Co-electrodeposition of Cu-Zn-Sn Film and Synthesis of Cu$_2$ZnSnS$_4$ Photovoltaic Material

Tubshin (Tubuxin) Hreid

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Thin film solar cells, power conversion efficiency, earth-abundant elements, p-type semiconductor, light absorber, kesterite, Cu$_2$ZnSnS$_4$, non-vacuum method, co-electrodeposition, Cu-Zn-Sn precursor film, growth mechanism, hydrogen evolution, alloy phases, concentration of metal ions
Abstract

Solar energy is a clean, renewable energy source utilized to overcome global energy shortages. Photovoltaic technology is a promising approach that directly converts sunlight to electricity. Over the past century, various types of photovoltaic materials and solar cells have been developed. Copper indium gallium selenide (CIGS) material-based, thin film solar cells have achieved more than 20% high power conversion efficiency and have successfully been manufactured in large-scale production. In recent years, low-cost and earth-abundant quarterly material–copper zinc tin sulphide (CZTS) has emerged as a promising and sustainable p-type semiconductor light absorber. A copper zinc tin (CZT) metallic film is extensively employed as the essential precursor to fabricate CZTS or copper zinc tin selenide (CZTSe) film. Although several techniques are present to prepare a CZT precursor film, electrodeposition is considered a low-cost, facile and environmentally-friendly method suitable for large-scale production. Different electrodeposition strategies are available for fabrication of CZT film, among them co-electrodeposition is the simplest and fastest approach for low-cost production.

The quality of CZT precursor film provides a solid foundation to develop an effective CZTS film for application on solar cells. It is important to understand the electrochemical formation of CZT film. In this work, a comprehensive study on co-electrodeposition of CZT film was conducted in electrolyte solutions containing Cu (II), Zn (II), and Sn (II) with tri-sodium as a complexing agent. Synthesis of a CZTS film with effective composition was also carried out.

Firstly, the effects of influencing factors, including applied potential concentrations of the complexing agent and pH of the electrolyte solution on the
composition and morphologies of electrodeposited CZT films were investigated. The following results were found:

i. Films with a nearly stoichiometric ratio of Cu: Zn: Sn = 2: 1: 1 are obtained in the potential range of -1.20 V to -1.25 V, while the crystallites within the CZT films increased in size as the applied potential became more negative, until the point where hydrogen evolution occurs which compromises the adhesive ability of the CZT film to the substrate.

ii. The metal content is controlled by the solubility of the precursor metal ions in the presence of tri-sodium citrate which also influences film homogeneity.

iii. The compositions of the CZT films are similar at pH = 4.1, 5.1 and 6.1, however, the Zn content is significantly lower at pH = 7.1. By optimizing each of these parameters it is possible to fabricate homogeneous CZT films with the desired stoichiometric ratio of 2: 1: 1, which is the ideal precursor to photovoltaic materials such as CZTS and CZTSe.

Secondly, the electrochemical growth mechanism of CZT film on a molybdenum coated soda lime glass (Mo/SLG) substrate has been revealed for the first time. The evolution of film thickness, nucleation morphology, composition, and alloying process over deposition time were investigated. It was found that a thin film consisting of only copper and tin was formed on Mo/SLG in the initial stage (30 sec) of deposition, whereas zinc was only incorporated into the film after 30 – 60 sec of the deposition. The phenomenon is ascribed to the influence of H₂ evolution. It also confirmed that the electrochemical growth (except for the first 1 minute) of a CZT film:
i. obeys Faraday's Law in that the film thickness is linearly dependent on the charge consumption, and the film grows at a constant rate.

ii. the composition of the CZT film remains constant throughout the deposition process and copper, tin and zinc are distributed evenly in the film.

iii. the content (as an atomic percentage) of the main phases Cu₀Sn₅ and Cu₅Zn₈ in the CZT film are constant during the growth of the film.

The ability to generate a homogeneous CZT film in such a controlled manner will have significant benefits for the production of CZTS or CZTSe film.

Thirdly, a kesterite CZTS film with the most effective composition of Cu/(Zn + Sn) ≈ 0.8, Zn/Sn ≈ 1.2 was successfully synthesised via co-electrodeposited CZT films with controllable composition achieved by finely adjusting the concentration of the metal ions in the electrolyte solutions. It was found that an atomic ratio of Cu/(Zn + Sn) and Zn/Sn in the CZT and CZTS film was dependent on the ratio of the elements in the precursor salt in the electrolyte solution. The deposition strategy demonstrated lays a foundation to yield high quality CZTS film with high-throughput for photovoltaic applications.

Finally, the effects of metal ions concentration on composition, morphology and alloy phases were systematically investigated. The metallic content (as a relative atomic percentage) in the film increased linearly with the increase of the metal ion concentration. This is the first time that the relationship of the compositions of the alloy phases in the co-electrodeposited CZT film with the concentration of metal ions has been revealed. The content of Cu₀Sn₅ and Cu₅Zn₈ alloy phases formed in the film were determined by the concentration of Cu (II) instead of Zn (II) and Sn (II). Morphologically, Sn (II) had significant impacts on the film which became more
porous as a result of the bigger nucleation size of tin. The changes of surface properties of the films were also confirmed by chronoamperometry characteristic \((i-t)\) deposition curve. By optimization of the metal ions concentrations in the electrolyte solution, a copper-poor and zinc-rich kesterite CZTS film was synthesized by sulfurization of the deposited CZT film. The solar cell with the CZTS film showed an energy conversion efficiency of 2.15 % under the illumination intensity of 100 mW cm\(^{-2}\).
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Journal articles:


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<th>Description</th>
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<tr>
<td>CIGS</td>
<td>Copper indium gallium selenide</td>
</tr>
<tr>
<td>CZT</td>
<td>Copper-Zinc-Tin</td>
</tr>
<tr>
<td>CZTS</td>
<td>Copper Zinc Tin Sulphide</td>
</tr>
<tr>
<td>CZTSe</td>
<td>Copper Zinc Tin Selenide</td>
</tr>
<tr>
<td>EC-ALE</td>
<td>Electrochemical Atomic Layer Epitaxy</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-Ray Spectroscopy</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident Photon-to-Current Efficiency</td>
</tr>
<tr>
<td>Mo/SLG</td>
<td>Molybdenum Coated Soda Lime Glass</td>
</tr>
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</tr>
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<td>SEL</td>
<td>Stacked Elemental Layer</td>
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<td>Under Potential Deposition</td>
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<td>XRD</td>
<td>X-Ray Diffraction</td>
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Statement of Original Authorship

The work contained in this thesis has not been previously submitted to meet requirements for an award at this or any other higher education institution. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made.

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Date: 17/03/2016
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Chapter 1: Introduction

1.1 RESEARCH BACKGROUND

Alloy films based on ternary metallic Cu-Zn-Sn (CZT) have been extensively employed in applications for decorative and protective purposes due to its strong adhesive properties, severability, and high corrosion resistance [1-3]. In recent years, alloy films have been widely used as the essential precursor film to fabricate the new p-type light absorber Cu$_2$ZnSnS$_4$ (CZTS) and Cu$_2$ZnSnSe$_4$ (CZTSe) films, and in sustainable thin film solar cells after the introduction of sulphur or selenium [4, 5]. There are various deposition techniques such as sputtering [6], evaporation [7], pulsed laser deposition [8], and electrodeposition [9] that can be used to fabricate CZT films. Of these, electrodeposition is considered the most facile, scalable, environmentally-friendly, and low-cost technique [9-11]. Generally, there are three strategies available to prepare the CZT precursor film by electrodeposition: (i) stacked Cu/Sn/Zn metal layers [12] (SEL) electrodeposited from three electrolyte solutions; (ii) stacked binary alloys layers [13] such as Cu-Zn and CuSn electrodeposited from two electrolyte solutions containing binary metal ions; and (iii) CZT film co-electrodeposited [14] in one step using a single electrolyte solution. Compared to the SEL deposition and stacked binary alloys, the co-electrodeposition approach is more favourable for large-scale and higher-throughout production as it uses less equipment, takes less time, and is a more simple procedure. However, some challenges still remain regarding the co-electrodeposition of CZT films.
1.2 RESEARCH CHALLENGES

Compared to the stacked elemental layers approach, it is more challenging to control the co-electrodeposition process of CZT film due to the complexity of the electrolyte system and the different reduction potentials of the metal ions. Generally, the electrolyte solution consists of the three metal salts with one or more complexing agents. The simultaneous presence of copper, tin and zinc metal ions with the complexing agent in the electrolyte solution can generate various metal complex species which may have different solubility and can lead to precipitation in the electrolyte solution. To understand the co-electrodeposition process of CZT film, two issues must be examined. Firstly, it is necessary to study the effects of critical factors including potential complexing agent and pH of electrolyte solution on the formation of CZT film. Secondly, it is necessary to uncover the mechanism of electrochemical growth of CZT film. Moreover, the influence of the concentration of metal ions on the electrodeposited CZT film must be investigated. It is crucial to control the content of copper, zinc and tin in the electrodeposited CZT precursor film in order to fabricate CZTS films with the desired composition.

1.3 RESEARCH AIMS AND OBJECTIVES

1.3.1 AIMS

This research project aims to comprehensively understand the formation and growth mechanism of CZT film fabricated by the co-electrodeposition method, and to synthesize high-quality kesterite CZTS film with copper-poor (Cu/ (Zn + Sn) \approx 0.8) zinc-rich (Zn/Sn \approx 1.2) composition which is well-known as the most effective composition in the application of solar cells.
1.3.2 OBJECTIVES

- To investigate the effects of potential, complexing agent and the pH of the electrolyte solution on the composition and morphology of the electrodeposited CZT film;
- To reveal the electrochemical growth mechanism of the CZT film including thickness evolution, composition, morphology and alloying process;
- To evaluate the effects of hydrogen evolution on the electrodeposition of Zn during the electrochemical formation of CZT film;
- To study the effects of concentration of each metal ion on the electrodeposited CZT film including analysis of composition, morphology and alloy phases;
- To synthesize high-quality kesterite CZTS film with controlled copper-poor, zinc-rich composition.

1.4 OUTLINE OF THIS THESIS AND LINKAGE BETWEEN CHAPTERS

This thesis consists of seven chapters, as illustrated in Figure 1-1. In Chapter 1, research background, research challenges, research aims and objectives, and connections between the chapters are introduced. Chapter 2 presents the literature review on the research topic, narrowing it from the general field of solar energy to the specific area of electrodeposition of metallic films. Five different electrochemical deposition strategies to fabricate CZTS films are classified in Chapter 2. Co-electrodeposition is chosen as the fabrication method of CZT film due to its simplicity, reduced equipment requirements, and time-saving methods that means it has a potential in application to large-scale and high-throughput production. The research work is divided into four chapters: from Chapters 3 to 6. In Chapter 3, the
effects of applied potential concentrations of complexing agent and pH of electrolyte solution on the composition and morphology of electrodeposited CZT films were investigated. In order to obtain a CZT film with nearly stoichiometric composition, uniform morphology and well-adhered, optimized parameters including potential of -1.25 V, 200 mM of tri-sodium citrate and pH = 6.1 were determined. In Chapter 4, the electrochemical growth mechanism of the CZT film is revealed through a comprehensive investigation of the film thickness, composition, morphology as well as alloying processes. The effect of hydrogen evolution on the electrodeposition of Zn was also investigated. The electrodeposition time of 10 minutes was determined to use in later work. In Chapter 5, a CZTS film is synthesized through sulfurization of electrodeposited CZT using the method demonstrated in Chapter 3 and Chapter 4. The obtained CZTS film did not have the optimal composition of copper-rich and zinc-poor required for solar cell application. In order to obtain the desired composition of Cu/ (Zn + Sn) ≈ 0.8 and Zn/Sn ≈ 1.2, the composition of the precursor CZT film was controlled via adjusting the concentrations of Cu (II), Zn (II) and Sn (II) in the electrolyte solution. To understand how each metal influenced the formation of CZT film, the effects of metal ion concentration on the composition, morphology and alloying processes of electrodeposited CZT are comprehensively investigated in Chapter 6. A kesterite CZTS film was synthesized and tested as a solar cell. In Chapter 7, outcomes of the research work and recommendations for future work are presented. Chapters 3, 4, 5 and 6 are written in a journal publication style. They contain the required abstract, introduction, experimental and conclusion parts, and some repetitive phrases and sentences may be noted.
Chapter 1: Introduction
Thesis outline, Research background, Research aims, Research objectives

Chapter 2: Literature Review
Solar energy, Photovoltaic technologies, CZTS solar cells, Electrochemical fabrication of CZTS thin film, Fundamentals in electrodeposition of metal/alloy film, (Review paper, will be submitted to Solar Energy)

Chapter 3: Research Part I
Identification of the critical parameters controlling the electrochemical formation of homogeneous Cu-Zn-Sn films, (Manuscript, will be submitted to Journal of Solid State Electrochemistry)

Chapter 4: Research Part II
Investigation of electrochemical growth mechanism of Cu-Zn-Sn film on a molybdenum substrate, Evaluation of hydrogen generation on electrodeposition of Zn (Manuscript, will be submitted to Electrochimica Acta)

Chapter 5: Research Part III

Chapter 6: Research Part IV
Effects of Cu (II), Zn (II) and Sn (II) concentrations on composition, morphology and formation of alloy phases in the Cu-Zn-Sn film, Application of kesterite Cu$_2$ZnSnS$_4$ film in solar cells (Published in RSC Advances, 2015, 5, 65114-65122)

Chapter 7: Conclusions and future work
Research outcomes, Recommendation for future work

Figure 1-1: Outline of thesis.
1.5 REFERENCES


Chapter 2: Literature Review

2.1 SOLAR ENERGY

The demand for energy consumption has been continuously increasing [1] due to the combined effects of the growth of the global population and human modernization. Since the Industrial Age, fossil fuels such as coal, fossil oil and natural gas have been the main energy source for human society. However, the consumption of fossil fuels has raised many issues and concerns. It has caused environmental contamination as well as climate change due to the emission of greenhouse gases. Additionally, fossil fuels will run out in the foreseeable future due to their limited reserves and unrenewable nature. Therefore, developing clean and renewable energy sources such as water, wind, biomass, geothermal and solar energy is essential to address these grave energy concerns. Among them, solar energy is the most promising and powerful energy source worldwide [2, 3]. It is estimated that more than 100,000 TW of sunlight strikes the Earth at any time each day and the illuminating power over the course of one hour equals the whole world’s annual energy consumption [2]. Moreover, solar energy is the fastest-growing green and renewable energy source available to increase energy production. It is predicted that solar energy will play an increasing role in electrical energy production over the next 60 years [4], as indicated in Figure 2-1.
2.2 PHOTOVOLTAIC (PV) TECHNOLOGIES AND MATERIALS

Photovoltaic (PV) represent a clean and green energising technology that converts sunlight directly into electricity. The photovoltaic effect was first demonstrated in 1839, and the first solid-state solar cell with efficiency of approximately 1% was created in 1883. Since the first practical silicon solar device was built in 1954 and later utilized in satellite by 1958 the photovoltaic device (or solar cell) has undergone a rapid development which can be divided into four generations [6], as shown in Figure 2-2. The first generation of the solar cell is mainly based on thick silicon crystalline that has high efficiency but is high cost. The second generation introduced thin film technology to significantly reduce the cost; however, this reduced the efficiency of the solar cell to some extent. This development did extend the material ranges to polycrystalline silicon [7, 8], CdTe/TeS [9, 10] and CIGS [11]. The third generation solar cell intends to achieve
higher efficiency than the second generation with low-cost production, and this development includes dye sensitized solar cells [12], quantum dot [13], tandem structure devices based on GaAs/Ge/GaInP₂ [14], organic/polymer [15] solar cells, solar cells using earth-abundant materials such as Cu₂ZnSn(S,Se)₄, and new concepts such as hot carrier cells [16]. The fourth generation of solar cell aims to achieve the development of a flexible device at low cost, using organic and inorganic hybrid materials.

Figure 2-2: Timeline of the four generations of solar cells and the photovoltaic materials (reproduced with permission from Ref.[6], copyright 2013, RSC).

2.3 CZTS THIN FILM SOLAR CELL

2.3.1 CZTS MATERIAL

Among the competitive solar cell technologies, recent progress in CuInₓGaₐSe₂ (CIGS) based solar cells has achieved high power conversion efficiency of more than
20% [17, 18], and 17.9% [19] in a large area of 900 cm². However, this material presents various concerns in terms of the high cost and scarcity of raw materials such as indium and gallium [20, 21]. This provides opportunities for the use of other materials which are lower-cost, less toxic, and more abundant. Cu₂ZnSn (Se, S)₄ is a promising new p-type light absorbing material for photovoltaic devices. The band gap of Cu₂ZnSn(Se, S)₄ can be tuned from 1.0 eV for Cu₂ZnSnSe₄ to 1.5 eV for Cu₂ZnSnS₄ through adjusting the relative amounts of the chalcogens in the compound [22].

![Figure 2-3](image)

**Figure 2-3:** Price ($ per kg) and annual production (ton per year) of the elements used in light absorbers for thin film solar cells (reproduced with permission from Ref. [5], copyright 2012, RSC).

To date, the world record of thin film solar cells based on Cu₂ZnSnS₄ (CZTS), Cu₂ZnSnSe₄ (CZTSe) [23] and Cu₂ZnSn(Se, S)₄ (CZTSSe) [24] materials has been achieved with power conversion efficiency of 9.2%, 11.1% and 12.6%, respectively. CZTS is structurally similar to CIGS but using low-cost, earth-abundant and non-toxic elements Zn, Sn and S, which substitute the expensive In, Ga and Se elements in CIGS, respectively. The prices and annual production of elemental raw materials in recent years are shown in **Figure 2-3** [5].
CZTS can be found naturally-occurring in some minerals [25]. The first CZTS thin films were fabricated and acknowledged as a photovoltaic effect semiconductor material by Ito and Nakazawa in 1988 [26]. CZTS has a semiconductor direct band gap energy of 1.4 - 1.6 eV and a high optical absorption coefficient greater than 1x10^4 Cm⁻¹ [26, 27]. These features have made CZTS a promising p-type absorber candidate for sustainable photovoltaic devices. The quaternary semiconductor CZTS (I₂-II-IV-VI₄) has two different crystal structures known as kesterite-type (space group I₄̅) and stannite-type (space group I₄̅ 2m) which are similar in structure except for the different space distribution of Cu and Zn atoms, as shown in Figure 2-4 [28]. Thermodynamically stable kesterite-type rather than stannite-type serves as the principal CZTS crystal phase [29].

![CZTS crystal structures](image)

*Figure 2-4: Crystalline structure of CZTS (reproduced with permission from Ref. [28], copyright 2009, AIP).*

There are two ways to synthesize CZTS material by solid-state chemical reactions: (i) reaction between ZnS, Cu₂S and SnS₂; and (ii) reaction between Cu₂SnS₃ and ZnS. However, the synthesis of high purity CZTS is challenging as other ternary and quaternary compounds can easily be formed in the synthesis process. The study [30]...
of phase equilibrium in the ZnS-Cu$_2$S-SnS$_2$ system indicates that a single-phase CZTS can be formed in a limited region labelled as ‘1’ in the middle of Figure 2-5 [30]. CZTS films used for highly effective solar cells should have characteristics including pure phase, large grains and uniform morphology. Structural defects, numerous grain boundaries and secondary phases are main factors to deteriorate solar cell performance in practice. The formation of the impurity phases can increase the electronic defects and negatively affect the optical and electronic properties of the material, leading to poor performance as a solar cell [31]. Nevertheless, studies [32, 33] show that copper-poor and zinc-rich conditions benefits the growth of single phase CZTS with less structural defects. Both theoretical [31] and experimental [24, 34, 35] results suggest that the copper-poor and zinc-rich CZTS films with Cu/(Zn+Sn) $\approx$ 0.8 and Zn/Sn $\approx$ 1.2 is the optimal composition for high-performance solar cells.

![Figure 2-5: Phase diagram of SnS-Cu$_2$S-ZnS system (reproduced with permission from Ref. [30], copyright 2004, Elsevier).]

Chapter 2: Literature Review
2.3.2 STRUCTURE OF CZTS THIN FILM SOLAR CELL

In general, a thin film solar cell consists of metal electrical contacts (front and back), transparent window layers, a p-type absorber layer, and an n-type buffer layer. A typical structure of a solar cell using CZTS as a light absorber is shown in Figure 2-6 [36]. After fabrication of a p-type semiconductor CZTS thin film (1–2 µm thick) on a Mo-coated soda lime glass (SLG) substrate (back electrical contact), the n-type semiconductor CdS (~100 nm thick) is coated by a chemical bath deposition. The remaining device is comprised of a sputtered intrinsic ZnO/Al-doped ZnO (~80 nm thick) as a window layer and front electrical contact [35, 37, 38].

![Figure 2-6: A schematic structure of CZTS thin film-based solar cell (reproduced with permission from Ref. [36], copyright 2011, Hindawi).](image)

2.3.3 WORKING PRINCIPLE OF CZTS THIN FILM SOLAR CELL

The p-n junction is the key part of the solar device, which is formed between the p-type hole-conducting absorber layer and the n-type electron-conducting buffer layer. Different semiconductor materials can absorb photons at various ranges of wavelengths depending on the band gap of the material. When a CZTS solar cell is
irradiated by incident photons, electrons are excited from the valance band to the conduction band in the p-type CZTS (band gap of ~1.5eV) semiconductor, leaving positively charged holes in the valance band as shown in Figure 2-7 [39]. The low-conduction band energy level in the n-type CdS layer results in the excited electrons being transported to the n-type layer, creating the electron-hole pair’s separation. If the two metal electrical contacts (cathode and anode) are connected by a wire, the electrons can pass through the external circuit [39-41].

![Figure 2-7](image.png)

**Figure 2-7**: (a) A schematic cross-section of p-n junction (b) Band diagram of p-n junction (reproduced with permission from Ref. [39], copyright 2011, De Gruyter).

### 2.3.4 CHARACTERIZATION OF CZTS THIN FILM-BASED SOLAR CELL

The performance of solar cells is evaluated by external quantum efficiency (EQE), also referred to as incident photon to current conversion efficiency (IPCE), and I-V measurements under simulated solar irradiation.

