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Synthesis, Processing, and Fundamental Phase Formation Study of CZTS Films for Solar Cell Applications

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

SYNTHESIS, PROCESSING, AND FUNDAMENTAL PHASE FORMATION STUDY
OF CZTS THIN FILMS FOR SOLAR CELL APPLICATIONS

A dissertation submitted in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

in

MATERIALS SCIENCE AND ENGINEERING

by

Osama Awadallah

2018

To: Dean John L. Volakis
College of Engineering and Computing

This dissertation, written by Osama Awadallah, and entitled Synthesis, Processing, and Fundamental Phase Formation Study of CZTS Films for Solar Cell Applications, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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Florida International University, 2018

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DEDICATION

I dedicate this dissertation to my parents. Without their love, support, and patience, it would have been impossible to complete this research.

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Foremost, I would like to express my sincere gratitude to my advisor Professor Zhe Cheng for the tremendous support, motivation, immense knowledge and insightful discussions throughout my PhD study and research.

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ABSTRACT OF THE THESIS

SYNTHESIS, PROCESSING, AND FUNDAMENTAL PHASE FORMATION STUDY
OF CZTS FILMS FOR SOLAR CELL APPLICATIONS

by

Osama Awadallah

Florida International University, 2018

Miami, Florida

Professor Zhe Cheng, Major Professor

Copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$ or CZTS) kesterite compound has attracted much attention in the last years as a new abundant, low cost, and environmentally benign material with desirable optoelectronic properties for Photovoltaic (PV) thin film solar cell applications. Among various synthesis routes for CZTS thin films, sol-gel processing is one of the most attractive routes to obtain CZTS films with superior quality and low cost. In this study, sol-gel sulfurization process parameters for CZTS thin films were systematically investigated to identify the proper process window. In addition, temperature dependent Raman spectroscopy was employed to monitor the CZTS sulfurization process in real time and gain fundamental information about the phase formation and degradation mechanisms of CZTS under the relevant processing conditions. It was found that CZTS thin films with different Cu stoichiometry can be prepared using parts-per-million (ppm) level of hydrogen sulfide (H_2S) gas as opposed to high percentage level of H_2S (e.g., $\geq 5\%$) in all previous studies. Samples sulfurized at lower temperatures of $\sim 350^\circ\text{C}$ and 125°C revealed the formation of CZTS phase as confirmed by XRD, Raman micro-spectroscopy, and sheet resistance measurement.

Local EDS analysis indicates that CZTS films prepared at those low temperatures have a near-stoichiometric composition and are sometimes accompanied by the formation of Cu_{2-x}S phase(s). Also, stoichiometric and Cu-rich precursor solutions tend to yield CZTS samples with better crystallinity and superior optical properties compared with the Cu-deficient solution.

Moreover, in situ Raman monitoring of phase formation of CZTS material was carried out from room temperature up to 350°C in a 100 ppm $\text{H}_2\text{S}+4\%\text{H}_2+\text{N}_2$ gas mixture. The results showed that CZTS phase formed in about 30 min via a direct reaction between the metal oxide precursor film and the $\text{H}_2\text{S}-\text{H}_2$ gas mixture at an intermediate temperature of 350°C and remained stable upon extended exposure. In comparison, at a lower temperature (170°C), the oxide precursor film had to be reduced first (e.g., in 4% H_2/N_2 forming gas) and then the CZTS phase emerged. However, continued sulfurization at a lower temperature (e.g., 170°C) led to the disintegration of CZTS and the formation of CuS impurity, which remains stable upon cooling the sample down to room temperature. Furthermore, results of in situ Raman monitoring of CZTS films in an oxygen rich atmosphere at elevated temperatures up to 600°C suggested that CZTS oxidizes first at $\sim 400^\circ\text{C}$ to form tin oxide (SnO_2) and binary sulfides of mainly copper sulfide (Cu_{2-x}S) and zinc sulfide (ZnS). Then, at temperatures higher than 400°C , the remaining sulfides oxidize to form zinc oxide (ZnO).

The outcomes of the current study set the directions for optimizing the CZTS film structure and stoichiometry toward developing low cost and high-performance CZTS solar cells in future.

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1. INTRODUCTION

1.1. Overview

Solar radiation is the most abundant, clean, and free source of energy on earth. Approximately, the sun emits 120,000 Terawatts (TW) of power on the earth's surface. Photovoltaic (PV) technology uses semiconductor materials for making solar panels to convert solar radiation directly into electricity. Currently, PV is the fastest growing renewable energy technology compared to other renewable energy sources. Additionally, compared to other sources of energy (e.g., hydrothermal and wind), PV technology does not require sophisticated changes of the landscape beside it is emission and noise free, which makes it the safest and cheapest sustainable alternative to fossil fuels and other energy sources.

The most fundamental component of a PV product is an “optoelectronic semiconductor” device that is called solar cell. The two major categories of PV solar cells are the inorganic and organic solar cells. The first category includes crystalline silicon as well as inorganic thin film solar cells (TFSCs), while the second category represents a class of solar cells with the organic component acting as the active absorber layer such as dye-sensitized solar cells (DSSCs).

Crystalline silicon solar cells are fabricated from Si wafers and assembled in modules. They have been the dominant technology in the PV industry for decades, with a market share close to 90%. However, they are limited by the rigidity of cells and modules, the extensive material and energy consumption involved in silicon wafer processing and the

need for flexible modules with much lighter weight and flexibility. Due to the drawbacks of crystalline silicon solar cells, another category of inorganic solar cells, named inorganic thin film solar cells, was introduced to the PV technology in which the light absorber is a layer of “inorganic semiconductor compound”, and comes as thin as 1 μm . The most important compounds that are currently used for TFSCs technology include cadmium telluride (CdTe) and copper indium gallium selenide ($\text{CuIn}_x\text{Ga}_{(1-x)}\text{Se}_2$, CIGS) and both materials are used to make flexible PV modules.

Nevertheless, both CdTe and CIGS suffer from significant drawbacks such as Cd toxicity, the scarce resources of In, Ga, and Te elements, and resulting price fluctuation, which might affect their market adoption in the future. Recently, copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$, CZTS) has been investigated as a promising candidate that offer great advantages over CdTe and CIGS. CZTS material has all earth abundant and non-toxic constituents along with excellent optoelectronic properties, which make it an environmentally friendly and more economical and sustainable alternative to both CdTe and CIGS. Furthermore, the same underlying device architecture for CdTe and CIGS could be implemented for CZTS, which would help accelerate the development of CZTS solar cells with superior power conversion efficiency.

1.2. Motivation of the Research

Typically, fabrication of CZTS thin films involves high temperature ($\geq 500^\circ\text{C}$) annealing of the film precursors in high concentrations (from 5% up to 60% vol.) of the toxic and corrosive hydrogen sulfide (H_2S) gas. At such high processing temperatures, stoichiometry control of CZTS phase becomes a challenge due to the high possibility for

the loss of low melting point elements such as zinc and tin or volatile metal chalcogenides such as tin sulfides (SnS_x). Also, the use of high concentration of H_2S causes severe safety and environmental concerns and requires the implementation of stringent safety measures and precautions. Furthermore, most of the vacuum-based techniques developed for CZTS film deposition such as thermal evaporation and sputtering have restricted stoichiometry control beside their complexity and high operating cost, while some existing solution based routes are either toxic and dangerous (such as the hydrazine-based solution route) or imply multiple-step deposition (such as the nanoparticle approach).

Therefore, it is necessary to develop a processing route that provides better stoichiometry control, helps mitigate the potential loss of volatile components in the system during sulfurization process, and adopts a more environmentally friendly and cost-effective procedure compared to the currently implemented methods in previous studies. In that sense, sol-gel sulfurization of oxide precursor in H_2S atmosphere is an attractive approach since it provides precise stoichiometry control on the molecular level and may be carried out lower sulfurization temperature with reduced H_2S concentration.

On the other hand, another major limitation of previous studies is the lack of understanding of the fundamental mechanism of CZTS phase formation during the actual sulfurization process of precursors under the relevant conditions and related transformation and decomposition that may be encountered. Such understanding is essential to CZTS sulfurization process optimization and eventually improving device performance.

1.3. Research Objectives and Technical Approaches

Based on the main challenges discussed previously, the following are the two primary objectives of the current study. The first is to produce high-quality CZTS films based on an environmentally friendly and cost-effective technique that utilizes the minimal concentration of H_2S gas (100 ppm by volume) as opposed to the highly toxic concentrations of (50,000 up to 600,000 ppm) typically used for processing this material. The second is to provide a better understanding of the phase formation mechanism during the evolution of CZTS material under the relevant processing conditions as well as phase transformation/decomposition mechanism under the conditions that lead to oxidation and degradation of CZTS films.

To achieve the above mentioned objectives, sol-gel sulfurization process of CZTS and other related binary and ternary sulfide films was carried out in 100 ppm $\text{H}_2\text{S}+\text{H}_2$ atmosphere at different temperatures. After that, films were characterized using various ex-situ techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS), light absorption spectroscopy to understand the influences of processing parameters on film chemical and physical properties.

On the other hand, characterization techniques such as in situ Raman microspectroscopy were used to study fundamental mechanisms for CZTS phase formation and decomposition in real time with support from other techniques.

In addition, thermodynamic analysis was also carried out to help understand the observed phenomena during sulfurization process under different conditions.

1.4. Organization of the Thesis

In the following, chapter II will provide background information about the basic concepts of solid-state PV solar cell devices, their basic classification, current status and prospects of PV technology. It will also provide a detailed literature review of CZTS kesterite material, focusing on its properties, synthesis routes including existing sol-gel sulfurization route and their limitations. Finally, it will address the previous work done on understanding the fundamental mechanism of phase formation and transformations in CZTS material as well as temperature dependent Raman spectroscopy studies on CZTS material. Chapter III will present the results of the study on CZTS preparation via the sol-gel sulfurization method using ppm level H_2S including the effect of different stoichiometric compositions of the precursor material. Results of characterization of the obtained CZTS films will also be presented in this chapter based on XRD, ex situ Raman spectroscopy, SEM/EDS, electrical conductivity, and optical absorption spectroscopy. Chapter IV will present the results of the in situ Raman monitoring of the sulfurization process for stoichiometric and Cu-rich sol-gel CZTS films and discuss the possible mechanisms for CZTS formation as well as related important transformations observed during the in situ Raman monitoring experiments. Also, a thermodynamic analysis of the sulfurization process under relevant in situ sulfurization conditions will be introduced in this chapter to help understand the observed phenomena. In Chapter V, the results of the in situ Raman monitoring of CZTS annealing process at elevated temperatures in oxygen rich atmosphere will be presented and the mechanism of CZTS film oxidation and related degradation under the relevant annealing conditions will be discussed.

Finally, chapter VI will summarize the main findings from this work and provide the directions and recommendations for future work.

2. BACKGROUND AND LITERATURE REVIEW

2.1. Principles of PV Solar Cells

The basic principle of PV solar cells is based on the photovoltaic effect that involves the generation of a potential difference at the interface of two semiconducting materials in response to electromagnetic radiation.

The energy of the light photons can be expressed as follows:

$$E = h\nu \quad (2.1)$$

where h is Planck's constant and ν is the frequency of the light.

Based on the PV effect, the working principle of a solar cell can be divided into three fundamental processes:

1. Generation of electron-hole pair due to photons absorption: when the material absorbs a photon, the photon energy excites an electron from its initial energy level E_i to a higher energy level E_f , as in Figure 2.1 (a). Photons can only be absorbed if the difference in electron energy levels equals or smaller than the photon energy, $h\nu = E_f - E_i$. Once an electron is excited from E_i to E_f , a void is created at E_i . This void behaves like a particle with a positive elementary charge that is called a hole. Therefore, the absorption of a photon leads to the creation of an electron-hole pair, as illustrated in Figure 2.1(c)-step 1.

2. Separation of the photo-generated charge carriers in the junction: the electron-hole pair tends to recombine which means the electron will fall back to the initial energy level E_i , as illustrated in Figure 2.1(c)-step 2.

Figure 2.1. (a) Absorption of a photon in a semiconductor with bandgap E_g . The photon with energy $E_{ph}=h\nu$ excites an electron from E_i to E_f . (b) Part of the energy is thermalized If $E_{ph} > E_g$. (c) A simple solar cell model. (Jager et al., 2014)

After that, the energy will be released as a photon or transferred to other electrons or holes. When two different semiconductor materials (p-type and n-type) are combined, electrons can flow out through the p-type material and holes can flow out through the n-type material, as in Figure 2.1(c)-step 3.

3. Charge collection: the charge carriers eventually is extracted from the solar cells using electrical contacts to an external circuit as shown in Figure 2.1(c)-step 4. Finally, after the electrons passed through the circuit, they will recombine with holes at the contact-absorber interface, as depicted in Figure 2.1(c)-step 5.

2.2. Classification of PV Solar Cells

This section briefly describes the different classes of PV solar cells and reviews the major achievements and the current status of each class of solar cell.

2.2.1. Crystalline Silicon Solar Cells: The First Generation of PV Solar Cells

Crystalline Silicon solar cells are currently dominating the PV industry with a market share of approximately 90%. Crystalline silicon solar cells, as appears in Figure 2.2(a) utilize a relatively thick layer (typically 100 μm) of high purity doped silicon to harvest solar radiation and convert it into electricity. Solar-grade purity silicon is produced from chemical treatment of metallurgical grade silicon processed at a temperature as high as 2000°C (Xakalashe and Tangstad, 2011). After that, silicon is further purified and solidified into large ingots, either in multi-crystalline or mono-crystalline form in a process named Czochralski process for single crystal ingots, and the Bridgman process for multi-crystalline silicon ingots (Markvart and Castañer, 2003). Following that, purified silicon ingots are subjected to subsequent mechanical processes such as surface grinding, wire sawing, and chemical etching to produce silicon wafers. After that, a chemical treatment process of the wafers called doping is implemented, which involves incorporation of an impurity such as phosphorus and boron to precisely alter their electronic properties near the surface and physically obtain the p-n junction structure as illustrated in Figure 2.2(b). Currently, power conversion efficiency, as measured in the laboratory, for single p-n junction polycrystalline solar cells reached 22.3% while that for single p-n junction monocrystalline is around 25.8%, both without the use of concentrators (from National Renewable Energy Laboratory (NREL) chart for Research Cell Record).

Owing to the thick wafer utilized in silicon solar cells to harness as much sunlight as possible, silicon solar cells and modules are usually rigid and heavy which requires

mechanical supporting. In addition, in order to achieve high power conversion efficiency, silicon must be purified to the high purity of $\geq 99.9999\%$ (6 nines, equivalent to 1 part impurity per million) which involves the use of toxic compounds such as chlorosilane and hydrochloric acid (Braga *et al.*, 2008) in addition to the intensive energy consumption during processing.

Figure 2.2. (a) Actual photo of monocrystalline (left) and polycrystalline (right) silicon solar cells. (a) Schematic of the basic structure of a single p-n junction silicon solar cell (from <http://www.arkimedesrl.it/Contents/SanyoHIT.htm>).

Furthermore, processing of silicon solar cells involves high manufacturing cost. Owing to all those drawbacks of silicon solar cells, the second generation in PV technology was developed with the capability to harness sunlight with much thinner ($1\ \mu\text{m}$) inorganic semiconductor light absorber layers that would enable flexible module production. In the next section, the most significant light absorber material that are used for thin film solar cells technology are discussed with emphasis on CZTS material and related compounds.

2.2.2. Thin Film Solar Cells (TFSCs): The Second Generation of PV Solar Cells

The primary challenge for silicon-based PV technology is to reduce further the material processing cost which accounts for approximately 50% of the total module cost (Louwen *et al.*, 2016). Besides providing flexible and much lighter solar panels to serve for different applications, another key motivation for the rise of the so-called TFSCs technology is the urgent need for solar panels that can be produced with a high throughput manufacturing technique (such as roll to roll production) with the minimum use of raw materials. In that sense, thin film solar cells provide a great alternative to silicon solar cells since they utilize much thinner light absorber layer (due to their direct bandgap and high absorption coefficient which is 100 time higher than silicon) to harness sunlight and also enable flexible modules which open the doors for entirely novel and more diverse applications.

Also, a significant advantage of thin film solar cell materials is that they are more tolerant to deviations in stoichiometry and phase purity and less stringent in material quality regarding crystallinity and grain structure compared to silicon, which requires highly crystalline and pure grade for solar cell application.

Amorphous silicon (a-Si), cadmium telluride (CdTe), copper indium gallium selenide (CIGS), copper zinc tin sulfide (CZTS) are the most important inorganic semiconductor compounds that are used as light absorber materials for thin film PV technology. Among those materials, only a-Si, CdTe and CIGS based solar cells are commercially available and share the other 10% of the market with crystalline silicon solar cells.

2.2.2.1. Amorphous Silicon (a-Si)

Amorphous Si is a light absorber material used in TFSCs due to its high absorption rate. Unlike crystalline Si, amorphous Si does not have a uniform crystal structure. Instead, it consists mainly of agglomerates of amorphous Si that are deposited onto a substrate. Amorphous Si absorbs 2.5 times more energy from the sun compared to crystalline silicon for the same thickness. However, a-Si solar cells suffer from instability after several hundred hours of operation due to intrinsic defects. The record efficiency for a stable a-Si solar cell is only 13% while initial efficiency was measured as 15.2% (Schiff, Hegedus and Deng, 2011). Figure 2.3(a) shows the basic structure of a-Si solar cell.

2.2.2.2. Cadmium Telluride (CdTe)

Over the past two decades, CdTe solar cells (shown in Figure 2.3(b)) have proved to be a key player in TFSCs and showed a significant market growth. CdTe is a II-VI semiconductor with a direct band gap of 1.5 eV and high light absorption coefficient of $>10^5 \text{ cm}^{-1}$.

CdTe module fabrication cost is among the cheapest of all types of commercially available PV technologies. Currently, CdTe thin film single junction solar cell has a record efficiency of 22.1% as reported by the National Renewable Energy Laboratory. In spite of that, the prospect of CdTe solar cell technology is a matter of debate due to the scarce resource of Te element and the toxicity of cadmium and its environmental impacts.

2.2.2.3. Copper Indium Gallium Selenide (CIGS)

Similar to CdTe, CIGS solar cells (shown in Figure 2.3(c)) is also highly attractive in TFSCs industry due to their near optimal band gap and less stringent requirements of crystal quality beside the wide variety of choice for the heterojunction buffer layer. According to the most recent NREL reports, the record efficiency for a single p-n junction CIGS solar cell is 22.6%. Nevertheless, the long term future of CIGS in TFSCs industry is also not very clear due to the scarce resource and significant fluctuations in market price of both In and Ga elements.

