Cadmium-free buffer layer for electrochemically deposited chalcopyrite solar cell

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NANYANG TECHNOLOGICAL UNIVERSITY

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**CADMIUM-FREE BUFFER LAYER FOR ELECTROCHEMICALLY DEPOSITED
CHALCOPYRITE SOLAR CELL**

SUN JUAN

SCHOOL OF MATERIAL SCIENCE AND ENGINEERING

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Abstract

The high efficiency CuInGaSe₂ (CIGS) based thin film solar cells have been demonstrated by various groups across the globe. At present, the highest efficiencies are obtained using CdS buffer layers deposited by chemical bath deposition with a record efficiency of 20.9%. However, because of both environmental reasons and the fact that the CdS layer with a band gap of about 2.4-2.5 eV limits the transmittance of the short wavelength light into the absorber, development of a wide-band gap Cd-free buffer layer is currently the most pivotal topic in CIGS thin film PV technology. This thesis focuses on three parts: (i) to establish electrodeposited CuInSe₂(CIS) as the absorber for the device fabrication, and (ii) to investigate the charge transport at absorber /buffer interface of the chemical bath deposited (CBD)-Zn(O,S) buffer layer, then last (iii) to develop low temperature solution based ZnSnO as alternative Cd-free buffer for CIS solar cells. Proof-of-concept devices of the electrodeposited CIS with these buffer layers yield power conversion efficiency (PCE) of ~4% for Zn(O,S)/CIS devices and 1.53% for ZnSnO/CIS devices.

The first part of the thesis explores a solution based method to fabricate the CIS absorber. Electrodeposition was investigated for this purpose. Two deposition approaches (i) one-step electrodeposition and (ii) stacked elemental layer (SEL) deposition were compared. It was difficult for one step electrodeposition to achieve Cu-poor CIS as a post-selenization etching step using the toxic KCN is required. Moreover, the selenized CIS was porous with small grain size. On the other hand, SEL approach can easily control the Cu/In ratio by controlling the thickness of each layer. Selenization process, which is the most important for the SEL approach, was studied in details. And after a series of analysis and optimization, CIS with Cu/In ratio of 0.85 achieved 3.25% PCE with CdS buffer layer.

The second part of the thesis focuses on the investigation of Zn(O,S) as a candidate of Cd-free buffer layer. As Zn(O,S) prepared by CBD method has a graded S/(S+O) composition, increasing the thickness of Zn(O,S) yields different composition profile. The optical and compositional properties of different thicknesses of Zn(O,S) were investigated. Next, the effect of thickness of Zn(O,S) on the buffer/absorber interface band alignment and charge relaxation was studied by XPS depth profiling and optical pump probe. It was found that the conduction band offset at the interface for different thicknesses Zn(O,S) /CIS was almost identical. Since the thinner Zn(O,S) has lower defect density, the thinner Zn(O,S)/CIS has much longer electron decay time than the thicker one. Both of these are the reasons why the J_{sc} and PCE of the 20nm Zn(O,S) is higher than the 50nm Zn(O,S) one. In addition, other solution based approach, such as spray pyrolysis was explored to control the S/(S+O) ratio inside the Zn(O, S) film.

Lastly, ZnSnO was also explored as alternative Cd-free buffer layer for CIS solar cell. Two methods: (i) conventional and (ii) combustion sol gel methods were compared. Combustion method can generate high energy locally and this energy can help ZnSnO precursors to convert to ZnSnO semiconductor at relative low temperature and minimize the damage to the CIS absorber. The band gap of ZnSnO can be tuned by controlling the Sn concentration in the precursor and thus the band alignment between the ZnSnO and CIS. Promising device PCE of 1.35% was achieved by the ZnSnO/ CIS solar cell with 20%Sn.

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Chapter 1. Introduction

1.1 Background and Motivation

In the last few decades, CIS has become one of the most important materials in polycrystalline thin film solar cell technology. It has established itself as a main contender in solar cells due to its properties such as direct band gap, extraordinary high-absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$) and long term optoelectronic stability [1-3]. The band gap of CIS can be altered either by replacing In with Ga, forming Cu(In,Ga)Se_2 (CIGS); or by replacing the Se with S, forming CuIn(S,Se)_2 (CISSe) [4]. The CIGS solar cell, which in general consists of a glass/Mo/CIGS/CdS/i-ZnO/ZnO:Al stack, has reached maturity for mass production. To date, the best performance CIGS-based solar cell (with PCE of 20.9% [5]) was fabricated with a vacuum co-evaporation method with CdS as the buffer. However, due to environmental reasons and the common fact that the CdS layer with a band gap energy of about 2.4-2.5 eV limits the level of optimum performance of the cells, especially in the short wavelength domain, one of the current key efforts in the CIGS technology is the development of Cd-free alternative buffer layer [6]. Substantial research has been conducted to develop suitable Cd-free buffer as the replacement for CBD-CdS. Among various materials that have been studied during the last decade, Zn-based compounds such as Zn(O,S), ZnMgO and ZnSnO have shown the comparable efficiency to those reference devices with CdS as buffer. The record efficiencies obtained by chemical bath deposition (CBD) Zn(O,S) 19.7% [7], atomic layer deposition (ALD) Zn(O,S) 18.5% [8], ALD ZnMgO 18.1% [9] and ALD ZnSnO 18.0% [10]. Besides Zn-based alternative buffer, indium-compounds have also been explored for the

application as buffer in CIGS solar cell, with current record efficiency obtained for CBD-In(S,O,OH)[11] and ALD-In₂S₃ [12] 15.7% and 16.4% respectively. Indium is much more expensive than Zinc; therefore, Zn-based Cd-free buffers are more popular and generate more research interest.

In the CIGS solar cell, the role of buffer layer is to form a p-n junction with the p type chalcopyrite absorber material CIGS to separate the electrons and holes created in the absorber layer by incident light[6]. The suitable buffer should have a large band gap and appropriate band alignment with absorber. ZnO has a larger band gap of 3.37eV. CIGS and ZnO can form the p-n junction and the cell without buffer still can work, however, the performance of cells is not as good as the one with an additional layer of buffer. The reason is that ZnO has a “bad” alignment with the absorber. At the ZnO/absorber interface, a downward step cliff was formed at the conduction band from the absorber to the ZnO-layer, which results in loss in the open circuit voltage V_{oc} and reduction in the short circuit current J_{sc} due to an enhanced recombination rate at the interface. Therefore, the band structure of ZnO should be modified[6]. Extensive research has been done in the modification of ZnO electronic properties by substituting either Zn or O atoms with other elements. Zn(O,S), ZnSnO and ZnMgO are the three most promising replacement candidates.