- **The definition of IPCE**

  IPCE indicates the ratio of the number of charge carriers collected by the solar cell to the number of photons of a given energy striking the solar device (incident photons). It depends on three parameters: LHE(λ), Φ_{mj} and η_{c}. 

Chapter 2: Literature Review
\[ \text{IPCE}(\lambda) = \text{LHE}(\lambda) \times \Phi_{\text{inj}} \times \eta_c \]  

(1)

In the equation (1), LHE (\(\lambda\)) is the light-harvesting efficiency for photons of wavelength \(\lambda\) and \(\Phi_{\text{inj}}\) is the quantum yield of charge injection, while \(\eta_c\) refers to the charge collection efficiency.

- **I-V characterization**

Characteristic parameters of a photovoltaic device are indicated by the I-V curve, as shown in Figure 2-8 where \(V_{oc}\) is the open circuit voltage and \(I_{sc}\) is the short circuit photocurrent. In solar cells, the theoretical \(V_{oc}\) is determined by the gap between the conductive bands of the p-type semiconductor (CZTS) and the n-type semiconductor (CdS), while \(I_{sc}\) depends on the overall charge produced in the device and is closely related to the IPCE value in the spectral response range. Therefore, a broad absorbance in the solar spectrum and a high IPCE are critical to achieve a high efficiency solar cell device. The overall efficiency of a solar cell is calculated from equation (2), where \(ff\) refers to fill factor which can be calculated from equation (3), and \(P_{in}\) is the power of incident light.

\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{I_{mp} \times V_{mp}}{P_{\text{in}}} \times 100\% \quad \text{Or} \quad \eta = \frac{ff \times I_{sc} \times V_{oc}}{P_{\text{in}}} \times 100\% \]  

(2)

\[ ff = \frac{I_{mp} \times V_{mp}}{I_{sc} \times V_{sc}} \times 100\% \]  

(3)
2.4 FABRICATION TECHNIQUES OF CZTS THIN FILM

CZTS films applied in photovoltaic devices are normally synthesised by the annealing of a precursor film with sulphur sources (S powder or H2S gas) in an inert atmosphere such as N2 and Ar. The precursor film could be metal, metal sulphides, a combination of metal and metal sulphides, or as deposited CZTS compounds. The annealing temperature normally varies between 400 °C - 600 °C, while the annealing duration varies from a few minutes to a few hours. The techniques employed to fabricate CZTS thin film can be classified into two main categories [36, 42, 43]: (i) vacuum-based method, and (ii) non-vacuum based method. The vacuum-based method uses special equipment which applies a suitable vacuum and temperature condition to generate the constitute atoms’ vapour of the CZTS compound in the machine chamber to form a precursor thin film on a substrate. The vacuum-based method includes sputtering [26, 44-46], evaporation [35, 47-49], and pulsed laser deposition [50-52]. The vacuum-based method has advantages of producing CZTS films with high uniformity that are reproducible and controllable. However, it requires high-energy consumption, low material utilization and long deposition time; therefore, it represents high-cost and slow production rate [68, 69]. For this reason, non-vacuum based techniques have

Figure 2-8: I-V curve of a solar cell.
been developed to provide a low-cost, quick-throughput production of CZTS films. This approach normally applies a process to make a CZTS precursor such as sol-gel and paste, and is then followed by the film-coating techniques and annealing process. The non-vacuum based method includes spray pyrolysis [53, 54], chemical vapour deposition [55, 56], screen printing [57, 58], chemical bath deposition [59], photochemical deposition [60], spin coating [61, 62] and electrodeposition [63-66]. Both approaches have been successfully used to fabricate pure CZTS thin film solar cells with considerable power conversion efficiency. The list of the highest efficiency CZTS thin film solar cells using different techniques is illustrated in Table 2-1. High efficiencies of more than 10% for solar cells based on CZTSe [23] and CZTSSe [24, 34] films made by solution process have been reported.

Table 2-1: Highest efficiency CZTS solar cell fabricated by different techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>V_{oc} (mV)</th>
<th>J_{sc} (mA cm^{-2})</th>
<th>FF (%)</th>
<th>\eta (%)</th>
<th>Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vacuum-based approach</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td>610</td>
<td>17.9</td>
<td>62.0</td>
<td>6.77</td>
<td>2008</td>
<td>[67]</td>
</tr>
<tr>
<td>Thermal evaporation</td>
<td>708</td>
<td>21.6</td>
<td>60.1</td>
<td>9.19</td>
<td>2013</td>
<td>[47]</td>
</tr>
<tr>
<td>Pulsed laser deposition</td>
<td>376</td>
<td>38.9</td>
<td>40.0</td>
<td>5.85</td>
<td>2014</td>
<td>[51]</td>
</tr>
<tr>
<td><strong>Non-vacuum based approach</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spray pyrolysis</td>
<td>620</td>
<td>15.5</td>
<td>45.0</td>
<td>4.32</td>
<td>2011</td>
<td>[53]</td>
</tr>
<tr>
<td>Chemical vapor deposition</td>
<td>658</td>
<td>16.5</td>
<td>55.0</td>
<td>6.03</td>
<td>2012</td>
<td>[55]</td>
</tr>
<tr>
<td>Spin coating</td>
<td>558</td>
<td>18.5</td>
<td>51.2</td>
<td>5.29</td>
<td>2014</td>
<td>[62]</td>
</tr>
<tr>
<td>Electrodeposition</td>
<td>705</td>
<td>18.0</td>
<td>63.2</td>
<td>8.10</td>
<td>2015</td>
<td>[66]</td>
</tr>
</tbody>
</table>
2.5 ELECTRODEPOSITION OF CZTS FILM

Up to date, CZTS solar cells fabricated by electrodeposition achieved the highest efficiency of 8.1 % as compared to other non-vacuum based techniques as shown in Table 2-1. Also, electrodeposition is considered a facile, low-cost, and environmentally-friendly method for fabrication of metals or semiconductor thin films [36, 68-70]. Electrodeposition has been successfully employed in the large-scale production of CdTe and CIGS-based thin film solar cells [71-73]. The electrodeposition of CZTS films can be accomplished by sulfurization of electrodeposited precursor films, including stacked metals Cu/Sn/Zn, binary alloys CuSn and Cu-Zn, ternary metallic Cu-Zn-Sn, and quaternary Cu-Zn-Sn-S. The procedure for the preparation of precursor films is facile: (i) insert the substrate into an electrolyte solution containing ions of the target precursor film; (ii) connect the substrate to the electrical equipment which provides stable voltage or current; and (iii) apply a suitable voltage or current to electrochemically reduce the wanted ions in the electrolyte solution to form the target precursor film. The electrodeposition is also cost effective because the deposition of the precursor film is conducted under room temperature and open-air conditions and normally takes a few minutes to an hour to complete the deposition. Moreover, the process of electrodeposition of the precursor film is environmentally-friendly as non-toxic chemicals are involved. On the basis of different strategies to electrodeposit a precursor film, electrodeposition of CZTS film can be divided to five sub-classifications: (i) stacked elemental layer (SEL) approach; (ii) stacked binary alloys; (iii) co-deposition; (iv) single step electrosynthesis; and (V) electrochemical atomic layer epitaxy (EC-ALE).
2.5.1 STACKED ELEMENTAL LAYER (SEL) APPROACH

![Diagram](image)

**Figure 2-9:** A schematic of stacked elemental layer (SEL) approach.

In this approach, copper, zinc and tin are subsequently deposited from the corresponding electrolyte solution. A schematic of the stacked elemental layer (SEL) approach is illustrated in **Figure 2-9**. The chemical compositions of the electrolyte solution used to electrodeposit the stacked metal layers in the literature are shown in **Table A-1** (Appendix).

The most commonly used electrolyte for copper deposition contains copper sulphate in acidic aqueous solution. Additives such as citric acid, sodium citrate and sorbitol are used as complexing agents to deposit a homogenous copper film. For electrodeposition of tin films, it can be achieved in both acidic and alkaline solutions. In the acidic condition, Sn (II) is unstable, therefore easily oxidized to Sn (IV) compounds which form colloids and then precipitation. Complexing agents such as CH₃SO₃H, sorbitol are applied to stabilize the Sn (II) in the electrolyte solution over a wide range of pH. Zinc chloride or zinc sulphate is commonly used as the precursor salt in the zinc electrodeposition. Acidic electrolyte is preferable for electrodeposition of zinc.

Although a different order of the three metals can be used to prepare the stacked metals, Cu/Sn/Zn is acknowledged as the optimal sequence to obtain high performance of the CZTS solar cells [38, 74]. This sequence benefits from good
metal exchange and stabilization of the metal layers [75, 76]. The CZTS solar cells by electrodeposition with high performance used the stacked elemental layer (SEL) approach combined with a soft annealing treatment. The stacked metal layers could be turned into homogenous and highly crystallized Cu-Zn-Sn metallic layers after the soft annealing process. This treatment can significantly improve the crystallinity and reduce structural failures of the CZTS film, and further boost the performance of solar cells [38, 64, 66, 74].

The sulfurization process used in the literature is shown in Table A-2 (Appendix) and is normally conducted under an inert environment such as N$_2$ or Ar with sulfur source such as sulfur powder or H$_2$S gas at 400 – 600 ºC. It was reported that H$_2$S showed better performance than sulfur powder for crystallization of CZTS film [78]. The literature shows sulfurization temperature in the range of 550 – 600 ºC is optimal for the formation of high quality CZTS films for solar cell application.

The advantage of this approach is to easily control the content of each metal so that the copper-poor and zinc-rich CZTS film is easily obtained. This can be done in various ways: (i) adjusting the concentration of each metal salt in the electrolyte solution [82]; (ii) controlling the current or potential for each metal deposition [38]; and (iii) controlling the duration of the deposition in each metal deposition [79, 83].

### 2.5.2 STACKED BINARY ALLOYS

![Figure 2-10: A schematic of stacked binary alloys.](image)

Chapter 2: Literature Review
In this method, the precursor alloy films Cu-Zn and CuSn are electrodedeposited on the Mo/SLG. A CZTS film is fabricated through sulfurization of the precursor alloy films, as illustrated in Figure 2-10. This method has only been reported once [88]. The chemical composition of the electrolyte solutions and sulfurization condition are shown in Table A-3 (Appendix).

2.5.3 CO-ELECTRODEPOSITION APPROACH

![Figure 2-11: A schematic of the co-electrodeposition approach.](image)

In this approach, a Cu-Zn-Sn metallic precursor film can be co-deposited from an electrolyte solution containing Cu, Zn and Sn cations. The CZTS film is subsequently synthesized by the sulfurization. The electrolyte solutions and experimental conditions used in the literature to fabricate CZTS film by co-electrodeposited Cu-Zn-Sn are listed in Table A-4 (Appendix). Compared to the SEL and stacked binary alloys, co-electrodeposition is simpler because the metallic film can be fabricated from an electrolyte solution at once. However, the co-deposition technique has some disadvantages. The electrolyte solution is unstable and precipitation may occur after a period of time. In addition, the composition of Cu-Zn-Sn metallic film is difficult to control because the electrolyte system is complexed and the metal ions have different reduction potentials. The reduction potential of the zinc cation is more negative than copper and tin cations. To
electrodeposit CZT metallic film, a suitable potential which is normally more negative than equilibrium reduction potential of zinc cation is needed to reduce the copper, tin and zinc cations on the surface of the substrate. A certain degree of hydrogen evolution often accompanies the co-electrodeposition process in the aqueous solvent because the reduction potential of the zinc cation is more negative than that of H⁺ [89]. In many cases, much higher concentration of zinc salt [90-96] than copper and tin salt were used to obtain CZT film with a nearly stoichiometric of Cu: Zn: Sn = 2: 1: 1. Tri-sodium citrate [89, 97] is widely used as a complexing agent in the electrolyte solution due to its effective complexing abilities to Cu (II), Zn (II) and Sn (II) ions and its environmentally-friendly nature. In some cases, tartaric acid [89, 96, 98, 99] was employed as an additive to adjust the pH of the electrolyte solution. The co-electrodeposition electrolyte solution may have problems with stability over a long period of time. Cu (II), Zn (II) and Sn (II) may interact with the citrate ion to form non-electroactive metal citrate complexes [97] such as ZnH₂Cit₂ and Zn₂Cit₂⁺ or precipitation compounds such as Cu₃SO₄(OH)₄, Cu₃SO₄(OH)₆, Zn₂Cit, Zn₄(OH)₆SO₄, and Sn(OH)₂. The presence of the non-electroactive species and precipitation components is dependent on the concentration of citrate and pH of the electrolyte solution. A weak acidic condition [97] with pH = 5 - 5.75 can offer a stable electrolyte solution when the concentration of citrate ion exceeds 0.4 M.
2.5.4 ONE-STEP ELECTROSYNTHESIS

![Diagram](Image)

**Figure 2-12**: A schematic of one-step electrosynthesis

In the single-step electrosynthesis of CZTS, the CZTS precursor thin film is directly electrodeposited on the conductive substrate from the electrolytic bath solution which contains Cu, Zn, and Sn cations as well as S-source such as Na$_2$S$_2$O$_3$. The as-deposited CZTS precursor film needs to be further crystallized via annealing under an inert environment such as Ar or N$_2$, as illustrated in **Figure 2-12**. However, to fabricate high-quality CZTS, additional sulfur sources such as S-powder or H$_2$S are still necessary in the annealing process, according to the literature [63, 106-108]. The electrolyte solutions and experimental conditions used in one-step electrolysis in the literature are listed in **Table A-5 (Appendix)**. Compared to the electrolyte used in the co-electrodeposition method, the electrolyte system employed in one-step synthesis is even more complex due to the presence of a sulfur source such as Na$_2$S$_2$O$_3$ with the metal species in the solution. Na$_2$S$_2$O$_3$ is fundamentally unstable and sulfur precipitation easily occurs in the moderately acidic solution by reaction (1) [70]:

$$\text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}^+ \leftrightarrow 2\text{Na}^+ + \text{SO}_2(\text{g}) + \text{S}_2(\text{g})^+ + \text{H}_2\text{O}(\text{l})$$  \hspace{1cm} (1)

This would affect the incorporation of S element in the deposits. The proposed mechanism in the formation of Cu$_2$ZnSnS$_4$ film in one-step electrolysis is shown in reaction (2) [109]:

$$2\text{Cu}^+ + \text{Zn}^{2+} + \text{Sn}^{2+} + 4\text{S}_2\text{O}_3^{2-} + 14\text{e}^- \leftrightarrow \text{Cu}_2\text{ZnSnS}_4 + 4\text{SO}_3^{2-}$$  \hspace{1cm} (2)
The pH of the electrolyte solution [110], concentration of the complexing agent [111, 112] and deposition potentials [94, 113] are important factors that influence the amount of sulfur incorporation and the properties of the deposited CZTS film.

2.5.5 ELECTROCHEMICAL ATOMIC LAYER EPITAXY (EC-ALE)

EC-ALE is an electrochemical technique based on alternative under-potential deposition (UPD) in which a monolayer can be formed on conductive substrates. UPD is a phenomenon of electrochemical surface limited reaction where an atomic layer of an element can be deposited upon another element under the potential that is required to deposit the element itself [122].

Fabrication of a CZTS thin film with a thickness of 113.22 nm on a Ag substrate by using EC-ALE was reported [123]. The elements were deposited in the order of S/Sn/S/Cu/S/Zn/S/Cu by cyclic voltammetry from separate electrolytic bath solutions of the four elemental sources: 2.5 mM Na$_2$S, 2.5 mM SnCl$_2$, 2.5 mM ZnSO$_4$ and 2.5 mM CuSO$_4$ in an ammonia buffer solution (pH = 9.6) with 5 mM EDTA. However, no work on CZTS solar cell by using the EC-ALE method has been reported.

2.5.6 CHOICE OF THE LOW-COST AND QUICK PRODUCTION STRATEGY AND PERSPECTIVES

The advantages, disadvantages and perspective remarks on the fabrication of CZTS thin films by using different electrodeposition methods are shown in Table 2-2, while the highest-efficiency solar cells are illustrated in Table 2-3. There are still considerable gaps between the most efficient CZTS solar cells fabricated by co-electrodeposition (3.87 %) and the one-step electrosynthesis (6.6 %) and SEL approach (8.1 %), as shown in Table 2-3. However, the SEL approach and one-step
electrosynthesis are more time-consuming and not suitable for high-throughput production; also, the SEL approach requires more equipment. Economically, co-electrodeposition tends to be more competitive than other methods because it has less equipment requirements and is an easier and quicker process. Moreover, for CZTSe based solar cell, the co-electrodeposition method [124] has achieved efficiency of 8.1% which is competitive for 8.2% in the SEL method [125]. It is generally accepted that homogeneous and uniform CZT film with a thickness of a few hundred nanometers and nearly stoichiometric (Cu: Zn: Sn = 2:1:1) composition is the preferable precursor to produce high quality CZTS or CZTSe films with a smooth and compact morphology [38, 75]. In the application to solar cells, CZTS films with smooth CZTS surface would reduce the carrier recombination that occurs at the interface between p-n junction (CZTS and CdS) and would enhance the performances of solar cells [64]. Moreover, compact morphology represents less voids and cracks which act as shunt baths leading to low FF of solar cells and decreases the efficiency. Indeed, post-annealing and sulfurization conditions also significantly influence crystallinity, phase formation, and even morphology of the final CZTS or CZTSe products, and subsequently the performances of solar cells [64, 74, 99].

To achieve more efficient CZTS solar cells using the co-electrodeposition method, several strategies are considered: (i) to understand the electrochemical formation mechanism of CZT films which can provide fundamental knowledge to control the co-electrodeposition process; (ii) to optimize the morphology of co-electrodeposited Cu-Zn-Sn films to grow high quality CZTS films; (iii) to build up an optimum sulfurization condition applicable to the precursor CZT films; (iv) to develop an optimum electrolyte solution for high quality CZT films.
Table 2-2: Comparison of the different electrodeposition strategies.

<table>
<thead>
<tr>
<th>Electrodeposition strategy</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Perspectives</th>
</tr>
</thead>
</table>
| Stacked elemental layer (SEL) approach | (1) easy to control composition of the CZT film  
(2) stable electrolytes  
(3) high quality of final CZTS film | (1) multiple electrolyte solutions and deposition steps  
(2) time-consuming | May be easily adaptable for industry, but not suitable for high-throughput production compared to co-electrodeposition |
| Stacked binary alloys       | Relatively easy to control composition of the CZT film than co-electrodeposition | (1) multiple electrolytes  
(2) multiple deposition steps  
(2) time-consuming | More work needed to evaluate the quality of the final CZTS film |
Table 2-3: Characteristic parameters reported for the most efficient CZTS solar cells by different electrodeposition methods.

<table>
<thead>
<tr>
<th>Electrodeposition Method</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stacked elemental layer approach</td>
<td>705</td>
<td>18.0</td>
<td>63.2</td>
<td>8.1</td>
<td>2015</td>
<td>[66]</td>
</tr>
<tr>
<td>Stacked binary alloys</td>
<td>668</td>
<td>12.6</td>
<td>43.7</td>
<td>3.67</td>
<td>2015</td>
<td>[88]</td>
</tr>
<tr>
<td>Co-deposition</td>
<td>512</td>
<td>15.6</td>
<td>48.0</td>
<td>3.87</td>
<td>2014</td>
<td>[65]</td>
</tr>
<tr>
<td>Single step electrosynthesis</td>
<td>581</td>
<td>19.9</td>
<td>57.2</td>
<td>6.6</td>
<td>2015</td>
<td>[63]</td>
</tr>
<tr>
<td>Electrochemical atomic layer epitaxy</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2.6 CHARACTERIZATION OF CZT AND CZTS FILMS

According to the literature [38, 64, 65, 74, 79, 91, 93, 95, 98, 99, 101, 102], ratios of Cu/(Zn+Sn) and Zn/Sn are used to characterize the composition of CZT and CZTS films. The quantitative analyses were made using either the Energy Dispersive X-ray Fluorescence (XRF) [38, 65, 79, 101, 102] or the Energy Dispersive X-ray Spectroscopy (EDS) [64, 74, 91, 93, 95, 98, 99] measurement.

The morphology of CZT and CZTS films was observed by utilising Scanning Electron Microscopy (SEM) [51, 74, 91, 95, 101]. The thicknesses of the films were measured by cross-sectional images of SEM [38, 74, 92, 93, 95, 102] or Transmission Electron Microscopy (TEM) [38, 64]. EDS mapping was used to detect the distribution of each element in the films [95, 99, 102].

Crystal structure of CZTS films was identified using X-ray diffraction (XRD) and Raman measurements [65, 74, 91, 96, 99, 104, 126]. The thermodynamically stable
phase kesterite-type CZTS shows strong XRD diffraction peaks at $2\theta = 18.24$, 28.44, 32.94, 47.30, 56.10, 69.09, and 76.36, which are attributed to (101) (112), (200), (220), (312), (008) and (332) orientation planes of tetragonal crystal structure (JCPDS 01-075-4122), respectively [126, 127]. Nevertheless, potential secondary phases such as cubic ZnS, cubic Cu$_2$SnS$_3$ and tetragonal Cu$_3$SnS$_4$ exhibit similar XRD diffraction peaks [126, 128]. Raman measurement is used to further distinguish these secondary phases from kesterite CZTS [126, 128, 129].

The p-type photoelectrochemical response of a CZTS film under a light illumination can be characterized in an Eu(NO$_3$)$_3$ aqueous solution using electrochemical three-electrodes system [77, 114, 126, 130, 131]. Photovoltaic performance of a CZTS film is measured by $I-V$ measurement after completing a CZTS solar cell, as presented in section 2.3.2 and 2.3.3.

2.7 FUNDAMENTALS IN ELECTRODEPOSITION OF METAL/ALLOY FILMS

2.7.1 MAIN INFLUENCING FACTORS OF ELECTRODEPOSITION

Electrodeposition of metal/alloys is the basis of a wide range of large industries. Considerable amounts of literature including articles, patents, and books [132-135] on the electrodeposition of metal/alloys have been published. According to the generally accepted principle [132], the main factors influencing the properties of the electrodeposited metal/alloys can be divided into operational and electrolyte solution factors. Operational factors include current density or potential, temperature, and agitation of working electrodes or electrolyte solution. All these factors can individually influence the compositions and morphologies of the alloy deposits. To co-electrodeposit multi-metals or alloys films, the co-reduction potential used is determined by the metal which has the most negative equilibrium potential. An increase in temperature usually decreases the polarization of deposition potential and
increases the diffusion rates of the metal cations which, in turn, enhances the deposition efficiency. Agitation of working electrodes or electrolyte solutions could improve the uniformity of the deposited film and could increase the deposition rate.