Figure 2.3. Basic structures of a-Si solar cell (a) (from <http://www.solars-china.com/solar08.html>), CdTe solar cell (b) (from <https://nice.asu.edu/nano/cadmium-telluride-cdte-thin-film-solar-cells>), and CIGS solar cell (from <https://www.energy.gov>)

2.2.2.4. Copper Zinc Tin Sulfide/Selenide (CZTS(Se))

During the last decade, considerable efforts have been made to resolve the challenging issues facing both CdTe and CIGS. Specifically for the case of the CIGS, the primary target is to substitute the two scarce elements In and Ga with another two abundant elements from another group in the periodic table while maintaining the same valance

electrons and number of atoms. Based on that concept, another class of materials, which is derived from chalcopyrite compounds, called kesterite compounds was established and can be expressed by the chemical formula $\text{Cu}_2\text{-II-IV-VI}_4$. In that formula, the VI element is one of the chalcogens (S or Se) while II and IV represent the divalent (Zn or Fe) and tetravalent (Sn, Ge, Si) elements respectively.

Among those kesterite compounds, $\text{Cu}_2\text{ZnSn(S,Se)}_4$ (CZTS(Se)) are of the most significance due to the unique optoelectronic properties that made them very promising candidates for TFSCs. CZTS(Se) materials are intrinsic p-type semiconductors, with a direct band gap energy of 1.0 eV for selenide based kesterite, (CZTSe) and 1.5 eV for sulfide-based kesterite (CZTS) which is close to the optimal bandgap for maximum solar radiation absorption. In addition, the direct bandgap gives a high absorption coefficient, which allows the utilization of one-micron thick layer to absorb most of the incoming sunlight.

2.2.3. Why Pure Sulfide (CZTS)?

In this thesis, the focus of the study is on the pure sulfide compound CZTS rather than the selenide-based compound CZTSe. The reason why pure sulfide compound was chosen lies in several key factors. First, selenium is a relatively scarce element compared to sulfur which is much more abundant. Second, elemental sulfur is non-toxic compared to selenium, which is considered toxic to humans upon intense or continued exposure. In addition, recently a noticeable improvement in CZTS device performance was reported when replacing the CdS buffer layer, which includes the toxic Cd element, by either ZnS or (Zn, Sn)O (Platzer-Björkman *et al.*, 2015). Third, CZTS is more suitable for both

single p-n junction as well as tandem structures (Green, 2016). The reason for such match is that CZTS has a perfect lattice match with Si and an optimal band gap in the range of 1.4 to 1.6 eV which makes it ideal as the top absorber layer with Si at the bottom in a tandem cell structure (Song *et al.*, 2015). All those factors make CZTS compound an attractive alternative to all other thin film light absorber materials for a green and sustainable thin film solar cells technology.

2.3. Properties of CZTS

CZTS has a tetragonal structure that is similar to the zinc blende structure of ZnS and is related to the (II-VI) compounds as shown in Figure 2.4 (a) by substituting the group II cation with Zn, Cu, and Sn cations in the appropriate proportion that maintain the charge neutrality of the crystal while keeping the group VI anion. Specifically, such substitution is done by substituting the Zn^{2+} cation with two atoms of the Cu^{1+} cation (group I), one Zn^{2+} cation (group II), and one Sn^{4+} cation (group IV) to balance the four S^{2-} anion (group VI) and eventually obtain the $(\text{I}_2\text{-II-IV-VI}_4)$ CZTS compound.

Figure 2.4(b) shows the lattice structure of the kesterite CZTS material. CZTS was found to have two different phases, known as kesterite (space group $\bar{1}\bar{4}$) and stannite (space group $\bar{1}\bar{4}2m$). However, kesterite was found to be thermodynamically favored at room temperature as evidenced by experimental observations and theoretical calculations (Schorr, Hoebler and Tovar, 2007) (Persson, 2010). From the optoelectronic properties point of view, CZTS is an intrinsic p-type semiconductor. The bandgap of CZTS reported in the literature for the synthesized material is between 1.4 and 1.6 eV (Bär *et al.*, 2011). However, Density Functional Theory (DFT) theoretical calculations for the ideal CZTS

structure shows value in the range between 1.5 to 1.65 eV (Persson, 2010) (Chen *et al.*, 2010).

Figure 2.4. (a) Derivation of kesterite compounds by gradual substitution of elements from different groups in the periodic table. (b) Structure of kesterite compounds. From (Zhou et al., 2013)

2.4. Synthesis of CZTS Thin Films

Several techniques have been investigated during the past two decades for the synthesis of CZTS thin films. CZTS synthesis routes can be classified into two major categories. The first one are vacuum-based techniques, which involve deposition of metal stacks followed by high-temperature annealing in a sulfur-rich atmosphere in a process known as sulfurization. Alternatively, co-deposition of binary sulfides mainly via thermal evaporation or magnetron sputtering might be carried out followed by annealing in an inert atmosphere such as Argon or nitrogen. The second category is solution based (sometimes-called non-vacuum) techniques, which involve solution deposition of a precursor layer followed by high-temperature sulfurization in either inert or sulfur-rich

atmosphere. The following sections briefly review the main methods for each category along with the notable progress achieved so far.

2.4.1. Vacuum Based Techniques

Physical vapor deposition (PVD) is a well-established method of depositing polycrystalline compound semiconductor materials. PVD includes several techniques such as thermal evaporation, sputtering, and pulsed laser deposition. PVD processes are typically carried out under high vacuum to minimize the residual gas in the system and maximize the yield of the deposited material on the substrate, which is vital for the purity of the deposited films. PVD techniques involve the evaporation of a source material, transport of the atoms in gas state to the substrate, and the condensation of the vapor atoms on the substrate. Thermal evaporation of CZTS typically involves the simultaneous deposition of different pure elements (Cu, Zn, and Sn) onto a heated substrate, and is usually called co-evaporation. In that case, sulfur may be incorporated during deposition process through a valved cracker source (Shimamune *et al.*, 2017) or in a separate step after the deposition which involves annealing in a sulfur rich atmosphere using either elemental sulfur or hydrogen sulfide gas (A Weber *et al.*, 2009). Thermal evaporation might also be carried out in alternative routes through co-evaporation of a combination of binary sulfide sources such as ZnS, Cu₂S, and SnS (Das and Mandal, 2012) or even a quaternary CZTS powder source (Shi *et al.*, 2012). An 8.4% record efficiency for a CZTS solar cell device made by thermal evaporation and has been achieved by (Shin *et al.*, 2013).

In sputtering deposition, Ar ions bombard a source material, which causes the metal atoms to sputter and deposit onto the substrate. Similar to evaporation, CZTS films can be obtained by sputtering of different sources such as Cu, Zn, and Sn metals to form the metal stack, which is subsequently sulfurized at high temperature to form CZTS. In addition, co-sputtering of Cu, ZnS, and SnS, as schematically illustrated in Figure 2.5(b) (Khalkar *et al.*, 2014), as well as the one step sputtering from quaternary CZTS source were also reported (Jheng, Liu and Wu, 2014). A power conversion efficiency of 6.8% is still the record for a sputtered CZTS solar cell (Katagiri *et al.*, 2008).

Figure 2.5. (a) Schematic diagram of co-evaporation of CZTS films (Shimamune *et al.*, 2017). (b) Schematic diagram of reactive sputtering of CZTS films (Khalkar *et al.*, 2014).

2.4.2. Solution Based Techniques

Basically, solution-based techniques comprise three major steps: first, preparation of precursor solution with specified cation (Cu, Zn, and Sn) and/or anion (S) concentration; second, deposition of the precursor solution onto a substrate; third, subsequent annealing in an inert (Ar or N₂) or sulfur-rich (elemental sulfur or H₂S) atmosphere to grow CZTS

and improve film crystallinity. The cation source is usually Cu, Zn, and Sn salts such as acetates or chlorides while sulfur anions can be obtained from sulfur-based organic or inorganic compounds such as thiourea and sodium sulfate.

2.4.2.1. Spray Pyrolysis Method

In spray pyrolysis route, a substrate is heated to a temperature ranges between 300 and 650°C (Song *et al.*, 2014) and then the precursor solution is sprayed onto the heated substrate. The high temperature will cause pyrolysis of the sprayed solution and will form a coat on the substrate surface. There have been only a few studies focused on spray pyrolysis of CZTS films (Kamoun, Bouzouita and Rezig, 2007) (Bhosale *et al.*, 2014). Nguyen *et al.* obtained CZTS solar cells with power conversion efficiency of 5.8% from spray-pyrolyzed CZTS films annealed at 580°C in sulfur vapor (Nguyen *et al.*, 2015). Recently, the same group reported an 8% efficiency achieved for a CZTS solar cell prepared through enhanced spray pyrolysis route (Nguyen *et al.*, 2016).

Figure 2.6. (a) Schematic diagram of spray pyrolysis system for CZTS film deposition (Shinde, Deokate, & Lokhande, 2013). (b) Schematic diagram of electrodeposition process of CZTS precursor films (Tsai *et al* 2016).

2.4.2.2. Electrodeposition Method

Electrodeposition has also been extensively investigated for the fabrication of CZTS films for solar cells. It involves the deposition of pure metallic layers or alloys of reduced cations in aqueous solutions through the application of an electrical potential from an external power circuit. Several approaches of electrodeposition have been implemented by either sequential deposition of Cu, Zn, and Sn metal layers to form a metal stack that is eventually annealed in sulfur vapor or co-deposition of Cu, ZnS, and SnS layers simultaneously in one solution mixture. Regardless of the exact electrodeposition route, annealing of the precursor film is necessary in order to obtain a complete transformation to CZTS and improve crystallinity. Tao et al. sequentially deposited Cu/Zn/Sn stack and implemented a two-step annealing with the first step for 30 minutes in N₂ at 350°C to form a metallic mixture followed by an additional 12 minutes annealing at 585°C in N₂ containing sulfur to form CZTS. Based on that route, they were able to achieve CZTS device efficiency of 7.3% (Tao *et al.*, 2016).

2.4.2.3. Sol-gel Method

Another interesting solution-processing route is the sol-gel method, which involves the preparation of sol precursor by dissolving metal salts (e.g., acetates and chlorides) in organic solvents followed by hydrolysis and polycondensation reactions. After that step, thin film is obtained by spin or dip coating, subsequent drying, and eventual annealing at high temperature to form the phases. Sol-gel processing is a simple and inexpensive route that could be implemented on large scale and over different substrates. In addition, sol-

gel technique also allows precise stoichiometry control and quantitative doping on the molecular level, which provide better structure and composition control compared with other techniques. Since sol-gel is the main processing route for CZTS films in this thesis, the previous studies mainly focusing on that particular route will be discussed in detail in section 2.5.

2.5. Previous Studies on Processing of Sol-Gel Sulfurized CZTS thin films

In this section, the most significant studies focusing on sol-gel processing of CZTS films are presented. In addition, previous results on the influence of sulfurization process parameters on the structural and optical properties of sol-gel sulfurized CZTS films are discussed.

Maeda et al. (Maeda, Tanaka, Fukui, *et al.*, 2011) investigated the influence of H₂S gas concentration on the structure, microstructure, and electronic properties of CZTS films. Sulfurization process was carried out at 250°C and 400°C for 1 minute and 500°C for 1 hour in H₂S+N₂ mixtures with 3%, 5%, 10%, and 20% vol. H₂S concentrations. The results showed that samples prepared using 3% H₂S concentration have the largest grain size of ~1 μm and relatively denser compared to other samples as shown in Figure 2.7(a). Moreover, as the H₂S gas concentration decreases from 20% to 5%, sulfur content in the films was found to increase. However, decreasing H₂S concentration to 3% was found to increase sulfur content. As shown in figure 2.7(b), the band gap of CZTS films does not show a strong dependence on the H₂S concentration during sulfurization. In another study by Maeda et al. (Maeda, Tanaka, Nakano and Uchiki, 2011), lower concentrations of

0.5% and 1% of H_2S gas were employed, and their influence of the quality of the produced CZTS films was investigated. All samples were sulfurized at 500°C for 1 hour except for the 0.5% H_2S samples which were sulfurized for a prolonged time of 4 hours. The results showed that samples sulfurized using 0.5% H_2S are slightly sulfur deficient and contains Cu_xS phase. However, investigation of the film structure and grain size based on SEM surface and cross section imaging as shown in Figure 2.8 revealed that CZTS films prepared using 0.5% H_2S have the largest grain size of $\sim 2\ \mu\text{m}$ and are densely packed compared to other samples sulfurized using both 1.0% and 3.0% H_2S gas concentrations.

Figure 2.7. (a) Surface SEM images of CZTS films sulfurized using different H_2S concentrations. (b) Optical absorption dependence on H_2S concentration (c) Chemical composition dependence on H_2S concentration. (Maeda, Tanaka, Fukui, et al., 2011)

Figure 2.8. Surface and cross section SEM images of CZTS films sulfurized at 500°C for 1 hour using different H₂S concentrations of (a, and d) 0.5%, (b, and e) 1.0%, and (c, and f) 3.0%. (Maeda, Tanaka, Nakano, & Uchiki, 2011)

Xiaoqi Yu et al. (Yu *et al.*, 2014) investigated the annealing of sol-gel based CZTS films prepared from sulfur-containing solutions in an inert atmosphere without sulfurization. CZTS samples with a different thickness of deposited layers with the 3 layers samples annealed at 250°C for 10 min and another 5 and 9 layers samples annealed at 500°C for 60 minutes under nitrogen atmosphere. XRD patterns (see Figure 2.9) shows that CZTS phase successfully formed in both the 5 and 9 layers samples and the 9 layer sample has better crystallinity.

Figure 2.9. (a) XRD patterns of the 5 and 9 layers CZTS films. (b) Raman spectrum of 9 layers CZTS thin film. (Yu et al., 2014)

In addition, Raman spectroscopy results (Figure 2.9(b)) for the 9 layers sample confirmed the formation of CZTS phase as observed by the two main characteristic peaks at 338 cm^{-1} and 287 cm^{-1} . Moreover, the SEM surface and cross-section images of the 9 layer annealed sample as in Figure 2.10 showed a nano-sized grain structure and relatively porous surface with the multi-layered structure as compared to the as-deposited sample. The reason for such structure was attributed to the different concentrations of the solution used for film deposition. The band gap for the 3 layers sample as extracted from the Tauc plot was 2.05 eV while for both the 5 and 9 layers samples was 1.46 eV which is close the typical values reported for CZTS.

Figure 2.10. Surface and cross-section SEM images of as 9 layers as deposited CZTS films (a and c) and annealed CZTS films (b and d). (Yu et al., 2014)

In another study by Tunuguntla *et al.*, 2015, 1,3-dimethyl-2-Imadazolidinone (DMI) was used as a solvent for the preparation of highly viscous, homogeneous, as well as nontoxic CZTS sol. Following the spin coating and air baking steps, CZTS films were sulfurized in 6% $\text{H}_2\text{S}+\text{N}_2$ gas mixture and elemental Sn and S are also added. They obtained CZTS films with grain size greater than $0.7\mu\text{m}$ and a minimal amount of carbon detected. Moreover, they found that external supply of Sn and S significantly suppress the loss of S_2 and SnS and thus lead to CZTS thin films with stoichiometric and homogeneous composition. Finally, an improved efficiency of 5.67% for the fabricated CZTS devices was achieved from samples prepared in 6% $\text{H}_2\text{S}-\text{Sn}-\text{S}$ atmosphere compared to the 2.89% efficiency obtained from CZTS samples sulfurized in 6% $\text{H}_2\text{S}+\text{N}_2$.

Figure 2.11. SEM cross-section and surface images for pristine CZTS samples (a, and d), CZTS samples sulfurized in 6% $\text{H}_2\text{S}+\text{N}_2$ (b, and e), CZTS samples sulfurized in 6% $\text{H}_2\text{S}+\text{N}_2$ and elemental Sn and S. (Tunuguntla et al., 2015)

Recently, T. Ozdal et al. (Özdal and Kavak, 2017) carried out a comprehensive study to investigate the influence of sol-gel processing and subsequent annealing/sulfurization parameters, such as spin coating speed, solution concentration, amount of stabilizer. Also, subsequent annealing conditions on the characteristics of the prepared CZTS films including composition, grain size, surface morphology, crystallinity and film thickness. Based on their analysis, there was no significant influence of spin coating speed on the quality of the prepared films while the amount of stabilizer used in the solution was found to control the film properties. Moreover, low solution concentration (molarity) led to both S and Sn loss and hence negatively affected the film stoichiometry. Air Baking the spin-coated films at 300°C was found to reduce the surface cracks, increase the grain size, and improve the film crystallinity. Furthermore, loss of volatile chalcogens (such as S_2 and SnS) was found to directly proportional to the sulfurization temperature. However,

N₂ gas flow was observed to significantly help reduce the loss of chalcogen components from the system and improve film crystallinity as well. Table 2.1 summarizes the main previous studies focused on the sol-gel sulfurization processing of CZTS films. It shows the basic sulfurization process parameters that have been previously investigated such as temperature and sulfur source. It is noted that in most of the previous studies, sulfurization process was investigated at high temperature and use high concentration ($\geq 5\%$ vol.) of H₂S gas.

Table 2.1. Summary of the main previous studies on sol-gel sulfurization processing of CZTS films.

Reference	Deposition technique	Temperature (°C)	Time (min)	Annealing/sulfurization atmosphere
(Tanaka, Moritake and Uchiki, 2007)	Sol-gel, spin coating	500	60	5% H ₂ S+N ₂
(Maeda, Tanaka, Fukui, <i>et al.</i> , 2011)	Sol-gel, spin coating	500	60	3%, 5%, 10%, 20% H ₂ S+N ₂
(Maeda, Tanaka, Nakano and Uchiki, 2011)	Sol-gel, spin coating	350, 400, 450, 500, 550, and 600	60	5% H ₂ S+N ₂
(Tunuguntla <i>et al.</i> , 2015)	Sol-gel, spin coating	610	8	6% H ₂ S+N ₂
(Su <i>et al.</i> , 2014)	Sol-gel, spin coating	560	60	N ₂ (thiourea was used as sulfur source in Sol preparation step)
(Yu <i>et al.</i> , 2014)	Sol-gel, spin coating	500	60	N ₂ (thiourea was used as sulfur source in Sol preparation step)
(Özdal and Kavak, 2017)	Sol-gel, spin coating	300, 350, 400, 450, 500 and 550	30	Air, N ₂ , and N ₂ + elemental S

2.6. Identification of secondary phases and their influence in CZTS system

Due to the single phase narrow region for CZTS (see Figure 2.12(a)), it is highly likely that other binary sulfide phases form during the annealing/sulfurization process and remain stable upon cooling down to room temperature (Nagoya *et al.*, 2010) (Kumar *et al.*, 2015). The most common sulfide phases reported to form in association with CZTS phase are ZnS, Cu_{2-x}S ($0 < x < 1$), SnS, SnS_2 , and Cu_2SnS_3 (CTS). ZnS is less harmful to device performance, since it has higher bandgap (band gap for cubic ZnS = 3.54 eV), compared to CZTS band gap of 1.5 eV.