For the Zn-based Cd-free buffer (Zn-O-X) (X can be S, Sn or Mg), one challenge is that the conduction band offset (CBO) between Zn-O-X and CIGS has to be well controlled to favor a small spike formation at the conduction band from the absorber to buffer. It is already common knowledge that the band gap and conduction band position of Zn-based buffer will vary with different X% atomic composition, such as S/(O+S) ratio for Zn(O,S)[13, 14] and

Sn/(Zn+Sn) ratio for ZnSnO[15]. However, currently the composition and band gap variation of Zn-O-X can only be done by vacuum based method (ALD, sputtering and Physical vapor deposition) [13, 15]. These vacuum approaches require expensive vacuum equipment and the production throughput is low, especially for the absorber produced by non-vacuum method. It needs additional process time to open the chamber and is difficult to achieve immediate deposition of buffer on CIGS after it is taken out from selenization furnace. Stability is also an issue as the cell efficiency will degrade significantly if there is a time lag before selenized CIGS is covered with buffer. Therefore, with the fast development of non-vacuum based CIGS, the industry needs a controllable solution based method to deposit Cd-free buffer layer and tune the electronic properties of buffer layer according to different requirements.

Chemical bath deposited Zn(O,S) is the most promising replacement and most studied for the buffer layer[6]. It has been reported that for the CBD-Zn(O,S), the oxygen-to-sulfur ratio is thickness dependent[16]. One technical obstacle for the CBD method is that it is quite difficult to systematically control the S/(S+O) ratio and thus tune the electronic properties of CBD-Zn(O,S). It is noted that for a fixed CBD deposition bath, the S/(S+O) ratio will vary with the thickness. This complicates the matter because it creates a graded composition across the thickness. To date, the graded composition effect on the solar cell performance has not been thoroughly well studied. For most research groups, the thickness of CBD-Zn(O,S) for CIGS solar cell is around 50-100nm [17-19]. However, recently several groups have found that the ultra-thin Zn(O,S) can achieve comparable efficiency to CdS [20, 21] [22], prepared by either CBD or ALD.

1.2 Objectives and scope

To address the gaps mentioned above, the main objective of this thesis is to develop and investigate the Cd-free Zinc based buffer layers by solution methods at low temperature.

The detailed breakdown is summarized as follows:

1.2.1 Develop low temperature solution based Cd-free buffer layer for CIS solar cells.

Three methods: (i) CBD (ii) spray pyrolysis and (iii) spin coating of combustion sol gel have been investigated to deposit the Cd-free buffer layer at low temperature. The challenge for CBD Zn(O,S) deposition is that it is difficult to control the S/(O+S) ratio for a fixed thickness and also the S/(O+S) ratio is thickness dependent. Therefore, we propose another method-spray pyrolysis for Zn(O,S) deposition to control the composition. Precise control of zinc and sulfur precursor ratio can vary the S/(S+O) in the Zn(O,S) film and careful selection of solvent will allow the reduction of the conversion temperature.

Another popular Zn-based Cd-free buffer, ZnSnO, can be synthesized by combustion sol gel method. This method can generate massive amount of localized heat in a very short duration. This heat can reduce the formation temperature of ZnSnO in the subsequent heat treatments. ZnSnO with varied Sn/Zn ratio can be synthesized by this method through controlling the ratio of different metal sources.

1.2.2 Study the absorber/buffer interface properties and their correlation with device performance

As mentioned earlier, one of the greatest hurdles to CBD-Zn(O,S) is that the composition is thickness dependent. The study will investigate the performance of the electrodeposited CIS solar cell with varying thicknesses of CBD Zn(O,S) buffer layers. The optical properties and composition of Zn(O,S) buffer layers with different thicknesses will be studied and compared. The conduction band offset of Zn(O,S)/CIS interface will also be investigated. The current density-voltage (J-V) characteristics of devices and the external quantum efficiency (EQE) offer a direct correlation to the effect of CBD-Zn(O,S) with different thicknesses.

The sprayed Zn(O,S) and combustion sol gel ZnSnO offer us the ability to investigate the effect of varied composition on the optical and electronic properties of buffer, which will be investigated and correlated to the device performance.

1.2.3 Investigate the photo-physical properties of absorber/buffer interface

CIS solar cells with varied buffer conditions have different device performance. To understand the detailed role of buffers on the charge transfer at the interface and the photo-physical properties of the interface, femtosecond optical pump-optical probe (OPOP) measurement will be carried out to compare the decay time and rise time of different absorber /buffer systems. The effect of different thicknesses CBD-Zn(O,S) and different composition of ZnSnO will be the focus of this study.

1.3 Thesis organization

The thesis is organized as follows:

In chapter 2, the chalcopyrite family materials, the structure and working principles of chalcopyrite solar cells are briefly introduced. In addition, the role of buffer layers in CIGS solar cell and properties of several types of buffer layers are reviewed and discussed.

Chapter 3 presents the synthesis procedures of CIS absorber and Zn(O,S), ZnSnO buffer. In addition, optical, electronic, chemical and photo-physical characterization details are also presented.

Chapter 4 presents the electrodeposition methods to fabricate the CIS absorber. Details of the optical, structural and chemical characterization of device-grade CIS are discussed. In addition, the benchmark solar cell with CdS on electrodeposited CIS is fabricated and characterized.

Chapter 5 comprises two sections. The first section studies the effect of thickness of CBD-Zn(O,S) on the device performance. The optical and compositional properties of buffer and buffer/absorber interface, band alignment and charge relaxation are studied and compared for buffers with different thicknesses. The second section describes another solution based method, i.e. spray pyrolysis, to control the composition of Zn(O,S) and thus tune the optical properties of Zn(O,S).