Electrolyte solution factors include complexing agent and additives, pH value of the solution, and concentration of the metal ions. Complexing agents or additives are important to the electrolyte solution. They exhibit multi-functions: (i) stabilizing the electrolyte solution via enhancing the solubility of metal ions with formation of stable metal complex; (ii) narrowing the gap between different reduction potentials of metals; (iii) improving the homogeneity and roughness of the deposited film with fine-grain size. The nature and volume of the complexing agent or additives can affect the compositions and morphologies of the deposited films. The choice of an optimal pH is beneficial for enhancing the solubility of metal ions and increasing the efficiency of the metal deposition. An increase of a particular metal cation in an electrolyte would normally result in an increase of the corresponding metal in the deposits.

2.7.2 VOLTMETRY AND CHRONOAMPEROMETRY

Voltammetry is one of the basic electroanalytical techniques by which electrochemical reduction and oxidation processes on the working electrode surface can be evaluated via analysing the recorded signal current changes as a function of applied potential. Voltammetry is widely employed in analytical chemistry and various industrial processes [136, 137]. In the electrodeposition of metal/alloys, the linear sweep voltammetry method is used to identify reduction potentials of metal cations species in electrolyte solutions [89, 95, 96].

Chronoamperometry is an electrochemical technique in which current changes occurring at working electrode surface as a function of time is recorded under applied potentials [134, 135]. Chronoamperometry can be used to study
nucleation and growth of electrodeposits [138, 139]. Also, it can be used to detect surface area changes of the deposited film during the electrodeposition process [140].

2.7.3 MASS TRANSFER PROCESS IN THE ELECTRODEPOSITION OF METAL/ALLOY

In the electrodeposition of metal/alloy films, electrode reactions (M\(^{n+}\) + ne\(^-\) → M) form metal thin films on the substrates from electrolyte solutions containing metallic cations. In general, a simple electrode reaction rate is only governed by mass transfer [128]. The mass transfer process is shown in Figure 2-13. The mass transfer is influenced by diffusion, migration, and convection. Migration is the movement of a charged body under the influence of an electric field (a gradient of electrical potential); diffusion refers to movement of a species under the influence of a gradient of chemical potential (a concentration gradient); and convection refers to the stirring or hydrodynamic transport (density gradients). Thus, the mass transfer to an electrode can be expressed by the Nernst-Planck’s equation (4) in one-dimension along the x-axis as [141]:

\[
J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x} + C_i \nu(x) \quad (4)
\]

Where \(i(x)\) is the flux of species \(i\) (mol s\(^{-1}\) cm\(^{-1}\)) at distance \(x\) from the electrode surface, \(D_i\) is the diffusion coefficient (cm\(^2\)/s), \(\partial \Phi(x)/\partial x\) is the concentration gradient at distance \(x\), \(\partial \Phi(x)/\partial x\) is the potential gradient, \(z_i\) and \(\nu\) are the charge (dimensionless) and concentration (mol cm\(^{-3}\)) of species \(i\), respectively, and \(\nu(x)\) is the velocity (cm/s) with which a volume element in solution moves along the axis. Therefore, in an electrodeposition with the same employed potential or current and
same stirring rate of electrolyte solution, the electrode reactions (M^{n+} + ne^{-} → M) rate is determined by the concentration of metallic cations in the electrolyte solution.

**Figure 2-13:** A schematic of electrochemical reaction for metallic deposition on the electrode.

## 2.8 SUMMARY

Low-cost and earth-abundant CZTS material as a promising p-type light absorber semiconductor has huge potential application to commercialized solar cells in the future. Electrodeposition is considered as a facile, low-cost and green technology to fabricate CZTS film on a large-scale. Among the different electrodeposition strategies to prepare CZTS films, co-electrodeposition is competitive: it allows for low-cost, high-throughput production of CZTS thin film due to its simplicity, time-efficiency and reduced equipment requirements. However, the efficiency of CZTS thin film solar cell by co-electrodeposition is still relatively low compared to other electrodeposition strategies. To solve this issue, fabrication of high quality CZT films is necessary. Although the literature reports the fabrication of CZTS film via co-electrodeposited CZT film, the studies focusing on understanding the mechanism or
process in co-electrodeposition of CZT is rare. The research conducted here is to understand the electrochemical formation mechanism of CZT film and to control the process to fabricate high quality of CZT films resulting in effective CZTS films for photovoltaic applications.
2.9 REFERENCES


Chapter 3: Identification of the critical parameters controlling the electrochemical formation of homogeneous Cu-Zn-Sn films

SYNOPSIS

According to generally accepted principles in electrodeposition of metal/alloy films, two types of factors could have significant impacts on the electrochemical formation of metallic films: (i) operational factors such as current density or potential, temperature, and agitation of working electrodes or electrolyte solution; and (ii) electrolyte solution factors such as complexing agent and additives, pH value of the solution, and concentration of the metal ions. In this chapter, the effects of factors such as applied potential, concentrations of complexing agent, pH of the composition, and morphologies on the electrodeposited CZT films were investigated. Electrodeposition of CZT films was conducted at room temperature (26±1°C) using a static aqueous solution with tri-sodium citrate as complexing agent. EDS was used to determine the composition of the CZT films. SEM was used to observe the morphologies of the CZT films. Linear sweep voltammogram technique was employed to observe the behaviour of the soluble metal species in the electrolyte solution. This chapter is written in a journal article style and the manuscript will be submitted to the Journal of Solid State Electrochemistry.
STATEMENT OF CONTRIBUTION

The authors listed below have certified that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;

2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;

3. there are no other authors of the publication according to these criteria;

4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and

5. they agree to the use of the publication in the student’s thesis and its publication on the Australian Digital Thesis database consistent with any limitation set by publisher requirements.

In the case of this chapter:

Identification of the critical parameters controlling the electrochemical formation of homogeneous Cu-Zn-Sn films

Tubshin Hreid, Anthony P O’Mullane, Geoffrey Will* and Hongxia Wang*

To be submitted to the Journal of Solid State Electrochemistry

<table>
<thead>
<tr>
<th>Contributor</th>
<th>Statement of contribution</th>
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<tbody>
<tr>
<td>Tubshin Hreid</td>
<td>Designed and conducted experiments, wrote the manuscript</td>
</tr>
<tr>
<td>Anthony P O’Mullane</td>
<td>Revised the manuscript</td>
</tr>
<tr>
<td>Geoffrey Will</td>
<td>Revised the manuscript and supervision</td>
</tr>
<tr>
<td>Hongxia Wang</td>
<td>Revised the manuscript and supervision</td>
</tr>
</tbody>
</table>

Principal Supervisor Confirmation

I have sighted email or other correspondence from all co-authors confirming their certifying authorship.

Geoffrey Will  

12/10/2015

Name  Signature  Date
Identification of the critical parameters controlling the electrochemical formation of homogeneous Cu-Zn-Sn films

Tubshin Hreid, Anthony P O’Mullane, Geoffrey Will* and Hongxia Wang*

School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, Brisbane, QLD. 4001, Australia

* Corresponding Authors: g.will@qut.edu.au; hx.wang@qut.edu.au

ABSTRACT

In this work, Cu-Zn-Sn (CZT) ternary alloy films were potentiostatically electrodeposited on molybdenum coated soda lime glass (Mo/SLG) substrates from an electrolyte solution containing 20 mM Cu (II), 10 mM Zn (II), 10 mM Sn (II) ions using tri-sodium citrate as a complexing agent. The effects of three main influencing factors–namely applied potential, concentration of the complexing agent and pH of the electrolyte solution on the composition, and morphology of the electrodeposited CZT films–were examined. The following results were noted:

i. films with a nearly stoichiometric ratio of Cu: Zn: Sn = 2: 1: 1 are obtained in the potential range of - 1.20 V to - 1.25 V, while the crystallites within the CZT films increased in size as the applied potential was made more negative until it reached a potential where hydrogen evolution occurs which compromises the adhesive ability of the CZT film to the substrate.

ii. the metal content is controlled by the solubility of the precursor metal ions in the presence of tri-sodium citrate which also influences film homogeneity.

iii. the compositions of the CZT films are similar at pH = 4.1, 5.1 and 6.1, however, the Zn content is significantly lower at pH = 7.1. From a study of the nucleation and growth mechanism it was found that CZT films grown
under different conditions are dominated by progressive nucleation growth, which explains the varying sizes of crystals found in each film. By optimising each of these parameters it is possible to fabricate homogeneous CZT films with the desired stoichiometric ratio of 2:1:1 which is the ideal precursor to photovoltaic materials such as Cu₂ZnSnS₄ (CZTS) and Cu₂ZnSnSe₄ (CZTSe).

3.1 INTRODUCTION

Cu-Zn-Sn (CZT) ternary alloys are extensively used for protective and decorative purposes due to their enhanced chemical and physical properties such as high corrosion resistance, strong adhesion, and solder-abilities [1-5]. In recent years, however, CZT ternary alloy films have gained significant attention in renewable energy research as an essential precursor to the fabrication of new photovoltaic materials such as Cu₂ZnSnS₄ (CZTS) and Cu₂ZnSnSe₄ (CZTSe) [6-9]. CZT has also demonstrated its potential as a material in electrochemical energy storage devices such as lithium ion batteries because it exhibits high capacity [10, 11].

Electrodeposition is a facile, low cost, and environmental friendly method to fabricate CZT films on conductive substrates [12-15]. With this approach, a suitable potential is required to co-electrodeposit copper, zinc and tin from an electrolyte solution that typically contains one or more complexing agents. In the field of metal and metal alloy electrodeposition [3], there are critical factors which influence alloy formation, composition, and film morphology such as the applied potential or current, the nature and/or concentration of the complexing agent, and the pH of the electrolyte solutions.
As the reduction potential for Zn (II) is more negative than that of Cu (II), Sn (II) and significantly hydrogen evolution, the reduction potential chosen for the electrodeposition of CZT film is determined to a large extent by the Zn (II) reduction process, and a certain degree of hydrogen evolution often accompanies the deposition process [16]. Complexing agents in the electrolyte solution play an important role in the electrodeposition of metal and metal alloy films [3, 16, 17] such as: (i) enhancing the solubility of metal ions in solution via the formation of stable metal complexes; (ii) narrowing the gap between the different reduction potentials of metal ions in solution; (iii) improving the homogeneity and roughness of the film by altering the grain size of the deposits. Several complexing agents such as Copper Glo [18, 19], ethylenediaminetetraacetic acid (EDTA) [1], citric acid [16], and tri-sodium citrate [2, 7, 20-26] have been used in aqueous electrolyte solutions for the electrodeposition of CZT films. Among them, tri-sodium citrate is the most widely used due to its effective complexing abilities to Cu (II), Zn (II) and Sn (II) ions and its environmentally friendly nature [2]. It was also reported that an electrodeposited CZT film using tri-sodium citrate showed superior performance when applied in a solar cell after converting into CZTS film, compared to a film with EDTA or tartaric acid [9]. The pH of the electrolyte solution is also a key factor in affecting how the complexing agent interacts with the metal cations and therefore their solubility [2]. Low solubility of the metal salts in the electrolyte solution decreases the efficiency of the metal deposition process. Overall, a CZT precursor film with a nearly stoichiometric ratio of Cu: Zn: Sn = 2: 1: 1 with a uniform morphology that is well-adhered to the underlying substrate is essential for synthesizing high quality CZTS and CZTSe photovoltaic films [15, 27].
In the present study, the effects of applied potential, concentration of tri-sodium citrate, and pH of the electrolyte solution on the composition and morphology of the electrodeposited CZT film were investigated. This research will offer a foundation for the preparation of CZT films with a range of composition and different morphologies, which can be utilized for a wide range of applications including CZTS and CZTSe solar cells, corrosion resistance, and lithium ion batteries.

3.2 EXPERIMENTAL

3.2.1 ELECTROCHEMICAL METHODS AND MATERIAL SYNTHESIS

Mo/SLG substrates were ultrasonically cleaned in acetone, ethanol and MilliQ water in sequence for 5 minutes and then dried under a flow of nitrogen. The electrochemical deposition was implemented with a three-electrode configuration consisting of a Mo/SLG substrate working electrode, Pt wire counter electrode, and a Ag/AgCl/saturated KCl reference electrode using an electrochemical workstation (VSP-300 Bio-logic). Freshly prepared electrolyte solutions containing 200 mM tri-sodium, 20 mM CuSO₄·5H₂O, 10 mM ZnSO₄·7H₂O and 10 mM SnSO₄ and tri-sodium citrate were used to electrodeposit CZT films. To examine the effect of applied potential on the formation of alloy metallic films, a potential range of -0.5 V to -1.35 V was employed to electrodeposit metallic films on the Mo/SLG. To investigate the effects of the complexing agent, concentrations on the electrodeposited CZT film of tri-sodium citrate with a range of concentrations 0 - 400 mM were employed. Moreover, pH = 4.1, 5.1, 6.1 and 7.1 were used to evaluate the effects of pH of electrolyte solutions on CZT films. The electrolyte solutions were adjusted to 6.10 ± 0.05 (AQUA-pH digital meter, TPS) by sulfuric acid or NaOH. The electrodeposition of the CZT films was carried out at a constant potential of -1.25 V for 10 minutes at ambient temperature (26 ± 1°C). The active area of the
films was 0.2 cm$^2$. All the films were electrodeposited from a 40 ml electrolyte solution to ensure the concentration change caused by the consumption of metal cations during the deposition process was negligible.

3.2.2 CHARACTERIZATION OF ELECTRODEPOSITED ALLOY FILM

The surface and cross-section morphology of the deposited thin films were characterized by field emission scanning electron microscopy (FESEM, JEOL 7001F). Compositional analysis and elemental mapping for the CZT thin films were characterized by energy dispersive X-ray spectroscopy (EDS, JEOL 7001F) at an acceleration voltage of 20.0 kV. The relative error of the EDS detector was within ±2.0 % for Cu, ±2.0 % for Zn, and ±3.0 % for Sn. The minimum EDS detection limitation for each metal element is 0.1 %. Linear sweep voltammograms were employed to detect the soluble metal species in the electrolyte solutions.

3.3 RESULTS AND DISCUSSION

3.3.1 POTENTIAL EFFECTS ON ELECTROCHEMICAL FORMATION OF METALLIC FILMS

Linear sweep voltammograms of the three metal cations in the electrolyte solution are shown in Figure 3-1a. It should be noted that the peak observed at -0.72V is attributed to the reduction of Sn (IV) to Sn (II). The latter originates from the simultaneous presence of Cu (II) and Sn (II) in the electrolyte solution that generates Sn (IV) based on the reaction [23]: Cu (II) + Sn (II) $\leftrightarrow$ Cu (I) + Sn (IV). The compositions of metallic films electrodeposited at different potentials for 10 minutes are shown in Figure 3-1b. The films were electrodeposited in two potential regions between -0.5 V to -0.80 V and -1.10 V to -1.35 V, with a potential interval of 0.05 V. Copper-tin binary films are formed between -0.55 V to -1.10 V, as illustrated in Figure 3-1b. -1.15 V is the starting potential for the electrodeposition of Zn and concomitantly the formation of a CZT film where 13 % Zn was observed.
The Zn content increased to 20 % at -1.20 V and then slightly increased to 21 % and 23 % at -1.25 V and -1.30 V, respectively, and finally decreased to 20 % at -1.35 V. Morphologically, similar circular-shaped agglomerated crystals with irregular sizes were formed in the CZT films when deposited over a potential range of -1.15 V to -1.35 V. The average sizes of the crystals gradually increased from less than 200 nm at -1.15 V and -1.20 V, to more than 200 nm at -1.25 V, as illustrated in Figure 3-2. Due to stronger hydrogen evolution at more negative potentials, a significant crack was found in the film deposited at -1.35 V, which compromises the adhesion of the film to Mo/SLG substrate. The elemental ratio of Cu: Zn: Sn in the CZT films deposited at -1.20 V, -1.25 V and -1.30 V are close to the desirable stoichiometric of 2: 1: 1. Herein, -1.25 V was chosen as an appropriate potential to deposit CZT films for the later experiments.
Figure 3-1: (a) Linear sweep voltammograms for electrodeposition of CZT film. Scan rate: 10 mV s^{-1}. The potential was started at 0 V and was scanned in the negative direction. (b) Composition of metallic film electrodeposited at different potentials, in an aqueous solution containing 20 mM CuSO₄·5H₂O + 10 mM ZnSO₄·7H₂O + 10mM SnSO₄ and 200 mM Na₃C₆H₅O₇·2H₂O.
Figure 3-2b: SEM images of metallic films electrodeposited in range of -1.10 V to -1.35 V.
Chronoamperometry was used to study the kinetics of electrocrystallization of metal and alloy deposits [28-31]. A typical chronoamperogram ($J$-$t$ curve) shows a peak current at the beginning of current–time response. The maximum cathodic current $J_m$ at deposition time ($t_m$) is labelled in a typical curve as shown in **Figure 3-3a**. The non-dimensional plots of $(J/J_m)^2$ vs. $t/t_m$ are widely employed to determine the nucleation and growth mechanism when electrodepositing materials on an electrode surface. The theoretical model developed by Sharifker and Hills [32] described two types of mechanism for the initial stages of 3D nucleation and 2D growth process: instantaneous and progressive. For the case of instantaneous nucleation growth, nucleation adatoms on the electrode surface grows at a constant rate with deposition time. On the contrary, initially deposited adatoms grow at a varying rate during progressive nucleation-growth. The theoretical curves $(J/J_m)^2$ vs.$t/t_m$ for instantaneous and progressive mechanisms are shown in **Figure 3-3b** and correspond to equations (1) and (2), respectively.

\[
\frac{J}{J_m} = \frac{3.9542}{(t/t_m)} [1 - \exp (-1.2564 \frac{t}{t_m})]^2 \quad (1)
\]

\[
\frac{J}{J_m} = \frac{1.2254}{(t/t_m)} \left\{\left[1 - \exp (-2.3367 \left( \frac{t}{t_m} \right)^2) \right] \right\}^2 \quad (2)
\]

**Figure 3-3b** also illustrates nucleation and growth types of CZT electrodeposited at different potentials. All $(J/J_m)^2$ vs. $t/t_m$ plots resulted from the corresponding chronoamperograms (**Figure 3-3a**)—including the binary CuSn deposited at -1.10 V and ternary CZT from -1.15 to -1.25 V all closely match the theoretical progressive nucleation-growth curve, suggesting initially deposited adatoms grow at a varying rate. This can explain why crystals with irregular sizes that form in all the deposits, as demonstrated by **Figure 3-2**. Chronoamperograms recorded at -1.30 V and -1.35
V did not show a clear maximum \( J_m \), therefore, were not applicable for generating \( (J/J_m)^2 \) vs. \( t/t_m \).

**Figure 3.3**: (a) Chronoamperograms for electrodeposition of binary Cu-Sn (-1.10 V) and ternary CZT films at different potentials; (b) Corresponding non-dimensional \( (J/J_m)^2 \) vs. \( t/t_m \) plots comparing with theoretical curves for instantaneous and progressive nucleation and growth mechanisms.
3.3.2 EFFECTS OF COMPLEXING AGENT CONCENTRATION ON ELECTRODEPOSITED CZT FILM

In order to investigate the effect of the concentration of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O on the electrodeposited film, the pH of all the electrolyte solutions were adjusted to 6.1 ±0.05 by H$_2$SO$_4$ or NaOH, ensuring same pH as the original solution containing 20 mM CuSO$_4$·5H$_2$O + 10 mM ZnSO$_4$·7H$_2$O + 10 mM SnSO$_4$ and 200 mM Na$_3$C$_6$H$_5$O$_7$·2H$_2$O. Before the adjustment, the electrolyte solutions with different concentrations of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O showed different pH values due to the alkaline properties of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O. The pH of these solutions is 2.7, 3.5, 4.7, 5.7, 6.1, and 6.8 when using 0 mM, 25 mM, 50 mM, 100 mM, 200 mM and 400 mM of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O, respectively. However, significant precipitations occurred in the solution without the complexing agent during the pH adjustment by NaOH. The precipitations should be mostly Sn(OH)$_2$ as a result of the reaction between NaOH and unstable Sn(II) species in the solution. Therefore, the solution could not be used as an effective electrolyte for the electrodeposition of a CZT film. The composition of the CZT films electrodeposited from the electrolyte solutions with 25 mM – 400 mM of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O are shown in Figure 3-4, and linear sweep voltammograms of the electrolyte solutions are illustrated in Figure 3-5. The CZT film electrodeposited from 25 mM Na$_3$C$_6$H$_5$O$_7$·2H$_2$O contains 62 % of Cu, 21 % of Sn and 16 % of Zn. When the concentration of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O was increased to 50 mM, the Sn content in the CZT film was significantly enhanced to 33 %, while the Cu content decreased to 49 % and the Zn content remained at a similar level. These compositional changes are attributed to the variation in solubility of the metal species caused by the concentration changes of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O. The tri-sodium citrate can react with Cu (II), Zn (II) and Sn (II) cations in the solution to form soluble metal species such as Cu$_2$HCit$^2$-, Cu$_2$Cit$^4$-, ZnHCit, and SnCit$^2$-, and some non-
electroactive species such as $\text{ZnH}_2\text{Cit}^{4-}$ and $\text{Zn}_2\text{Cit}^{4-}$, and precipitation can also occur via the formation of species such as $\text{Cu}_3\text{SO}_4(\text{OH})_4$, $\text{Cu}_4\text{SO}_4(\text{OH})_4$, $\text{Zn}_2\text{Cit}$, $\text{Zn}_4(\text{OH})_6\text{SO}_4$, $\text{Sn(OH)}_2$ and $\text{SnH}_2\text{Cit}$ [2].