Figure 2.12. (a) Calculated chemical potential stability diagram for Cu rich CZTS in 2D plane. (Nagoya *et al.*, 2010) (b) Simulated XRD patterns for CZTS, CTS, and ZnS phases showing the overlap of the main peaks. (Walsh, Chen, Wei, & Gong, 2012)

On the other hand, both SnS and CTS phases are very detrimental to device performance due to their lower bandgap compared to CZTS. In particular, the presence of CTS phase in CZTS films is more challenging since it is difficult to distinguish from CZTS due to

the similarity in the crystal structure which results in overlapping of the main XRD peaks for both phases (see Figure 2.12(b)).

To resolve that issue, Raman spectroscopy is employed to complement XRD and help detect other secondary phases associated with CZTS. Green laser excitation with a wavelength of 514.5 nm can be used to identify the main Raman modes of CZTS phase and all other secondary phases reported (see Table 2.2) except for ZnS which is not sensitive to that particular wavelength excitation.

Table 2.2. Raman modes for CZTS and other common secondary phases.

Phase	Raman Shift (cm ⁻¹)	Reference
CZTS	288, 338, 351, 368	(Fontane' <i>et al.</i> , 2011)
Monoclinic Cu₂SnS₃	290, 352	(Berg <i>et al.</i> , 2012)
Cu₃SnS₄	318	(Berg <i>et al.</i> , 2012)
Cu_{2-x}S	264, 475	(Dimitrievska <i>et al.</i> , 2014)
ZnS	275, 352	(Nilsen, 1969)
SnS	163, 189, 223	(Berg <i>et al.</i> , 2014)
SnS₂	215, 315	(Fontane' <i>et al.</i> , 2011)
Sn₂S₃	52, 60, 307	(Altamura and Vidal, 2016)

It is reported in previous studies that ZnS can be detected efficiently using ultraviolet (UV) laser excitation with a wavelength of 325 nm (Berg *et al.*, 2014). However, in the absence of UV laser, energy dispersive X-ray spectroscopy (EDX) can be used in combination with XRD and 514.5 nm laser Raman to detect the localized composition of ZnS.

2.7. Understanding Phase Formation Mechanism of CZTS

Understanding the fundamental phase formation mechanism and the related phase transformations of CZTS system is crucial to the optimization of the sulfurization process. In addition, a better understanding of how material processing influence the characteristics allows tuning its properties to obtain superior opt-electronic properties that are beneficial to CZTS based device performance. Many previous studies investigated the phase formation of CZTS films based on different synthesis technique using various ex-situ as well as in situ characterization tools. In this section, some of the previous studies aiming to understand the fundamental phase formation mechanism for sol-gel derived CZTS thin films.

Conceptually, the formation of CZTS phase are briefly reviewed via sol-gel processing comprises three main steps regardless of the synthesis technique. The first one is the formation of precursor material, which is typically a mixture of amorphous metal oxides. Secondly, sulfur incorporation through inter-diffusion which yields binary or ternary sulfides. Lastly, the reaction between those sulfides leads to the evolution and crystallization of CZTS phase.

Su et al. (Su *et al.*, 2014) investigated the formation mechanism of sol-gel deposited CZTS films. CZTS films were prepared by spin coating of non-aqueous precursor solution containing Cu, Zn, Sn ions and thiourea was used as a sulfur source. Films were dried at 200°C in air before the high-temperature annealing at 560°C for 1 hour in nitrogen as illustrated in Figure 2.13.

Figure 2.13. Schematic diagram of the formation of the CZTS thin films via thermal decomposition and reaction by the sol-gel route. (Su et al., 2014)

The suggested mechanism for CZTS phase formation includes a set of reactions from (1) to (6). First, metal salts react with alcohols to form metal alkoxides. Then, nanoparticles are formed with an average size of several nm after alcoholysis and polycondensation between the metal salt and metal alkoxides. The excess thiourea used in this study reacts with the metal ions to form thiourea-metal complexes, and these complexes are subsequently subjected to alcoholysis and condensation reactions with 2-methoxyethanol to form CZTS nanoparticles.

In the those equations, the symbols (M, X, Tu, and R) represent metal ions (Cu^{2+} , Zn^{2+} , Sn^{2+}), anions (CH_3COO or Cl), thiourea and organic molecular chains of 2-methoxyethanol, respectively. The volatile matter is the gases generated during the annealing process, such as CS_2 , CO_2 , NO_2 , SO_2 , H_2O , and NH_4Cl . Equation (1) displays the complexing process between thiourea and the metal ions.

2.8. Previous studies on temperature dependent Raman monitoring of CZTS

In this section, previous studies focusing on the investigation of CZTS Raman spectral behavior and the influence of temperature on both structure and phase stability of CZTS will be presented. Van Duren et al. (Van Duren *et al.*, 2017) investigated the feasibility of using in situ Raman spectroscopy to monitor the evolution of CZTS films in real time. The films were prepared via co-evaporation of Cu, Sn and ZnS layers in a sulfur atmosphere. Following that, in situ Raman monitoring was carried out at elevated temperatures (from room temperature up to 550°C) using a Linkam heating stage (THMS600) under a nitrogen atmosphere. Above 350°C , the temperature step was decreased to 25°C to better observe the ongoing transformations in the film.

Figure 2.14(a) illustrates the evolution from the Cu, Sn and ZnS precursor stack to kesterite. The process starts with the observation of Raman modes for monoclinic CTS phase characterized by the two main Raman modes at 292 and 352 cm^{-1} at 50°C . After that, continued heating up to a temperature of 400°C was observed to broaden and attenuate CTS peaks. The main A-mode of CZTS was first observed at 400°C and

gradually becomes more dominant as indicated by the arrows in Figure 2.14(a). At 550°C, the main mode for CZTS can be seen to dominate the spectrum.

Figure 2.14. (a) Raman spectra of the Mo/CTS/ZnS precursor stack during annealing from 50 to 550°C. (b) Evolution of peak positions of CTS, CZTS references and CZTS from CTS/ZnS precursor stack. (Stephan Van Duren et al., 2017)

The evolution of the peak positions with temperature is shown in Figure 2.14(b). For comparison, evolution of peak position from previous studies is included. It can be concluded that data from Duren's study is identical to Sarswat's study also at lower temperature regime up to 180°C. While, data from Singh showed slight deviation in the peak position although it has the similar trend.

In addition, it can be observed from Figure 2.14(b) that CZTS formed from the stack slightly deviates from the CZTS reference sample, which might be attributed to the influence of CTS phase that initially existed in the stack. However, at 475 $^{\circ}\text{C}$ and higher, the stack data overlaps with the CZTS reference, confirming the presence of the kesterite phase.

In another study, Scragg et al. (Scragg *et al.*, 2014) studied the influence of temperature on the structural ordering of CZTS phase using near-resonant Raman scattering. The two CZTS reference samples were cooled down at different rates, sample (VS) was slowly cooled at a rate of 10K/hour while sample (VF) was quenched in ice water. Raman spectra of both samples were collected in a Renishaw system using 532 nm and 785 nm laser excitations.

Figure 2.15. (a) Raman spectra with peak fitting for CZTS reference samples VS (slowly cooled) and VF (rapidly cooled) examined with 532 and 785 nm lasers. (b) Raman spectra using 785 nm, for an as-prepared CZTS film at different temperatures. (Scragg et al., 2014)

Figure 2.15(a) shows spectra of VS and VF for 532 nm and 785 nm excitation wavelengths. For both excitation wavelengths, sample VF gives a general broadening that is attributed to Cu/Zn disorder. In the 785 nm spectra, the differences between VS and VF are more dramatic. For the slowly cooled sample, the second A mode at 288 cm⁻¹ (labelled m_{2A}) has roughly double the intensity of the E and B modes at 368 and 376 cm⁻¹ (labelled m_{4E} and m_{5B}). In the fast cooled sample, both of the main A modes m_{1A} and m_{2A}

drop significantly relative to the rest of the spectrum, so that m_{2A} becomes similar in intensity to the previously minor A mode at 304 cm^{-1} (m_{3A}), while m_{4E} and m_{5B} have much higher relative intensity. A possible explanation for these variations is that the near-resonant conditions with the 785 nm excitation wavelength make the spectrum sensitive to small changes in band gap that is occurring because of structure disorder.

In another study by Sarswat et al. (Sarswat, Free and Tiwari, 2011), the temperature influence on the CZTS Raman peaks was investigated at the range of 98 – 378 K. The Raman spectra of CZTS thin film were collected over the range of $315\text{--}365\text{ cm}^{-1}$ are shown in Figure 2.16(a). The highest intensity Raman peak was observed at room temperature at 338 cm^{-1} , which matches well with previously published results for kesterite phase of CZTS. A decrease in the frequency and intensity of A-mode is observed with an increase in temperatures shown in Figure 2.16(a).

Figure 2.16. (a) Raman spectra for CZTS thin film recorded at various temperatures. The shift in peak frequency versus temperature. (b) The shift in peak frequency versus temperature. (c) The shift in linewidth versus temperature. (Sarswat et al., 2011)

The variation of peak frequency of the A-mode with temperature is shown in Figure 2.16(b).

Figure 2.16(c) shows the variation of the linewidth between 98 and 378 K. Fitting of experimentally observed linewidth data is also shown. Based on least square fit analysis, a theoretical fit using the 3-phonon process demonstrated which is valid only for a short (100–250 K) temperature range while the agreement between experimental data points and theoretical fitting is best found for the 4-phonon process for the entire temperature range (100–350 K).

3. FORMATION OF SOL-GEL BASED CZTS THIN FILMS USING PPM-LEVEL HYDROGEN SULFIDE

3.1. Introduction

Recently, extensive research has been carried out on copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$ or CZTS) material as an absorber layer for thin film solar cell applications (Katagiri *et al.*, 2009; Ramasamy, Malik, and O'Brien, 2012). CZTS material is considered as a non-toxic, abundant, and inexpensive alternative to conventional chalcogenide solar absorber materials such as copper indium gallium selenide ($\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$, CIGS) or cadmium telluride (CdTe) that suffer from resource limitation (e.g., for In and Ga) and/or toxicity (e.g., for Cd) (Taylor and Scott M. McLennan, 1985). Beside the excellent physical properties of CZTS such as a tunable band gap between 1.04 to 1.48 eV with Se incorporation (Woo *et al.*, 2013) and a high absorption coefficient greater than 10^4 cm^{-1} (Ito and Nakazawa, 1988), researchers expect the well-established device technology for CIGS solar cells could also be implemented for CZTS to achieve high performance yet low cost CZTS solar cells in the near future.

Different techniques have been adopted for CZTS thin films preparation such as vacuum based techniques of thermal evaporation (Shi *et al.*, 2012), magnetron sputtering (Tanaka *et al.*, 2005; Dhakal *et al.*, 2014), and pulsed laser deposition (Moholkar *et al.*, 2011) and non-vacuum based techniques such as electrodeposition (Ge *et al.*, 2014), nanoparticles (Guo *et al.*, 2014), spray pyrolysis deposition (Nakayama and Ito, 1996; Swami *et al.*, 2015), and sol-gel sulfurization (Tanaka, Moritake and Uchiki, 2007; Maeda, Tanaka, Nakano and Uchiki, 2011; Kahraman *et al.*, 2013). Vacuum based techniques such as

thermal evaporation or magnetron sputtering produce densely packed thin films with large grains of CZTS but are expensive due to the need for high vacuum and the complexity added to the system. In comparison, almost all *non-vacuum* based techniques adopt some form of solution processing, which offers simplified processing and reduced device fabrication cost. In particular, *sol-gel sulfurization* is one of the simplest and cheapest options for CZTS thin film preparation among all solution processing techniques. Typically, sol-gel sulfurized CZTS thin films are prepared by spin coating and baking of solutions containing Cu, Zn, and Sn metal ions to form metal oxide precursors that are eventually sulfurized in a sulfur-rich atmosphere at elevated temperature (e.g., $\sim 550^{\circ}\text{C}$) to obtain densely packed large grain CZTS films. It has advantages in terms of simplicity and, potentially, cost over other non-vacuum processes: for example, the nanoparticles approach starts from solutions but has the added steps of nanoparticles synthesis, while the electrodeposition process usually consists of multiple deposition steps due to different metal layers involved. Tanaka et al. (Tanaka, Moritake and Uchiki, 2007) were the first group to prepare CZTS films based on the sol-gel sulfurization processing. The maximum efficiency achieved was 2.03% (Maeda, Tanaka, Nakano, Fukui, *et al.*, 2011). Recently, champion power conversion efficiency of $\sim 5\%$ and higher for sol-gel based CZTS devices had been reported (Su *et al.*, 2014; Tunuguntla *et al.*, 2015).

Compared to elemental sulfur, hydrogen sulfide (H_2S) gas balanced by nitrogen (e.g., 5% H_2S by volume balanced by N_2 (Tanaka, Moritake and Uchiki, 2007), or, in short, abbreviated as 5% $\text{H}_2\text{S}+\text{N}_2$. *Note all concentrations for gas mixtures mentioned in this thesis are by volume.*) is often preferred for the sulfurization process in order to obtain

chemically homogenous CZTS films, partly due to the complexity associated with elemental sulfur evaporation resulting in multiple gas allotropes such as S_2 as well as S_4 , S_6 , S_8 (Jackson, Tiana and Walsh, 2016). In addition, some other studies reported better CZTS crystallinity when using H_2S gas as the sulfurizing agent compared to elemental sulfur (Scragg, Dale and Peter, 2009). However, hydrogen sulfide is well known to be an extremely toxic, highly corrosive gas with stinky, “rotten egg” like odor, especially with the high concentration levels (5 up to 60% H_2S) utilized for CZTS preparation as reported in almost all CZTS studies including non-sol-gel processes (Ramasamy, Malik and O’Brien, 2012; Xie *et al.*, 2013). This would result in complicated safety considerations and corresponding stringent measures in process engineering in order to eliminate any potential risk of human toxicity and environmental damage.

Therefore, the great appeal of sol-gel sulfurization approach and the serious safety/environmental concerns with using high concentration H_2S for preparing CZTS motivate the study aimed at searching for better and safer ways to prepare CZTS thin films using *significantly lower* concentration of H_2S gas as the sulfurizing agent. On the other hand, it is conceived not impossible to form CZTS phase with significantly reduced H_2S concentration. The rationale is that the equilibrium H_2S concentration to form many metal sulfides tends to *decrease* dramatically (by several orders of magnitude) with decreasing sulfurization temperature. For example, for the sulfide of Ni_3S_2 , the equilibrium pH_2S/pH_2 for Ni_3S_2 to form by reaction between Ni and H_2S decreases from ~1% at 1050°C to only 100 ppm at ~400°C, while for NiS, the equilibrium pH_2S/pH_2 decreases from ~4% at 727°C to only 38 ppm at ~227°C (Cheng and Liu, 2007).

Previously, only Maeda et al. used lower percentage level of 0.5% $\text{H}_2\text{S}+\text{N}_2$ to prepare CZTS thin films, but impurity phases of Cu_xS was clearly observed by XRD (Maeda, Tanaka, Fukui, *et al.*, 2011). The work reported here investigates the feasibility of preparing CZTS with *low parts per million (ppm)-level* H_2S and understand the influence of the relevant processing conditions on the quality of the sulfurized Cu-Zn-Sn-S films. Moreover, the current study also provides insights about the complexity associated with CZTS preparation and highlights the practical limits for the sulfurization process from thermodynamic point of view.

3.2. Experimental Procedure

The Cu-Zn-Sn precursor solutions were prepared from metal precursors reported in Tanaka's study (Tanaka, Moritake and Uchiki, 2007). Three solution batches were prepared with different metal ions ratio as explained below. The first solution batch named as recipe R2 has a *stoichiometric composition* with Cu:Zn:Sn metal ions ratio of exactly 2.0 : 1.0 : 1.0.

The second solution batch named recipe R7 was designed to be *copper-rich (or tin-and-zinc-poor)* with Cu:Zn:Sn metals ions ratio of 2.2 : 1.0 : 1.0, while the third solution batch named R8 has a *copper-poor composition* with Cu:Zn:Sn metal ions ratio of 1.90 : 1.0 : 1.0. The reason for using both Cu-poor and Cu-rich compositions is to investigate the influence of different precursor solution compositions on the structure, phase purity, and homogeneity of the prepared CZTS films. In addition, although traditionally Cu-poor compositions were often used to prepare CZTS, some recent studies including authors' own work suggest Cu-rich CZTS(Se) thin films seem to offer benefits of larger grains

and denser layers, which is important to device performance (Guo *et al.*, 2014). For recipe R2, the precursor solution was prepared by dissolving 8.73 g of copper acetate monohydrate (>98% - Sigma Aldrich), 4.80 g of zinc acetate dihydrate (>99% - Sigma Aldrich), 4.93 g of tin(II) chloride dihydrate (98% - Sigma Aldrich) into 50 mL of 2-methoxyethanol (99% - Alfa Aesar). After that, 5 mL of monoethanolamine (99+% - Alfa Aesar) was added to the solution to prevent precipitation during stirring at 55°C for 60 minutes. Precursor solutions for recipes R7 and R8 were prepared based on the same procedure with varying amount of copper acetate monohydrate as designed. In all three cases after stirring, a clear dark blue solution formed. The solutions were then filtered using 0.2 μm PTFE syringe filter before spin coating. Seven layers of Cu-Zn-Sn oxide precursor films were prepared by spin coating using the precursor solutions on 1 mm thick soda lime glass (SLG) substrates at 3000 rpm for 30 seconds followed by air baking at 300°C

for 5 minutes for each layer, and the total film thickness is $\sim 1.2 \mu\text{m}$. Following the sol-gel preparation of the oxide precursors, sulfurization process was performed under various conditions to convert the oxide precursors to sulfide(s). Table 1 specifies the sample designation and corresponding detailed sulfurization conditions. The sulfurization process was performed in a tube furnace in which samples were purged with ultrahigh purity N_2 (UHP grade, Airgas) before heating up in N_2 . The sulfurization atmosphere is provided by a gas mixture of 100 ppm $\text{H}_2\text{S} + \text{H}_2$ (Airgas) at the target annealing temperature. *The choice of 100 ppm H_2S is rational because above that concentration, H_2S exposure will cause loss of smell and pose serious danger to production personnel* (OSHA, no date). The samples listed in Table 3.1 contain two sub-sets: set 1 involved

only a *single* annealing step for sulfurization while set 2 involved two annealing steps for sulfurization, as explained below in detail. For samples designated as R2-350S, R8-350S, R7-350S, R2-450S, R7-450S, R2-550S, and R7-550S belonging to set 1 single-step sulfurization, the samples were heated up in N₂ to the target temperature (350°C, 450°C, or 550°C) and the gas was then switched to 100 ppm H₂S+H₂ and sulfurized for 60 minutes at those respective temperatures followed by cooling to room temperature (RT) in N₂. For the two-step sulfurization, a sample designated as R7-400H-125S was prepared based on recipe R7: the sample was heated up to 400°C in N₂ and reduced in 4% H₂+N₂ for 60 minutes. After that, the sample was cooled in N₂ to 125°C and then sulfurized for 180 minutes in 100 ppm H₂S+H₂ followed by cooling to RT in N₂. In all processing, the typical heating rate was ~22°C/min and the cooling rate is limited by heat dissipation and was measured to be ~2°C/min.