Chapter 6 explores ZnSnO as another Cd-free buffer layer for CIS solar cell. Two methods (i) conventional and (ii) combustion sol gel methods are compared. The optical and photo-physical properties of ZnSnO are studied systematically with varied Sn concentration.

Chapter 7 brings the overall summary and conclusion. Along with the conclusion, future prospects addressing the quantitative characterization of the defect level and optimization of ZnSnO as buffer are proposed.

1.4 Contributions of thesis

The original contributions arising from my PhD work are listed as follows:

Technologic contribution

- Successfully demonstrate that ultra-thin CBD-Zn(O,S) without light soaking can work better than the thicker Zn(O,S), which is comparable to CdS for electrodeposited CIS.
- Propose a new method to evaluate the carrier relaxation dynamics at the buffer/absorber interface by pump probe.
- Establish a solution based method to control the S/Zn in the Zn(O,S) film by spray pyrolysis and correlate the S/Zn ratio to band gap for solution processed Zn(O,S).
- Develop a new low T solution based method to deposit ZnSnO and systematically investigate the effect of the constituent composition on the optical & electronic properties.

Scientific contribution

- Detailed analysis for in-depth understanding of the effect of thickness of CBD-Zn(O,S) with graded composition and correlate the varied device performance to the defect density of different buffers.
- Understanding that not only CBO , but also carrier life time plays an important role in the absorber/buffer interface
- Deep understanding the effect of post annealing after CBD process by pump probe measurement that it enhances the charge transfer and carrier lifetime
- Zn(O,S) prepared by spray pyrolysis has a band gap, crystal structure and defect states evolution over the composition change

Chapter 2. Literature overview

2.1 CIGS chalcopyrite solar cell

2.1.1 Chalcopyrite family material

CuInSe₂ (CIS) is among the most promising absorber materials for thin film solar cells. CIS and its alloys with Ga and S have shown highest conversion efficiency of 20.9%[5] with reasonable stability. It belongs to the semiconducting I-III-VI₂ materials family and crystallizes in the tetragonal chalcopyrite structure. **Figure 2.1** shows the unit cell of chalcopyrite structure. Each I (Cu) or III (In) atom has four bonds to the VI (Se) atom. In turn, each Se atom has two bonds to Cu and two to In. In this structure, In site can be substituted by Ga atom, and Se atom can be substituted by S atom, thus forming CuGaSe₂, CuInS₂, Cu(In,Ga)Se₂, CuIn(S,Se)₂ and Cu(In,Ga)(S,Se)₂[23].

As a result of this atomic substitution, the band gap of CuInSe₂ can be tuned within a wide range. The band gap of CuInSe₂ is 1.05 eV and it normally absorbs the red and some infra-red photons; while CuGaSe₂, with a band gap of 1.7 eV, mainly absorbs the short wavelength visible light. By increasingly substituting In with Ga, the band gap of CIS can be increased continuously over a wide range up to 1.7 eV as a function of Ga content and absorb the intermediate light. The trend for the band gap evolution of CuIn_{1-x}Ga_xSe₂ can be described by the following equation 2.1:

$$E_g = 1.010 + 0.626x - 0.167x(1 - x)[24] \quad (2.1)$$

Similarly, the band gap can also be increased by substituting Se with S up to 1.55 eV. It can even be increased up to 2.4 eV by substituting the In and Se with Ga and S simultaneously.

Figure 2.1 Unit cell of chalcopyrite structure[24]

2.1.2 CIGS solar cell structure and working principle

Structure of the CIGS heterojunction solar cell

A typical architecture of a ZnO/CdS/CIGS hetero-junction solar cell is shown in **Figure 2.2 (a)**. The device consists of a 0.5-1 μm thick Mo layer deposited by sputtering on a soda-lime glass substrate and serving as the back contact for solar cell. The CIGS is then deposited on top of Mo back electrode as the photovoltaic absorber material. This absorber layer has a thickness of 1-2 μm and can be prepared by various vacuum and non-vacuum methods. The heterojunction is then completed by CBD of CdS (typically 50nm thick) and by the sputtering deposition of a nominally undoped (intrinsic) i-ZnO layer (usually of thickness 50-70nm) and then a heavily Al doped ZnO layer. Finally, the front electrode Ni:Al is then deposited onto ZnO:Al by thermal evaporation.

The band diagram of ZnO:Al/ZnO/CdS/CIGS heterostructure is shown in **Figure 2.2(b)**. When light enters from the front electrode, the short wavelength light with the energy $(h\nu) > E_g$ of the respective semiconductors on the top is absorbed. The longer wavelength light is transmitted to CIGS layer and excites electron & hole in this layer. Hole will transport through p-CIGS to the Mo back contact; while electrons will transport to n-CdS side and be collected at the front electrode.

Figure 2.2 (a) Basic structure of CIGS solar cell[23]; (b) Band diagram of CIGS solar cell[23]

Essential parameters for device performance

Figure 2.3 shows a typical I-V characteristic observed in solar cell. The most commonly used parameters in describing the performance of a solar cell are: open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (PCE)[25]. V_{oc} depends on the charge separation and transport efficiency. J_{sc} is very much dependent on the light absorption, charge separation, transport and collection efficiency. Fill factor is calculated

as the ratio of maximum power delivered at the point V_m and I_m , over the total area of $V_{oc} \times I_{sc}$.

FF can also be associated with the series and parallel resistance of the solar cell.

$$FF = \frac{I_{\max} \cdot V_{\max}}{I_{sc} \cdot V_{oc}} \quad (2.2)$$

Efficiency (η), which is the most important measurement of device performance, gives the ratio of generated power over the input power

$$PCE = \frac{P_{out}}{P_{in}} = \frac{I_{sc} \cdot V_{oc} \cdot FF}{Ps.A} \quad (2.3)$$

Research has shown the dependency of these parameters to various factors that occur within the CIGS solar cell. Since the band gap of buffer layer is fixed and the band gap of CIGS absorber can be tuned within a wide region, the V_{oc} of CIGS solar cell is therefore hugely dependent on the band gap of CIGS absorber. V_{oc} also depends on the CIS-type film quality, trapping and recombination at the absorber/Mo interface and absorber/buffer interface. J_{sc} depends on the light intensity, CIGS absorber band gap and thickness, the transparency of buffer and window layer, the charge diffusion length, carrier mobility and the contact between absorber and Mo substrate. FF is usually associated with the charge collection efficiency which is largely affected by the quality of the semiconductor/metal interfaces. The power conversion efficiency (PCE) of the solar cell is affected by all these parameters.