**Figure 3-4:** Composition of CZT films electrodeposited from an aqueous solution containing 20 mM CuSO$_4\cdot$5H$_2$O + 10 mM ZnSO$_4\cdot$7H$_2$O + 10 mM SnSO$_4$ with different concentrations of Na$_3$C$_6$H$_5$O$_7\cdot$2H$_2$O.

**Figure 3-5:** Linear sweep voltammograms for CZT films electrodeposited in an aqueous solution containing 20 mM CuSO$_4\cdot$5H$_2$O + 10 mM ZnSO$_4\cdot$7H$_2$O + 10 mM SnSO$_4$, with different concentrations of Na$_3$C$_6$H$_5$O$_7\cdot$2H$_2$O.
The reduction peaks of the metal cations observed in the linear sweep voltammograms (Figure 3-5) reflect only the soluble metal species in the solution. It should be noted that a certain amount of soluble Sn (IV) species is also present in the solution. The reduction peak of Sn (IV) species is more positive than that of Sn (IV) as confirmed in Figure 3-1a, section 3.3.1. The two sharp peaks for Sn (II) and Sn (IV) species (except for 25 mM) are circled in the ellipse middle of Figure 3-5. No peak for the reduction of Sn (IV) was observed in the solution containing 25 mM of Na₃C₆H₅O₇·2H₂O. Compared to the peak current for the reduction of Sn (II) in 25 mM of Na₃C₆H₅O₇·2H₂O, a much higher peak current for the reduction of both Sn (IV) and Sn(II) species was observed in 50 mM of Na₃C₆H₅O₇·2H₂O. Both soluble Sn (II) and Sn (IV) species can be reduced to Sn at a potential of -1.25 V. Therefore, the significant increase of soluble Sn species in the solution is responsible for the increased Sn content in the CZT film when using 50 mM Na₃C₆H₅O₇·2H₂O. It was found that the Cu content increased while the Sn content decreased in the CZT film when using 100 mM Na₃C₆H₅O₇·2H₂O as compared to 50 mM Na₃C₆H₅O₇·2H₂O. This is attributed to the increased solubility of Cu species, which is reflected in the significant increase in the reduction peak current for Cu (II) reduction, as illustrated in Figure 3-5. The Zn content significantly increased from 15 % in the CZT film with 100 mM Na₃C₆H₅O₇·2H₂O to 21 % in the CZT film with 200 mM of the complexing agent, which can be explained by the enhanced solubility of Zn (II) species in the solution. A prominent Zn (II) reduction peak could be observed at this concentration (Figure 3-5). Similar linear sweep voltammograms were recorded except for the high H₂ peak observed in the case of 400 mM Na₃C₆H₅O₇·2H₂O.
Figure 3-6: SEM images of CZT film electrodeposited in an aqueous solution containing 20 mM CuSO$_4$·5H$_2$O + 10 mM ZnSO$_4$·7H$_2$O + 10 mM SnSO$_4$ with different concentration of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O.

It was reported previously that H$_2$ evolution is facilitated by the presence of citrate [16]. SEM images of the CZT films electrodeposited from electrolyte solutions containing 25 to 400 mM Na$_3$C$_6$H$_5$O$_7$·2H$_2$O are given in Figure 3-6. Non-uniform clusters with size ranges from nanometres to micrometres were found when using 25 mM Na$_3$C$_6$H$_5$O$_7$·2H$_2$O, while the large, round-shaped clusters consist of agglomerated compact nano grains.
Figure 3-7: (a) Chronoamperograms for electrodeposition of CZT films from electrolyte solutions containing different concentration of tri-sodium citrates; (b) corresponding non-dimensional \((J/J_m)^2\) vs. \(t/t_m\) plots compared with theoretical curves for instantaneous and progressive nucleation and growth mechanisms.

It was also found that the film had partially fallen off when rinsed with water after the deposition, indicating the adhesive ability of the film to the substrate is poor. As the concentration of the \(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\cdot2\text{H}_2\text{O}\) increases, the uniformity of the CZT film increases with a narrower size distribution of clusters, which are better adhered to the
substrate. When using 50 mM and 100 mM Na₃C₆H₅O₇·2H₂O clusters ranging in
diameter from 20 nm to more than 200 nm are observed. In contrast, uniform and
round shaped crystals with sizes of ~ 200 nm are observed when using 200 mM and
400 mM Na₃C₆H₅O₇·2H₂O. Nevertheless, compared to the 200 mM case, more
regular crystals are formed with 400 mM Na₃C₆H₅O₇·2H₂O, with more defined
spaces between the deposits. This can be attributed to more H₂ evolution occurring
during the electrodeposition process which is facilitated by the higher concentration
of citrate, as confirmed by prominent H₂ peak current shown in Figure 3-5.

Figure 3-7b shows a comparison of the non-dimensional plots \((J/J_m)^2\) vs. \(t/t_m\)
(calculated from their chronoamperograms in Figure 3-7a) for CZT deposited
from electrolyte solutions containing 25 mM - 200 mM tri-sodium citrate
with the theoretical curves. The plots of 25 mM and 50 mM partially matching the
progressive nucleation-growth therotical curve while those of 100 mM and 200
mM closely match the progressive curve, indicating again a progressive
nucleation and growth mechanism and is in agreement with irregular sized crystals
formed in the all CZT films as illustrated in Figure 3-6. The
chronoamperogram of 400 mM is not applicable for generating the non-
dimensional plots \((J/J_m)^2\) vs. \(t/t_m\) due to an unclear \(J_m\) value.

3.3.3 EFFECTS OF PH OF ELECTROLYTE SOLUTION ON ELECTRODEPOSITED CZT

The composition of the CZT films electrodeposited from electrolyte solutions with
different pH are illustrated in Figure 3-8. The composition of CZT films with pH =
4.1, 5.1 and 6.1 are quite similar. However, the Zn content significantly decreased in
the film with a pH = 6.1. This is attributed to the decreased solubility of Zn (II) in the
solution, which is detected in the linear sweep voltammogram (Figure 3-9). No
significant Zn (II) reduction peak occurred in the electrolyte solution with pH = 7.1; however, this is not the case for the other solutions with pH = 4.1, 5.1 and 6.1. This is in agreement with the results of the speciation diagram for Zn (II) in the citrate solution that a large amount of non-electroactive species such as ZnH$_2$Cit$_2^{4+}$ and Zn$_2$Cit$_2^{4+}$ [2], and precipitates like Zn$_2$Cit and Zn$_4$(OH)$_6$SO$_4$ are formed when the pH is around pH = 7.1; therefore, the amount of soluble Zn (II) species is significantly decreased. It should also be noted in Figure 3-8 that the position of the reduction peaks for Cu (II), Sn (II) and Sn (IV) are shifted negatively as the pH of the solution is increased from 4.1 to 7.1. Also, the cathodic current at -1.25 V significantly decreased with an increase of pH, as indicated in Figure 3-9. This indicates that the hydrogen evolution becomes inhibited in solution of a higher pH when the CZT film is electrodeposited at -1.25 V. The morphology of the CZT films is remarkably changed by the contribution of the hydrogen evolution reaction at different pH, as illustrated in Figure 3-10. The CZT film deposited from a solution with pH = 4.1 is mostly composed of triangle crystals with an average size of ~ 500 nm. The film exhibits a rough surface as a result of strong hydrogen evolution during the electrodeposition of the film. In contrast, the CZT films electrodeposited from a solution with pH = 5.1, 6.1 and 7.1 consist of round shaped crystals and smoother and compact films are obtained due to less hydrogen evolution. The average size of the crystals decrease from ~ 300 nm (pH = 5.1) to ~ 200 nm (pH = 6.1) and less than ~100 nm (pH = 7.1).
Figure 3-8: Composition of CZT films electrodeposited in an aqueous solution containing 20 mM CuSO₄·5H₂O + 10 mM ZnSO₄·7H₂O + 10 mM SnSO₄ and 200 mM Na₅C₆H₅O₇·2H₂O with different pH.

Figure 3-9: Linear sweep voltammograms for CZT films electrodeposited in an aqueous solution containing 20 mM CuSO₄·5H₂O + 10 mM ZnSO₄·7H₂O + 10 mM SnSO₄ with different concentrations of Na₅C₆H₅O₇·2H₂O.
Figure 3-10: SEM images of CZT film electrodeposited in an aqueous solution containing 20 mM CuSO₄·5H₂O + 10 mM ZnSO₄·7H₂O + 10 mM SnSO₄ and 200 mM of Na₃C₆H₅O₇·2H₂O with different pH.

Analysis of the plots of \((J/J_m)^2\) vs. \(t/t_m\) (Figure 3-11b) made from the corresponding chronoamperograms (Figure 3-11b) were made for CZT deposited from electrolyte solutions with pH = 6.1 and pH = 7.1. The results indicate that CZT nucleation and growth in both the solutions is progressive. This is in agreement with different sizes of CZT crystals observed under both conditions as shown in Figure 3-10. Chronoamperograms for pH = 4.1 and pH = 5.1 are not applicable for generating a plot of \((J/J_m)^2\) vs. \(t/t_m\).
Figure 3-11: (a) Chronoamperograms for electrodeposition of CZT films from electrolyte solutions with different pH; (b) Corresponding non-dimensional $(J/J_m)^2$ vs. $t/t_m$ plots compared with theoretical curves for instantaneous and progressive nucleation and growth mechanisms.
3.4 CONCLUSIONS

In this work, the effects of applied potential, concentration of a tri-sodium citrate complexing agent, and pH of electrolyte solution on the composition and morphology of electrodeposited CZT films were evaluated in an aqueous electrolyte solution containing 20 mM Cu (II), 10 mM Sn (II) and 10 mM Zn (II). The results of the study showed that a potential range of -1.20 to -1.25 V, a tri-sodium citrate concentration of 200 mM to 400 mM, and a pH of 5.1 - 6.1 are the optimal conditions needed to be employed to obtain CZT films with a nearly stoichiometric ratio of Cu: Zn: Sn = 2: 1: 1 with uniform morphology, and excellent adherence to the Mo substrate.
3.5 REFERENCES


Chapter 4: Electrochemical growth mechanism of a Cu-Zn-Sn film on a Molybdenum Substrate

SYNOPSIS

In this chapter, the electrochemical growth mechanism of the CZT film on a Mo/SLG substrate has been revealed by analysis of the film thickness, charge consumption, elemental and phase composition, and surface morphology. The CZT films were electrodeposited for 30 sec – 20 min using optimized experimental conditions in Chapter 3: potential of -1.25 V, 200 mM of tri-sodium citrate, pH of 6.1. The film thickness was measured by SEM cross-sectional image. The charge consumption during the electrodeposition was measured by I-T curve. The composition of the CZT films was determined by EDS measurement. The morphology of the CZT film was observed by SEM. H₂ evolution on different substrates was evaluated by linear sweep voltammetry. The phase composition in the CZT films was calculated through Rietveld refinement of XRD patterns of the films. This chapter is written in a journal article-style and the manuscript will be submitted to Electrochimica Acta.
STATEMENT OF CONTRIBUTION

The authors listed below have certified that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and
5. they agree to the use of the publication in the student’s thesis and its publication on the Australian Digital Thesis database consistent with any limitation set by publisher requirements.

In the case of this chapter:

Electrochemical growth mechanism of a Cu-Zn-Sn film on a Molybdenum Substrate

Tubshin Hreid, Anthony P O’Mullane, Henry J. Spratt, Geoffrey Will* and Hongxia Wang*

To be submitted to Electrochimica Acta

<table>
<thead>
<tr>
<th>Contributor</th>
<th>Statement of contribution</th>
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<tbody>
<tr>
<td>Tubshin Hreid</td>
<td>Designed and conducted experiments, wrote the manuscript.</td>
</tr>
<tr>
<td>Anthony P O’Mullane</td>
<td>Revised the manuscript</td>
</tr>
<tr>
<td>Henry J. Spratt</td>
<td>Refinement of XRD patterns</td>
</tr>
<tr>
<td>Geoffrey Will</td>
<td>Revised the manuscript and supervision</td>
</tr>
<tr>
<td>Hongxia Wang</td>
<td>Revised the manuscript and supervision</td>
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Principal Supervisor Confirmation

I have sighted email or other correspondence from all co-authors confirming their certifying authorship.

QUT Verified Signature

Geoffrey Will

12/10/2015

Name Signature Date
Electrochemical growth mechanism of a Cu-Zn-Sn film on a Molybdenum Substrate

Tubshin Hreid*, Anthony P O’Mullane*, Henry J. Sprattb, Geoffrey Will*** and Hongxia Wang***

*School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, Brisbane, QLD, 4001, Australia

b Central Analytical Research Facility, Institute for Future Environments, Queensland University of Technology, Brisbane, QLD, 4001, Australia

a* Corresponding Authors: g.will@qut.edu.au ; hx.wang@qut.edu.au

ABSTRACT

Cu-Zn-Sn (CZT) metallic films were electrodeposited on molybdenum coated soda lime glass (Mo/SLG) substrates at a constant potential using an aqueous electrolyte solution containing Cu (II), Zn (II), Sn (II) ions and tri-sodium citrate. The electrochemical growth mechanism of the CZT film has been elucidated by analysis of the film thickness, charge consumption, elemental and phase composition and surface morphology. In the initial stage (30 sec) of the deposition, a thin film consisting of copper and tin was formed on the Mo/SLG substrate whereas zinc was only incorporated in the film after 30–60 sec of deposition. It was found that copper and tin can be easily electrodeposited onto the surface of Mo/SLG; however, this was not the case for zinc, due to the influence of H₂ evolution. However, zinc was successfully deposited on the substrate consisting of a CuSn alloy due to its weak catalytic activity for H₂ evolution. It was also confirmed that the electrochemical growth (except for the first 1 minute) of a CZT film: (i) obeys Faraday’s Law in that the film thickness is linearly dependent on the charge consumption, and the film grows at a constant rate; (ii) the composition of the CZT film remains constant throughout the deposition process and copper, tin and zinc are distributed evenly in
the film; and (iii) the content (at %) of the main phases Cu₆Sn₅ and Cu₅Zn₈ in the CZT film are constant during the growth of the film. The ability to generate a homogeneous CZT film in such a controlled manner will have significant benefits for the production of solar active materials.

4.1 INTRODUCTION

Electrodeposition has been widely used to coat metal/alloy films for both decorative and protective purposes due to its advantages such as simplicity, low-cost, environmental friendliness, and its viability for large-scale production [1-5]. Compared to a single metal film, alloy films usually have superior properties such as greater corrosion resistance and higher magnetic permeability, which can be designed to meet special mechanical and/or chemical requirements [1, 6, 7]. Over recent years, alloy films based on the three metals of copper, zinc and tin (Cu-Zn-Sn or CZT) have attracted attention because it is widely used as an essential precursor film to synthesize new sustainable photovoltaic materials such as Cu₃ZnSnS₄ (CZTS) and Cu₃ZnSnSe₄ (CZTSe) after being sulfurized or selenized respectively [8-12].

Mo/SLG is generally used as the back contact substrate for CZTS and CZTSe thin film-based solar cells due to its optimal band alignment and strong ohmic contact behaviour [13, 14]. A precursor CZT alloy film is initially electrodeposited on a Mo/SLG substrate prior to further treatment to form CZTS and CZTSe thin films [12, 15, 16]. The nature of the substrate is important for the electrodeposition of metal/alloy films, as it offers the seed sites for the initial nucleation of the metal deposits. A citrate electrolyte solution with pH = 5.0 - 6.0 has been developed for the electrodeposition of CZT films due to its environmentally-friendly nature and strong complexing abilities to Cu (II), Zn (II) and Sn (II) cations [12, 17, 18], allowing CZT films to be fabricated from a single electrolyte bath. In many cases, a much higher concentration of zinc salt was
required in the plating mixture to ensure that CZT films were fabricated with the
desired stoichiometry of Cu: Zn: Sn = 2: 1: 1 [15, 19- 24]. This indicates that the
electrodeposition of zinc is most likely less effective than that of copper and tin.
Since the reduction potential of zinc is more negative than the onset potential of
hydrogen evolution, a certain degree of hydrogen bubbling often accompanies the
electrodeposition of a CZT film. Indeed, the effect of hydrogen on electrodeposited
metals/alloys such as embrittlement and the formation of metal hydrides have
been described in the literature [25, 26].

Although many works [15-18, 20, 21, 23, 24, 27, 28] have been published on the
electrodeposition of CZT metallic films on Mo/SLG substrates, the literature has not
reported the detailed electro-reduction behaviours of Cu (II), Zn (II) and Sn (II)
ions during the electrochemical growth of a CZT film. Nevertheless, an in-depth
understanding of the electrochemical growth mechanism of CZT films is of high
importance because it can provide essential information on the nucleation, growth
and alloying process of the CZT film that can be used to develop effective
electrodeposition routes for the preparation of CZTS or CZTSe films. Besides, a
detailed study on the compositional homogeneity during the electrodeposition of a
CZT film from a single electrolyte bath is essential and important to produce new
knowledge that can benefit the preparation of high quality CZTS or CZTSe films. It
is well known that a compositionally homogeneous CZT precursor film is highly
desirable for the formation of high purity CZTS films [29]. In comparison to the
electrodeposition of a single metal, the co-electrodeposition of copper, zinc and tin is
much more complicated. The formation of binary alloys that are likely to be present
during the co-electrodeposition of three metal salt precursors could, in principle,
significantly affect the compositional homogeneity of the CZT film.
In the present work, CZT films were electrodedeposited on Mo/SLG substrates from a citrate electrolyte aqueous solution containing Cu (II), Zn (II) and Sn (II) ions at constant potential. The films with different thicknesses were made with deposition times ranging from 30 sec – 20 min. The electrochemical growth mechanism of the CZT film is revealed through a comprehensive investigation of the film thickness, composition, and morphology as well as identification of an alloying process of Cu with Sn and Zn. This research offers new knowledge into the fundamental understanding of the electrodeposition of CZT films.

4.2 EXPERIMENTAL

4.2.1 ELECTROCHEMICAL METHODS AND MATERIAL SYNTHESIS

Mo/SLG substrates were ultrasonically cleaned in acetone, ethanol and MilliQ water in sequence for 5 minutes and then dried under a flow of nitrogen. The electrochemical deposition was implemented with a three-electrode configuration consisting of a Mo/SLG substrate working electrode, Pt wire counter electrode and an Ag/AgCl/saturated KCl reference electrode using an electrochemical workstation (VSP-300 Bio-logic). Freshly prepared aqueous solutions with the same pH = 6.10 ± 0.05 (adjusted by sulfuric acid) were used for the electrodeposition of different metallic thin films. The composition of the electrolyte solutions is shown in Table 4-1. All the chemicals used were of analytical grade and supplied by Alfa Aesar. The electrodeposition of the films was carried out at a constant potential of -1.25 V at ambient temperature (26 ± 1°C). The active area of the films was 0.2 cm². All the films were electrodeposited from a 40 ml electrolyte solution to ensure the concentration change caused by the consumption of metal cations during the deposition process was negligible.
Table 4-1: Electrolyte solutions for electrodeposition of different metallic thin films

<table>
<thead>
<tr>
<th>No.</th>
<th>Target Film</th>
<th>Chemical composition</th>
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<tbody>
<tr>
<td>(a)</td>
<td>CZT</td>
<td>200 mM Na₃C₆H₅O₇·2H₂O + 20 mM CuSO₄·5H₂O + 10 mM ZnSO₄·7H₂O + 10 mM SnSO₄·7H₂O</td>
</tr>
<tr>
<td>(b)</td>
<td>Cu</td>
<td>200 mM Na₃C₆H₅O₇·2H₂O + 20 mM CuSO₄·5H₂O</td>
</tr>
<tr>
<td>(c)</td>
<td>Sn</td>
<td>200 mM Na₃C₆H₅O₇·2H₂O + 10 mM SnSO₄·7H₂O</td>
</tr>
<tr>
<td>(d)</td>
<td>Zn</td>
<td>200 mM Na₃C₆H₅O₇·2H₂O + 10 mM ZnSO₄·7H₂O</td>
</tr>
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4.2.2 CHARACTERIZATION

The surface and cross-section morphology of the deposited thin films were characterized by field emission scanning electron microscopy (FESEM, JEOL 7001F). Compositional analysis and elemental mapping for the CZT thin films were characterized by energy dispersive X-ray spectroscopy (EDS, JEOL 7001F) at an acceleration voltage of 20.0 kV. The relative error of the EDS detector was approximately ±2.0 % for Cu, ±2.0 % for Zn and ±3.0 % for Sn. The minimum EDS detection limitation for each metal element is 0.1 % (atomic percentage). The X-Ray diffraction patterns of CZT films were collected using a PANalytical X’Pert Pro diffractometer operating at 40 kV using Cu Kα radiation in Bragg-Brentano geometry. The relative molar percentages of the crystal phases in the CZT films were determined by refining the XRD diffraction patterns. The Rietveld refinement against the collected XRD patterns was performed using Total Pattern Analysis Solutions (Topas V5, Bruker). The CuKa5_Berger emission profile was used to describe the incident X-rays. The XRD data between 2θ = 36 to 42 and 71 to 76 ° were excluded in the refinement as these regions contained the intense XRD peaks due to the Mo/SLG substrate.
4.3 RESULTS AND DISCUSSION

4.3.1 REDUCTION POTENTIAL OF THE METAL CATIONS IN THE ELECTROLYTE SOLUTION

Figure 4-1a shows the linear sweep voltammograms recorded in the electrolytes (Table 4-1) investigated in this work. The peak potentials for the reduction of Cu (II), Sn (II) and Zn (II) ions on the Mo/SLG electrode are well-separated and occur at -0.32 V (pink line), -0.85 V (blue line) and -1.20 V (cyan line), respectively. In the presence of all three metal cations it is observed that the reduction potential for Sn (II) is shifted positively to -0.77 V (black line). This is ascribed to the fact that under these conditions Sn (II) is now being reduced on an electrode surface containing Cu instead of solely Mo. It should be noted that in the majority of cases there is a distinct cathodic peak at cathodic -0.93 V, which is also present in the absence of any metal cation in solution. This can be attributed to the generation of hydrogen which is facilitated by the presence of citrate in the electrolyte according to the mechanism reported in reference [17] and is illustrated in reaction [1] and [2].

\[
H_3(C_6H_4O_6)OH \leftrightarrow (C_6H_4O_6)OH^3^- + 3H^+ \quad [1]
\]

\[
2H^+ + 2e^- \leftrightarrow H_2 \quad [2]
\]

