent PL spectra for CZTS with different NaF content: a) no NaF, b) 1 nm NaF, c) 4.5 nm NaF, and d) 23 nm NaF.

Figure 6.2.1.2 (a) V_{oc} vs Temperature data and its linear extrapolation to 0 K indicating the activation energy EA of the recombination process. (b) Time-resolved PL traces measured at a wavelength near bandgap that yields maximum PL signal.

Figure 6.2.1.3 C-AFM conductivity images for (a) undoped and (b) Li-doped CZTSSe thin films.

Figure 6.2.1.4 (a) AFM topography image, (b) potential image, and (c) topography and potential linescans of Li-doped CZTSSe films. (d) AFM topography, (e) potential image, and (f) topography and potential linescans of undoped CZTSSe films.

6.2.2 Application of alkali elemental doping in flexible devices

Thin film flexible CIGS and CZTS solar cells are attractive and promising for future large scale industrial and household applications. Currently, flexible devices are fabricated on metal foils or polymer substrates [80-83], whereas one of the biggest challenges is to form absorber layers with suitable optical and electrical properties at low annealing temperature. Since the metal foils and polymer substrates are alkali deficit, external addition of alkali doping is required for high efficiency devices. As a result, developing precise controlled incorporation of optimum amount of alkali elements especially Na and K will make a great difference on the development and future application of flexible devices.

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