Figure 2.3 Typical I-V characteristic of a solar cell[24]

2.1.3 Absorber preparation method

Overview of various absorber preparation methods

A wide variety of thin-film deposition methods have been used to deposit CIGS thin films. It can be divided into two general approaches: vacuum-based methods and non-vacuum methods [26, 27]. Vacuum methods mainly refer to co-evaporation and sputtering techniques. The world record efficiency 20.9%[5] has been produced by co-evaporation under high vacuum. However, these vacuum methods are normally high energy-consuming, which make them relatively expensive.

Non-vacuum fabrication of thin film photovoltaic device provides an attractive cost saving opportunity that has generated a considerable amount of research interest [28, 29], and have achieved quite high efficiency up to 15.9% by Nexcis[3]. Such efficiency value proves adequate for commercial up-scaling and several companies are now trying to develop products based on non-vacuum deposited CIGS absorbers. Depending on the deposition method and

the scale of mixing of the precursor materials, non-vacuum approaches could be roughly divided into three different categories[30]: (1) electrochemical deposition, with the highest reported efficiency of 15.9% by Nexcis[3]; (2) particulate-based processes that use solid particles dispersed in a solvent to form an ink, which can be coated onto a substrate. Nanosolar has reported 14% efficient cells using mixed selenide nanoparticles and a single-stage annealing treatment[31]; (3) solution process that coat molecular precursor solutions onto a substrate by mechanical means such as spraying or spin coating. In 2004, Mitzi et al[32] reported the hydrazine-based approach. In this approach, the hydrazine precursors are prepared by simply mixing appropriate amounts of metal chalcogenides and chalcogens in hydrazine and stirring at room temperature. The precursor solution is coated onto substrates using various wet coating methods (e.g. spin coating, drop casting). Upon heating, volatile hydrazine species leave the system and a CIGS thin film is formed directly. Up to now, cell efficiency 15.2% for CIGS has been reported by their group[33].

Electrochemical deposition

Of the various non-vacuum methods, electrodeposition is a highly attractive proposition for mass production of low cost CIS thin film solar cells [2, 34]. The advantages of electrodeposition include low equipment cost, high deposition speed, negligible waste of chemicals, good scalability as well as ability to deposit films on a complex surface[35]. Furthermore, simple tweaks to the process parameters allow for easy control of the deposited film thickness, morphology and composition.

There are two main approaches of the electrochemical deposition methods: Co-electrodeposition of Cu-(In,Ga)-(Se,S) from a single electrolyte and electrodeposition of stacked layers of metals, alloys or binary selenides.

Bhattacharya was the first to develop a one-step route for the electrodeposition of Cu-In-Se[36]. Co-electrodeposition baths normally have a low pH[37]. Generally, Cu, In, Ga salts and selenic acid (H_2SeO_3) were used as the precursors. In most cases, the metallic elements are introduced as sulphate[38] or chloride[39] salts and more rarely as nitrate salts. The electrodeposition of CIGS from a single solution is difficult due to the wide differences between the standard reduction potentials of Se ($E^\circ = +0.75\text{V}$ vs. NHE), Cu ($E^\circ = +0.34\text{V}$ vs. NHE), In ($E^\circ = -0.34\text{V}$ vs. NHE) and Ga ($E^\circ = -0.53\text{V}$ vs. NHE). Copper-rich films are usually produced when a cathodic deposition potential is applied. Copper in these deposited films is found to be both in CIGS chalcopyrite phase and in Cu_{2-x}Se secondary phase [40]; the latter is identified to be responsible for low efficiencies of CIGS films [40]. Decreasing the activities of Cu^{2+} via a complexation process was reported as an attractive approach to lower down the potential gap between Cu^{2+}/Cu and In^{3+}/In redox couples by shifting the redox potential of Cu^{2+}/Cu couple to a more negative potential. Sodium citrate[41], tartaric acid[42], potassium thiocyanate[43] and triethanolamine[44] were examined as copper chelating agents. Even though the exact mechanism of co-electrodeposition of CIGS is not well established, it is most probably caused by the combination of electrochemical and chemical reactions as follows:

After the deposition, selenization is required to improve the film quality and grain size.

Solar cell devices based on Cu-In-Se electrodeposited precursors with PCE of up to 11.4% have been reported [45].

Due to the high electro-negativity, incorporation of In and Ga by co-electrodeposition is very difficult. To overcome the intrinsic difficulty in In and Ga incorporation, one alternative strategy has been developed, which often involves the deposition of stacked elemental Cu, In and Ga layers followed by the selenization or sulfurization treatment [46, 47].

Another strategy based on the sequential electrodeposition of bilayer of binary or ternary selenide precursors was proposed [26, 30, 48]. CuInGaSe₂ films were prepared by selenizing precursors containing layers of: Cu-Se and In-Se, In and Cu-Se, CuSe and evaporated In-Ga and Cu, In₂Se₃ and Cu_{2-x}Se.

The as-electrodeposited CIS and CIGS films are usually amorphous or poorly crystalline and consist of small grains. They tend to be Cu-rich and contain frequently degenerate Cu_{2-x}Se phases that are detrimental to the device performance. The films may also contain impurities that originate from the aqueous deposition solution or from the complexing agents. For these reasons, the films require at least annealing under an inert atmosphere prior to completing the device. Often the film stoichiometry needs to be corrected too, for instance by annealing under

a Se-containing atmosphere and/or by selective etching in cyanide-containing solutions to remove the excess Cu and Se [49-51].

2.2 Buffer layer in CIGS solar cell

2.2.1 Role of buffer layer

Functions of buffer layer

As shown in **Figure 2.2 (a)**, in a standard CIGS solar, there exists a layer of buffer between the CIGS and ZnO window layer. Although CIGS and ZnO can form the p-n junction and the cell without buffer still can work, the performance of cells with an additional layer of buffer will be much improved.