To confirm whether this is in fact a hydrogen evolution response, linear sweep voltammograms were recorded at the Mo/SLG electrode in 200 mM Na$_3$C$_6$H$_5$O$_7$·2H$_2$O where the pH was adjusted from 4.8 to 8.0, as shown in Figure 4-1b. Clearly, the peak for H$_2$ generation significantly increases when the pH of the solution decreases. It is found that this H$_2$ evolution peak occurs at -0.93 V (green line) in a solution with pH = 6.1 on the surface of the Mo electrode. However, in the presence of metal cations different behaviour was observed. The potential of H$_2$ evolution is positively shifted to -0.85 V (pink line, Figure 4-1a) on the surface of
copper while it was more negative at -0.97 V with a significantly reduced intensity (a weak and broad peak, black line, Figure 4-1a) when all three metal cations are present in the solution. It should be noted that at this potential only Cu and Sn would have been deposited on the electrode surface at this potential. A weak Zn (II) reduction peak at -1.20 V was recorded at the surface of both Mo/SLG (cyan line) and a surface consisting of electrodeposited Cu and Sn (black line). Therefore, to reduce Cu (II), Sn (II) and Zn (II) together to form a CZT film, a potential of -1.25 V was used with the expectation that hydrogen generation also evolved.
Figure 4-1: (a) Linear sweep voltammograms for the reduction of indicated metal cations in an aqueous solution containing 200 mM Na₃C₆H₅O₇·2H₂O, pH of all the other electrolyte solutions were adjusted to 6.10 ± 0.05 by sulfuric acid; (b) Linear sweep voltammograms showing H₂ evolution on the surface of Mo/SLG in the background electrolyte solutions of 200mM Na₃C₆H₅O₇·2H₂O and at pH = 8.0, 6.1 and 4.8 respectively, adjusted by sulfuric acid.
4.3.2 FILM THICKNESS AND CHARGE CONSUMPTION FOR CZT FILM GROWTH

Figure 4-2a shows the current and charge passed during the electrodeposition of a CZT film as a function of time (blue line). At the beginning of the deposition process, the cathodic current density decreases rapidly, which indicates a decrease in the concentration of Cu (II), Sn (II) and Zn (II) ions in the vicinity of electrode surface due to their electro-reduction. After the initial rapid decrease in the current it becomes steady indicating the reductions of the diffused metal cation from the bulk solution. The consumed charge increases linearly with deposition time as shown in Figure 4-2a. The deposition rates and film thickness of the CZT film with time are shown in Figure 4-2b. The CZT film deposited for 5, 10, 15 and 20 minutes shows a near constant deposition rate of ~ 57 nm/ min with a linear relationship between the film thickness and deposition time from 5 minutes onwards. In contrast, the deposition rate of the film in the initial period is much higher than that from 5 minutes onwards. The deposition rate is 106 nm/ min and 94 nm/ min, in the first 30 seconds and 1 minute, respectively, as indicated in Figure 4-2b. The CZT film thickness and deposition rates are derived from the cross-sectional SEM data presented in Figure 4-3. It should be noted that the 30 second electrodeposited film (Figure 4-3a) only consists of copper and tin as confirmed in section 4.3.4. Therefore, it is labelled as 30 sec CuSn instead of 30 sec CZT. The above results indicate that the CZT film growth obeys Faraday’s law as illustrated in equation 1 [6]:

\[ H = \frac{Q}{nFD} \]  

(Eq.1)

where \( H \) is the film thickness, \( Q \) is the consumed charge, \( A \) is the atomic weight of the metal, \( S \) is the surface area, \( d \) is the density of the metal, \( n \) is the number of electrons involved in the reaction, and \( F \) is Faraday’s constant (96485 C/mol).
Figure 4-2: (a) J-T deposition curve for CZT film formation (blue line) and the corresponding J-Q line (red line); (b) CZT film deposition rate at different duration (blue line) and film thickness over deposition duration (red line).
Figure 4-3: SEM cross-section images of CZT films electrodeposited for (a) 30 sec, (b) 1 min, (c) 5 min, (d) 10 min, (e) 15 min, and (f) 20 min.

4.3.3 CZT FILM MORPHOLOGY AND COMPOSITION

The surface morphology of the CZT films deposited for different durations is shown in Figure 4-4 and the compositions of these films are shown in Figure 4-5. It should be noted that each EDS compositional value shown is the average value of four samples prepared under the same experimental conditions. During the initial nucleation and growth of metals in the first 30 sec of deposition, only copper (62 %) and tin (38 %) are found in the non-fully covered film which consists of small nano grains of ~ 20-30 nm in diameter (the SEM image of bare Mo is given in Figure 4-7 in section 4.3.4). When the deposition time increases to 1 min, zinc (10 %) was found in the film and the surface of the Mo becomes fully covered by a compact and smooth CZT film with grain sizes of around 30-50 nm in diameter. This indicates that zinc starts to incorporate into the film when the deposition time is beyond 30 seconds. The investigation of the mechanism behind this phenomenon will be presented in section 4.3.4. When the deposition time was extended from 5 to 20 minutes, the surface of the film becomes rougher and large clusters of grains were formed.
Figure 4-4: SEM images of CZT films electrodeposited for (a) 30 sec, (b) 1 min, (c) 5 min, (d) 10 min (e) 15 min, and (f) 20 min.

The grain sizes increase in size with deposition time. The average grain sizes are in the range of 100-150 nm after 5 min, 150-200 nm after 10 min, 180-230 nm after 15 min and 200-300 nm after 20 min electrodeposition time, respectively, as shown in Figure 4-4 (c, d, e and f). Correspondingly, the relative content of copper, zinc and tin showed nearly parallel lines after 5 minutes of electrodeposition (Figure 4-5), indicating that copper, zinc and tin are deposited into the film at a constant rate after the initial deposition of the film. The relatively minor deviation from the dashed line at the 5 minutes time point can be attributed to the bottom layer of film that does not contain zinc which accounts for 50 nm (Figure 4-3a) of the CZT film within a thickness of 290 nm at this time point (Figure 4-3c). Also, it can be seen in the EDS elemental mapping in Figure 4-6 that copper, zinc and tin are evenly distributed throughout the film electrodeposited for 20 minutes.
Figure 4-5: Composition of the CZT films electrodeposited for 30 sec – 20 minutes.

Figure 4-6: EDS mapping of the CZT film electrodeposited for 20 minutes.
4.3.4 SUBSTRATE EFFECTS ON THE ELECTRODEPOSITION OF ZINC

As confirmed in the previous section, the deposition of Zn did not begin until after 30 - 60 seconds of electrodeposition, where a thin layer consisting of Cu and Sn would have formed (Figure 4-5). The electrodeposition of Zn on a bare Mo/SLG substrate (Figure 4-7a) was also conducted at -1.25 V for 10 minutes using an electrolyte solution containing only Zn (II) ions (Table 4-1d). Interestingly, it was found that Zn was not detected on the surface of Mo/SLG, as confirmed by the EDS measurement in Fig S1a [supporting information]. SEM imaging also indicated that there was no deposit on the surface of Mo/SLG as the image is essentially the same as Bare Mo (Figure 4-7a). In contrast, a considerable amount of Zn was detected on the surface of the 30 sec CuSn/Mo/SLG substrate (as shown in Figure 4-3a and 4-4a) under the same conditions as the attempted electrodeposition of Zn on the Mo/SLG substrate, as confirmed by the EDS measurement in Figure 4-S1 (d) [supporting information]. In order to examine Zn electrodeposition on different metallic substrates, individual copper and tin layers were deposited on the Mo/SLG at -1.25 V for 30 sec from electrolyte solutions (Table 4-1a and 1b) containing copper and tin cations only, respectively. The morphologies of the electrodeposited copper and tin are shown in Figure 4-7b and 7c. Copper is formed as a uniform and compact layer consisting of ~ 30 nm nano-grains (Figure 4-7b). In contrast, tin showed a bigger grain size in a range between 40 nm - 200 nm. The substrates were then used for the electrodeposition of Zn. However, similar to the bare Mo/SLG case, Zn was not detected on the surface of copper or tin substrates either after being electrodeposited at -1.25 V for 10 minutes. This was also confirmed by the EDS spectra in Figure 4-S1 (b) and (c) [supporting information].
Cyclic voltammograms of Zn (II) reduction on the surface of different metallic substrates were conducted to further examine the ability of these metallic layers to facilitate the deposition of zinc onto the substrate (Figure 4-8). A weak and broad Zn (II) reduction peak was found between the potentials of -1.10 V and -1.30 V on the surface of Mo (green line), Cu/Mo (pink line), and Sn/Mo (blue line); however, there is no corresponding Zn oxidation peak appearing in the reverse scan, which indicates that metallic zinc is not present on the surface in the timescale of this experiment. This is in agreement with the failed deposition of Zn on these substrates. Even though a reduction process for Zn (II) electrodeposition is clear from the voltammetric data, a layer of zinc is undetectable on the surface of the substrates via EDS measurement after deposition for 10 minutes at -1.25 V. This suggests that
although Zn is likely to nucleate on the surface, its growth is inhibited and subsequently removed from the surface under the influence of hydrogen evolution. In contrast, pronounced Zn (II) reduction and Zn$^0$ oxidation peaks are observed in the cyclic voltammetric curves using substrates based on Cu/Sn/Mo (Figure 4-8, black line). Therefore, it appears that H$_2$ evolution on the substrates has a significant effect on the Zn deposition process. For the 30 sec CuSn/Mo/SLG substrate no significant peak attributed to the evolution of H$_2$ (at cathodic -0.97 V) is observed (Figure 4-8, black) which is in agreement with the weak H$_2$ peak that was observed on the CuSn surface (Figure 4-1, black line) in section 4.3.1. As a result, Zn is successfully electrodeposited on this 30 sec CuSn/Mo/SLG substrate. In contrast, significant H$_2$ peaks (Figure 4-8 green, pink and blue lines) are found for bare Mo, Cu/Mo and Sn/Mo, which could explain why Zn was not able to be electrodeposited on these substrates.

Figure 4-8: Cyclic voltammograms of different substrates immersed in 200 mM Na$_3$C$_6$H$_5$O$_7$·2H$_2$O + 10 mM ZnSO$_4$·7H$_2$O aqueous solution. Scan rate: 10 mV s$^{-1}$. The potential was started at 0 V and was scanned in the negative direction.
It is known that H₂ evolution on substrates can inhibit the crystallization of Zn by formation of zinc hydride and zinc hydroxide [30, 31] as well as creating a physical barrier. It should be noted in Figure 4-8 that significant reduction peaks at -0.23 V (pink line) and -0.71 V (blue line) are found on the surface of Cu/Mo and Sn/Mo, respectively. This indicates that copper oxide/ hydroxide and tin oxide/ hydroxide exist on the copper and tin films, respectively [26].

The catalytic abilities of the different substrates for H₂ evolution were investigated by examination through a linear sweep voltammetry in an aqueous solution containing 200 mM Na₃C₆H₅O₇·2H₂O. Figure 4-9 shows the cathodic current density recorded at different substrates at an applied potential of -1.25 V where only the reaction of 2H⁺ + 2e⁻ = H₂ occurs. The results indicate that the catalytic activity for H₂ evolution on the substrates are in the order of Cu > Mo > Sn > 30 s CuSn. This conclusion can explain the incorporation of Zn into the film after 30 seconds of electrodeposition of the CZT film.
Zn deposition is inhibited in the initial stage due to strong H₂ evolution on the Mo substrate. However, Cu and Sn are easily electrodeposited on the Mo/SLG at the same potential with H₂ evolution as discussed previously. At an applied potential of -1.25 V the rate of Cu and Sn deposition will be significantly higher than that for hydrogen evolution when the standard reduction potentials are considered. In contrast, the rate of Zn deposition will be significantly lower than that for Cu and Sn and will not be able to compete with the evolution of hydrogen from the surface. Presumably, during the electrodeposition of CZT, Cu and Sn are initially electrodeposited as a CuSn alloy film in the initial stages (first 30 seconds) as the morphology of CuSn (Figure 4-4a) is different from the individually deposited copper (Figure 4-7b) and tin (Figure 4-7c). Once the rate of reduction of Zn (II) to Zn⁰ overcomes H₂ evolution from the surface, which is suppressed by the formation of CuSn (Figure 4-9), Zn can be deposited. The CuSn alloy is less active for H₂
evolution compared to Mo, Cu or Sn, and therefore, once CuSn is formed on the Mo surface, Zn starts to be deposited as confirmed in Figure 4-5.

4.3.5 ALLOYING PROCESS OF THE CZT FILM

The XRD patterns of the CZT films are shown in Figure 4-10a. CuSn electrodeposited for 30 seconds and the CZT film electrodeposited for 1 minute are too thin to be detected by XRD. Alloy phases of Cu₆Sn₃, Cu₅Zn₈ and CuZn₅ are found in the films after 5, 10, 15 and 20 minutes of electrodeposition and the diffraction patterns of these phases are stronger with prolonged deposition time. The relative molar composition of the two main phases Cu₆Sn₃ and Cu₅Zn₈ remains largely stable within a range of (40.8±2.2) % and (59.6±2.6) % respectively, during the electrochemical growth of the CZT film, as illustrated in Figure 4-10b. This can be attributed to the constant and homogenous deposition of individual copper, zinc, and tin during the CZT film growth (1–20 min) as confirmed in section 4.3.3 (Figure 4-5). The content of the phase composition was determined via Rietveld refinement of the XRD patterns (Figure 4-10). The diffraction pattern at 2θ = 42° for the CuZn₅ phase was excluded in the refinement due to close proximity of the strong peak from Mo/SLG.
Figure 4-10: (a) XRD patterns; and (b) phase compositions of the CZT films electrodeposited for different duration.

4.4 CONCLUSIONS

In this work, homogeneous metallic thin films consisting of Cu, Zn and Sn (CZT) were co-electrodeposited from an electrolyte solution containing Cu (II), Zn (II) and Sn (II) ions on a molybdenum coated soda lime glass substrate. The formation mechanism of the CZT film was investigated through a thorough investigation of the evolution of the film thickness, composition, and morphology as well as crystal
phases. The results showed that only Cu and Sn were deposited on the molybdenum substrate in the initial stage of the deposition process before Zn was introduced into the film at a later stage. This is attributed to the fact that Zn deposition is inhibited by strong hydrogen evolution occurring on the surface of Mo. The CZT film was found to grow at a constant rate after this initial stage and obeyed Faraday’s law of electrolysis. During CZT film growth (except for the first minute), the relative content of Cu, Zn and Sn remained constant and were evenly distributed in the film. Further study by XRD confirmed that alloys of Cu₆Sn₃ and Cu₅Zn₈ and CuZn₅ were formed in the CZT film, suggesting a simultaneous alloying process. It was found in the XRD refinement that the content of the main alloys phases of Cu₆Sn₃ and Cu₅Zn₈ were constant during CZT film growth.

4.5 SUPPORTING INFORMATION

![Figure 4-S1: EDS spectrum of different substrates after electrodeposition of Zn for 10 min (a) Bare Mo/SLG, (b) 30 sec Cu on Mo/SLG, (c) 30 sec Sn on Mo/SLG; and (d) 30 sec Sn on Mo/SLG.](image-url)
4.6 REFERENCES


Chapter 5: Precisely Controlled Synthesis of High Quality Kesterite Cu$_2$ZnSnS$_4$ Thin Film via Co-electrodeposited Cu-Zn-Sn Alloy Film

SYNOPSIS

This chapter outlines how CZTS films were fabricated by the sulfurization of CZT films. All of the CZT films were electrodeposited for 10 minutes to obtain film thickness of less than 560 nm. Different concentrations of metal cations were used to deposit CZT films with a range of compositions. Finally, a pure kesterite CZTS film with a desired composition of Cu/ (Zn + Sn) $\approx$ 0.8 and Zn/Sn $\approx$ 1.2 was synthesised. The composition of the CZTS films was determined by EDS measurement. Morphology of the CZT and CZTS films was observed by SEM. Distribution of elements in the CZT and CZTS films was detected by EDS mapping scans. Phase identification of the CZTS film was determined by XRD and Raman measurements. Photoelectrochemical test of the CZTS film was conducted in 0.2 M Eu(NO$_3$)$_3$ (pH = 2.3) aqueous solution under the illumination of green light. This chapter is written in a journal article-style and was published in the Journal of Nanotechnology and Nanoscience (2015) 15, 1-6.
STATEMENT OF CONTRIBUTION

The authors listed below have certified that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and
5. they agree to the use of the publication in the student’s thesis and its publication on the Australian Digital Thesis database consistent with any limitation set by publisher requirements.

In the case of this chapter:

**Precisely Controlled Synthesis of High Quality Kesterite Cu₂ZnSnS₄ Thin Film via Co-electrodeposited Cu-Zn-Sn Alloy Film**

Tubshin Hreid, Vincent Tiing Tiong, Molang Cai, Hongxia Wang*, Geoffrey Will*

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<th>Contributor</th>
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<tr>
<td>Tubshin Hreid</td>
<td>Designed and conducted experiments, wrote the manuscript.</td>
</tr>
<tr>
<td>Vincent Tiing Tiong</td>
<td>Aided in Raman measurement</td>
</tr>
<tr>
<td>Molang Cai</td>
<td>Aided in XRD measurement</td>
</tr>
<tr>
<td>Hongxia Wang</td>
<td>Revised manuscript and supervision</td>
</tr>
<tr>
<td>Geoffrey Will</td>
<td>Revised manuscript and supervision</td>
</tr>
</tbody>
</table>

Principal Supervisor Confirmation

I have sighted email or other correspondence from all co-authors confirming their certifying authorship.  

QUT Verified Signature

Geoffrey Will  
12/10/2015

Name  Signature  Date
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Chapter 6: Effects of metal ions concentration on electrodeposited Cu-Zn-Sn film and its application in kesterite Cu$_2$ZnSnS$_4$ solar cells

SYNOPSIS

In this paper, the effects of Cu (II), Zn (II) and Sn (II) concentration on composition, morphology, and alloy phases content of electrodeposited Cu-Zn-Sn films were comprehensively studied. All the CZT films were electrodeposited for 10 minutes. The composition of the CZT films was determined by EDS. The morphology study of the CZT films was investigated by SEM. Content of alloy phases in the CZT films was calculated through Rietveld refinement of XRD patterns. XRD and Raman techniques were used to identify the CZTS film phase. Finally, a kesterite CZTS film solar cell was fabricated and it exhibited 2.15 % of power conversion efficiency under illumination intensity of 100 mA cm$^{-2}$. This chapter is written in a journal article-style and it was published in RSC Advances (2015) 5, 65114-65122.
STATEMENT OF CONTRIBUTION

The authors listed below have certified that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and
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In the case of this chapter:

Effects of metal ions concentration on electrodeposited Cu-Zn-Sn film and its application in kesterite Cu$_2$ZnSnS$_4$ solar cells

Tubshin Hreid$^a$, Jianjun Li$^b$, Yi Zhang$^b$, Henry J. Spratt$^c$, Hongxia Wang$^{a*}$, Geoffrey Will$^{a*}$

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<tr>
<td>Tubshin Hreid</td>
<td>Designed and conducted experiments, wrote the manuscript.</td>
</tr>
<tr>
<td>Jianjun Li</td>
<td>Tested the CZTS solar cell</td>
</tr>
<tr>
<td>Yi Zhang</td>
<td>Fabricated the i-ZnO/ZnO:Al/Ni:Al layers of solar cell</td>
</tr>
<tr>
<td>Henry J. Spratt</td>
<td>Refinement of XRD patterns</td>
</tr>
<tr>
<td>Hongxia Wang</td>
<td>Revised manuscript and supervision</td>
</tr>
<tr>
<td>Geoffrey Will</td>
<td>Revised manuscript and supervision</td>
</tr>
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</table>

Principal Supervisor Confirmation

I have sighted email or other correspondence from all co-authors confirming their certifying authorship.

Geoffrey Will 12/10/2015

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Name                  Signature                  Date

QUT Verified Signature
Effects of metal ions concentration on electrodeposited Cu-Zn-Sn film and its application in kesterite Cu₂ZnSnS₄ solar cells

Tubshin Hreid¹, Jianjun Li², Yi Zhang³, Henry J. Spratt⁴, Hongxia Wang⁵, Geoffrey Will⁶

¹School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, Brisbane, QLD. 4001, Australia

²Institute of Photoelectronic Thin Film Devices and Technology, Nankai University, Tianjin 300071, China

³Central Analytical Research Facility, Institute for Future Environments, Queensland University of Technology, Brisbane, QLD. 4001, Australia

a* Corresponding Authors: hx.wang@qut.edu.au; g.will@qut.edu.au

ABSTRACT

In this work, the effects of the concentrations of Cu (II), Zn (II) and Sn (II) ions in electrolytic bath solution on the properties of electrochemically deposited CuZnSn (CZT) films were investigated. The study of the composition of the CZT film has shown that the metallic content (relative atomic ratio) in the film increased linearly with the increase of the metal ion concentration. It is the first time that the relationship of the composition of the alloy phases in the co-electrodeposited CZT film with the concentration of metal ions has been revealed. The results have confirmed that the formation and content of Cu₆Sn₃, Cu₃Zn₈ alloy phases in the film were directly controlled by the concentration of Cu (II). SEM measurements have shown that Sn (II) had significant impacts on the film morphology which became more porous as a result of the larger nucleation size of tin. The changes of surface properties of the film was also confirmed by chronoamperometry characteristic (i - t) deposition curve. By optimization of the metal ions concentrations in the electrolyte solution, a copper-poor and zinc-rich kesterite
Cu$_2$ZnSnS$_4$ (CZTS) film was synthesized by sulfurization of the deposited CZT film. The solar cell with the CZTS film showed an energy conversion efficiency of 2.15% under the illumination intensity of 100 mW cm$^{-2}$.