Upon sulfurization, all samples were examined by X-ray diffraction (XRD) (diffractometer: Siemens 500D) for phase identification using Cu K_α radiation with wavelength $\lambda=1.5406 \text{ \AA}$ in the range of $2\theta = 20^\circ$ to 80° . Raman spectroscopy was used to complement XRD analysis for selected samples and carried out using air cooled Argon ion laser system (Spectra Physics, model 177G02) with excitation wavelength of 514.5 nm and spectrograph (HoloSpec f/1.8i, Kaiser Optical Systems) in the range of 200 to 2000 cm⁻¹ Raman shift.

Table 3.1. Sample designation and corresponding detailed sulfurization conditions for the two designed experiment sets.

Exp. set	Sample designation	First annealing		Second annealing	
		Temperature (°C) /time (min)	Atmosphere	Temperature (°C) /time (min)	Atmosphere
Set 1	R2-350S	350/60	100 ppm H ₂ S+H ₂	NA	NA
	R8-350S	350/60			
	R7-350S	350/60			
	R2-450S	450/60			
	R7-450S	450/60			
	R2-550S	550/60			
	R7-550S	550/60			
Set 2	R7-400H-125S	400/60	4% H ₂ +N ₂	125/180	100 ppm H ₂ S+H ₂

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were carried out using JOEL 6330 system for thin films morphology study and local chemical composition analysis. In addition, electrical resistivity measurements were carried out for the prepared Cu-Zn-Sn-S thin films using an Ecopia HMS 3000 Hall Measurement System. The system was initially calibrated using a standard indium tin oxide (ITO) sample. Optical property including light absorbance/transmittance and resulting band gap information was measured using a custom configured system with spectrometer (Ocean Optics USB 2000+ VIS and NIR spectrometer). The light source used is Deuterium-Halogen Light Source (DH 2000) for the UV-Vis-NIR spectroscopy.

3.3. Results and Discussion

3.3.1. Single-step sulfurization process

After sol-gel processing and 300°C air baking, the obtained Cu-Zn-Sn oxide precursor films before sulfurization are typically amorphous. As an example, Figure 3.1 gives the XRD pattern for the Cu-Zn-Sn oxide precursor film prepared based on recipe R7 showing no crystalline peaks.

Figure 3.1. XRD pattern of a Cu-Zn-Sn oxide precursor thin film for recipe R7 after spin coating and air baking (300°C/5 min).

Table 3.2 shows the EDS data for the air baked Cu-Zn-Sn oxide precursor film from the same recipe. The measured initial Cu:Zn:Sn metal ratio of ~25 : 12 : 11 matches closely the expected ratio of 2.2 : 1.0 : 1.0 for R7 that is designed to be slightly copper-rich. On the other hand, oxygen content for the air-baked oxide precursor film was found to be lower than stoichiometry for the expected oxides, while carbon content is very significant, suggesting incomplete organics burnout even after repeated hard baking at 300°C in open air.

Table 3.2. EDS data showing atomic percentage of the Cu-Zn-Sn oxide precursor thin film after 300°C air baking for recipe R7.

Element	Cu	Zn	Sn	O	C
at. %	25	12	11	9	43

A photo of the oxide precursor film for recipe R7 is shown in Figure 3.2 (a). The thin film appears transparent with slight brownish color, suggesting metal oxides such as Cu₂O and/or residue carbon as coke. Other oxide precursor films for recipes R2 and R8 are similar to recipe R7. For sulfurization of the Cu-Zn-Sn oxide precursor, the simplest process would follow the typical single-step sulfurization procedure as adopted by many other researchers with the exception of replacing the >5% H₂S+N₂ by low ppm level H₂S-containing gas mixture, which is 100 ppm H₂S+H₂ here. (It is noted that the balance gas for ppm-level H₂S here is H₂ instead of N₂. The reason for this change was to help improve the metal oxide reduction since the ppm-level H₂S concentration used in this study is much lower than the normally used 5%, which can produce significant H₂ at elevated temperature due to the reaction of $2\text{H}_2\text{S} = \text{S}_2 + 2\text{H}_2$).

Figure 3.2 (b to e) show pictures of the sulfurized samples of R8-350S, R7-350S, R7-450S, and R7-550S, respectively, according to the processing conditions stated in Table 1. Samples of R8-350S and R7-350S are dark black, while R7-450S and R7-550S show brownish color with distinct metallic reflection especially in certain angles as seen clearly for R7-450S.

Figure 3.2. Pictures of the amorphous oxide precursor thin film prepared based on recipe R7 after 300°C/5 min air baking (a) and the single-step sulfurized samples of R8-350S (b), R7-350S (c), R7-450S (d), R7-550S (e).

Figure 3.3 and Figure 3.4 show the XRD patterns for samples of set 1 prepared from recipe R7 (10 mol.% Cu-rich) and R2 (stoichiometric) respectively and sulfurized in a single step for 60 minutes in 100 ppm $\text{H}_2\text{S}+\text{H}_2$ at different temperatures. For the R7-550S and R2-550S and R7-450S samples, XRD patterns clearly show the formation of metallic alloy phase of Cu_3Sn , as evidenced by the major XRD peaks observed at 2θ of 37.6° , 41.7° , 43.2° , and 68.1° (JCPDS card no. 01-077-8587). The identification of alloy phase of Cu_3Sn also explains the metallic reflection observed for those samples such as R7-450S as shown before in Figure 3.2(d). In addition, for these samples, XRD peaks were also observed at 2θ of 28.5° , 47.4° , and 56.4° . It is well known that these peaks might belong to either CZTS or ZnS or Cu_2SnS_3 (JCPDS cards no. 00-026-0575, 01-071-5976, and 01-089-4714, respectively). However, based on the appearance of strong peaks of Cu_3Sn in these sample (R2-550S, R7-450S, and R7-550S), it is rational to assign the peaks at 28.5° , 47.4° , 56.4° primarily to ZnS instead of CZTS or Cu_2SnS_3 for those samples. In comparison, the XRD patterns for samples of R7-350S and R2-350S only show peaks at 28.5° , 47.4° , 56.4° for ZnS or CZTS but without any other major

crystalline phases. As both samples sulfurized at 350°C appeared dark black without metallic reflection, XRD alone could not determine if ZnS or CZTS actually formed. (It is noted that XRD for sample R2-450S also only shows peaks at 28.5°, 32.9°, 47.4°, 56.4°.

Figure 3.3. XRD patterns of samples of R7-350S, R7-450S, and R7-550S, which were prepared from copper-rich recipe R7 and sulfurized in a single-step at 350°C, 450°C, and 550°C for 60 minutes in 100 ppm $\text{H}_2\text{S}+\text{H}_2$.

However, that EDS (shown later) suggests R2-450S sample is severely sulfur deficient and rules out the possibility of CZTS formation for that sample.). Figure 3.5 shows the XRD patterns for samples of set 1 prepared at 350°C for the three recipes R2, R8, and R7. The poor crystallinity of sample R8-350S from copper-deficient solution R8 is noted as only two diffraction peaks for that sample are clearly visible with lower intensity and higher background noise compared to the other two samples of R2-350S and R7-350S.

Figure 3.4. XRD patterns of samples of R2-350S, R2-450S, and R2-550S, which were prepared from stoichiometric recipe R2 and sulfurized in a single-step at 350°C, 450°C, and 550°C for 60 minutes in 100 ppm $\text{H}_2\text{S}+\text{H}_2$.

In order to help determine the exact sulfide phases formed after sulfurization at 350°C, Raman was carried out for samples of R2-350S, R8-350S, and R7-350S, and the obtained Raman spectra are shown in Figure 3.6. For R7-350S, the pattern revealed three distinct major peaks at 338, 288, and 352 cm^{-1} and one minor, wide peak at 368 cm^{-1} that match well with those typically assigned to CZTS phase (Zhang *et al.*, 2014). Raman spectrum for the sample of R2-350S showed a major peak at 331 cm^{-1} with minor peaks at 288 cm^{-1} and a wide shoulder around 368 cm^{-1} .

The reason for the major peak shift from 338 to 331 cm^{-1} is not clear at the moment. Nevertheless, the strongest peak corresponding to ZnS at $\sim 351 \text{ cm}^{-1}$ is not obvious in both patterns, suggesting ZnS is not the major crystalline phase in the prepared thin films. The obtained Raman spectra for the 350°C sulfurized samples also contain a peak at 476

cm^{-1} , and it is attributed to Cu_{2-x}S phase, which is common during CZTS preparation (Schubert *et al.*, 2011). However, Raman analysis for copper deficient R8-350S sample shows only high background with poor signal to noise ratio, which might be attributed to the partial formation of CZTS phase and association of secondary phases with high degree of surface inhomogeneity of that sample. Further analysis will be needed to understand the exact reason for this.

Figure 3.5. XRD patterns of sulfurized samples of R2-350S, R8-350S, and R7-350S which were prepared from stoichiometric, Cu-poor, and Cu-rich recipes respectively and sulfurized in a single-step at 350°C for 60 minutes in 100 ppm $\text{H}_2\text{S}+\text{H}_2$.

To further substantiate the study from XRD and Raman, SEM-EDS analysis was also carried out to help characterize thin film structure and local composition. The surface SEM images for single-step sulfurized samples of R7-450S, R7-350S, and R8-350S are shown in Figure 3.7 along with a reference CZTS sample prepared at 550°C using 5% $\text{H}_2\text{S}+\text{N}_2$. Figure 3.7(a) is for sample R7-450S, and it shows the surface is relatively dense and uniform. However, as stated before, XRD suggests the film for R7-450S is a mixture

of ZnS and Cu₃Sn metallic phase. Figure 3.7(b) and (c) are for the surface of sample R7-350S and R8-350S, respectively, which appear to be relatively dense with reasonably large grains. On the other hand, it is noted that the surface for these two samples appears to have some inhomogeneity: micron-sized particles were observed on the surface and were distributed across all examined areas of the thin film. The origin for such surface inhomogeneity is not yet clear at this moment, and local EDS analysis and Raman micro spectroscopy study has not been conclusive and this will be investigated further in future.

Figure 3.6. Room temperature Raman spectra for single-step sulfurized samples of R2-350S, R8-350S, and R7-350S which were prepared from stoichiometric, Cu-poor, and Cu-rich recipes respectively and sulfurized in a single-step at 350°C for 60 minutes in 100 ppm H₂S+H₂.

Nevertheless, the overall surface quality in terms of film density and grain size of both R8-350S and R7-350S samples prepared at reduced temperature of 350°C using low concentration 100 ppm H₂S+H₂ is comparable to the reference CZTS sample (Figure 3.7(d)) prepared at 550°C using 5% H₂S+N₂.

Table 3.3 gives the chemical composition obtained by EDS over surface for selected single-step sulfurized Cu-Zn-Sn-S thin film samples prepared with 100 ppm H₂S+H₂ mixture compared to the reference CZTS, which is prepared by sol-gel sulfurization at 550°C for 60 minutes using 5% H₂S+N₂ mixture following literature procedure (Tanaka, Moritake and Uchiki, 2007). The reference CZTS sample is very close to stoichiometry in terms of total metal to sulfur atomic ratio with slight Cu-poor and Zn-rich composition. It is noted from Table 3.3 that as the single-step sulfurization temperature decreases, the sulfur content in the film obtained by sulfurization in 100 ppm H₂S+H₂ increases significantly.

Samples sulfurized at higher temperatures such as R7-450S, R2-450S, R7-550S all show severe sulfur deficiency with sulfur to total metal molar ratio much lower than the expected 1 : 1 value for stoichiometric CZTS. This is consistent with the XRD patterns showing metallic Cu₃Sn phases as well as ZnS phase for those samples (see Figure 3.3 and Figure 3.4). In addition, EDS also indicates for those samples such as R7-450S, there are local surface particles (e.g., see SEM image in insert for Figure 3.7(a)) with Cu:Sn atomic ratio close to 3:1 and very poor in sulfur and zinc content. Those small particles are presumably Cu₃Sn metallic phase, which is consistent with XRD patterns for those samples. In comparison, EDS in Table 3 indicates that the three samples of R2-350S, R8-350S, and R7-350S have compositions very close to CZTS, with total sulfur to metal ratios of nearly 1:1 and slight Cu-poor/Zn-rich stoichiometry. It is noted that the S to total metal ratio for these three samples still appears to be slightly lower than 1. Such minor deviation might be related to experimental error for EDS analysis considering the

standard deviation given in Table 3.3 and/or the possibility that the sulfurization temperature of 350°C is still slightly higher than ideal and further optimization will be needed.

Figure 3.7. Surface SEM images for single-step sulfurized samples of R7-450S (a), R7-350S (b), R8-350S (c), and the reference CZTS sample (d). The yellow arrow in the insert points toward the particle identified by EDS as Cu₃Sn for R7-450S sample.

Nevertheless, these results, together with XRD (Figure 3.3 to 3.5) and Raman (Figure 3.6) lead to the conclusion that CZTS are formed in the samples of R2-350S and R7-350S through the sulfurization process in 100 ppm H₂S+H₂ at 350°C. However, for sample R8-350S, it is difficult to confirm whether CZTS formed or not since Raman data for that particular sample is not conclusive and further analysis will be needed to understand such observations.

In addition, it is noted that some local regions on the surface for those three samples appear to be rich in Cu and S with very low Zn and Sn content, which is consistent with the appearance of the Raman peak at 476 cm^{-1} characteristic of Cu_{2-x}S (Figure 3.6).

Table 3.3. EDS for single-step sulfurized samples in 100 ppm $\text{H}_2\text{S}+\text{H}_2$ and a reference CZTS sample. (The reference CZTS sample was prepared by sol-gel sulfurization at 550°C for 60 minutes in $5\%\text{H}_2\text{S}+\text{N}_2$.)

Sample designation	Cu (at. %)	Zn (at. %)	Sn (at. %)	S (at. %)
R2-350S	22 ± 1.1	23 ± 1.1	9 ± 0.5	46 ± 1.5
R8-350S	22 ± 1.1	13 ± 0.97	18 ± 1.8	46 ± 2.0
R7-350S	22 ± 2.3	18 ± 1.7	12 ± 1.1	48 ± 2.5
R2-450S	35 ± 4.9	20 ± 0.2	16 ± 0.6	35 ± 0.7
R7-450S	40	18	20	22
R7-550S	51	25	19	5
Reference CZTS	21 ± 0.9	18 ± 4.0	12 ± 0.3	49 ± 3.4

Because XRD pattern for those samples do not reveal additional crystalline phase other than CZTS, it is hypothesized that the amount of Cu_{2-x}S phase formed in the thin films is either amorphous or very little (e.g., $<\sim 2\%$).

SEM cross section images for samples R7-350S, R8-350S, and reference CZTS are shown in Figure 3.8(a), (b), and (c), respectively. It appears that all three samples show bilayer structures across the ~ 1 micron thick films with larger grains on top and smaller one underneath the surface and close to the substrate. Consistent with surface SEM images, sample R7-350S prepared at 350°C from Cu-rich recipe in 100 ppm $\text{H}_2\text{S}+\text{H}_2$ give similar or even larger grain size comparing to that obtained at high temperature (550°C) using high H_2S concentration ($\geq 5.0\text{ vol.}\%$), as shown for the reference CZTS sample (Figure 3.8(c)). In order to further complement previous analyses concerning phase

formation, electrical resistivity measurements were carried out for selected thin film samples. Table 4 lists measured sheet resistance and calculated electrical resistivity values at room temperature for some single-step sulfurized samples using 100 ppm $\text{H}_2\text{S}+\text{H}_2$. It is clearly seen that electrical resistivity values of samples of R7-450S and R7-550S sulfurized at 450 to 550°C using 100 ppm $\text{H}_2\text{S}+\text{H}_2$ are significantly lower than the values typically reported in literature for CZTS by several orders of magnitude (Xinkun *et al.*, 2012). Such results are consistent with the XRD patterns and EDS analysis suggesting the presence of Cu_3Sn metallic phase and much lower sulfur to metal ratio for those samples.

Figure 3.8. Cross section SEM images for single-step sulfurized samples of R7-350S (a), R8-350S (b), and the reference CZTS sample (c).

In comparison, for the R7-350S sample with near-stoichiometric sulfur to metal ratio and no crystalline phase other than CZTS, the measured resistivity value of $0.11 \, \Omega \cdot \text{cm}$ falls in the lower range reported in literature, probably due to excess carbon in the film (Yu *et al.*, 2014).

Table 3.4. Summary of electrical resistivity measurement for single-step sulfurized Cu-Zn-Sn thin film samples.

Sample designation	Avg. Sheet resistance ($\Omega/\square$)	Resistivity ($\Omega\cdot\text{cm}$)
R7-350S	923	0.11
R7-450S	2.0	2.4×10^{-4}
R7-550S	39.1	4.7×10^{-3}

Finally, optical properties of transmittance and absorbance were measured. Both reference CZTS and R7-350S samples have almost zero transmittance and closely matching absorbance. In comparison, sample R8-350S shows lower absorption and higher transmission compared to the other two samples. The extrapolation of Tauc plot between $(\alpha h\nu)^2$ versus photon energy ($h\nu$) to zero absorption coefficient gives the optical band gap of each sample, and the results are shown in Figure 3.9. The band gap for the reference CZTS sample is 1.48 eV (Tanaka *et al.*, 2011), while sample R7-350S gives a band gap of 1.41 eV, both of which are within the range (i.e., between 1.40 and 1.50 eV) normally reported for CZTS.

Figure 3.9. Plot showing calculated band gap from Tauc plot of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) based on measured optical properties of absorbance and transmittance for single-step sulfurized samples of R7-350S, R8-350S, and the reference CZTS sample.