The following functions are ascribed to buffer layers in CIGS solar cells. Firstly, buffer layer can protect the absorber surface from damage by the high energy sputtering of window layer (i-ZnO and Al-ZnO) [52]. Secondly, buffer layers are usually highly resistive and can prevent shunting between the TCO and absorber [6]. Thirdly, chemical constituents of buffer material normally can dope the CIGS near interface layer or passivate the CIGS surface defects. The most important function of the buffer layer is to mitigate the band alignment between the p-n junction. This band alignment is important because it will affect the conduction band offset at the junction and consequently affect the charge recombination and transportation.

Criteria for buffer-layer selection

There are some general requirements for the buffer material in CIGS solar cells. To form a good p-n junction with absorber, the buffer must be n-type and very thin (30-100 nm) to minimize the absorption of photons. Buffer materials also need to have good lattice match with the absorber layer. From the electronic point of view, buffer layer must have a sufficiently wide band gap to minimize the optical absorption. And most importantly, it should have a suitable conduction band alignment with the absorber at the interface. The nature of the absorber/buffer hetero-interface is crucial for solar-cell operation. In order to achieve high efficiency, such interface should not favor the carrier recombination.

Figure 2.4 shows the p-n junction band diagram in different cases. In an ideal band structure for normal semiconductor(**Figure 2.4a**), the p-n junction is very flat[53], which is good for the injection of electrons and holes to the respective electrodes after separated at the space charge region. However, for the CIGS solar cell, the requirement for the band alignment at the interface is different from normal semiconductor solar cell. With CdS as buffer layer, the conduction band minimum of CdS is higher than that of CIGS, $\Delta E_c > 0$ (**Figure 2.4b**), which is so-called spike. In conventional solar cell, this spike would impede the e- injecting from the p side to n side. However, in CIGS solar cell case, this spike can create n type inversion and increase the space charge region (SCR) width, shifting the SCR towards CIGS side, and thus reduces the recombination at the absorber/buffer interface, enhancing the performance of solar cell. For the CdS/CIGS, the conduction band offset (CBO) is just nice, around 0.3 eV, to reduce the interface recombination but not to limit the charge injection at the interface. However, in the most cases of Cd-free buffer layers, such as ZnS, one of the main problems

is the large CBO between the conduction band minimum of buffer and that of CIGS. The CBO at the interface is around 1eV (**Figure 2.4c**). A higher spike impedes the injection of e⁻ from p side to n side, reducing the J_{sc} and FF sharply. Therefore, the CBO at the absorber /buffer interface needs well control.

Figure 2.4 (a) p-n junction in idealized band structure for normal semiconductor[53]; (b) CdS/CIGS band diagram; (c) ZnS/CIGS band diagram.

Conduction band offset (CBO) at the buffer/CIGS interface was calculated as follows:

$$CBO_{CIGS/buffer} = E_{g_{buffer}} - E_{g_{CIGS}} - VBO_{CIGS/buffer} [54] \quad (2.8)$$

2.2.2 Buffer materials in CIGS solar cell

CdS buffer layer by CBD

The CBD-CdS is the most established buffer layer in CIGS solar cell. The device that reported record efficiency of 20.9% [5] utilized CdS as the buffer layer in the cell. Chemical bath deposition (CBD) is the most frequently adopted method for the deposition of buffer layer in CIGS solar cell. It has been suggested that the buffer layer functions not only as a p-n

heterojunction partner, but it also protects the p-n junction from plasma damage during the subsequent ZnO sputtering process[6]. Moreover, the ammonia used in most CBD recipes is thought to chemically etch away the oxides and other impurities on the surface of CIGS and thus have an obvious surface cleaning effect [55, 56]. Finally, the CBD process permits a conformal and pinhole-free coating of buffer layer on the absorber.

Besides the benefits of common CBD buffer layer stated in the above section, CdS also has some additional intrinsic advantages. The lattice of CdS matches quite well with that of CIGS[57]. Due to the similar diameter of Cd and Cu ions, Cd can diffuse a certain extent into the Cu-poor surface layer of the absorber material, and form $\text{Cd}_x\text{Cu}_{1-x}\text{GS}$ [55, 58, 59], which will further improve the lattice matching between CIGS and CdS and also smooth the heterojunction between CIGS and CdS. From the electrical point of view, CdS forms very good band alignment with CIGS. There is a small conduction band spike [60] [61] with CIGS at the heterojunction interface (**Figure 2.4b**). This small spike tends to minimize the interface recombination.

The challenges of CdS buffer layer result from the toxicity of Cd, limiting its application and market share in those countries and regions where Cd is banned[62]. Another issue arises from the low band gap (2.4-2.5 eV) of CdS. When light enters from the front contact, CdS can also absorb some portion of short wavelength light and thus decrease the J_{sc} [63]. Therefore, one of the major objectives in the CIGS technology is to develop alternative Cd-free buffer layer with a wider band gap.

Zn (O, S) buffer layer by CBD and ALD/Sputtering

Many alternative materials have been tried in the past decades for a Cd-free buffer layer in CIGS solar cells. Of all the Cd-free buffer layers, ZnS-based buffer layer has proved to be high promising due to its good lattice match with CIGS, wide band gap (3.67eV), environmental friendly and low cost[62, 64].

As such, CBD-ZnS remains one of the most studied Cd-free buffer layer for replacing CBD-CdS. It was reported that CIGS cells fabricated with CBD-Zn(O,S) buffer layer yielded 19.7% efficiency[7] comparable to those with CdS buffer used as a control in that study.

The CBD-Zn (O, S) films have often been synthesized in basic medium using a zinc salt, with Thiourea as sulfur precursor and ammonia as complexing agent. The growth mechanism of CBD-ZnS is as follows[65]:

Although the deposition conditions could affect the composition of the deposited film, in most cases a composition of the type $\text{Zn}(\text{S},\text{O},\text{OH})$ is obtained. Therefore, the deposited layer is a mixture of ZnS , ZnO , and $\text{Zn}(\text{OH})_2$. For optimal performance of the CIGS solar cells, buffer films must be annealed after deposition on the absorber, possibly causing a partial removal of water, transformation of hydroxide to oxide, or a slight modification of the absorber at the interface[64].