6.1 INTRODUCTION

The approach based on electrodeposition has been extensively used in practice to fabricate metal/alloy film [1-3] and materials [4, 5] due to the fact that it is facile, low-cost, environmentally-friendly, and viable for large-scale production. Ternary alloys based on CuZnSn (CZT) have long been employed in industries for decorative and protective purposes [6]. In recent years, it has been widely used as an essential precursor to synthesize new sustainable photovoltaic materials, such as Cu$_2$ZnSnS$_4$ (CZTS) [7-10] and Cu$_2$ZnSnSe$_4$ (CZTSe) [11-14]. Solar cells using electrodeposited Cu$_2$ZnSnS$_4$ (CZTS) and Cu$_2$ZnSnSe$_4$ (CZTSe) with efficiency up to 8.0% [15-18] have been reported.

Generally, electrodeposition of CZT metallic film can be achieved by the deposition of Cu/Zn/Sn stacked elemental layers using separate electrolyte solutions containing each metal ion via a multi-step method [18-22], or by co-deposition using a single solution containing all metal ions in one step [23-27]. The method based on co-electrodeposition has advantages over the stacked elemental layers method because of its simpler procedure, which is more favourable for high-throughput production. However, compared to the stacked elemental layers approach, it is more challenging to control the co-electrodeposition process of CZT film due to the complexity of the electrolyte system and the different reduction potentials of the metal ions. The simultaneous presence of copper, tin and zinc metal ions with the complexing agent in the electrolyte solution can generate various complex species which may have different solubility and can lead to precipitation in the electrolyte.
solution [28, 29]. Moreover, in the deposition process, the CZT film deposited from copper, zinc and tin ions may contain a mixture of metals and binary alloys phases such as \( \eta \)-Cu\(_{6.26}\)Sn\(_5\), Sn and \( \gamma \)-CuZn\(_5\) [30] and Zn, Sn, Cu\(_6\)Sn\(_3\) and CuZn\(_2\) [8]. It has been reported that the alloy phases such as Cu\(_6\)Sn\(_5\) and Cu\(_5\)Zn\(_8\) in the CZT film have significant effects on the morphology of the CZTS film [10].

It is important to develop an effective electrodeposition route for the fabrication of CZT film as a high-quality CZT precursor film is one of the prerequisites to synthesize CZTS film with desired optical and electronic properties for application in solar cells. According to the generally accepted electrodeposition principles [6], two types of variables can influence the properties of the deposited film: (i) electrolyte solution variables such as the concentration of metal ion, the nature of complexing agent, and the pH of the electrolyte solution; (ii) operational variables such as the electrodeposited current density or potential, deposition temperature, and stirring of solution. A complexing agent is an important component in an electroplating solution as it can narrow the gap between different reduction potentials of metals ions and enhance the solubility of metal ions [28]. It can also reduce the grain size of the deposits and improve the homogeneity and roughness of the deposited film [6]. Different complexing agents such as Copper Glo [31, 32], EDTA [33], citric acid [28], and tri-sodium citrate [8, 12-15, 17, 26, 27, 34, 35] have been used in aqueous electrolyte solutions for the electrodeposition of CZT films. Among them, tri-sodium citrate is the most widely used because of its effective complexing abilities to Cu (II), Zn (II) and Sn (II) ions and its environmentally-friendly nature [28, 29]. Recently, the effects of the concentration of tri-sodium citrate on the electrodeposition process of CZT film and on the compositions of the deposits were investigated by M. Slupska et al. [29] while the effects of the applied potentials on the composition
of CZT films were studied by C. Gougaud et al. [28]. However, the report on
the influence of the concentration of metal ions on the electrodeposited CZT film
using tri-sodium citrate as complexing agent is rare. The concentration of metal ions
could have great impact on CZT film formation through influencing the mass
transfer process. Therefore, it is important both fundamentally and practically to
distinguish the effects of metal ions concentration on the properties of
electrodeposited CZT film in order to gain an in-depth understanding of the
formation mechanism of CZT film. This work has investigated the effect of the
concentration of each metal ion on the composition, morphology, and crystal
structure of the electrodeposited CZT film using static electrolyte solutions
containing a constant content of tri-sodium citrate as complexing agent. For the first
time, the dependence of the formation of alloys in the co-electrodeposited CZT film
on the concentrations of metal ions in the electrolyte was determined
quantitatively. A kesterite CZTS film with desired copper-poor and zinc-rich
composition was synthesized by controlling the concentrations of the metal ions in
the electrolyte solution. The corresponding CZTS solar cell showed energy
conversion efficiency of 2.15 % under illumination intensity of 100 mA cm⁻².
The research provides new insights into the preparation of high quality CZT and
CZTS films for solar cell applications through controlling the electrodeposition
procedure.

6.2 EXPERIMENTAL

6.2.1 CHEMICALS

Molybdenum coated soda lime glass (Mo/SLG) substrates were
ultrasonically cleaned by acetone, ethanol and MiliQ water in sequence for 5
minutes and dried under nitrogen flow gas. All the chemicals used were
analytical agents and supplied by Alfa Aesar unless otherwise stated.
6.2.2 PREPARATION OF CZT AND CZTS FILMS

The electrodeposition of CZT films was implemented with a three-electrode configuration consisting of Mo/SLG substrate working electrodes, Pt wire counter electrodes and Ag/AgCl/Saturated KCl reference electrodes using an electrochemical workstation (VSP-300 Bio-logic). In order to investigate the effects of the concentration of each metal ion on the property of the deposited CZT film, freshly prepared aqueous solutions containing different concentrations of metal ions were used as electrolytic baths. The detailed compositions and the pH value of each solution are shown in Table 6-1. The solutions containing different concentrations of Cu (II) are named as A-series (A1B1C1 – B5), of Zn (II) are labelled as B-series (A1B1C1 – B5), and of Sn (II) as C-series (A1B1C1 – C5). The starting electrolyte solution is labelled as A1B1C1, which contains 10.0 mM of each metal ion. For the electrodeposition of copper, zinc and tin individual metal, the electrolyte solution consisted of 10.0 mM of each metal sulphate and 200 mM Na3C6H5O7·2H2O. The pH value of each electrolyte solution was adjusted to 6.2 using sulfuric acid. Due to the difficulty of direct deposition of Zn on Mo substrate, the substrate for the electrodeposition of the metal was based on a thin layer of CZT film which was made by electrodeposition of the solution A1B1C1 for 10 minutes. The reduction potential of each metal ion was determined by a linear sweep voltammetry [Figure 6-S1, Supplementary information].
Table 6-1: Chemical composition and pH of electrolyte solutions containing different concentrations of metal ions

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<tr>
<td><strong>Different concentrations of copper ion</strong></td>
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<tr>
<td><strong>Different concentrations of zinc ion</strong></td>
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<td>B2</td>
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</table>

A negative constant potential of -1.25 V (vs. Ag/AgCl/Saturated KCl) was applied to deposit CZT films for 10 minutes as well as individual metal films at temperature 26±1 °C. Mo/SLG substrates with an active area of 0.2 cm² (circle shape) were used in the electrodeposition for the investigation of the effects of metal ions concentration on CZT films, as well as for electrodeposition of individual metal. A larger area of CZT film (2.2 cm × 2.2 cm) with thickness of ~ 800 nm was prepared for the fabrication of thin film solar cell. The CZTS film was synthesized by sulfurizing the electrodeposited CZT film at 550 °C for 30 minutes in a rapid thermal processing (RTP) furnace (OTF-1200X, MTI) filled with argon (12.0 Torr). The internal
temperature of the furnace chamber was heated from ambient temperature to 550 °C in 1 minute.

6.2.3 FABRICATION OF CZTS SOLAR CELL

The CZTS thin film solar cell adopted an architecture of Mo/CZTS/CdS/i-ZnO/ZnO:Al/Ni:Al with an active area of 0.34 cm². The cell was made by following the procedure below. A 60 nm CdS buffer layer was deposited above the CZTS film using a chemical bath solution containing 1.0 mM Cd₂(CH₃COO)₂, 6.0 mM CH₃COONH₃, 5.0 mM thiourea and 25% ammonia water (5 ml in 250ml bath aqueous solution) by putting the film in the solution for 10 minutes at 82 ± 2 °C. This was followed by the deposition of the window layer consisting of 50 nm i-ZnO and 500 nm ZnO : Al layers by sputtering. The cell was completed by deposition of Ni/Al grid contact by electron beam evaporation [36].

6.2.4 CHARACTERIZATION

The composition of the CZT and CZTS films were determined by energy dispersive X-ray spectroscopy (EDS, JEOL 7001F) at an acceleration voltage of 20.0 kV. The relative error of the EDS detector was approximately ±2.0% for Cu, ±2.0% for Zn, and ±3.0% for Sn. The surface and cross-sectional morphology of CZT and CZTS films were measured by field emission scanning electron microscopy (FESEM, JEOL 7001F). The X-Ray diffraction patterns of CZT and CZTS films were collected using a PANalytical X’Pert Pro diffractometer operating at 40 kV using Cu Kα radiation in Bragg-Brentano geometry. The relative molar percentages of the crystal phases in the CZT films were determined by refining the XRD diffraction patterns. The Rietveld refinement against the collected XRD patterns was performed using
Total Pattern Analysis Solutions (*Topas* V5, Bruker). CuKa5_Berger emission profile was used to describe the incident X-rays. The XRD data between 2θ = 36° and 42° and 71° to 76° were excluded in the refinement as these regions contained the intense XRD peaks due to Mo/SLG substrate. A Raman spectrometer (Renishaw inVia Raman microscope) was used to measure the Raman spectrum of the CZTS thin film. The laser excitation wavelength at 532 nm and 785 nm were used in the Raman measurement respectively. The *J-V* characteristic performance of the CZTS solar cell was measured using a solar simulator with AM1.5 spectrum and an illumination intensity of 100 mW cm⁻².

### 6.3 RESULTS AND DISCUSSION

#### 6.3.1 EFFECTS OF CONCENTRATION OF METAL IONS ON THE COMPOSITIONS OF CZT FILMS

The dependence of the content of electrodeposited metal (Cu, Zn and Sn) in the film on the concentration of corresponding metals ions is shown in **Figure 6-1** (a, b and c). The compositional result is an average of three samples prepared under the same conditions. For the electrolyte solution with a concentration of 10.0 mM for all the three metal salts (**A1B1C1**), a CZT film with a composition (molar ratio) of Cu: Zn: Sn = 1.48: 1.37: 1.00 was obtained. The deviation of the composition from the ratio of the metal ion concentration (1: 1: 1) in the solution suggests the three metals have different deposition rates. Specifically, the deposition rates of the metal ions should be in the order of Cu (II) > Zn (II) > Sn (II). It has been reported that the metal ions can interact with the complexing agent to form non-electroactive metal citrate complexes [29] such as $\text{ZnH}_2\text{Cit}_2$ and $\text{Zn}_2\text{Cit}_2^{4+}$ or precipitation components such as $\text{Cu}_3\text{SO}_4(\text{OH})_4$, $\text{Cu}_3\text{SO}_4(\text{OH})_6$, $\text{Zn}_2\text{Cit}$, $\text{Zn}_4(\text{OH})_6\text{SO}_4$, $\text{Sn}(\text{OH})_2$, which could decrease the effective deposition of metal ions on the substrate.
Figure 6-1: Dependence of metal content in the electrodeposited CZT films as a function of different concentrations of metal ions: (a) Cu (II); (b) Zn (II); and (c) Sn (II) in the electrolyte solutions.
Nevertheless, it is observed that the content of specific metal in the CZT films increases linearly with the increase of the corresponding metal ion concentration in the electrolyte solution while the relative content of the other two metals decrease linearly. It is also observed in Figure 6-1 (a, b and c) that the slopes of the plots for the two metals with constant concentration (10.0 mM) in the electrolyte solution are different. This should be attributed to the different deposition rates of the metals and the fact that the electrodeposition of CZT film involves the formation of alloys, including Cu₆Sn₅, Cu₅Zn₈ phases, instead of pure metals. Therefore, a change of each metal ion concentration would change the surface property of the CZT film, which affects the deposition rate of each metal as shown in the following section.

6.3.2 EFFECTS OF CONCENTRATION OF METAL IONS ON MATERIAL PHASES IN CZT FILMS

X-ray diffraction was employed to characterize the material phases in the CZT film (Figure 6-2 a, b and c). It was found that alloys of Cu₆Sn₅ and Cu₅Zn₈ exist in the film together with metal tin. The relative contents of the material phases of Cu₆Sn₅, Cu₅Zn₈ and Sn were determined by Rietveld refinement and are correlated with the concentration of each metal ion as shown in Figure 6-2 (d, e and f). In the CZT film deposited from the electrolytic solution A1B1C1, the film is dominated by the metal Sn phase which accounts for 59.54 %, while the alloy of Cu₆Sn₅ only accounts for 11.33 % of the film. However, as the concentration of Cu (II) in the solution increases, the contents of both Cu₆Sn₅ and Cu₅Zn₈ phases increase while the content of Sn phase decreases rapidly.
Figure 6-2: XRD patterns (a, b and c) and the phases compositions (d, e and f) of the electrodeposited CZT films from electrolyte solutions containing different concentrations of Cu (II) (a, d), Zn (II) (b, e), and Sn (II) (c, f). The contents of each material phase were calculated by Rietveld refinement of the corresponding XRD patterns.
There is no Sn phase detected by XRD in the film deposited with 17.5 mM of Cu (II) in the electrolyte solution. This indicates that the increase of the Cu (II) concentration favours the formation of Cu₆Sn₅ and Cu₅Zn₈ alloys and suppresses Sn in the deposited film. However, with the increase of the concentration of Zn (II) in the electrolyte bath, the content of the Cu₅Zn₈ phase remain largely constant, the Sn phase slightly increases, while Cu₆Sn₅ phase decreases until there is no Cu₆Sn₅ phase when the Zn (II) concentration reaches 15.0 mM (Figure 6-2e). Furthermore, the increase in Sn (II) concentration is found to facilitate the formation of the Sn phase while hindering the Cu₅Zn₈ phase and has almost no effects on Cu₆Sn₅, as shown in Figure 6-2f. The results suggest that formation of both Cu₅Zn₈ and Cu₆Sn₅ alloy phases is determined by the concentration of Cu (II) instead of Zn (II) and Sn (II).

6.3.3 EFFECTS OF CONCENTRATION OF METAL IONS ON MORPHOLOGY OF CZT FILMS

The evolution of the morphology of the CZT films deposited from different concentrations of metal ions is illustrated in Figure 6-3. It is found that the morphology of the CZT films deposited from solutions (A1B1C1 - A5) containing different concentrations of Cu (II) is similar, indicating the negligible effect of the content of copper on the CZT film morphology. The films are mainly composed of ~ 200 nm crystals formed from nano-scaled grains. In contrast, the morphology of the CZT film changes slightly with the increase of Zn (II) concentration. As shown in Figure 6-3 (A1B1C1 - B5), the increasing content of zinc in the film leads to the more defined spaces between crystal grains and rougher film surface. Meanwhile, Sn (II) on the CZT film morphology is even more pronounced. When the concentration of Sn (II) increases, the film becomes porous and more rough as illustrated in Figure 6-3.
Chapter 6: Effects of metal ions concentration on electrodeposited Cu-Zn-Sn film and its application in kesterite Cu2ZnSnS4 solar cells

(A1B1C1 – C5). The agglomerations of grains are also observed in higher concentrations of Sn (II), as shown in Figure 6-3 (C3 – C5).

**Figure 6-3:** SEM images of CZT films electrodeposited from electrolyte solutions containing different concentrations of metal ions; Cu (II) (A series), Zn (II) (B series), and Sn (II) (C series).
The different morphological behaviour induced by the metal ions should be related to the different nucleation mechanism associated with the metals Cu, Zn and Sn respectively in the electrodeposited film. In order to clarify this, the morphology of the films of copper, tin and zinc separately electrodeposited on a CZT/Mo/SLG substrate was investigated. Mo/SLG was not used as substrate for the deposition because it was found that Zn could not be electrodeposited on the surface of Mo/SLG under the reduction potential used. The results show that the average particle size of the film with copper is around 40 nm (Figure 6-4a) and that of zinc varies from several nanometres to a few hundred nanometres (Figure 6-4b), while the film with tin is composed of micro- meters sized islands composed of few hundred nanometres crystals (Figure 6-4c). This confirms the larger nucleation size of tin compared to copper and zinc. The different morphologies of the films in Figure 6-4 infer that the morphologies of Cu₆Sn₅ and Cu₅Zn₈ alloys should be indirectly affected by the nucleation size of each metal copper and zinc and tin.

Figure 6-4: SEM images of electrodeposited individual metal (a) Cu, (b) Zn and (c) Sn on CZT/Mo/SLG substrate.

Obviously, tin has the most significant influence on morphology of the CZT film. The increase of tin content (Figure 6-1c) made the film rougher and more porous as seen in Figure 6-3 (A1B1C1 - C5). The XRD pattern in Figure 6-2c shows that the tin crystal grows along the preferred directions of
(020). This is also supported by the plate-like crystals formed in the film as marked by a blue circle in the inserted plot in Figure 6-3 (C5).

6.3.4 CHRONOAMPEROMETRY CHARACTERISTIC (I-T) CURVE

The chronoamperometry characteristic (i-t) curve for the electrochemical deposition of CZT films can also indicate the changes of interface between the deposited metal film and the electrolyte solution during the deposition process [37]. The i-t curves of the CZT films deposited using different electrolyte solutions are illustrated in Figure 6-5 (a, b and c). As demonstrated, the cathodic current density decreases rapidly at the initial stage (about the first 50 seconds for A1B1C1) of the deposition. This is due to the decrease of concentrations of metal ions in the vicinity of the electrode surface caused by electrochemical reduction. After this instance, the current becomes stable. The i-t curve of each metal ion concentration displays different features. In the case of varying the concentration of Cu (II), all the i-t curves show a similar trend, with the cathodic current becoming constant after 50 seconds, as shown in Figure 6-5a, suggesting a constant surface area of the films during the deposition. This is in agreement with the similar morphologies of the films with different concentrations of Cu (II), shown in Figure 6-3 (A1B1C1 - A5). However, for the deposition with different concentrations of Zn (II) in the electrolyte solution, the cathodic current at the plateau region increases with the increase of Zn (II) concentration, as shown in Figure 6-5b. This indicates the enhancement of the surface area of the deposited films, which is consistent with the more rough surface morphology of the film, shown in the Figure 6-3 (A1B1C1 - B5).
Figure 6-5: Comparison of the $i-t$ curves for the electrodeposition of CZT films with different concentrations of (a) Cu (II); (b) Zn (II); and (c) Sn (II).
It should be noted that significant peaks (Figure 6-5b) are observed in the i-t curves at the deposition time between 30–100 seconds for different Zn (II) concentrations, and the peak intensity increases with the concentration of Zn (II). This is attributed to the fact that the reduction of Zn (II) does not occur until sufficient CuSn are present on the surface of the Mo. This appears to occur at 30–60 seconds and is speculated to be due to a lack of reduction ability of Zn (II) to deposit on Mo at the voltage [Figure 6-S2, supplementary information]. Remarkably, with the increase of Sn (II) concentration, the cathodic current at the plateau region increases rapidly and cannot reach a steady value at all, as illustrated in Figure 5c. This is ascribed to the enhanced surface area of the films as a result of the formation of porous structured films shown in Figure 6-3 (A1B1C1 – C5). Nevertheless, a common trend of the increased cathodic currents in the plateau region with the increasing concentration of each metal ion has been observed in all the electrolyte solutions (Figure 6-5, a b and c). It suggests the deposition current is dependent on the concentration of each metal ion.

6.3.5 CHARACTERIZATION OF CZTS FILM

A CZTS film with copper-poor (Cu/(Zn + Sn) ≈ 0.8) and zinc-rich (Zn/Sn ≈ 1.2) composition has been reported to benefit the performance of solar cells [38, 39]. Therefore, it is important to control the contents of copper, zinc and tin in the CZT precursor film in order to fabricate CZTS films with the desired composition. As demonstrated above, this can be achieved by finely tuning the concentration of the metal ions in the electrolyte solution. By optimization of the concentrations of the metal ions, a CZT film with composition (atomic ratio) of Cu/ (Zn + Sn) = 0.69, Zn/Sn = 1.02 was deposited from an aqueous electrolyte solution containing 13.0 mM
CuSO₄•5H₂O, 12.0 mM ZnSO₄•7H₂O and 10.0 mM SnSO₄ with 200 mM Na₃C₆H₅O₇•2H₂O. The thickness of the deposited CZT film is 0.83 µm according to the measurement of the cross-sectional SEM image (Figure 6-6a). The film is uniformly composed of spherical crystallites measuring 200 nm (Figure 6-6b) and is well-adhered to the Mo/SLG substrate. The CZT film was transformed into CZTS through a high temperature sulfurization process at 550 °C for 30 minutes. The CZTS thin film had the composition (atomic ratio) of Cu/ (Zn + Sn) = 0.74, Zn/ Sn = 1.33 and S/ (Cu+ Zn+ Sn) = 1.05, based on EDS measurement. The composition of the film falls in the desired compositional range of CZTS films which have shown good performance in solar cells. It is found that the ratios of Cu/ (Zn + Sn) and Zn/Sn in the CZTS film are higher than the ratios in corresponding CZT film. This is attributed to the loss of tin during the high temperature sulfurization process [40, 41]. The thickness of the CZTS film is 1.78 µm and large polycrystalline grains of 0.3 - 1.0 µm can be seen in the compact CZTS film, as shown in Figure 6-6c and 6-6d.
Figure 6-6: SEM cross-sectional and surface images of optimal CZT film (a and b) and corresponding CZTS film (c and d).