On the other hand, the band gap for sample R8-350S is significantly higher at 1.79 eV, which might be due to the presence of impurity phases such as ZnS. Further investigation using Raman spectroscopy based on multiple wavelength excitations (e.g., 325 nm) will be needed to understand the exact reason behind the reported high band gap for this sample.

3.3.2. Thermodynamic analysis

Thermodynamic analysis was carried out using available data in the literature to further help understand the processing window to obtain CZTS, including at temperatures even lower than 350°C using the ppm-level H_2S . The following set of reactions (equations (1) to (3)) that describe the reactions for binary sulfides formation from metals (obtained from reduction of corresponding metal oxides in a hydrogen-containing atmosphere):

(It is recognized that upon reduction, the metal elements could form Cu-Sn and Cu-Zn alloys that would then react with H_2S . However, for simplicity, direct reaction between individual metal element and H_2S is analyzed.) Upon binary sulfides formation, a final reaction between those binary sulfides would lead to CZTS formation as follows:

Alternatively, CZTS might also form from metals and H_2S in a single step:

However, due to the limited thermochemical data for CZTS, as a first approximation, only formation of binary sulfides was considered from thermodynamics point of view. For each binary sulfide, values of standard Gibbs free energy of formation (ΔG_f°) at a given temperature can be found in databases (Richard Hemingway, 1995). Based on those standard Gibbs formation energy values, the equilibrium ratio of partial pressure of H_2S to H_2 or $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ can be predicted according to equation (6):

$$\frac{p_{\text{H}_2\text{S}}}{p_{\text{H}_2}} = \exp\left(\frac{\Delta G_f^\circ}{RT}\right) \quad (6)$$

in which ΔG_f° is the standard free energy change for the reaction at temperature T as calculated from the Gibbs formation energy. This way, for a given $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ ratio (for example by using the gas mixture of 100 ppm $\text{H}_2\text{S}+\text{H}_2$, i.e., $p_{\text{H}_2\text{S}}/p_{\text{H}_2} = 10^{-4} = 100 \text{ ppm}$),

the stability-limit temperature T_s for each sulfide can be calculated based on equation (6): below T_s , the binary sulfide phase will be thermodynamically stable while above that the metal element is stable.

Figure 3.10 depicts the calculated stability-limit temperature T_s for sulfurization reaction corresponding to different p_{H_2S}/p_{H_2} for Cu_2S , ZnS , $Sn(II)S$, and $Sn(IV)S_2$ phases. Generally, as p_{H_2S}/p_{H_2} decreases, the stability limit temperature T_s becomes lower. It is seen that Zn can be sulfurized easily with p_{H_2S}/p_{H_2} as low as 0.01 ppm at temperatures of $550^{\circ}C$, which is expected given the high stability for ZnS . In comparison, Cu and Sn need much higher H_2S concentration or, at a fixed p_{H_2S}/p_{H_2} ratio, much lower temperature in order for the corresponding sulfide phases to be thermodynamically stable. Specifically, with $p_{H_2S}/p_{H_2} = 100$ ppm as used in this study, for Cu to form Cu_2S , the sulfurization temperature has to be lower than $\sim 450^{\circ}C$; for Sn to form $Sn(II)S$, reaction temperature below $\sim 400^{\circ}C$ is necessary; on the other hand, for Sn to form $Sn(IV)S_2$, the temperature has to be below $\sim 150^{\circ}C$.

Figure 3.10. Stability-limit temperature T_s as a function of equilibrium H_2S concentration in H_2 ($p\text{H}_2\text{S}/p\text{H}_2$, in ppm) for binary sulfides of ZnS, Cu_2S , Sn(II)S, and Sn(IV) S_2 .

In summary, from the thermodynamic analysis, using 100 ppm $\text{H}_2\text{S}+\text{H}_2$, it seems possible to form CZTS in which Sn exist in Sn(II) state at temperature below $\sim 350^\circ\text{C}$; while to make sure Sn to be at Sn(IV) state, sulfurization at even lower temperature such as $\sim 150^\circ\text{C}$ might be needed.

3.3.3. Two-step low temperature sulfurization process

Based on the results of single-step sulfurization giving CZTS associated with minor or amorphous Cu_{2-x}S phase after sulfurization in 100 ppm $\text{H}_2\text{S}+\text{H}_2$ at temperature of 350°C and the thermodynamic analysis, additional experiment was carried out with two-step sulfurization at even lower temperature of 125°C .

As described before, the sample was first heated up to 400°C in $4\%\text{H}_2+\text{N}_2$ and held for 60 minutes to reduce the metal oxide precursor to metallic alloys and then cooled down

to 125°C and hold for 180 minutes in 100 ppm H₂S+H₂. Figure 3.11 shows XRD pattern for the R7-400H-125S sample with diffraction peaks that could belong to either ZnS or CZTS. The pattern has high background that might be due to the low temperature used for sulfurization. The SEM images in Figure 3.12 show a uniform and reasonably dense thin film. Also, EDS analysis as shown in Table 3.5 confirmed that sample R7-400H-125S has stoichiometry that matches closely with the expected CZTS phase. In addition, EDS for some surface particles showed high content of Cu and S and almost zero Zn and Sn content, suggesting surface Cu_{2-x}S phase(s). Further investigation based on Raman spectroscopy as in Fig. 13 revealed four distinct peaks at 338, 288, 352, and 368 cm⁻¹ all belong to CZTS.

Figure 3.11. XRD pattern and picture (insert) of the two-step sulfurized sample R7-400H-125S that was prepared by annealing sol-gel obtained Cu-Zn-Sn oxide precursor at 400°C in 4% H₂+N₂ followed by sulfurization at 125°C in 100 ppm H₂S+H₂.

Moreover, one additional peak at 476 cm⁻¹ with relatively high intensity belongs to Cu_{2-x}S. Cu_{2-x}S was identified, which is consistent with the identification of Cu_{2-x}S peaks in XRD and

SEM-EDS analysis on the thin film surface. The combined results from XRD, SEM-EDS, and Raman proved that the thin film formed after sulfurization of the film at 125°C in 100 ppm H₂S+H₂ is primarily Cu₂ZnSnS₄ with minor amount of Cu_{2-x}S. It should be mentioned that single-step sulfurization of the Cu-Zn-Sn oxide precursor films using 100 ppm H₂S + H₂ at temperature ~300°C and below had been carried out but it only yielded amorphous film. This suggests inactivity of the oxide precursor film after air baking, which might be due to the slow reaction kinetics for oxides at lower temperature.

Figure 3.12. SEM images at different magnification for the two-step sulfurized sample R7-400H-125S.

Table 3.5. EDS data for two-step sulfurized sample R7-400H-125S.

	Cu (at. %)	Zn (at. %)	Sn (at. %)	S (at. %)
R7-400H-125S	24±2.0	12±1.5	12±0.7	52±1.5

This is the rationale for using the two-step sulfurization with the first step reducing the oxide precursor to metals in forming gas at 400°C, which is then followed by the second step sulfurization at lower temperature of 125°C.

Figure 3.13. Room temperature Raman spectrum for the two-step sulfurized sample R7-400H-125S.

3.4. Conclusion

Sulfurization of Cu-Zn-Sn oxide precursor thin films prepared by sol-gel method from different stoichiometric solutions was carried out using 100 *ppm* H₂S+H₂ gas mixture for CZTS thin films preparation. At high sulfurization temperatures (e.g. 450 and 550°C), ZnS was the main sulfide phase observed, while Cu and Sn were primarily found to exist as Cu₃Sn metallic alloy phase, which lead to low sulfur to metal ratio (as determined by EDS analysis) and metallic like-low electrical resistivity values for those films. On the other hand, at low sulfurization temperatures (e.g. 350°C in single step sulfurization or even as low as 125°C in the reduction-then-sulfurization two-step process), near stoichiometric CZTS phase was obtained, which is often accompanied by minor Cu_{2-x}S phase(s) as confirmed by XRD, EDS, Raman spectroscopy, and measurements of

electrical resistivity and optical properties of the obtained thin films. This study demonstrates the complexity of CZTS sulfurization process, while the discovery of the CZTS formation using sol-gel sulfurization with significantly lower H₂S concentration at the ppm-level paves the way for developing safe, environmentally friendly, and inexpensive processing route for CZTS based solar cells. Further study is needed to optimize the sulfurization process to eliminate the formation of Cu_{2-x}S phase(s), improve the surface homogeneity, and evaluate the performance and limitations for CZTS solar cells prepared using this approach as compared with those from standard preparation techniques that rely on the use of high concentration (e.g., 5% and higher) H₂S gas.

4. STUDY OF THE FUNDAMENTAL PHASE FORMATION MECHANISM OF SOL-GEL SULFURIZED CZTS FILMS IN PPM LEVEL H₂S

4.1. Introduction

Preparation of high-quality CZTS thin films for solar cell applications remained a challenge due to the intrinsic complexity of the quaternary CZTS system (Wang *et al.*, 2014). Regardless of the adopted processing route, there is a lack of understanding about CZTS formation and other side-reactions that might lead to various harmful secondary phases (e.g., ZnS, Cu_{2-x}S, and Cu-Sn-S) during processing, which contribute to the limited device efficiency. Such knowledge regarding the fundamental mechanism of CZTS formation and associated transformation is crucial to process optimization to obtain CZTS thin films with better quality and hence higher device performance.

To address this issue, several attempts have been made using different *ex situ* characterization techniques such as multiwavelength Raman scattering (Dimitrievska *et al.*, 2014), Room Temperature Photoluminescence (RT-PL) (Grossberg *et al.*, 2014), Secondary Ion Mass Spectroscopy (SIMS), and X-ray Spectroscopy (XPS) combined with SEM and EDS (Salomé *et al.*, 2011)(Vora *et al.*, 2012)(Djemour *et al.*, 2013). However, these techniques usually do *not* provide information regarding the real-time emergence and transformation of CZTS phase and other by-products.

On the other hand, *in situ* XRD technique has been adopted to complement those *ex situ* techniques and provide useful information regarding the evolution of CZTS and other phases in real time (Brandl *et al.*, 2015)(Schorr and Gonzalez-Aviles, 2009). However, XRD alone is not adequate in differentiating between CZTS and some closely-related

phases such as ZnS and Cu_2SnS_3 (CTS) and it also suffers from poor spatial resolution (Alfons Weber *et al.*, 2009).

In contrast, *in situ* Raman microspectroscopy, as a multiphase sensitive, non-destructive, and high spatial resolution (down to $\sim 1\text{ }\mu\text{m}$) tool, offers great potential to investigate the phase formation mechanism of CZTS material under real processing conditions and provide useful information regarding the process kinetics. Previous studies on CZTS using Raman spectroscopy were focused on structure transitions (Scragg *et al.*, 2014) and temperature influence up to only $\sim 100^\circ\text{C}$ on Raman peaks of CZTS thin films (Sarswat, Free and Tiwari, 2011). Recently, the authors of this work demonstrated that CZTS material is Raman active at elevated temperatures up to $\sim 600^\circ\text{C}$ and it would undergo significant oxidation in air starting from $\sim 400^\circ\text{C}$ (Awadallah and Cheng, 2016). Wang *et al.* used *in situ* Raman to investigate the evolution of CZTS nanocrystals via the reaction between SnS_x , ZnS, and Cu_xS binary sulfide nanoparticles on a TiO_2 mesoscopic scaffold in nitrogen atmosphere (Wang, Elouatik and Demopoulos, 2016), and found that kesterite starts to form at 170°C under continuous heating condition.

However, to the best of our knowledge, there is no reported *in situ* Raman study for monitoring the phase formation of CZTS directly from sol-gel derived Cu-Zn-Sn oxide precursor in a sulfur rich atmosphere. Therefore, one of the main objectives of this work is to reveal the fundamentals about the phase formation process of CZTS thin films via sulfurization of Cu-Zn-Sn oxide precursor obtained by sol-gel processing in a hydrogen sulfide (H_2S)-containing atmosphere using the unique capability of the *in situ* Raman microspectroscopy technique.

Moreover, information related to formation of impurities for CZTS (Chakrabarti and Laughlin, 1983) (Kawai, 1973), are not available, especially under real time condition when quaternary CZTS system are processed. Of particular concern, how do impurity such as Cu_{2-x}S , SnS and Cu_2SnS_3 phases form during processing which have band gaps lower than CZTS and could be detrimental to the device performance (Siebentritt, 2013).

Therefore, studying each binary and ternary sulfide system individually will also provide fundamental information regarding the stability limit of those systems and their formation mechanism, which eventually help understand complex quaternary compound CZTS system.

The insights from this study would also help optimize the formation of CZTS via sulfurization of sol-gel derived oxide precursor in ppm-level H_2S at relatively low temperatures ($\sim 350^\circ\text{C}$ and below) as demonstrated earlier in chapter 3 (Awadallah and Cheng, 2017) aiming to produce CZTS thin films with superior quality via safe and low cost processing. It will also be beneficial to general CZTS-related study by providing insights about how to reduce formation of unwanted impurities.

4.2. Materials and Methods

The Cu-Zn-Sn metal oxide precursor thin films were prepared based on two different solutions: stoichiometric and Cu-rich. The reason for using the Cu-rich solution in the current study is that some reports recently suggest that Cu-rich CZTSSe films might offer

denser layers and larger grains which is beneficial to the device performance (Awadallah and Cheng, 2017) (Guo *et al.*, 2014).

The stoichiometric solution has Cu : Zn : Sn atomic ratio of 2 : 1 : 1 while the Cu-rich solution has Cu : Zn : Sn atomic ratio of 2.2 : 1 : 1 (i.e., 10 at.% Cu-rich). For stoichiometric solution, 4.37 g of copper acetate monohydrate (+99%, Sigma Aldrich), 2.40 g of zinc acetate dihydrate (+99%, Sigma Aldrich), and 2.47 g of tin chloride (+99%, Sigma Aldrich) were dissolved into 50 mL of 2-methoxyethanol (Afla Aesar) and the solution was stirred on a hot plate at 60°C for 1 hour. 2 mL of Monoethanolamine (MEA, Alfa Aesar) was also added to the solution to help dissolve the metal salts through the formation of complex intermediates. It also helps film adhesion and prevents defects (e.g., voids and cracking) formation (Ito, 2015)(Kahraman *et al.*, 2014). Then, the dark blue solution that formed was left to cool down to room temperature and filtered with 0.2 μ m PTFE filter. After that, samples were prepared by spin coating on bare soda lime glass substrates at 3000 rpm for 30 seconds and air baked on a plate at 300°C for 5 min. The coating and air-baking steps were repeated 5 times to obtain the desired film thickness of ~ 800 nm. The same procedure was adopted for the preparation of Cu-rich samples except for the starting amount of copper acetate monohydrate used was 4.78 g. Eventually, the oxide precursor samples were annealed in an H₂S-containing atmosphere in the *in situ* Raman monitoring cell that is specially designed for that purpose as described in detail below.

Similar to Cu-Zn-Sn metal oxide precursor, precursor films of Cu, Sn, and stoichiometric Cu-Sn (molar ratio of Cu:Sn is 2:1) were prepared. The reason for not considering sulfurization of Zn-O precursor in the current study is that ZnO is well known as one of

the effective sorbents that is commonly used for H₂S wash (Rosso *et al.*, 2003). Besides, ZnS is the least harmful phase to the device performance compared with other binary and ternary sulfides associated with CZTS (Siebentritt, 2013).

Table 4.1 shows the Table 2 includes the sample designation and the corresponding sulfurization conditions for each sample. The in situ Raman experiments are classified based on the processing temperature into two categories; intermediate and low temperature. The first category of experiments is a single step sulfurization process carried out at intermediate temperature of 350°C while the second category involves a two-step process in which a high temperature Forming Gas Annealing (FGA) is carried out at 400°C using 5% H₂+Ar (Airgas, UHP) gas mixture, followed by low temperature sulfurization at 170°C.

Table 4.1. List of designated sulfurization and in situ Raman monitoring experiments with detailed sulfurization conditions.

Sample designation	Oxide precursor	Sulfurization temperature (°C)	Sulfurization time (min)	FGA temperature (°C)	FGA time (min)
Sn-350	SnO ₂	350	≥60	N.A.	N.A.
Cu-350	CuO/Cu ₂ O				
Cu-Sn-350	Cu-Sn-O				
CZT-350	Cu-Zn-Sn-O				
Sn-170	SnO ₂	170	≥60	400	60
Cu-170	CuO/Cu ₂ O				
Cu-Sn-170	Cu-Sn-O				
CZT-170	Cu-Zn-Sn-O				

Figure 4.1(a) is a top view photo without the viewport lid to show the configuration inside the Raman cell. The thin film sample on glass substrate would lay down horizontally on the top of the heating wire that is connected to the power supply. To provide accurate temperature measurement inside the cell, a type-K thermocouple connected to the temperature controller is inserted into the cell and touches the back surface of the glass substrate. A cross section model view of the cell assembled with other Raman system components is shown in Figure 4.1(b). The laser beam is focused onto the sample vertically using a reflecting mirror and the objective lens and passes through a glass window with thickness of 200 μm that allows signal transmission with minimum intensity attenuation. The whole Raman cell is fixed on a 3-axis stage to allow precise laser focus and examine different areas of the sample. Figure 4.1(c) shows a schematic drawing of the in-house built Raman micro-spectroscopy system with the heating cell installed. All experiments were carried out using an in-house Raman system equipped with an air-cooled Ar ion laser (Spectra Physics Model 177, 514 nm, 400mW, spot size 20 μm) and the Raman spectra were collected using a spectrograph (HoloSpec f/1.8i, Kaiser Optical System) with a total accumulation time of 5 min. After the *in situ* Raman monitoring experiments, samples were also examined with different *ex situ* characterization tools: X-ray diffraction was carried out using Siemens 500D diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation and 2θ in the range of 20 - 80° for phase identification. SEM combined with EDS was performed on a JEOL 6330F microscope at 15.0 kV accelerating voltage to investigate the surface morphology and assess the local chemical composition of the sample surface and cross section.

Figure 4.1. (a) Top view of the in situ Raman cell with the top lid open showing the sample and other gas and electrical connections (b) Cross sectional model view of the in situ Raman cell and stage. (c) Schematic of the in-house built Raman system.

4.3. Results and Discussion

4.3.1. In situ Raman Monitoring of Cu-O Films Sulfurization

As shown in Figure 4.2(a), sulfurization of Cu-O film in 100 ppm H₂S+4%H₂+N₂ at 350°C for 120 min showed no evidence for the formation of any copper sulfide phase as no peaks correspond to any Cu_{2-x}S phase(s) were detected. No change on the Raman spectra was observed upon cooling the sample down to room temperature in Argon.