Nakada group and Showa shell[64] were two notable groups that had successfully established the CBD $\text{Zn}(\text{O},\text{S})$ as alternative buffer layers with compromised efficiency. Though some people believe the NH_3 in the CBD bath had a leading role for the formation of $\text{Zn}(\text{O},\text{S})$ layer, use of very high and low concentration of NH_3 were both reported. Nakada et al.[18, 64] employed a very high NH_3 concentration in the CBD process. The final thickness of the buffer layer was 120nm achieved by 3 deposition cycles. Conversely, Showa shell[64] group used a relatively low NH_3 concentration to deposit a $\text{Zn}(\text{O},\text{S})$ buffer which had thickness around 50nm. Although there are differences in the deposition methods used by the various groups, it is noted that most of the research groups employed $\text{Zn}(\text{O},\text{S})$ buffer with thickness around 50-100nm [17-19]. Recently, very thin CBD grown $\text{Zn}(\text{O},\text{S})$ buffer layer was reported as highly promising buffer layer[20]. This result was also echoed by reports from other research group [21] who compared the 15nm CBD- $\text{Zn}(\text{O},\text{S})$ with the control 50nm CdS buffer layer for CIGS solar cell applications. The excellent performance of ultra-thin $\text{Zn}(\text{O},\text{S})$ buffers were reported either by CBD[20-21] method or the atomic layer deposition (ALD)[22]. However, the results are largely empirical and the fundamental science to explain the reasons for the equivalent or better performance of the ultra-thin buffer layer compared to the thicker one is still unclear.

And it is also reported that for the CBD-Zn(O,S), the sulfur-to-oxygen ratio is thickness dependent[16]. So for CBD method, it is quite difficult to systematically control the S/(S+O) ratio and thus tune the electronic properties of CBD-Zn(O,S). The conduction band offset between the CBD-Zn(O,S) and CIGS is almost identical with varied CBD deposition conditions (Table 2.1)[66].

Besides solution based CBD method, Zn(O,S) have also been reported to be prepared by vacuum based methods. ALD and sputtering can control the S/(O+S) ratio of Zn(O,S) very well and tune the band gap[67, 68] from 2.6 eV to 3.7 eV as shown in Table 2.1. Cell efficiency value up to 18.5% with AR coating was shown for deposition at 120°C by ALD with thickness of about 20 nm[8].

ZnSnO by ALD

Recent Cd-free work has also focused on ZnSnO based buffers produced by ALD [15, 69, 70]. The record efficiency with ALD ZnSnO is 18.0% [10]. The $\text{Zn}_{1-x}\text{Sn}_x\text{O}_y$ films are measured (by means of soft X-ray spectroscopy analysis) to have a variable band gap from 3.3 eV (ZnO) to 2.5 eV ($\text{Zn}_{0.87}\text{Sn}_{0.13}\text{O}_y$) and then to 2.2 eV (SnO_x)[15]. This change in the band gap is found to mainly result from a shift in the valence band edge towards higher energies with increasing Sn concentration, whereas only a moderate shift is observed in the conduction band edge with the same Sn concentration (as shown in table 2.1)[15]. Good solar cell performance is found for Sn concentration to be in the range of 0.15 – 0.21[70].

ZnMgO by ALD/sputtering

ZnMgO alloy is another Cd-free buffer layer that has large band gap and controllable conduction band energy level[71]. Compared to their CdS/ZnO-based counterpart, CIGS devices incorporating ZnMgO demonstrate similar or superior performance, with one work reporting efficiency 18.1%[9] with 26% Mg/(Zn+Mg). ZnMgO with an adjustable Mg/Zn ratio can be prepared both by sputtering and ALD, with the latter more promising. The band gap of ZnMgO films increases linearly with the magnesium content until phase segregation of cubic MgO occurs. At x-value 0.33, single-phase wurtzite film was obtained, corresponding to a band gap of 4.0 eV[6]. With inclusion of Mg, the conduction band of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ is increased, resulting in improved band alignment with CIGS and thus better device efficiency.

Table 2-1 summary of band gap and band alignment of Zn-based buffer with varied composition

Zn-based buffer	band gap with varied composition	Band alignment with varied composition	Composition at highest efficiency
$\text{ZnO}_{1-x}\text{S}_x$ [65-67]			$\text{S/Zn} \approx 0.6$ for CBD $\text{S/Zn} \approx 0.3$ for ALD
$\text{Zn}_{1-x}\text{Sn}_x\text{O}_y$ [15]			$\text{Sn}/(\text{Zn}+\text{Sn})$ ≈ 0.18
$\text{Zn}_{1-x}\text{Mg}_x\text{O}$ [71]			$\text{Mg}/(\text{Zn}+\text{Mg}) \approx 0.26$

Chapter 3. Experiment

3.1 Preparation and characterization of p-type CIS absorber material

3.1.1 One step electrodeposition of single phase CIS

All chemical compounds were purchased from Sigma Aldrich and used as received without any further purification. For electrochemical experiments, a conventional three-electrode configuration was employed. This setup consists of a Pt mesh counter electrode, Ag/AgCl/KCl (3M) reference electrode, and freshly cleaned glassy carbon ($S = 0.071 \text{ cm}^2$) or fluorine doped tin oxide (FTO, $S = 1 \text{ cm}^2$) working electrode.

The deposition bath was prepared by dissolving CuCl_2 (4mM), InCl_3 (8mM), and H_2SeO_3 (8mM) in deionized (DI) water. It was then adjusted to pH 2 by adding appropriate amount of HCl, acetic acid or oxalic acid.

To determine the reduction potentials of precursors in the deposition bath, linear sweep voltammograms were recorded on glassy carbon electrode for the deposition bath. Potential polarization was performed in cathodic direction with a potential scan rate of 10 mV.s^{-1} .

CIS film was deposited onto clean FTO electrode, with typical surface area of 1 cm^2 , at a fixed cathodic potential (between -0.6 and -1.0V vs. Ag/AgCl) for 20 minutes. The as-deposited CIS films were carefully rinsed under DI water and dried under a N_2 flux. Lastly, the films were annealed in N_2 at 350°C for 1.5 hours. The crystal structure and chemical composition of the deposited CIS films were characterized by thin-film XRD, field emission scanning

electron microscope (FESEM), Raman spectroscopy and energy dispersive spectroscopy (EDS).