Moreover, the crystal structure of the CZTS film adopts kesterite phase (JCPDS 01 - 075 - 4122) as confirmed by the XRD pattern shown in Figure 6-7a. Nevertheless, XRD alone cannot rule out the existence of secondary phases such as Cu$_2$SnS$_3$ and cubic ZnS in the film because these materials have similar XRD patterns with CZTS [42]. Hence, Raman spectroscopy was used to distinguish these potential impurities from that of CZTS. Herein, both the 532 nm and 785 nm laser were applied as excitation source in the Raman measurement. The Raman peaks in Figure 6-7b show that no peaks, due to Cu$_2$SnS$_3$, are observed. However, a cubic ZnS phase may exist in the film because the characteristic scattering peak of ZnS at around 350 cm$^{-1}$ is observed in the Raman spectrum with 785 nm laser excitation, although the intensity of the peak (located at 353 cm$^{-1}$) is quite weak [43]. The other peaks in both spectra can be assigned to the Raman scattering of kieserite CZTS that have been reported previously [43, 44]. Compared to the spectrum measured by 532 nm laser excitation, more peaks were detected by the 785 nm laser. This is attributed to the effect of vibration resonance because the 785 nm excitation is close to the bandgap (1.5 eV) of CZTS.
6.3.6 PERFORMANCE OF CZTS SOLAR CELL

The performance of the thin film solar cell using the CZTS film under the illumination of 100 mW cm$^{-2}$ (AM 1.5) is shown in Figure 6-8. The solar cell shows an energy conversion efficiency of 2.15% with $J_{sc} = 11.16$ mA cm$^{-2}$,
Voc = 0.47 V and ff = 0.47. All these characteristic parameters are lower than those reported (η = 3.74 %, Jsc = 13.4 mA cm⁻², Voc = 0.595 and ff = 0.47) in the highest efficiency solar cell made by the co-electrodeposition method [24]. Jiang et al. [18] have demonstrated that preheating treatment can significantly improve the performance of solar cells made from electrodeposited stacked metal layers precursor films. A similar effect would be expected for the film made by co-electrodeposition. It has been noticed that a preheating treatment of CZT film was employed in the work of the high efficiency co-electrodeposited CZTS solar cells [24] before the CZT film was sulfurized to form CZTS, while no such procedure was used in this work. Thus the lower performance of the solar cell in this work could be related with the different thermal treatment used in the film fabrication. The series resistance (R_s = 22.69 Ω cm²) and shunt-resistance (R_sh = 290.13 Ω cm²) of the solar cell are shown in **Figure 8**. It is well known that a high efficient solar cell requires low R_s and high R_sh. The relatively high R_s value of 22.69 Ω cm² in this work compared to what has been reported in a high efficiency solar cell¹⁴ (R_s = 4.10 Ω cm² and η = 7.3 %) should be one of the factors for the lower ff in the present work.
The higher $R_s$ is probably a result of the voids and small-sized crystals formed in the bottom layer of the CZTS film (Figure 6-6c). These voids may also work as recombination centres to cause lower $J_{sc}$ and $V_{oc}$, and further decrease the conversion efficiency of the solar cell.

### 6.4 CONCLUSIONS

The effects of the concentrations of Cu (II), Zn (II) and Sn (II) ions in the electrolyte solution on the composition, material phases and morphologies of the electrodeposited CZT films were systematically studied in this work. It has been found that the content of metal in the CZT films was linearly dependent on the concentration of the corresponding metal ion in the electrolyte solution. Moreover, it has been found that the increase of Cu (II) concentration in the solution facilitated the formation of Cu$_6$Sn$_5$ and Cu$_5$Zn$_8$ alloy phases. However, the increase of Zn (II) and Sn (II) concentration had no influence on the formation of these alloys. The investigation of the film by SEM has shown that Cu (II) had no effect on the CZT film morphology while Zn (II) increased both crystal size and surface roughness of
the film. Sn (II) showed the most dramatic effect on the CZT film morphology with the formation of porous film. The different morphological dependence with different metals was attributed to the various electrochemical nucleation sizes of the metals.

The changes of the surface property of the CZT with different metal contents were also confirmed by chronoamperometry characteristic (i-t) deposition curves. Through tailoring concentrations of the metal precursor salts in the electrolyte solution, a copper-poor and zinc-rich CZTS film with kesterite structure was synthesized and the corresponding solar cell exhibited an energy conversion efficiency of 2.15% under the illumination intensity of 100 mW cm$^{-2}$. 
6.5 SUPPORTING INFORMATION

Supplementary data associated with this article can be found in Figure 6-S1 and 6-S2 as mentioned in the main text.

**Figure 6-S1:** Linear sweep voltammogram of the co-electrodeposition of copper tin and zinc (Mo/SLG substrate working electrodes, Pt counter electrodes and Ag/AgCl/Saturated KCl Reference electrodes) immersed in 200 mM Na$_3$C$_6$H$_5$O$_7$·2H$_2$O and 20 mM CuSO$_4$·5H$_2$O, 10 mM ZnSO$_4$·7H$_2$O and 10 mM SnSO$_4$. Scan rate: 10 mV s$^{-1}$. The potential started at 0 V and was scanned in the negative direction.
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Figure 6-S2: EDS spectrum of the electrodeposited alloy film with different duration (a) 30 sec and (b) 1 min film, both deposited from the electrolyte solution containing 200 mM Na3C6H5O7·2H2O and 20 mM CuSO4·5H2O, 10 mM ZnSO4·7H2O and 10 mM SnSO4.
6.6 REFERENCES


Chapter 6: Effects of metal ions concentration on electrodeposited Cu-Zn-Sn film and its application in kesterite Cu2ZnSnS4 solar cells


Chapter 7: Conclusions and Future Work

7.1 CONCLUSIONS

This work contributes to the electrochemical fabrication of CZT film and the promising photovoltaic material of CZTS film. In recent years, CZT film has been employed as an essential precursor to synthesize CZTS films for applications in low-cost and sustainable solar cells. Electrodeposition provides a low-cost, facile and environmentally-friendly method to fabricate CZT films. In particular, the one-step electrodeposition approach is simple and time-saving. It has a potential application in large-scale and high-throughput production of CZT films, and for CZTS or CZTSe films after they have been sulfurized or selenized. In this work, one-step electrodeposition of CZT films on molybdenum substrates were comprehensively investigated using an aqueous electrolyte solution containing Cu (II), Zn (II), Sn (II) cations and tri-sodium as complexing agent. The contributions arising from this work to knowledge in research findings in science are illustrated below.

The applied potential, concentrations of complexing agent (tri-sodium citrate), and pH of electrolyte solutions are important impact factors influencing the electrochemical formation of metal/alloy films. The effects of these factors on morphology and composition of electrodeposited CZT films are investigated in this work. A CZT precursor film with a nearly stoichiometric ratio of Cu: Zn: Sn = 2: 1: 1, uniform morphology and strong adhesion to substrate is preferable for the synthesis of high quality CZTS and CZTSe photovoltaic films. The results of this study have demonstrated that a potential in the range of -1.20 to -1.25 V, tri-sodium citrate concentration of 200 mM - 400 m, and pH of 5.1 - 6.1 are the optimal ranges to
obtain a CZT film with a nearly stoichiometric ratio, uniform morphology and strong adhesion to substrate.

For the first time, electrochemical growth mechanism including nucleation, growth rate and alloying process of CZT film on a molybdenum substrate was revealed. Also, the study of compositional and alloy homogeneity during the CZT film growth was conducted. The study of electrochemical growth mechanism has shown that only Cu and Sn were deposited on the molybdenum substrate in the initial stage of the deposition process before Zn was introduced into the film at a later stage. This is attributed to the fact that Zn deposition is inhibited by strong hydrogen evolution occurring on the surface of Mo. The CZT film was found to grow at a constant rate after the initial stage and the growth obeys Faraday’s law of electrolysis. Moreover, alloys of Cu$_6$Sn$_5$ and Cu$_5$Zn$_8$ and CuZn$_5$ were formed in the CZT film, suggesting a simultaneous alloying process. It was found that the main phases of Cu$_6$Sn$_5$ and Cu$_5$Zn$_8$ were constantly formed during the growth of CZT film. The results of this compositional study have indicated that during the CZT film growth (except for the first minute), the relative content of Cu, Zn and Sn remained constant and were evenly distributed in the film. The ability to generate a homogeneous CZT film in such a controlled manner will have significant benefits for further synthesis of CZTS photovoltaic film.

It has been a challenge to precisely control the composition of CZTS film via co-electrodeposited CZT precursor film because of the complexity of the electrolyte system. One way to overcome this issue is by adjusting the concentrations of the metal cations in the electrolyte solution. This method has been developed in this work to obtain CZT precursor films with controllable composition, and CZTS film with desired composition. A high quality kesterite CZTS film with the effective
composition of Cu/(Zn+ Sn) \approx 0.8, \text{ Zn/Sn} \approx 1.2 was successfully fabricated via finely controlled CZT film by co-electrodeposition. It has been found that the ratios of Cu/(Zn+ Sn) and Zn/Sn in the CZT and CZTS films are strongly dependent on the ratios of corresponding cations in the electrolyte solution. The deposition strategy demonstrated in the work can lay a foundation to yield high quality CZTS film with high-throughput for photovoltaic applications.

The concentration of metal ions in the electrolyte solution is an important factor to influence the electrochemical formation of CZT films. The effects of the concentrations of Cu (II), Zn (II), and Sn (II) ions on the composition, material phases and morphologies of the electrodeposited CZT films were systematically studied in this work. It has been found that the content of metal in the CZT films was linearly dependent on the concentration of the corresponding metal ion in the electrolyte solution. Importantly, it is the first time that the dependence of the formation of alloys in the co-electrodeposited CZT film on the concentrations of metal ions was determined quantitatively. It has been found that the increase of Cu (II) concentration in the solution facilitated the formation of Cu₅Sn₅ and Cu₅Zn₈ alloy phases. However, the concentration of Zn (II) and Sn (II) had no influence on the formation of these alloys. The morphology study of the films has shown that Cu (II) had no effect on the CZT film morphology, while Zn (II) increased both crystal size and surface roughness of the film. Sn (II) showed the most dramatic effect on the CZT film morphology with the formation of porous film. The different morphological dependence with different metals was attributed to the different electrochemical nucleation sizes of the metals. The changes of the surface properties of the CZT films with different content of metals were also confirmed by chronoamperometry characteristic \((i-t)\) deposition curves. Finally, a copper-poor and
zinc-rich CZTS film with kesterite structure was synthesized and the corresponding solar cell exhibited an energy conversion efficiency of 2.15% under the illumination intensity of 100 mW cm\(^{-2}\).

7.2 FUTURE WORK

7.2.1 EFFECTS OF ALLOY PHASES ON FORMATION OF CZTS FILM AND PERFORMANCES OF SOLAR CELLS

Although the content of the alloy phases in CZT films electrodeposited from electrolyte solutions containing different concentrations of metal ions was analysed in Chapter 6, the effects of different content of alloy phases on the formation of CZTS film including morphologies and crystal phases and their influences on the performances of solar cells are not yet evaluated. The same thickness of CZT films with different contents of alloy phases will be needed in the fabrication of CZTS films to be used for comparison of solar cell performances. It has been confirmed in Figure 4-2b in Chapter 4 that the thickness of the CZT film is linearly increased by the charge consumption involved in the electrodeposition. Therefore, electrodeposition with same charge consumption will be used to prepare CZT films from the electrolyte solutions containing different concentrations of metal ions, ensuring same thickness of CZT films.

7.2.2 STUDY OF INTERFACES BETWEEN CZTS FILM AND MOLYBEDNUM SUBSTRATE

The CZTS film synthesised in this work has exhibited a solar cell with a power conversion efficiency of 2.15%, as illustrated in Figure 6-8 in Chapter 6. It found that voids and small crystals were formed in the bottom layer of the CZTS film, as confirmed in Figure 6-6c in Chapter 6. This may originally related to the lack of Zn in the initial layer ~ 50 nm of CZT film, which is confirmed in Figure 4-4 in chapter 4. Moreover, as summarized in Table 2-8 in Chapter 2, the power conversion
efficiency of CZTS solar cell by co-electrodeposition method is considerably lower than other methods. An interfacial issue is one of the main reasons for the lower performances of solar cells. An in-depth study to confirm the connection between lack of zinc in the bottom layer of CZT film and voids and small crystals in the bottom layer of CZTS film is recommended for future. One possible solution to address this problem is that an ultra-thin film of Zn could be deposited on the Mo substrate prior to the deposition of CZT.
## Appendix

### Notes:
The references cited in tables are listed in section 2.8, Chapter 2.

**Table A-1:** Electrolyte solutions used in the literature for electrodeposition of stacked metal layers

<table>
<thead>
<tr>
<th>Substrate, Stacked metal layers and active area</th>
<th>Chemical composition of copper electrolyte and condition of Cu deposition</th>
<th>Chemical composition of zinc electrolyte and condition of Sn deposition</th>
<th>Chemical composition of tin electrolyte and condition of Zn deposition</th>
<th>Year and Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/Cu/Sn/Zn 10mm*10mm</td>
<td>0.1 M sorbitol, 1.5 M NaOH and 50 mM CuCl₂, -1.14 V (vs. Ag/AgCl)</td>
<td>0.45 M sorbitol, 2.25 M NaOH and 55 mM SnCl₂, -1.21 V (vs. Ag/AgCl)</td>
<td>pH=3 hydron buffer, 0.15 M ZnCl₂, -1.20 V (vs. Ag/AgCl)</td>
<td>2008 [77]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Cu/Zn 25mm*25mm</td>
<td>0.2 M sorbitol, 3.0 M NaOH and 0.1 M CuSO₄·5H₂O, -1.15 V (vs. Ag/AgCl)</td>
<td>0.3 M sorbitol, 2.25 M NaOH and 0.05 mM SnCl₂·5H₂O, -1.21 V (vs. Ag/AgCl)</td>
<td>pH=3 hydron buffer, 1.0 M KCl, 0.55 M ZnCl₂, -1.20 V (vs. Ag/AgCl)</td>
<td>2009 [78]</td>
</tr>
<tr>
<td>Mo/Pd/Cu/Sn/Zn</td>
<td>0.594 M CuSO₄ and H₂SO₄ (10 vol%)</td>
<td>0.0931 M SnSO₄ and H₂SO₄ (8.15 vol%)</td>
<td>0.515M ZnSO₄</td>
<td>2009 [79]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn 12mm*12mm</td>
<td>0.1 M Sorbitol, 1.5 M NaOH and 50 mM CuCl₂, -1.14 V (vs. Ag/AgCl)</td>
<td>0.45 M Sorbitol, 2.25 M NaOH and 55 mM CuCl₂, -1.21 V (vs. Ag/AgCl)</td>
<td>pH=3 hydron buffer, 0.15 M ZnCl₂, -1.20 V (vs. Ag/AgCl)</td>
<td>2009 [80]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn 25mm*25mm</td>
<td>0.9 mM Empigen BB (surfactant), 0.2 M sorbitol, 3.0 M NaOH and 0.1 M CuSO₄, -1.20 V (vs. Ag/AgCl), 150 rpm rotation</td>
<td>3.6 mM Empigen BB, 50 mM Sn(SO₂CH₃)₂ and 1.0 M CH₃SO₃H, -0.72V (vs. Ag/AgCl), 100 rpm rotation</td>
<td>pH=3 hydron buffer, 0.1 M ZnSO₄·7H₂O, and 0.5 M K₂SO₄, -1.20 V (vs. Ag/AgCl), 150 rpm rotation</td>
<td>2010 [75]</td>
</tr>
<tr>
<td>FTO/Zn/Cu/Sn 1.5 - 2.0 cm²</td>
<td>0.78 M CuCN, 1.3 M NaCN, 0.017 M Na₂SO₄, 0.068 M ZnCN, and 0.018M Na₂SnO₃·3H₂O, 1.6 V, ~10 mA/cm², 58 °C</td>
<td>0.49 M sodium potassium tartrate and 0.088 M SnCl₂, -1.6V, ~0.45 mA/cm², 58 °C</td>
<td>0.49 M sodium potassium tartrate and 0.088 M ZnCl₂, -1.6V, ~4.5 mA/cm², 58 °C</td>
<td>2012 [81]</td>
</tr>
<tr>
<td>Material</td>
<td>Dimension</td>
<td>Electrolyte Details</td>
<td>Electrolyte Details</td>
<td>pH Details</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn</td>
<td>157.3 g/L CuSO₄·5H₂O and 10 g/L H₂SO₄, 10 mA/cm²</td>
<td>Commercial chemistry 89 RTU, 20 mA/cm²</td>
<td>0.2 M ZnSO₄·7H₂O and 0.5 M methane sulfonic acid, pH=2.0, 10 mA/cm²</td>
<td>2012 [38]</td>
</tr>
<tr>
<td>Cu plate/Sn/Cu/Zn, 2 cm*2 cm</td>
<td>0.2 M sorbitol, Empigen BB, 0.01 M Cu(NO₃)₂</td>
<td>1.0 M Sn(SO₄)₂ and Empigen BB, 50 mM ZnCl₂ and 2.0 M KCl</td>
<td></td>
<td>2013 [82]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn</td>
<td>0.05 M CuSO₄·5H₂O, 0.02 M citric acid and 0.04 M trisodium citrate, -0.4 V (vs. Ag/AgCl)</td>
<td>1.0 M CH₃SO₃H and 0.05 M Sn(SO₄)₂ and 1.0 M Empigen BB, -0.54 V (vs. Ag/AgCl)</td>
<td>pH=3 hydron buffer, 0.1 M ZnSO₄·7H₂O and 0.5 M K₂SO₄, -1.2 V (vs. Ag/AgCl)</td>
<td>2014 [64]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn</td>
<td>0.05 M CuSO₄·5H₂O, 0.02 M citric acid and 0.04 M trisodium citrate, -0.4 V (vs. Ag/AgCl)</td>
<td>1.0 M CH₃SO₃H and 0.05 M Sn(SO₄)₂ and 1.0 M Empigen BB, -0.55 V (vs. Ag/AgCl)</td>
<td>pH=3 hydron buffer, 0.1 M ZnSO₄·7H₂O and 0.5 M K₂SO₄, -1.2 V (vs. Ag/AgCl)</td>
<td>2014 [74]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Cu/Zn</td>
<td>0.2 M sorbitol, 3.0 M NaOH and 1.0 mmol CuCl₂, -1.3 V (vs. Ag/AgCl)</td>
<td>0.3 M sorbitol, 1.5 M NaOH and 0.25 mmol SnCl₂, -0.7 V (vs. Ag/AgCl)</td>
<td>pH=3 hydron buffer, 0.5 mmol ZnCl₂ and 1.0 M KCl, -0.9 V (vs. Ag/AgCl)</td>
<td>2014 [83]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn</td>
<td>0.05 M CuSO₄·5H₂O, 0.02 M citric acid and 0.04 M trisodium citrate, -0.4 V (vs. Ag/AgCl)</td>
<td>1.0 M CH₃SO₃H and 0.05 M Sn(SO₄)₂ and 1.0 M Empigen BB, -0.54 V (vs. Ag/AgCl)</td>
<td>pH=3 hydron buffer, 0.1 M ZnSO₄·7H₂O and 0.5 M K₂SO₄, -1.2 V (vs. Ag/AgCl)</td>
<td>2014 [84]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn 2.5 cm * 2.5 cm</td>
<td>0.1 M CuSO₄·5H₂O, 0.4 mM KCl (or 3.0 M NaOH), thiourea (or D-sorbitol) and 150 ppm PEG 4000, (pH=2.5, 2.9 and 14), 1.5 mA/cm²</td>
<td>0.08 M SnCl₂·2H₂O, 0.12 M NaCl, 0.65 M Na-citrate, 1 mM PEG 200, pH=5, 2.0 mA/cm²</td>
<td>0.1 M ZnCl₂, 2.8 M KCl, 0.32 M H₃PO₄, 1 mM PEG 200, pH=4, 1.5 mA/cm²</td>
<td>2015 [85]</td>
</tr>
<tr>
<td>Mo/Cu/Zn/Sn</td>
<td>0.2 M Cu₂P₂O₇, 1.06 M K₆P₂O₇·5H₂O, 0.09 mM SeO₂</td>
<td>0.1 M SnCl₃, 1.2 mmol CuCl₂, 0.16 mol C₆H₇N₃O₇</td>
<td>0.1 mol ZnSO₄, 0.13 mol Na₂SO₄, 0.06 mol H₃BO₃</td>
<td>2015 [86]</td>
</tr>
<tr>
<td>Mo/Cu/Zn/Sn 15cm² 15cm</td>
<td>Commercial solution 5 mA/cm² deposition time &lt; 120s</td>
<td>Commercial solution 10 mA/cm² deposition time &lt; 120s</td>
<td>Commercial solution 20 mA/cm² deposition time &lt; 120s</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>-------------------------------------------------</td>
<td>-------------------------------------------------</td>
<td>-------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn</td>
<td>0.05 M CuSO₄·5H₂O, 0.02 M citric acid and 0.04 M trisodium citrate, -0.4 V (vs. Ag/AgCl)</td>
<td>1.0 M CH₃SO₃H and 0.05 M Sn(SO₂CH₃)₂ and 1.0 M Empigen BB, -0.54 V (vs. Ag/AgCl)</td>
<td>pH=3 hydron buffer, 0.1 M ZnSO₄·7H₂O and 0.5 M K₂SO₄, -1.2 V (vs. Ag/AgCl)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2015 [87]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2015 [66]</td>
<td></td>
</tr>
</tbody>
</table>
Table A-2: Experimental conditions used in literature regarding synthesis of CZTS film by electrodeposited stacked metal layers