On the other hand, in situ Raman monitoring for the two step sulfurization of Cu-O sample at 170°C, as shown in Figure 4.3(a), revealed the emergence of one peaks at 471 cm^{-1} after 45 min of sulfurization. Further sulfurization till 60 min led to significant increase in the peak intensity accompanied by slight shift to higher wavenumber of 472 cm^{-1} . No further change was noticed on the peak intensity or position when sulfurization continued till 80 min. After that, sample was cooled down to room temperature and Raman signal was collected with no noticeable changes observed on its intensity or position. The observed peak during the in situ Raman monitoring most likely belongs to Cu_{2-x}S phase (Fernandes, Salomé and da Cunha, 2011).

Figure 4.2. (a) In situ Raman spectra collected at different sulfurization times for Cu-350 sample sulfurized at 350°C.

Figure 4.3. (a) In situ Raman spectra collected at different sulfurization times for Cu-170 sample sulfurized at 170°C. (b) XRD patterns for Cu-O precursor, Cu-350, and Cu-170 samples.

Further investigation of the sample's composition after in situ Raman monitoring was carried out using XRD and EDS. Figure 4.3(b), shows XRD pattern for Cu-O precursor sample which primarily consists of CuO and the main peaks were identified at 2θ of 35.5 and 38.7°, which matches the database for CuO (JCPDS #041-0254). The XRD pattern of sample Cu-350 shown in Fig. 3(b) clearly matches the one for the oxide precursor sample. Moreover, the EDS data (Table 4.2) for sample Cu-350 confirmed the sample content is primarily Cu and O with atomic ratio close to Cu:O ~1:1, which is consistent with both in situ Raman observations and XRD results.

On the other hand, XRD pattern for sample Cu-170 showed two distinctive peaks belong to Cu metal at 2θ of 43.2 and 50.4° (JCPDS#-004-0836). Another two low intensity peaks at 2θ of 31.7 and 36.9 were identified which might belong to CuS (JCPDS#-006-0464) and hexagonal Cu₂S (JCPDS#-012-0176) phases respectively. The high intensity of the Cu metal XRD peaks relative to other phases suggests that CuO undergoes

complete reduction to Cu metal during the initial FGA step at 400°C and then the Cu metal reacts with H₂S gas at 170°C to form Cu_{2-x}S phase(s) as identified by Raman spectroscopy. The EDS data (Table 4.2) for sample Cu-170 showed sulfur atomic content of 25% while Cu content was found to be 62%. The reason for the high Cu content is that most of the Cu in the sample exists in the metal form while the Cu_{2-x}S amount is very little, as consistent with the XRD result. Those results from in situ Raman as well as XRD and EDS are not conclusive about which Cu_{2-x}S (CuS or Cu₂S) phase exist in the sample since the two phase (CuS and Cu₂S) have a matching Raman shift and only one peak is identified in XRD for each phase. Continued sulfurization for longer time under these conditions is expected to completely transform the Cu metal to Cu_{2-x}S phase.

4.3.2. In situ Raman Monitoring of Sn-O Films Sulfurization

Sulfurization of Sn-O thin film at 350°C for 80 min using 100 ppm H₂S+4%H₂+N₂ mixture showed no evidence for the formation of any tin sulfide phase(s) (e.g., SnS, SnS₂, or Sn₂S₃) as in Figure 4.4(a). The in situ Raman data for sample Sn-350 is presented in the range of Raman shift between 100 and 400 cm⁻¹.

On the other hand, the two-step sulfurization process led to sulfurization of Sn-O precursor to form tin sulfide. Figure 4.4(b) shows the in situ Raman data for Sn-170 sample sulfurized at 170°C for 80 min. The first peak emerged after 30 min of sulfurization and was observed at 310 cm⁻¹. After 80 min of sulfurization, the peaks at 310 cm⁻¹ was observed to shift to 312 cm⁻¹ and its intensity slightly increased. It was also

noticed that one peak that might belong to SnS phase (Altamura and Vidal, 2016) appeared at 162 cm^{-1} , however, it disappeared with continued sulfurization and after cooling the sample down to room temperature. Upon cooling the sample down to room temperature, only one peak was observed at 315 cm^{-1} which most likely belongs to SnS_2 phase as identified in previous reports (Altamura and Vidal, 2016) (Lund *et al.*, 2014).

Figure 4.4. In situ Raman spectra for SnO_2 sulfurized samples at 350°C (a) and 170°C (b) collected at different sulfurization times. RT Raman spectra for samples before and after sulfurization are provided for comparison.

Further investigation of the Sn-O precursor sample as well as sulfurized samples using both XRD and EDS was also carried out. The XRD analysis of Sn-O precursor sample (Fig. 5) shows the three peaks identified at 2θ of 26.6, 33.8, and 51.7 which belong to SnO_2 and matches database for SnO_2 phase (JCPDS#-041-1445). In addition, EDS analysis of the Sn-O precursor sample showed that it has a Sn atomic content of 30% while O atomic content was 70%, this ratio of Sn:O $\sim 1:2$ matches the XRD results. Sulfurization of sample Sn-350 revealed no change from the oxide form as confirmed by

XRD analysis (Fig. 5(a)) of the sample, which showed a pattern identical to that of the precursor oxide. Furthermore, the EDS analysis of sample Sn-350 (Table 4.1) matches both in situ Raman and XRD observation as it showed the sample has only 1% content of sulfur and is significantly Sn-deficient with Sn atomic content of 20% and the remaining is oxygen.

XRD analysis of sample Sn-170 (Figure 5(b)) matches in situ Raman observation. The XRD pattern for sample Sn-170 shows the two characteristic peaks correspond to SnS_2 phase at 2θ of 15.0° , 41.8° and no peaks belong SnO_2 were observed. This result matches database for SnS_2 phase (JCPDS#-023-0677). However, EDS data for sample Sn-170 shows a Sn:S content of $\sim 1 : 1.35$ which slightly deviates from the SnS_2 composition. The reason for such sulfur deficiency is not clear.

Figure 4.5. XRD patterns for Sn-oxide precursor and samples Sn-350 and Sn-170.

4.3.3. In situ Raman Monitoring of Cu-Sn-O Films Sulfurization

The next step toward understanding the formation pathway for CZTS phase is to study the ternary sulfide systems, in particular Cu-Sn-system. Figure 4.6(a) shows the in situ Raman spectra for Cu-Sn-350 sample sulfurized at 350°C for 60 min at different sulfurization time. No Raman peaks were observed during the 60 min of sulfurization and all collected Raman spectra were featureless. The sample was then cooled down to room temperature and no change was observed on the Raman spectrum at room temperature.

For the two-step sulfurization of the Cu-Sn-O precursor film at 170°C, the *in situ* Raman data in Fig. 6(b) show no evidence for the formation of any copper tin sulfide phase. However, upon cooling the sample down to room temperature, Raman spectrum of the sample clearly showed one peak identified at 474 cm⁻¹ which more likely belongs to Cu₂-_xS phase (Fernandes, Salomé and da Cunha, 2011). The spike at 364 cm⁻¹ is originated from the cosmic ray in the background and does not belong to any Cu-Sn sulfide phase.

Figure 4.6. In situ Raman spectra for Cu-Sn-O samples sulfurized at 350°C (a) and 170°C (b) collected at different sulfurization times. RT Raman spectra for samples before and after sulfurization are provided for comparison.

4.3.4. In situ Raman monitoring of CZTS phase formation at 350°C

The first *in situ* Raman monitoring experiment for the Cu-Zn-Sn-O precursor was carried out using a gas mixture of 100 ppm H₂S+4%H₂ balanced by N₂ (all gas composition

specified by volume in this thesis) at 350°C with sulfurization time up to 180 min. The Cu-Zn-Sn oxide precursor sample as described before was placed in the Raman cell and heated up in Ar (Ultra-high purity (UHP) grade, Airgas) atmosphere at 25°C/min rate. Then, the gas was switched from Ar to the gas mixture of 100 ppm H₂S+4%H₂+N₂. During the sulfurization process, Raman signals were collected at different time intervals. After that, the sample was cooled down in Ar atmosphere to room temperature and Raman spectrum was collected again. It is noted that no sulfur deposits was observed on the glass window during or after the *in situ* Raman monitoring experiments when using 100 ppm H₂S for sulfurization. In comparison, a separate *in situ* sulfurization experiment was also carried out using elemental sulfur and it completely covered the internal surface of the glass window as expected due to sulfur evaporation and deposition on the relatively colder surfaces of the Raman cell including the glass window. Those observations indicate the effectiveness of using low ppm-H₂S as opposed to elemental sulfur for *in situ* Raman monitoring of the sulfurization process.

Figure 4.7(a) shows the Raman spectra collected between Raman shift of 200 to 600 cm⁻¹ at different time intervals up to a total sulfurization time of 180 min during the *in situ* Raman monitoring of the sulfurization process for the sample from the stoichiometric solution. The Raman spectrum collected at room temperature (RT) for the oxide precursor showed no peaks indicating the amorphous nature of the oxide precursor sample. After heating the sample up to 350°C and switching the gas from Ar to 100 ppm H₂S+4%H₂+N₂, no peaks were observed during the first 15 min of sulfurization.

Figure 4.7. Raman spectra collected at different sulfurization times during the in situ Raman monitoring experiment at 350°C for the stoichiometric sample sulfurized for 180 min (a) and the Cu-rich sample sulfurized for 60 min (b).

However, after ~30 min of sulfurization, a peak centered at Raman shift of $\sim 330 \text{ cm}^{-1}$ emerged, which most likely corresponds to CZTS phase at elevated temperature (Awadallah and Cheng, 2016), while no peaks belonging to other sulfides (e.g., Cu_xS , ZnS , or SnS_2) were observed. Subsequent annealing for longer time of 60 min and eventually 180 min did not seem to cause any additional changes in the Raman spectra except that Raman peaks became slightly higher in intensity. After that, the experiment

was ceased and the sample was cooled down naturally in Ar atmosphere to room temperature when a Raman spectrum of the sample was collected again. As shown in Figure 4.7(a) for the Raman spectrum collected at room temperature for the stoichiometric sample *after* the *in situ* monitoring experiment, the major Raman peak shifted to 338 cm^{-1} , which is characteristic to CZTS and matches well with the literature data (Dimitrievska *et al.*, 2014), and the shift to higher frequency with decreasing temperature is consistent with expectation. On the other hand, no peaks belonging to other sulfides (e.g., Cu_xS , ZnS , or SnS_2) were observed, suggesting relatively high purity of the CZTS thin film formed. (It is noted that a “peak” at $\sim 212\text{ cm}^{-1}$ seem to appear in all Raman spectra collected at elevated temperatures during sulfurization and at room temperature after cooling the sample down. It even appears for the oxide precursor sample! The authors believe it is not related to the sample and most likely originated from the cosmic rays in the background collected during the *in situ* Raman monitoring experiments given the relatively long signal acquisition time of 300 seconds or longer.)

In comparison, Figure 4.7(b) summarizes the result of the *in situ* Raman monitoring experiment at 350°C for the Cu-rich sample. Similar to the stoichiometric sample, sulfurization for $\sim 30\text{ min}$ led to the appearance of a distinctive peak at Raman shift of $\sim 331\text{ cm}^{-1}$ that most likely belongs to the CZTS phase. Further sulfurization for 60 min seems to lead to a slight shift in the observed peak from 331 cm^{-1} to 334 cm^{-1} . At the same time, another peak emerged at 467 cm^{-1} , which is attributed to Cu_{2-x}S at elevated temperature (Dimitrievska *et al.*, 2014). The exact reason for the observed peak shift for the Cu-rich CZTS is not clear and it might be related to the composition change

associated with the emergence of Cu_{2-x}S phase. After that, the sample was cooled down in Ar atmosphere and Raman data was collected again at room temperature, which showed two distinctive peaks characteristic to CZTS phase at 338 cm^{-1} and 287 cm^{-1} , and the other peak at 471 cm^{-1} is identified as Cu_{2-x}S .

Further investigation of both the stoichiometric and the Cu-rich samples was carried after the *in situ* Raman monitoring experiments. The room temperature XRD patterns of the 350°C *in situ* examined stoichiometric sample after sulfurization for 180 min and the Cu-rich sample after sulfurization for 60 min as well as the oxide precursor are shown in Figure 4.8. The oxide precursor sample showed a completely amorphous pattern while the *in situ* Raman examined samples were crystalline and showed the same main peaks identified for both samples at 2θ of 28.4° , 47.3° , and 56.0° , which can be attributed to CZTS (JCPDS # 026-0575).

One possible reason why Cu_{2-x}S phase in the Cu-rich sample, as detected by Raman from the sample surface (see Figure 4.8(b)), is not observed in the XRD pattern might be that the amount of Cu_{2-x}S formed during sulfurization is relatively small (i.e., less than ~5 wt.%) and below the detection limit for the XRD system used. Another possibility is that Cu_{2-x}S phase formed has poor crystallinity, which is common for the Cu-S system. It is also noted that the XRD patterns contain a bump in the 2θ range of $\sim 20\text{-}35^\circ$.

Figure 4.8. Room temperature XRD patterns of in situ Raman examined stoichiometric sample sulfurized for 180 min and Cu-rich sample sulfurized for 60 min at 350°C in 100 ppm $\text{H}_2\text{S}+4\%\text{H}_2+\text{N}_2$. The amorphous oxide precursor XRD pattern is included for reference.

This might be attributed to the glass substrate beneath the thin film sample, as its thickness is only $\sim 0.5\ \mu\text{m}$, as seen later for the SEM images of the samples cross-section. (The possibility of the bump belong to untransformed oxide is low due to the low oxygen content in those films, as confirmed by EDS.)

Figure 4.9(a) is an SEM image for the surface of a stoichiometric sample sulfurized at 350°C for 180 min. It showed the sample was relatively dense with small submicron grains, which is expected given the sulfurization temperature was only 350°C. In comparison, the Cu-rich sample showed a different morphology with a relatively flat layer decorated with large number of micron size particles on top as in Figure 4.9(b). The EDS analysis of the flat surface of stoichiometric sample (Table 4.1: sample 350-60-S1) showed that it has near stoichiometric composition. It is noted that Figure 4.9(a) on the stoichiometric sample surface also shows a few large bright particles. However, when

they were probed by EDS, they do not give a consistent composition such as Cu_{2-x}S . Since those particles are not in large number as opposed to the Cu-rich sample, they will be studied in future as needed to reveal their exact origin.

Figure 4.9. SEM images for the surface of the in situ Raman examined (a) stoichiometric sample sulfurized for 180 min and (b) Cu-rich sample sulfurized for 60 min. The large surface particles in (b) have been identified by EDS to have composition very close to Cu_2S .

For the Cu-rich sample, the flat surface regions (Table 4.1: sample 350-60-S2) give similar composition. In addition, analysis of the surface particles of the Cu-rich sample (Table 4.1: sample 350-60-S2-SP) showed they have low content of Zn and Sn and high content of Cu with Cu : S atomic ratio close to $\sim 2 : 1$, which most likely corresponds to the Cu_2S phase. Based on the *in situ* Raman monitoring data collected at 350°C for the stoichiometric sample, it is concluded that other than CZTS, none of the main peaks for other sulfides (i.e., monoclinic- Cu_2SnS_3 sulfide at 290 cm^{-1} and 352 cm^{-1} (Berg *et al.*, 2012)(Suryawanshi *et al.*, 2016), ZnS at 352 cm^{-1} , 700 cm^{-1} and 275 cm^{-1} (Duren *et al.*, 2015)(Nilsen, 1969), SnS_2 at 314 cm^{-1} (Berg *et al.*, 2012)) were observed during the *in situ* Raman monitoring experiments at 350°C .

Table 4.2. EDS data for in situ Raman examined samples sulfurized at different conditions using 100 ppm H₂S+4%H₂+N₂ mixture.

Sample designation	Cu (at. %)	Zn (at. %)	Sn (at. %)	S (at. %)	O (at. %)
Cu-350	55	NA	NA	1	44
Cu-170	62	NA	NA	25	0
Sn-350	NA	NA	20	1	79
Sn-170	NA	NA	41	55	0
350-60-S1(stoich.)	27±3.1	14±2.7	11±1.1	48±3.2	0
350-60-S2(Cu-rich)	25±8.7	15±5.0	10±1.0	48±1.8	0
350-60-S2-SP(Cu-rich)	64±9.2	3±6.4	7±1.0	26±3.8	0
170-60-S	26±4.2	14±3.8	14±1.5	46±2.5	0
170-180-SP	49±1.8	4±1.4	4±0.7	43±1.4	0

Therefore, it is most likely that CZTS phase forms through a direct reaction between the metal oxides and the gas mixture of 100 ppm H₂S+4%H₂ at 350°C, and the CZTS remains stable since it is the only thermodynamically stable phase for the stoichiometric sample under that condition. On the other hand, when using the Cu-rich solution, apart from forming CZTS, small amount of Cu_{2-x}S phase also form on the film surface upon continued sulfurization conditions and CZTS and Cu_{2-x}S would co-exist in equilibrium due to the Cu-rich composition of that sample.

4.3.5. In situ Raman monitoring of CZTS phase formation at 170°C

Previously, it has been reported CZTS could also form from sol-gel oxide precursor via a two-step sulfurization with the first step of forming gas (e.g., 4% H₂+N₂) annealing at 400°C and the second step of sulfurization in 100 ppm H₂S+H₂ gas mixture at further reduced temperature as low as 125°C (Awadallah and Cheng, 2017). (It is noted that the first step of forming gas annealing converts some of the metal oxides (Sn and Cu) to metallic phases. Without this forming gas annealing (FGA) step, direct sulfurization of the sol-gel oxide precursor at low temperature such as 125°C did not yield the desired CZTS phase (Awadallah and Cheng, 2017). On the other hand, Cu_{2-x}S phase was often observed for those samples sulfurized in 100 ppm H₂S+H₂ at lower temperature (i.e., <~200°C). This section discusses in detail the results of *in situ* Raman experiment simulating the two-step sulfurization to understand the CZTS and related impurity phase formation under this condition.