To investigate the photo-electrochemical properties of deposited CIS films, generated photocurrents under white light irradiation (150W Halogen lamp) at applied bias of -0.4V vs. Ag/AgCl was measured. Light intensity reached CIS electrode was adjusted to 100mW.cm⁻². A pH 7 phosphate buffer electrolyte solution was employed. Details of experimental setup, sample preparation etc. were described in our previous work[72].

3.1.2 Stacked elemental layer deposition followed by selenization

The substrates used in this work were standard soda-lime glass (SLG) coated with 500nm thick Mo prepared by direct current sputtering (approximately 1.5cm by 2.5cm). The Mo substrates were first cleaned by subsequent sonication in decon soap solution, acetone and DI water. After drying under N₂, the Mo substrates were further cleaned under Ar plasma for 15mins.

The electrodeposition of Cu layer was carried out on the potential state CHI660D with three-electrode configuration. The deposition bath consisted of 0.075M CuSO₄·5H₂O and 0.25M sodium citrate (Na₃C₆H₅O₇·2H₂O) in aqueous solution. Here the conventional three electrodes configuration described above was adopted. Cu was deposited at -0.9V vs Ag/AgCl at constant potential mode for 5mins.

While for the Indium deposition, the set up was a two-electrode configuration with Indium strip as the counter electrode. The deposition bath consisted of 0.26M InCl₃, 1.26M sodium

sulfamate, 0.78M NaCl, 8g/L glucose and 2.29g/L triethanolamine in aqueous solution. pH was adjusted to 1.6 by adding sulfamic acid. Indium layer was deposited onto the as-deposited Cu electrode by holding constant deposition current of 25mA/cm². The deposition time was adjusted according to the total reduction charge accumulated for the deposition of Cu. The Cu/In molar ratio was kept at the range of 0.7-1.1. After deposition, the Mo/Cu/In stacked layer was rinsed with DI water and dried under N₂. Subsequently, the Mo/Cu/In samples were placed into the tube furnace (as shown in **Figure 3.1**) together with solid selenium powder for selenization. Pumping and purging cycles were used to remove the air inside the tube furnace. The purging gas used was Ar. After 3 cycles of pumping and purging, the furnace was filled with Ar and the Ar flow rate was set at 10ccm. The selenization pressure was maintained at 1 atmosphere.

Figure 3.1 Schematic drawing of the selenization furnace

The next stage was the heating programme (**Figure 3.2**). The samples were first annealed (150°C for 30mins) to form Cu-In alloy, then during the low temperature selenization (300°C for 20mins), selenium was incorporated to form selenide and lastly during the high temperature selenization (520°C for 10mins), with a fast ramping rate, the film was recrystallized to form CIS with big grain size.

Figure 3.2 Temperature profile for the selenization process

3.2 Preparation and characterization of n-type buffers

3.2.1 Chemical bath deposition (CBD) of CdS layer

The CdS layer was deposited onto plasma cleaned UV transparent quartz substrate (for Ultraviolet-Visible (UV-Vis) spectroscopy measurement) or selenized CIS (for device fabrication) by a CBD method as schematized in **Figure 3.3**. The chemical bath was comprised of 2.68 mM $\text{Cd}(\text{Ac})_2$, 0.02 M NH_4Ac and 0.01M Thiourea (TU) in water. The chemicals were added into the reaction bottle by the following sequence. $\text{Cd}(\text{Ac})_2$ powder was first added into 200 ml DI water, followed by NH_4Ac and lastly TU powder. When the temperature of water bath was close to 85°C , several drops of concentrated NH_4OH were added into the reaction bottle at the last step to adjust the pH of the deposition bath to 9. The glass substrate or CIS sample were immersed into the reaction bottle. The whole bottle of mixed precursor solution was placed into the water bath with stirring. After around 10mins,

when the solution turned transparent yellow, the sample was taken out, rinsed with DI water and then dried under N_2 flow. Finally the film was annealed at 150°C for 20mins.

Figure 3.3 Typical set up for CBD process

3.2.2 Chemical Bath Deposition (CBD) of $Zn(O,S)$ layer

In order to prepare the $Zn(O,S)$ CBD bath, Zinc acetate dihydrate (Sigma Aldrich, ACS reagent grade, $\geq 98\%$), Thiourea (Sigma Aldrich, ACS reagent grade, 99%) and Ammonia hydroxide (Sigma Aldrich, ACS reagent grade, 28-30%) were used as received.

The setup for CBD- $Zn(O,S)$ was same as that of CdS as illustrated in **Figure 3.3**. To study the optical properties of $Zn(O,S)$ film, the film was deposited onto plasma cleaned UV-transparent quartz substrate. The chemical bath solution comprised of 0.08M $Zn(Ac)_2$, 5M Thiourea (TU) and 7M NH_3 in water. $Zn(Ac)_2$ powder was first added into DI water then followed by TU powder. When the temperature of water bath reached close to 85°C , concentrated NH_3 was added. The whole bottle of mixed precursor solution was placed into the water bath with stirring. And then the reaction started. The pH of the solution was

maintained between 10 and 11. The NH_3 was believed to act as a complexing agent to form complexation with Zn^{2+} and then control the growth of Zn(O,S) . The deposition time was varied between 12mins and 25mins to vary the thickness of deposited Zn(O,S) film. The quartz substrate with deposited film was then taken out from the chemical bath and washed in NH_3 solution (aqueous 2.5% solution) in order to avoid an uncontrollable precipitation of Zn(OH)_2 on the surface due to the drastic reduction of ammonia concentration[16]. At last, the film was rinsed with DI water and dried under N_2 flow. Then the films were annealed at 200°C for 20mins to convert Zn(OH)_2 within Zn(O,S) film to ZnO .

The optical properties of Zn(O,S) films on quartz substrate were measured by UV-Vis spectroscopy. The planar and cross-section images of $\text{Zn(O,S)}/\text{CIS}$ samples were obtained by FESEM, JEOL JSM-7600F. The valence band offset (VBO) at $\text{Zn(O,S)}/\text{CIS}$ interface was measured by X-ray photoelectron spectroscopy(XPS) depth profile. In order to study the ultrafast carrier relaxation dynamics in CIS films, femtosecond optical pump-optical probe (OPOP) measurement was carried out. Second harmonic generation of fundamental 800 nm (400 nm) wavelength was used as pump; and beam from optical parametric amplifier was used as probe. Differential probe signals were collected using photodiode and lock-in amplifier, with respect to pump delay. In this experiment, the pump and probe pulses were orthogonally polarized with the incident angle between both the beams less than three degrees. The ratio of energy between the pump and the probe pulses was less than 5 %.