<table>
<thead>
<tr>
<th>Substrate, Stacked metal layers and active area</th>
<th>Soft annealing condition</th>
<th>Sulfurization condition</th>
<th>CZTS film thickness</th>
<th>Efficiency of the best solar cell (active area)</th>
<th>Year and Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/Cu/Sn/Zn 10mm*10mm</td>
<td>non</td>
<td>100 - fold excess of sulfur, 1 bar argon, 40 °C min⁻¹, 550°C, 2h</td>
<td>unknown</td>
<td>non</td>
<td>2008 [77]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Cu/Zn</td>
<td>non</td>
<td>100 - fold excess of sulfur or H₂S (5% in argon), 1 bar argon, 40°C min⁻¹, Small argon flow, 550°C, 2h</td>
<td>unknown</td>
<td>non</td>
<td>2009 [78]</td>
</tr>
<tr>
<td>Mo/Pd/Cu/Sn/Zn</td>
<td>non</td>
<td>10sc, N₂ flow, 600 °C, 2h</td>
<td>unknown</td>
<td>0.98 % (0.129 cm²)</td>
<td>2009 [79]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn 12mm*12mm</td>
<td>non</td>
<td>50 mg sulfur, 10 mbar H₂(10%) + N₂, 40°C min⁻¹, 580°C, 30min</td>
<td>unknown</td>
<td>non</td>
<td>2009 [80]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn 25mm*25mm</td>
<td>non</td>
<td>100 mg sulfur, 500mbar H₂(10%) + N₂, 575 °C, 2h</td>
<td>~1.5 µm</td>
<td>3.2 % (0.234 cm²)</td>
<td>2010 [75]</td>
</tr>
<tr>
<td>FTO/Zn/Cu/Sn 1.5 - 2.0 cm²</td>
<td>non</td>
<td>argon, 550 °C, 2h</td>
<td>unknown</td>
<td>non</td>
<td>2012 [81]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn</td>
<td>210 - 350 °C N₂, 30 min</td>
<td>N₂, 540 - 590 °C, 5 - 15 min</td>
<td>~2.0 µm</td>
<td>7.3 % (unknown)</td>
<td>2012 [38]</td>
</tr>
<tr>
<td>Cu plate/Sn/Cu/Zn, 2 cm*2 cm</td>
<td>non</td>
<td>50 mg sulfur, N₂ flow, 100 °C min⁻¹, 580°C, 2h</td>
<td>~1.5 µm</td>
<td>non</td>
<td>2013 [82]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn</td>
<td>310 °C, 40 - 150 min</td>
<td>5 - 10 mg sulfur, 590 °C, 10 min</td>
<td>~1.3 µm</td>
<td>8.0 % (0.03 cm²)</td>
<td>2014 [64]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn</td>
<td>350 °C, 20 - 40 min</td>
<td>5 mg sulfur, 580 °C, 10 min</td>
<td>~2.0 µm</td>
<td>5.6 % (unknown)</td>
<td>2014 [74]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Cu/Zn Mo/Cu/Zn/Cu/Sn Mo/Zn/Cu/Sn/Cu Mo/Sn/Cu/Zn/Cu 2cm*2cm</td>
<td>non</td>
<td>N₂ flow, 40 ml min⁻¹, 30 g sulfur, 240 °C, 2h, crystallised at 580 °C, 2h</td>
<td>~2.0 µm</td>
<td>2.3 % (unknown)</td>
<td>2014 [83]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn</td>
<td>310 °C 2.5 h</td>
<td>sulfur 590 °C, 10 min</td>
<td>~1.2 µm</td>
<td>6.43 % (unknown)</td>
<td>2014 [84]</td>
</tr>
<tr>
<td>-------------</td>
<td>-------------</td>
<td>------------------------</td>
<td>---------</td>
<td>------------------</td>
<td>--------</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn 2.5 cm * 2.5 cm</td>
<td>Non</td>
<td>sulfur, N₂ 10°C min⁻¹, 550°C, 1h</td>
<td>~0.6 µm</td>
<td>non</td>
<td>2015 [85]</td>
</tr>
<tr>
<td>Mo/Cu/Sn/Zn Mo/Cu/Sn/Zn Mo/Cu/Sn/Zn/Cu Mo/Cu/Sn/Zn/Cu Sn Mo/Cu/Sn/Zn/Cu Sn</td>
<td>200 °C 30 min</td>
<td>Ar + H₂S, 560 torr 500°C, 1h</td>
<td>~1.5 µm</td>
<td>non</td>
<td>2015 [86]</td>
</tr>
<tr>
<td>Mo/Cu/Zn/Sn 15cm* 15cm</td>
<td>non</td>
<td>7 - 500 mbar, Ar, 10 °C S⁻¹, 350 - 550°C, 3 - 10 min</td>
<td>~2.0 µm</td>
<td>2.4 % (0.435 cm²)</td>
<td>2015 [87]</td>
</tr>
<tr>
<td>Mo/Cu/Zn/Sn</td>
<td>20 - 200 min</td>
<td>5 - 10 mg sulfur 590 °C, 10 min</td>
<td>~1.5 µm</td>
<td>8.1 % (0.05 cm²)</td>
<td>2015 [66]</td>
</tr>
</tbody>
</table>

Table A-3: Electrolyte solutions and experimental condition used in the literature regarding synthesis of CZTS film by using stacked binary alloys.

<table>
<thead>
<tr>
<th>Chemical composition of electrolyte solution and deposition condition</th>
<th>Sulfurization condition</th>
<th>CZTS film thickness</th>
<th>Efficiency of the best solar cell (active area)</th>
<th>Year and Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Zn deposition 45 mM CuSO₄·5H₂O + 220 mM ZnSO₄·7H₂O + 0.5 M Na₃C₆H₇O₆·2H₂O + 0.1 M KNaC₂H₄O₆·4H₂O, -1.25 V (vs. SCE)</td>
<td>0.05 Mpa sulfur 10°C min⁻¹, 580 °C, 30min</td>
<td>~1.2 µm</td>
<td>3.67 % (unknown)</td>
<td>2015 [88]</td>
</tr>
<tr>
<td>CuSn deposition 12 mM CuSO₄·5H₂O + 35 mM SnSO₄ + 0.5 M Na₃C₆H₇O₆·2H₂O + 0.1 M KNaC₂H₄O₆·4H₂O, - 0.9 V (vs. SCE)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table A-4: Electrolyte solution and experimental condition used in the literature regarding synthesis of CZTS film by using co-electrodeposited Cu-Zn-Sn

<table>
<thead>
<tr>
<th>Substrate used and deposited area</th>
<th>Chemical composition of electrolyte solution and deposition condition</th>
<th>Sulfurization condition</th>
<th>CZTS film thickness</th>
<th>Efficiency of the best solar cell (active area)</th>
<th>Year and Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo 2 cm*2 cm</td>
<td>0.02 M CuSO₄·5H₂O + 0.2 M ZnSO₄·7H₂O + 0.01 M SnCl₂·2H₂O + 0.5 M tri-sodium citrate, -1.1 ~ -1.2 V (vs.Ag/AgCl), 20 min</td>
<td>10 sccm, N₂, 10°C min⁻¹, 580 °C, 30 min</td>
<td>~ 3 µm</td>
<td>3.16% unknown</td>
<td>2009 [101]</td>
</tr>
<tr>
<td>Mo 10 cm*10 cm</td>
<td>3 mM Cu(II) + 3 mM Zn(II) + 30 mM Sn(V) + complexing agents + additives, 500 µg cm⁻¹, 20 min</td>
<td>Ar + H₂S (5%) 2 °C min⁻¹, 550 °C, 30 min</td>
<td>~ 1.5 µm</td>
<td>3.4% 0.5 cm²</td>
<td>2009 [102]</td>
</tr>
<tr>
<td>Cu</td>
<td>CuCl₂ + SnCl₂ + ZnCl₂ dissolved in C₆H₄OHCl and C₂H₅OH₂ (1:2) ~1.15 V (vs.Ag/AgCl)</td>
<td>sulfur, Ar 450 °C 1.5 h</td>
<td>1.0 - 4.0 µm</td>
<td>non</td>
<td>2010 [100]</td>
</tr>
<tr>
<td>Mo and FTO 0.25 - 0.50 cm²</td>
<td>0.004 M CuSO₄·5H₂O + 0.15 M ZnCl₂·7H₂O + 0.018 M Na₂Sn(OH)₆, -1.6 V</td>
<td>sulfur, Ar 2 h</td>
<td>~ 1.0 µm</td>
<td>non</td>
<td>2012 [90]</td>
</tr>
<tr>
<td>Mo 2 cm*2 cm</td>
<td>0.02 M CuSO₄·5H₂O + 0.035 M ZnSO₄·7H₂O + 0.014 M SnCl₂·2H₂O + 0.5 M tri-sodium citrate, -1.21 V (vs.Ag/AgCl), 20-40min</td>
<td>sulfur, Ar 550 °C, 10 min</td>
<td>~ 2.2 µm</td>
<td>non</td>
<td>2013 [95]</td>
</tr>
<tr>
<td>Mo 2 cm*2 cm</td>
<td>30 mM CuSO₄·5H₂O + 100 mM ZnSO₄·7H₂O + 10 mM SnSO₄·2H₂O + 100 mM tri-sodium citrate, -1.15 V (vs.SCE), 40min</td>
<td>Ar + H₂S (5%) 2 °C min⁻¹, 580 °C, 2 h</td>
<td>~0.5 – ~2.0 µm</td>
<td>non</td>
<td>2013 [92]</td>
</tr>
<tr>
<td>Mo 1 cm*6 cm</td>
<td>0.16 M CuSO₄·5H₂O + 0.33 M ZnSO₄·7H₂O + 0.08 M SnCl₂·2H₂O + 1.36 M Cu₂H₄Na₃O₂ + 1.00 M Cu₂H₄O₆, -1.62 V (vs. Ag/AgCl), 10min</td>
<td>1 bar, N₂ 10 °C min⁻¹, 200 - 600 °C, 1h</td>
<td>~ 0.5 µm</td>
<td>non</td>
<td>2013 [96]</td>
</tr>
<tr>
<td>Mo</td>
<td>35 mM CuSO₄·5H₂O + 200 mM ZnSO₄·7H₂O + 20 mM SnSO₄ + 0.5 M Cu₂H₄Na₃O₂·2H₂O + 0.1 M KNa₂CuH₄O₆·4H₂O, (pH=6, by NaOH), -1.2 V (vs. Hg/Hg₂Cl₂/KCl)</td>
<td>sulfur, 0.05M Pa, Ar 10 °C min⁻¹, 580 °C, 1 h</td>
<td>~ 2.0 µm</td>
<td>3.62% unknown</td>
<td>2014 [93]</td>
</tr>
<tr>
<td>Mo foil</td>
<td>2 cm x 1 cm</td>
<td>0.016 M CuSO₄·5H₂O + 0.072 M ZnSO₄·7H₂O + 0.037 M Na₂SnO₃·3H₂O + 0.6 M K₃P₂O₇ + additives, 5.5 mA/cm², 6 min</td>
<td>30 mg sulfur small N₂ flow 2 °C min⁻¹ or 20 °C min⁻¹, 550 °C, 15 min or 2 h</td>
<td>2.4 µm</td>
<td>non</td>
</tr>
<tr>
<td>Mo</td>
<td>0.7 cm²</td>
<td>0.02 M CuSO₄·5H₂O + 0.01 M ZnSO₄·7H₂O + 0.02 M SnSO₄ + 0.05 M (C₆H₅Na₃O₇·2H₂O or C₅H₆O₆, or EDTA) (pH=4.75, by HCl lactate acid), -1.2 V (vs. Hg/Hg₂Cl₂/KCl)</td>
<td>0.5 g sulfur N₂ + H₂S (5%, 30 torr) 580 °C, 2 h</td>
<td>~ 2.0 µm</td>
<td>2.94% unknown</td>
</tr>
<tr>
<td>Mo flexible foil</td>
<td></td>
<td>4 mM CuSO₄ + 3 mM ZnSO₄ + 3 mM SnSO₄, no complexing agent, pulse voltammetry method</td>
<td>N₂ + H₂S (5%, 30 torr) 550 °C, 1 h</td>
<td>~ 2.0 µm</td>
<td>3.82%</td>
</tr>
<tr>
<td>Mo/Cu</td>
<td></td>
<td>5 mmol CuCl₂ + 20 mmol ZnCl₂ + 20 mM SnCl₂ dissolved in choline chloride and urea (1:2) -1.2 V (vs. Hg/Hg₂Cl₂/KCl)</td>
<td>N₂ + H₂S (5%) 550 °C, 1 h</td>
<td>~ 1.0 µm</td>
<td>3.87% unknown</td>
</tr>
<tr>
<td>Mo</td>
<td></td>
<td>30 mM CuSO₄·5H₂O + 200 mM ZnSO₄·7H₂O + 25 mM SnSO₄ + 0.5 M C₆H₅Na₃O₇·2H₂O + 0.1 M KNaC₅H₄O₆·4H₂O, pH=6, -1.22 V (vs. Hg/Hg₂Cl₂/KCl), 500 s</td>
<td>0.05 M Pa, Ar 10 °C min⁻¹ 580 °C, 1 h</td>
<td>1.8 µm</td>
<td>3.74% unknown</td>
</tr>
<tr>
<td>Mo</td>
<td>2 cm x 2 cm</td>
<td>0.02 M CuCl₂ + 0.01 M ZnCl₂ + 0.02 M SnCl₂ + 0.2 M C₆H₅Na₃O₇ + 0.1 M C₅H₄O₆, pH = 4.5 – 5.5, -1.15 V (vs. Ag/AgCl), 45 min</td>
<td>0.5 g sulfur N₂ + H₂ (5%) 10 °C min⁻¹ 460 - 580 °C, 2 h</td>
<td>~ 2.5 µm</td>
<td>2.69%</td>
</tr>
<tr>
<td>Mo</td>
<td>2 cm x 1 cm</td>
<td>0.016 M CuSO₄·5H₂O + 0.072 M ZnSO₄·7H₂O + 0.037 M Na₂SnO₃·3H₂O + 0.6 M K₃P₂O₇ + additives</td>
<td>small N₂ flow 20 °C min⁻¹ 550 °C, 1 h</td>
<td>~ 1.5 µm</td>
<td>non</td>
</tr>
</tbody>
</table>
Table A-5: Electrolyte solutions and experimental conditions used in the literature regarding synthesis of CZTS film by using one-step electrolysis

<table>
<thead>
<tr>
<th>Substrate used and deposited area</th>
<th>Chemical composition of electrolyte solution and deposition condition</th>
<th>Sulfurization or crystallization condition</th>
<th>CZTS film thickness</th>
<th>Efficiencty of the best solar cell (active area)</th>
<th>Year and Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo 2 cm*2 cm</td>
<td>0.02 M CuSO₄ + 0.01 M ZnSO₄ + 0.02 M SnSO₄ + 0.02 M Na₂S₂O₃ + 0.2 M C₄H₆Na₃O₇ + 0.1 M C₆H₆O₆, -1.05 V (vs. SCE), 45 min</td>
<td>Ar, 150 – 550 °C, 1 h</td>
<td>unknown</td>
<td>non</td>
<td>2010 [114]</td>
</tr>
<tr>
<td>Mo 2 cm*2 cm</td>
<td>0.02 M CuSO₄ + 0.01 M ZnSO₄ + 0.02 M SnSO₄ + 0.02 M Na₂S₂O₃ + (0.0 - 0.6 M C₄H₆Na₃O₇, pH= 4.5 -5.0) by C₆H₆O₆, -1.05 V (vs. SCE), 45 min</td>
<td>Ar, 550 °C ,1 h</td>
<td>unknown</td>
<td>non</td>
<td>2010 [111]</td>
</tr>
<tr>
<td>Mo and ITO 2 cm*2 cm</td>
<td>0.02 M CuSO₄ + 0.01 M ZnSO₄ + 0.02 M SnSO₄ + 0.02 M Na₂S₂O₃ + 0.2 M C₄H₆Na₃O₇ + C₆H₆O₆, pH= 5.0 by C₆H₆O₆, -1.05 V (vs. SCE), 45 min</td>
<td>Ar or N₂, N₂ + H₂S 550 °C 1 h</td>
<td>unknown</td>
<td>non</td>
<td>2011 [108]</td>
</tr>
<tr>
<td>Mo 2 cm*2 cm</td>
<td>CuSO₄ · 5H₂O + ZnSO₄ · 7H₂O + SnSO₄ + Na₂S₂O₃ + 0.2 M C₄H₆Na₃O₇ + C₆H₆O₆, pH= 5.0 by C₆H₆O₆, -1.05 V (vs. SCE), 40min</td>
<td>N₂ 500 °C 30 min</td>
<td>unknown</td>
<td>non</td>
<td>2011 [115]</td>
</tr>
<tr>
<td>Mo and ITO 2 cm*2 cm</td>
<td>0.02 M CuSO₄ · 5H₂O + 0.015 M ZnSO₄ · 7H₂O + 0.02 M SnCl₂ · 2H₂O + Na₂S₂O₃ (0.001 M – 0.015 M) + 0.2 M C₄H₆Na₃O₇ + 0.01 M C₆H₆K₂O₆ · 1/2H₂O, pH= 5.0 by C₆H₆O₆, -1.05 V to -1.15 V (vs. Ag/AgCl), 15 min</td>
<td>N₂ + H₂S 550 °C 1 h</td>
<td>unknown</td>
<td>non</td>
<td>2011 [116]</td>
</tr>
<tr>
<td>Mo and ITO 2 cm*2 cm</td>
<td>0.02 M CuSO₄ · 5H₂O + 0.01 M ZnSO₄ · 7H₂O + 0.02 M SnSO₄ + 0.02 M Na₂S₂O₃ + 0.2 M C₆H₆Na₃O₇ + 0.1 M C₆H₆O₆, pH= 4.5 -5.0, -1.05 V (vs. Ag/AgCl), 45 min</td>
<td>N₂ + H₂S (5 %) 550 °C 1 h</td>
<td>0.5 - 0.6 µm</td>
<td>1.21 % unknown</td>
<td>2012 [117]</td>
</tr>
<tr>
<td>Material</td>
<td>Reaction</td>
<td>Conditions</td>
<td>Product</td>
<td>Flow Rate</td>
<td>Diameter</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>------------</td>
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<td>-----------</td>
</tr>
<tr>
<td><strong>FTO</strong></td>
<td>CuCl₂·2H₂O + ZnCl₂ + SnCl₂·2H₂O + Na₂S₂O₅, pH = 2.7, -1.1 V</td>
<td>Small N₂ flow, 50 °C min⁻¹, 400 °C, 30 min</td>
<td>N₂ + H₂S (5 %)</td>
<td>~2.0 µm</td>
<td>non</td>
</tr>
<tr>
<td><strong>ITO</strong></td>
<td>Cu⁺ + Zn²⁺ + Sn²⁺ + Na₂S₂O₃ (10 mM in total), 4 M KCNS + 0.4 M acetic buffer (pH = 5)</td>
<td>N₂ + H₂S (5 %)</td>
<td>550 °C, 1 h</td>
<td>1.0 - 1.5 µm</td>
<td>non</td>
</tr>
<tr>
<td><strong>Mo</strong></td>
<td>0.02 M CuSO₄ + 0.01 M ZnSO₄ + 0.02 M SnCl₂+ 0.02 M Na₂S₂O₅ + 0.2 M C₆H₅Na₂O₇ + 0.2 M C₂H₅OH, pH = 4.0 - 5.0, -1.0 - -2.0 V (vs. SCE), 45 min</td>
<td>50mg sulfur, 450 °C - 580 °C, 15 min</td>
<td>2.08 µm</td>
<td>non</td>
<td>2014</td>
</tr>
<tr>
<td><strong>FTO</strong></td>
<td>CuCl₂·2H₂O + ZnCl₂ + SnCl₂·2H₂O + Na₂S₂O₅, pH = 2.7, -1.1 V</td>
<td>Argon flow sulfur, 550 °C, 30 min</td>
<td>1.7 µm</td>
<td>non</td>
<td>2014</td>
</tr>
<tr>
<td><strong>Mo</strong></td>
<td>0.01 M CuSO₄·5H₂O + 0.02 M ZnSO₄·7H₂O + 0.02 M SnCl₂+ 0.02 M Na₂S₂O₅ + 0.2 M C₆H₅Na₂O₇ + 0.01 M C₂H₅OH, pH = 4.0 - 5.0, -1.10 - -1.15 V (vs. Ag/AgCl), 20 min</td>
<td>0.5 g sulfur, 100 °C min⁻¹, 550 °C, 30 min</td>
<td>~1.0 µm</td>
<td>3.68 % (unknown)</td>
<td>2014</td>
</tr>
<tr>
<td><strong>ITO</strong></td>
<td>Cu(I) + 0.05 M Zn(II) + 0.01 M Sn(II) + 0.005 M Na₂S₂O₃ + 0.1 M C₆H₅Na₂O₇ + 0.005 M C₂H₅OH, pH = 6.1, -1.15 V (vs. Ag/AgCl), 30 min</td>
<td>10 torr, Ar + H₂S (5 %)</td>
<td>20 °C min⁻¹, 520 °C, 30 min</td>
<td>~1.0 µm</td>
<td>3.4 % (0.07 cm²)</td>
</tr>
<tr>
<td><strong>Mo</strong></td>
<td>Cu(I) + 0.015 M Zn(II) + 0.01 M Sn(II) + 0.005 M Na₂S₂O₃ + 0.1 M C₆H₅Na₂O₇ + 0.005 M C₂H₅OH, pH = 6.1, -1.15 V (vs. Ag/AgCl), 30 min</td>
<td>sulfur</td>
<td>20 °C min⁻¹, 590 °C, 15 min</td>
<td>~1.0 µm</td>
<td>5.5 % (0.2 cm²)</td>
</tr>
<tr>
<td><strong>ITO</strong></td>
<td>CuCl₂·2H₂O + ZnCl₂ + SnCl₂·2H₂O + Na₂S₂O₅, pH = 2.7, -1.1 V</td>
<td>10 torr, Ar + H₂S (6.5 %)</td>
<td>50 °C min⁻¹, 500 - 580 °C, 30 min</td>
<td>~1.0 - 2.0 µm</td>
<td>1.98 % (0.25 cm²)</td>
</tr>
<tr>
<td></td>
<td>Reaction</td>
<td>N₂ flow</td>
<td>Temperature</td>
<td>Yield</td>
<td>Year</td>
</tr>
<tr>
<td>----------------</td>
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</tr>
<tr>
<td>Mo 4.0 cm²</td>
<td>0.04 M CuCl₂·2H₂O + 0.02 M ZnCl₂·2H₂O + 0.12 M SnCl₂·2H₂O + 0.1 M NH₂CSNH₂ + 0.14 M C₆H₃Na₂O₇ + 0.1 M C₆H₅O₆, pH = 4.0, pulsed triangle wave, 0 - 1.2 V (vs Ag/AgCl)</td>
<td>40 ml min⁻¹</td>
<td>580 °C</td>
<td>2 h</td>
<td>2.3 µm</td>
</tr>
<tr>
<td>Mo 2.5 cm²</td>
<td>0.01 M CuSO₄·5H₂O + 0.02 M ZnSO₄·7H₂O + 0.02 M SnSO₄·H₂O + 0.02 M C₆H₃Na₂O₇ + 0.02 M C₆H₅O₆K₂·1/2H₂O, pH= 4.5 - 5.0, -1.10 - -1.15 V (vs Ag/AgCl), 20 min</td>
<td>0.5 g sulfur</td>
<td>100 °C</td>
<td>30 min</td>
<td>1.2 µm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40 ml min⁻¹</td>
<td>550 °C, 30 min</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>