Due to the tendency of Cu_{2-x}S impurity formation in the Cu-rich sample as shown before for the 350°C sulfurized sample, only stoichiometric samples were employed for the low temperature (i.e., <~200°C) *in situ* Raman monitoring experiments. Similar to the previous procedure, the oxide precursor sample from sol-gel processing after spin coating and air-baking was heated up to 400°C at 25°C/min rate in the Raman cell with flowing Ar atmosphere. At 400°C, the gas was switched to forming gas of 5% H₂+Ar mixture and the sample was annealed for 60 min. (This forming gas annealing step basically converts Sn and Cu oxide into their alloys while ZnO largely remains as oxide.) The XRD analysis of the annealed sample (Figure 4.6) showed two peaks belong to Sn at 2θ of 31.7 and

66.0° (JCPDS #04-0673) and another 2 peaks belong to Cu at 2θ of 43.0 and 51° (JCPDS #04-0836). In addition, there is a low intensity peak at 2θ of 42.8 that belongs to Cu_6Sn_5 phase (JCPDS #081-8261). There was no peak identified for Zn metal, which indicates it remains in the amorphous oxide form after the FGA step. The Cross section SEM images showed the annealed precursor film thickness is 400 nm as they experienced shrinkage during transformation from metal oxides to pure metals or alloy mixture. After that, the Raman cell with the sample was cooled down naturally to 170°C for subsequent sulfurization. In particular, at 170°C, the gas flow was changed from the 5% H_2 +Ar forming gas to the 100 ppm H_2S +4% H_2 + N_2 gas mixture and the sulfurization was carried out for up to 180 min, and the Raman spectra were recorded from the sample at 170°C at different time intervals. Finally, the sample was cooled down naturally in Ar atmosphere. The *in situ* Raman data collected at 170°C during the sulfurization are shown in Figure 4.10. The first hint of a weak Raman peak emerged after ~30 min of sulfurization at ~335 cm^{-1} , which is attributed to CZTS. This appears to be longer than the what it took (~5 min) for the similar bump to appear after exposure to the same gas mixture of 100 ppm H_2S +4% H_2 + N_2 at 350°C, and the delay might be due to the slower reaction kinetics for CZTS formation at reduced temperature of 170°C. As the sulfurization process continued for 60 min, roughly the same Raman pattern for CZTS phase was observed without obvious shift of the peaks, while the peak intensity increased. Also, no peaks for other sulfides were detected. It is noted that if the *in situ* Raman experiment was ceased at this moment (i.e, 60 min of sulfurization at 170°C), and the sample was cooled down to room temperature in Ar, the Raman collected showed the distinctive peak corresponding to

CZTS phase at 338 cm^{-1} , while no Raman peaks corresponding to other sulfide phases were observed.

However, it was observed that significant amount of Cu_{2-x}S was often detected by Raman for the low temperature sulfurized sample. In order to verify when Cu_{2-x}S impurity would appear and whether the CZTS phase formed is stable under continuous sulfurization conditions beyond 60 min, the two-step *in situ* Raman experiment was repeated under the same conditions and the sulfurization time was extended to 180 min at 170°C . The first 60 min of sulfurization gave similar result as before. Then, after ~ 80 min of sulfurization, apart from the CZTS peak at 335 cm^{-1} , another peak at 467 cm^{-1} that corresponds to CuS phase started to emerge.

Figure 4.10. Raman spectra collected at different sulfurization times for the stoichiometric sample during the *in situ* Raman monitoring experiment at 170°C in 100 ppm H_2S +4% H_2 + N_2 gas mixture for up to 180 min.

(It is noted that Cu_{2-x}S with x in the range of 0 to 1 have the same Raman peak at $\sim 470\text{ cm}^{-1}$ (Hurma and Kose, 2016). CuS can be viewed as Cu_{2-x}S with $x \approx 1$. The rationale to specify the copper sulfide as CuS instead of Cu_2S is due to EDS analysis, as explained later.), Continued sulfurization up to 180 min led to further increase in intensity of the CuS Raman peak at 467 cm^{-1} accompanied with lowering of the CZTS peak. Finally, upon cooling the 180 min sulfurized sample down to room temperature, the CZTS peak intensity become much weaker, while the CuS peak shifted from 471 cm^{-1} at 170°C to 475 cm^{-1} with further increased intensity. This observation, together with the *absence* of the CuS peak during the first 60 min of sulfurization, strongly suggests that under sulfurization condition explored (170°C in $100\text{ ppm H}_2\text{S}+4\% \text{ H}_2$), CZTS forms first from the post FGA precursor film and then, upon extended sulfurization, CuS gradually forms from CZTS accompanied with (partial) decomposition of CZTS. The observation of the sulfur-rich CuS formation at low sulfurization temperature (i.e., $\leq 250^\circ\text{C}$) has been reported in several studies (Maeda, Tanaka, Fukui, *et al.*, 2011)(Wibowo *et al.*, 2007). Although the conditions are all somewhat different, it seems that, similar to the observation here, CuS occurrence is generally exaggerated under prolonged sulfurization and it is particularly significant at lower temperature. For example, in the study by Wang *et al.*, Cu_xS Raman peak always seems to increase during cooling as the temperature decreases and it was particularly obvious when temperature decreases to below $\sim 200^\circ\text{C}$ (Wang, Elouatik and Demopoulos, 2016). To further understand the observed phenomena during the low temperature *in situ* Raman experiment, other *ex situ* characterization techniques were performed. The XRD patterns for the *in situ* Raman examined samples after sulfurization at 170°C for 60 min as well as 180 min are given in Figure 4.11.

For the 60 min sulfurized sample, the XRD patterns shows three peaks that belong to CZTS phase at 2θ of 28.4, 47.3, and 56.0°. However, XRD pattern indicates there is another peak at 2θ of 31.7°, which might correspond to unreacted metallic Sn (JCPDS #04-0673). Continuous sulfurization for 180 min leads to the disappearance of the peaks corresponding to CZTS, suggesting its subsequent disintegration. Based on Raman spectra showing strong peak for CuS, the formation of CuS phase is suspected.

However, as shown Figure 4.11 for the 180 min sulfurized sample, the high background and very weak XRD peaks suggest the CuS phases and other related phases (upon CZTS decomposition) are all not well crystallized.

Figure 4.11. Room temperature XRD patterns for in situ Raman samples examined at 170°C for 60 and 180 min.

Further investigation of the morphology of the sample sulfurization at 170°C for 60 min based on SEM as in Figure 4.12(a, b) revealed that the sample seems to have a bilayered structure with a flat and dense layer at the bottom and flower-like structures on the top,

which have larger grain size. The EDS analysis of the dense layer near the substrate surface (Table 4.1, sample: 170-60-S) showed a slightly sulfur deficient sample with atomic content of 46% while Cu/Zn+Sn ratio appeared to be almost stoichiometric (Cu/Zn+Sn=0.93).

Figure 4.12. SEM surface (a, c) and cross section (b, d) images of the in situ Raman samples (stoichiometric composition) examined at 170°C for 60 min (a, b) and 180 min (c, d), respectively. The yellow arrows point toward particles identified by EDS as CuS.

The SEM surface and cross section images (Figure 4.12(c, d)) of the sample sulfurization at 170°C for 180 min showed a bilayer structure similar to that obtained for 60 min. However, the top surface particles in this case were observed to have grown into faceted structure with larger grain size. Further investigation of the large faceted particles on the surface (as indicated by yellow arrows in Figure 4.12(c)) by EDS (Table 4.1, sample: 170-180-SP) showed those particles are rich in Cu and S with ratio of Cu:S of ~1 with

almost no Zn and Sn, suggesting the surface particles are CuS. Such an explanation would seem to match both *in situ* Raman and XRD data.

4.3.3. Discussion on formation process of CZTS from sulfurization from sol-gel oxide precursor

It should be mentioned that all experiment were repeated several times on different samples and the same results were obtained, confirming the reproducibility for the observations made. From the results of all the *in situ* Raman monitoring experiments at different sulfurization conditions and the structural and compositional analyses of the *in situ* examined samples, the formation mechanism for CZTS derived from sol-gel oxide precursors is discussed in the following.

Regarding the CZTS formation from oxide precursor during sulfurization in 100 ppm H₂S at intermediate temperature such as 350°C, several scenarios might be possible. The first one is that metal oxides initially react with hydrogen in the 100 ppm H₂S+4%H₂+N₂ gas mixture to form a mixture of metals (or their alloy) and remaining unreacted oxides (primarily ZnO). After that, this mixture could then undergo sulfurization by reacting with H₂S to form binary sulfides (ZnS, Cu₂S and Sn(II)S) or ternary sulfide Cu₂SnS₃ (CTS). Eventually, those binary/ternary sulfides react to form CZTS phase according to reaction (R1)

It is also possible that Cu and Sn form an alloy mixture, which is then sulfurized to form CTS phase. After that, ZnS react with CTS phase to form CZTS according to reaction (R2)

Another possibility is that after the (partial) reduction, the mixture of metals with unreacted oxides react directly with H_2S and forms CZTS as in reaction (R3)

Nevertheless, given the relatively short reaction time (only ~15-30 min) and the absence of Raman peaks for other sulfides such as Cu_2S , SnS , SnS_2 , ZnS , or CTS in the period before CZTS Raman peak appearance, the most likely scenario is that the CZTS formation from the mixed amorphous oxide precursor finishes in one step as below:

The CZTS formed is thermodynamically stable, as evidenced in continued exposure to the same atmosphere for extended time showing persistence of the CZTS Raman and XRD fingerprints. That Cu-rich sample started to yield Cu_2S after 60 min of exposure, which is expected due to the Cu excess in the sample.

In comparison, for the two-step *in situ* Raman monitoring experiment carried out at 170°C , the first-step of forming gas annealing (FGA) at 400°C using the $5.0\%\text{H}_2+\text{Ar}$ reduced Sn and Cu metal oxides to Cu-Sn metal alloy (mixture), while ZnO remains as oxide (Theses and Weirich, 1926). Then in the second step of exposing the post FGA sample containing Sn-Cu alloy and ZnO to 100 ppm $\text{H}_2\text{S}+4\%\text{H}_2+\text{N}_2$ at 170°C due to the absence of Raman peaks for other sulfides in the first 60 min, it is believed that CZTS phase form from the Cu-Sn alloy and ZnO precursor in a single step through the reaction of R5:

Continued sulfurization for more than 60 min under this condition (170°C using 100 ppm H₂S+4%H₂+N₂) for the sample seems to lead to “over-sulfurization” - the formation of sulfur-rich phase of CuS with Cu at 2+ valence versus 1+ in CZTS (Thota *et al.*, 2017). The *in situ* Raman data collected over time along with the XRD pattern indicate that under the specific sulfurization condition investigated (170°C using 100 ppm H₂S+4%H₂+N₂), CZTS phase is not the thermodynamically most stable phase. Instead, CZTS may be the phase that is kinetically faster to form, while the sulfur-rich phase of CuS is thermodynamically stable. As a result, CZTS forms first. But overtime, as local sulfur concentration builds up (probably due to gradual building up of elemental sulfur from H₂S decomposition), Cu in CZTS migrates out and react to form CuS, which leads to decomposition of CZTS, as in reaction R6

Such an explanation is further supported by the EDS data for the samples: As mentioned before in Table 4.1, the 170°C-60min sulfurized sample has surface composition of near stoichiometry CZTS while the 170°C-180min sulfurized sample show faceted particles on surface with very low Zn and Sn content and Cu:S ratio ~1:1, suggesting they are sulfur-rich phase of CuS. The reaction products are not well crystalline after cooling the sample down to room temperature, which is common for the many metal sulfide such as the Cu-S and Sn-S systems (Quintana-Ramirez *et al.*, 2014).

Finally, in terms of the implications to future CZTS fabrication optimization, the results of the current study suggest that in order to avoid the copper-rich Cu₂S impurity

formation in CZTS, it is critical to control the stoichiometry of the starting solution. In addition, the process of intermediate temperature sulfurization of oxide precursor in low concentration H₂S-containing atmosphere (e.g., the 100 ppm H₂S+4% H₂ as used here) seems attractive because it may help avoid Sn and Zn loss due to absence of higher temperature processing, which can be tricky to control. As long as the solution is stoichiometric, the CZTS would be the only thermodynamically stable phase. On the other hand, to avoid the sulfur-rich CuS impurity formation, low temperature (e.g., <200°C) holding of CZTS in any sulfur-rich atmosphere (either in the form of H₂S or elemental sulfur) should be avoided as Cu will be thermodynamically more stable to exist in the 2+ state as in CuS as opposed to in 1+ state as in CZTS. However, it is recognized that the study has been limited to chemical and structural analysis of the CZTS absorber material and it has *not* been done on the typical Cu-poor Zn-rich composition. Therefore, further study on other compositions and also on actual device fabrication and characterization will be needed to confirm the real efficacy of the current processing procedure.

4.4. Conclusion

In conclusion, the current study investigated the fundamental formation process of CZTS thin films from sol-gel based oxide precursor at different sulfurization conditions using ppm-level H₂S-containing gas mixture. From the *in situ* Raman monitoring experiments and subsequent *ex situ* materials characterizations, CZTS phase was observed to emerge within ~30 min of sulfurization at an intermediate temperature of 350°C using 100 ppm

$\text{H}_2\text{S}+4\%\text{H}_2+\text{N}_2$ gas mixture and seems to form directly from the oxide precursor in a single-step reaction bypassing the individual sulfide phases (e.g., Cu_2SnS_3 and ZnS). On the other hand, for the two-step sulfurization process, the first step of forming gas annealing at 400°C reduces some of the oxides (i.e., Cu and Sn oxides) into metal alloys. Then, for the second step at an even lower temperature of 170°C , CZTS phase start to form in a single-step after ~ 30 min in the 100 ppm H_2S containing gas mixture. Moreover, continued sulfurization at low temperature ($<200^\circ\text{C}$) for extended time (e.g., >1 h) may lead to the formation of the sulfur-rich CuS phase accompanied with disintegration of the CZTS phase. Overall, the study suggests that sol-gel stoichiometry and sulfurization condition including both temperature and time needs to be carefully controlled to stabilize CZTS phase and avoid the formation of other impurity phases, such as Cu_xS ($1 \leq x \leq 2$) phase, which would deteriorate the quality of CZTS films. On the other hand, the study shows that *in situ* Raman microspectroscopy technique is a valuable tool that would help understand the fundamental phase formation mechanism of sol-gel based CZTS thin films in real time under relevant processing conditions. It could be used to guide further optimization of CZTS processing to obtain high quality films and better solar cell device performance. This technique is also expected to be helpful for investigating other multi-component systems such as CIGS.

5. IN-SITU RAMAN MONITORING OF CZTS OXIDATION AND RELATED DECOMPOSITION AT ELEVATED TEMPERATURES

5.1. Introduction

So far, the fundamental mechanisms for the formation of CZTS phase and other relevant sulfide phases using the sol-gel sulfurization in ppm level H_2S were proposed in chapter 4 based on the observations from in-situ Raman spectroscopy as well as other ex-situ characterization tools. However, the annealing of CZTS films in different environments opposed to the sulfurization conditions as might be encountered in subsequent device processing has not been addressed in any previous study. Such investigation is important to gain knowledge about the stability limits of sol-gel sulfurized CZTS films and understand their oxidation and degradation mechanisms in oxygen rich atmosphere at elevated temperatures. The objective of this chapter is to present the results for the use of in-situ Raman micro-spectroscopy combined with other techniques to study CZTS phase stability at elevated temperatures including its thermal oxidation and decomposition.

5.2. Experimental

5.2.1. CZTS Thin Film samples Preparation

The copper zinc tin based precursor solution is prepared by dissolving 2.0 grams of copper acetate monohydrate (>98%, Sigma Aldrich 217557), 1.0 gram of zinc acetate dihydrate (>99%, Sigma Aldrich 96459) and 1.0 gram of Tin (II) 2-ethylhexanoate (Alfa Aesar 18590) into 25.0 mL of anhydrous 2-methoxyethanol (99%, Alfa Aesar A1749) and the mixture was stirred for several minutes. A few drops of ethanolamine (99%, Alfa

Aesar 36260) are added during stirring to prevent precipitation (Tanaka, Moritake and Uchiki, 2007). The prepared solution is filtered using 0.2 μm syringe filter and spin coated on SLG substrates at 3000 rpm for 30 seconds. (Note that bare SLG was used in this study instead of the typical Mo-metal coated SLG to simplify the system for this study.) The films are then baked at 300 $^{\circ}\text{C}$ for 10 minutes in open air. Seven layers are deposited and baked to obtain a film thickness of $\sim 1\ \mu\text{m}$. Finally, the deposited thin films are sulfurized at 550 $^{\circ}\text{C}$ for 1 hour using 5.0 vol% H_2S balanced by N_2 gas mixture in a 2-inch diameter tube furnace with total gas flow rate of 200 cc/min to obtain the CZTS thin film.

5.2.2. Characterization Techniques

All the produced thin films were examined by X – ray diffraction (Diffractometer Siemens 500D) for phase identification. The X- ray diffraction patterns were obtained by Cu K α 1 ($\lambda = 1.5406\ \text{\AA}$) radiation with 2θ in the range of 20 - 80 $^{\circ}$. SEM combined with EDS was performed on JEOL 6330F microscope at 15.0 kV accelerating voltage to investigate the surface morphology and assess the chemical composition of the produced CZTS thin films. Air cooled Ar ion Laser system with excitation wavelength of 514.5 nm placed horizontally was used for Raman micro-spectroscopy. The spectral collection range was 200 – 2000 cm^{-1} . A special heating cell was developed by the Center for the study of Matter at Extreme Conditions (CeSMEC) at Florida International University and used for the *in situ* Raman experiments. The cell consists of a chamber heated by nichrome coil which is connected to a power supply and its temperature is controlled by a

thermo controller. Figure 5.1 shows schematic for the *in situ* Raman system with the thin film sample loaded into the heating cell. Raman spectra were collected both at room temperature and at elevated temperatures under different *in situ* conditions.

Figure 5.1. (a) Schematic representation of the heating cell and sample used for *in situ* Raman micro-spectroscopy experiments. (b) Photo of the “sealed” CZTS thin film sample used for the first *in situ* Raman experiment.

The samples were inserted into the heating cell and set to be vertical and perpendicular to the laser beam. The sample temperature was measured from thermocouple directly touching the back of the glass substrate for CZTS thin film. The attached optical microscope system was used for adjusting the focus of the sample.

Three *in situ* Raman experiments were performed. The first *in situ* Raman experiment was performed on a *sealed* CZTS thin film sample (see Figure 5.1(b)) at room temperature and under *in situ* conditions at 300 °C and 400 °C. The purpose of this experiment is to investigate if the CZTS phase is Raman active at elevated temperatures. In order to seal the sample, ceramic bonding material (Ceramabond® 552) was applied to

“glue” a thin piece of cover glass directly touching the front of the CZTS thin film sample before loading it into the heating cell. The second *in situ* Raman experiment involved exposure of the CZTS thin film sample to open air at 400 °C and soaked for 3 hours. The importance of this experiment is to investigate the onset of CZTS phase oxidation/decomposition in air and to identify how fast this process is. The third *in situ* Raman experiment was also performed in open air at temperature ranging from room temperature up to 650 °C. The purpose of this experiment is to investigate the oxidation and related decomposition process as well as the stability limit of CZTS phase at relatively high temperatures of up to ~650 °C.

For *in situ* Raman experiments, samples are heated up following the temperature profiles shown in Figure 5.2. Before collecting signal for each step, the temperature was usually held constant for 8 to 15 minutes to allow homogenous heat distribution inside the chamber. The signal was collected based on accumulation acquisition mode with 1.0 second shutter close and collection time of 5 to 8 minutes. As complementary techniques to the *in situ* Raman experiments, XRD, as well as EDS analysis, are carried out for all *in situ* examined samples afterward to identify the formed phases and the chemical composition.

Figure 5.2. Temperature profiles for both second (solid red line) and third (blue dash line) in situ Raman experiments.

5.3. Results and Discussion

5.3.1. Prepared CZTS Thin Film Samples

For XRD pattern, the main characteristic peaks of CZTS phase are observed (JCPDS card no.00-26-0575) for the prepared CZTS thin films as shown in Figure 5.3. SEM images for the surface and cross-section of the prepared CZTS thin film sample are shown in Figure 5.4.

It can be seen that the prepared films are relatively dense, forming grains as large as 1 μm at the surface upon sulfurization. In contrast to those large surface grains, cross-section images indicate the presence of small grains inside the film near the SLG substrate surface. The origin for such structure for sol-gel sulfurization processed CZTS is not exactly clear, but is hypothesized to be due to the higher sulfur concentration (or activity)

over the surface and lower values inside the film, which cause superficial grains to grow larger while the grains near the substrate surface tend to remain small.

Figure 5.3. XRD pattern for prepared CZTS thin film.

The EDS analysis (Table 5.1) of the thin film indicates an average surface composition that is Zn rich and Cu poor. (Three different readings are gathered from separate areas across the film surface and averaged as indicated in Table 5.1). In addition, SEM images of the thin film seem to show some particles on the surface that are “brighter” than surrounding as indicated by yellow arrows in Figure 5.4(a). However, EDS point analysis of those particles shows similar Zn rich and copper poor composition, as given in Table 5.1. The observed Zn rich and Cu poor composition for the prepared CZTS film may be off-stoichiometric CZTS or may be related to the preferred formation of ZnS near the surface under the sulfurization condition, but the exact origin is still under investigation.

Figure 5.4. SEM images for the prepared CZTS thin film surface (a) and cross-section (b). Particles indicated by yellow arrows are Zn-rich phase as confirmed by EDS point analysis (see Table 5.1).

Table 5.1. Average chemical composition of the prepared CZTS films.

Element	Cu	Zn	Sn	S
CZTS thin film	18.0±0.9	26.0±4.0	10.2±0.3	45.7±3.4
bright surface particles	16.4±3.7	23.8±3.7	10.9±2.1	48.8±3.8

5.3.2. Ex situ Raman Micro-spectroscopy Analysis

In order to distinguish between CZTS phase and other secondary phases, Raman spectra were collected and further confirmed the formation of the desired CZTS phase as shown in Figure 5.5. The collected data at room temperature for thin film sample show the main CZTS characteristic peaks at 338, 287, and minor peaks at 367 and 374. The broad peak at 252 cm^{-1} can be also observed (Dimitrievska *et al.*, 2014) (Fernandes, Salomé and da Cunha, 2009) .

Figure 5.5. Raman spectra for prepared CZTS thin film samples.

5.3.3. In situ Raman Micro-spectroscopy Analysis of the CZTS Thin Film Samples

As explained, the first *in situ* Raman experiment involves monitoring change of Raman spectra for a sealed CZTS thin film sample. The result, as shown in Figure 5.6, revealed a slight peak shift to the lower frequency values as temperature increases from 338 cm⁻¹ at room temperature to 330 cm⁻¹ at 400°C upon heating the sample. The peak shift to lower frequency values is expected and is attributed to the reduced stiffness of the atomic bonds at elevated temperatures. No major morphological changes are observed on the sample after cooling down to room temperature. These results suggest the CZTS phase is Raman active with no phase change under inert atmosphere at temperature at least of up to 400°C. It is noted that at temperature higher than 400°C, the sealed sample started to experience degradation, probably due to interactions with sealant materials used and the CZTS thin film.

Figure 5.6. In situ Raman spectra for the sealed thin film sample, collected at room temperature and under in situ condition at temperatures of 300 °C and 400 °C (first in situ Raman experiment).

The second *in situ* Raman experiment was carried out in open air at 300 – 400 °C over time on the CZTS thin film samples to study the on-set of oxidation of CZTS phase. At 300 °C, Raman spectra showed the same peak shift toward lower frequency values as observed in the first experiment. However, as the temperature is further increased to 400 °C in air, the spectrum shows dramatically decreased peak intensity. For example, after one hour of *in situ* testing in air at 400°C, as shown in Figure 5.7, the signal to noise ratio decreased dramatically which is attributed to the degradation of the thin film and most likely the start of its oxidation. By the end of the second hour, the sample slightly changed color from originally dark brown to light brown and maintained that color till the end of the experiment, which is about 3 hour of air exposure at 400°C. The second *in*

in situ experiment suggests that CZTS phase will go through significant oxidation in air at temperatures as low as 400°C in less than one hour.

Figure 5.7. In situ Raman spectra for a thin film sample, collected at room temperature and under in situ condition at 400 °C for up to three hours in open air (second in situ Raman experiment).

For the third *in situ* Raman experiment, which is also carried out in open air for thin film CZTS samples, the temperature was raised at a faster rate. Consistent with the second *in situ* Raman experiment, the main characteristic Raman peak of CZTS at 338 cm⁻¹ shifted toward lower wavenumbers (Figure 5.8) as temperature increased. Due to the relatively fast heating and short holding times, the CZTS characteristic Raman peak was obtained at temperatures as high as ~600°C, as in Figure 5.8. However, the sample gradually changed color and started to show non-uniformity due to oxidation at that high temperature of ~600 °C. At 650 °C, the sample became colorless and transparent and the

Raman spectrum became almost featureless, probably because the oxidation products formed do not crystallize well under such condition.

Figure 5.8. In situ Raman spectra for thin film sample collected at room temperature and under in situ condition at temperatures from 300 °C to 650 °C in open air (third in situ Raman experiment).

This experiment suggests that CZTS is Raman active at temperatures up to ~600 °C, and *in situ* Raman could be used to help study the phase transformation of CZTS under different real time processing conditions and differentiate between other phases. XRD and EDS analyses of the samples from the second and third *in situ* Raman experiments were carried out to help identify the formed phases.

5.3.4. XRD and EDS Analysis of the in situ Raman Examined Thin Films

XRD pattern of the second *in situ* examined CZTS thin film sample after 400°C - 3 hour exposure to open air is given in Figure 5.9. The four main peaks of CZTS and/or ZnS phase are observed at 28.4°, 47.2°, 56.0°, and 33.0° according to the decreasing intensity

order, which matches the standard JCPDS cards no.01-071-5976 for ZnS and no.00-26-0575 for CZTS respectively. Copper sulfide (Cu_2S) peaks are observed at 46.1° , 32.1° , and 54.6° , which matches the JCPDS card no. 00-053-0522 for cubic Cu_2S , while SnO_2 peaks are observed at 26.6° , 33.8° , 37.9° , and 51.8° according to the decreasing intensity order, which matches the JCPDS card no.00-041-1445 for SnO_2 . This result means that tin is the element first to experience phase change from sulfide to oxide while copper and zinc remain in sulfide phases under such *in situ* condition (400°C in air). XRD analysis of the *in situ* examined thin film sample for the third experiment after exposure to air up to $\sim 650^\circ\text{C}$ is given in Figure 5.10. CZTS/ZnS peaks disappear completely, while SnO_2 peaks show up strongly

In addition, ZnO peaks are observed at 36.2° , 31.7° , 34.4° , and 56.6° , which matches the standard JCPDS card no. 00-036-1451 for ZnO, while CuSO_4 peaks are observed at 34.2° and 25.0° , which matches the standard JCPDS card no.04-007-5185 for CuSO_4 .

Figure 5.9. XRD pattern of in situ examined CZTS thin film sample in air at temperature 400°C for three hours (second in situ Raman experiment).

There are also some unidentified impurity phases in the thin film sample after 650 °C oxidation in air and further analysis is needed to clarify them. Based on the XRD analysis of the samples from both the second and third *in situ* Raman experiments, it can be concluded that tin (Sn) is the first element to experience a sulfide to oxide oxidation/transformation at an intermediate temperature of ~400°C (equation 1) followed by zinc and copper at temperatures higher than 400 °C (equation 2).

Figure 5.10. XRD pattern of in situ examined CZTS thin film sample in air at temperature up to 650 °C (third in situ Raman experiment)

The overall oxidation and related decomposition of CZTS phase can be expressed by a two-step reaction as follows:

$$T \leq 400 \text{ }^{\circ}\text{C}$$

$$T \geq 400 \text{ }^{\circ}\text{C}$$

Table 5.2 illustrates the results of EDS analysis of the *in situ* examined samples, which show high oxygen content for both samples in addition to the four elements of CZTS. (Only one data point was collected.)

Relative to other metal elements, the copper percentage was found to be lower than expected. This might be attributed to the re-distribution of the copper elements in the oxidation process, which prefers to oxidize tin and then zinc species first, causing them to diffuse upward towards thin film surface and reduce relative copper concentration. Further studies including EDS along the cross-section of the oxidized sample and statistical analysis are needed to understand such observations fully. Based on the current study, it is not clear if CZTS directly oxidize and decompose into the Cu_2S , ZnS , and SnO_2 at 400°C air exposure or first oxidize partially to form oxygen-containing CZTS (Washio *et al.*, 2012).

Finally, it is worth mentioning that the 514.5 nm excitation wavelength used for collecting the Raman spectra typically has an effective analysis depth of 150 nm (Fernandes, Salomé and da Cunha, 2011). Consequently, the current *in situ* Raman analysis is limited to the very narrow superficial layer of the thin film. Characterizing deeper layers of the prepared CZTS film require the utilization of higher excitation wavelength such as 785.0 nm. This would be also helpful in fluorescence suppression and detection of various secondary phases and oxides. Further *in situ* Raman experiments will be carried out in the future on thin film samples using different excitation wavelengths to provide more details about the formation of CZTS in real time under

conditions relevant to real processing and identification of secondary phases and their distribution during CZTS processing.

Table 5.2. Chemical composition of the in situ examined CZTS thin films (for the second and third experiments).

Element	Cu	Zn	Sn	S	O
Second in situ Raman exp. (400 °C – 3hrs)	7.2	21.5	6.5	10.5	39.3
Third in situ Raman exp. (650 °C)	12.3	28.3	10.1	24.9	24.2

5.4. Conclusion

In the present work, CZTS thin films are successfully prepared using a simple sol-gel sulfurization procedure as confirmed by XRD and Raman spectroscopy. The SEM and EDS results showed the thin film CZTS material appears to be zinc rich and copper poor. In addition, use of *in situ* Raman micro-spectroscopy for characterizing CZTS materials at elevated temperature was demonstrated for the first time using 514.5 nm wavelength excitation laser. Preliminary results show CZTS phase remains Raman active up to ~600 °C. Moreover, the *in situ* Raman micro-spectroscopy for the CZTS thin films at high temperature revealed useful information regarding the CZTS phase oxidation and related decomposition in real time. The results suggest a two-step oxidation reaction in which CZTS oxidizes first at temperatures of ~400 °C to form SnO₂, Cu₂S, and ZnS. Then at temperatures higher than ~400 °C, ZnS and Cu₂S continue to oxidize to form ZnO and CuSO₄.

6. SUMMARY AND RECOMMENDATIONS

6.1. Summary

The main conclusions from the current study are as follows:

- 1- Sol-gel sulfurization of Cu-Zn-Sn-O precursor films in 100 ppm $\text{H}_2\text{S}+\text{H}_2$, as opposed to traditional high H_2S concentration, successfully led to the formation of near stoichiometric CZTS films at temperature as low as 125°C and up to 350°C . At 450°C and above, sulfurized samples primarily consisted of ZnS and Cu_3Sn metallic alloy phase.
- 2- CZTS phase derived from sol-gel sulfurization of precursor oxides was observed to emerge relatively fast (within ~ 30 min of sulfurization) at an intermediate temperature of 350°C in 100 ppm $\text{H}_2\text{S}+4\%\text{H}_2+\text{N}_2$ gas mixture. CZTS phase was observed to form directly from the oxide precursor in a single-step reaction bypassing the formation of binary and ternary sulfide phases (e.g., Cu_2SnS_3 and ZnS) reaction step.
- 3- CZTS phase can also be formed from oxide precursor in a two-step sulfurization process at lower sulfurization temperature ($125\text{--}170^\circ\text{C}$) in 100 ppm $\text{H}_2\text{S}+\text{H}_2$. The first step is a Forming Gas Annealing (FGA) at 400°C . In the second step, CZTS was observed to form directly after ~ 30 min in 100 ppm $\text{H}_2\text{S}+4\%\text{H}_2+\text{N}_2$ gas mixture from Cu-Sn alloy and ZnO. However, continued sulfurization at low temperature ($<200^\circ\text{C}$) for extended time (e.g., >1 h) led to the formation of the sulfur-rich CuS phase accompanied with disintegration of the CZTS phase.
- 4- Investigation of CZTS phase stability in an oxygen-rich atmosphere at elevated temperatures suggest a two-step oxidation reaction in which CZTS oxidizes first at

temperatures of ~ 400 °C to form SnO_2 , Cu_2S , and ZnS . Then at temperatures higher than ~ 400 °C, ZnS and Cu_2S continue to oxidize to form ZnO and CuSO_4 respectively.

6.2. Recommendations for Future Work

For future investigations of sol-gel based CZTS films for solar cell applications, addressing the following areas is recommended:

- 1- Multiwavelength as well as surface enhanced Raman spectroscopy can be used to provide a more effective identification of CZTS phase and distinguish from other secondary phases (mainly ZnS , which is sensitive to UV laser excitation). They will help further understand CZTS impurity formation and how to void them.
- 3- Flexible CZTS solar cells can be fabricated and performance can be systematically characterized to establish the relationship between the sol-gel processing condition and CZTS material property and solar cell performance.

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APPENDICES

APPENDIX A: CZTS SOLAR CELL DEVICE FARICATION AND CHARACTERIZATION

1- CZTS Solar Cell Device architecture

Figure A-1. (a) Conventional CZTS solar cell device configuration. (b) CZTS solar cell device configuration used in this study.

2- CZTS Solar Cell Device Fabrication Condition

1- Back Contact Molybdenum Sputtering

- DC – 200 W – 1.0×10^{-6} Torr – 12 mTorr for 10 minutes then 3 mTorr for 40 minutes – Ar, 10 sccm – full rotation.
- Thickness from profilometer ~ 775 nm
- Thickness from SEM cross section image ~ 800 nm

Figure A-2. (a) XRD pattern of the as sputtered Molybdenum film. (b) Actual image of the as sputtered Molybdenum film.

Figure A-3. SEM surface (a) and cross section (b) images of the sputtered Molybdenum films.

2- Cu-Zn-Sn Oxide Precursor Film Deposition

- Recipe 2 (Stoichiometric solution with Cu:Zn:Sn ratio is 2:1:1) – 6 layers – 2000 rpm/25 seconds – 300°C/5 minutes.

3- CZTS (Solar Absorber Layer) Sulfurization Process

- 350°C/ 1hour – 100 ppm H₂S+4% H₂+96N₂ – heating 25 °C/min – cooling: 2 °C/min – heating and cooling in UHP Ar.

Figure A-4. XRD pattern (a) and (b) SEM surface image of the CZTS film on Mo/SLG substrate.

Table A-1. EDS data of the sulfurized CZTS film.

Element	Cu (at%)	Zn (at%)	Sn (at%)	S (at%)
Atomic content	11	25	17	47

Figure A-5. Absorption (a) and transmittance (b) spectra for CZTS samples of different stoichiometry (Cu-rich and Cu-poor) in comparison to a reference sample. (c) Tauc plot showing the band gap information for the Cu-rich, Cu-poor, and reference CZTS samples.

4- CdS (Buffer Layer) Chemical Bath Deposition

- Chemical Bath: 50 mL of 0.015M CdSO₄ solution, 25 mL of 1.5M of thiourea solution, 65.2 mL of 28%-30% NH₄OH solution and 366 mL of DI water -
- Deposition Time: 30 min
- Deposition Temperature: 85°C.

Figure A-6. XRD pattern of the deposited CdS film on bare soda lime glass substrate. The insert is an actual image of the deposited CdS film.

5- i-ZnO (Passivation Layer) Sputtering

- RF – 100 W – 5.0×10^{-6} Torr – 20 mTorr for 30 minutes – Ar, 10 sccm – full rotation.
- Thickness from profilometer ~ 100 nm.

Figure A-7. XRD pattern (a) and (b) SEM surface image of the sputtered ZnO on bare SLG substrate. The insert is an actual image of the sputtered ZnO film.

6- Gold (Front Contact) Sputtering

- The front contact pattern is deposited using a shadow mask made of Polyimide sheet and cut using laser engraving.
- DC – 100 W – 1.0×10^{-6} Torr – 3 mTorr for 30 minutes – Ar, 10 sccm – no rotation.

Figure A-8. (a) Actual photos of the shadow mask (left) used for the front contact deposition and a sample of four complete CZTS solar cell devices (right). (b) The four CZTS solar cell devices shown after scribing.

3- CZTS Solar Cell Device Characterization

Solar Cell Performance parameters:

Open circuit voltage (V_{oc}): voltage with zero external current

$$V_{oc} = (kT/q) \ln((I_{sc}/I_0)+1)$$

Short circuit current (I_{sc}): current at zero voltage

Maximum Power (P_m):

$$P_m = I_{mp} \times V_{mp}$$

Fill Factor (FF):

$$FF = I_{mp} \times V_{mp} / I_{sc} \times V_{oc}$$

Power Conversion Efficiency (PCE):

$$\eta (\%) = J_{sc} \times V_{oc} \times FF/P_o$$

Figure A-9. (a) SEM cross section images of the conventional (b) and suggested CZTS solar cell devices.

Figure A-10. Comparison of I-V curves for the CZTS solar cells fabricated according to the two different device architectures indicated in figure A-1.

APENDIX B: IN-SITU RAMAN REACTOR ENGINEERING DRAWING

Figure B-1. (a), (b) Three dimensional model. (c), (d) realistic rendered model of the in-situ Raman reactor. (e), (f) Actual photo of the in-situ Raman reactor and the in-house built Raman system used for the in-situ Raman experiments.

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SELECTED JOURNAL PUBLICATIONS AND CONFERENCE PRESENTATIONS

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