The transient optical properties of the $\text{Zn(O,S)}/\text{CIS}$ interfaces were also measured by time resolved photoluminescence (TRPL). Optical parametric amplifier was pumped by an amplified-femtosecond pulsed laser system (Spectra physics, Mai Tai-Spitfire Ace-TOPAS

Prime). The output wavelength can be continuously tuned from 250 nm to 2.6 μm . The pulse-width and repetition rate were 100fs and 1 KHz, respectively. The Zn(O,S) film samples were excited at a wavelength of 325 nm, beam spot size of 3 mm. The PL signals from the sample were dispersed by a 3/4 m monochromator (Princeton instruments, adjusted to 550 nm) assisted with a pair of collection lenses and a long-pass filter (cut-off wavelength: 350 nm) and recorded by an Optronics streak camera system with time resolution of $\sim 50\text{ps}$ [73].

3.2.3 *Spray pyrolysis of Zn(O,S)*

Zn(O,S) films have been deposited by spraying a solution containing $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CS}(\text{NH}_2)(\text{CH}_3)$ (thioactamide-TAA) salts in mixture solvent of water and alcohols. In order to prepare the precursor solution, zinc chloride (3mmol, 408mg, Sigma Aldrich, reagent grade, $\geq 98\%$) was dissolved in 50ml solvent. Different amount (114mg, 228mg, 684mg.etc.) of TAA (Sigma Aldrich, ACS reagent, $\geq 99\%$) was then added to keep different TAA/ ZnCl_2 molar ratios (0.5,1.0,3.0,etc.). Nitrogen was used as the carrier gas and substrate temperature was kept in the range of 200 – 250°C. The spray pressure was maintained at 3.5 bars and the solution was sprayed at a constant speed of 2.5ml/min. By varying the TAA/ ZnCl_2 molar ratio, the S/Zn ratio was systematically varied and subsequently the optical and electronic properties were tuned.

The crystal structure and chemical composition of the sprayed Zn(O,S) films were characterized by Fourier Transform Infra-red (FTIR), thin-film XRD, UV-Vis spectroscopy, FESEM, EDS, XPS and photoluminescence spectroscopy. The films with varied S/Zn ratios were deposited onto CIS for device fabrication.

3.2.4 Spin coating of ZnSnO

Conventional spin coating

The solution for fabrication of ZnSnO was prepared by mixing different molar ratios of 0.1M ZnCl₂ and 0.1M SnCl₂ in acetonitrile solvent. The stock solution of each metal salt was prepared by adding 681.6mg ZnCl₂ or 948.1mg SnCl₂ into 50ml acetonitrile separately. In order to increase the stability of the stock solution, 2.5ml concentrated acetic acid was added into each stock solution. After stirring at room temperature for 12 h, different molar ratios of ZnCl₂ and SnCl₂ were mixed together and stirred at room temperature for 2 h. The mixed solution was filtered by 0.45µm filter and then spin-coated @3000 rpm followed by annealing at 100°C. The thicknesses of the films were varied by controlling number of spin-coating deposition cycles. Finally, the as-deposited films were annealed at different higher temperature followed by UV annealing under mercury lamp with the power intensity of 300W/cm² for 30mins.

Combustion sol-gel spin coating

The Zn and Sn precursor solution was prepared individually, by dissolving 2975 mg Zn(NO₃)₂ · 6H₂O or 1896 mg SnCl₂ with 1602 mg NH₄NO₃ in 50ml 2-methoxyethanol, then adding 2 ml acetylacetone into each precursor solution. The ideal precursor for the tin salt is tin nitrate. However, as the pure tin nitrate is reported to be unstable in an ambient environment, we prepared an alternative solution by mixing SnCl₂ and NH₄NO₃ in 2-methoxyethanol. After stirring for several minutes, 1.14ml (for Zn) or 0.57 ml (for Sn) concentrated NH₃ was added and the stock solution was aged for 12 h at room temperature. Different Sn/(Sn+Zn) ratios

(5%,10%,20%,30%, etc.) were obtained by mixing appropriate pre-calculated amount of these two stock solutions and stirring 2 h before used for spin coating.

The combustion sol gel solution was spin coated @ 2000rpm for 30s and anneal at 70°C after each cycle. After several cycles, the film was annealed at elevated temperature. The whole process is illustrated in (**Figure 3.4**).

Figure 3.4 Process flow of combustion sol gel spin coating

To compare the differences between the conventional method and combustion sol-gel method described here, Differential Scanning Calorimeter (DSC) and Thermo gravimetric analysis (TGA) analysis were carried out. Similar to the sprayed Zn(O,S), ZnSnO films with different Sn concentration were also characterized by thin film XRD, FESEM, UV-Vis spectroscopy, XPS and also OPOP and TRPL as mentioned in section 3.2.2 for CBD-Zn(O,S). The ZnSnO films were also deposited onto selenized CIS to fabricate solar cell.

3.3 Device fabrication and characterizations

The typical solar cell fabrication process is shown in **Figure 3.5**. To fabricate the CIS solar cell, a 500nm-thick molybdenum (Mo) back contact was deposited by direct current magnetron sputtering on SLG substrates. Elemental Cu and In were deposited onto Mo substrate sequentially by electrodeposition method. The Cu/In ratio was kept around 0.85. A layer of 1.5µm-thick CIS was formed through the selenization of Cu and In metallic layer in

the tube furnace at 520°C. Then the buffer layer (CdS or Zn(O,S) or ZnSnO) was deposited immediately onto the selenized CIS. Different thicknesses of buffer were deposited onto CIS by varying the deposition time. After buffer/CIS were deposited, washed, rinsed, dried and annealed at 200°C for 20mins, i-ZnO/AZO/Al were deposited to complete the solar cell structure.

Figure 3.5 Typical solar cell fabrication processes

The current density-voltage (J-V) characteristics of cells were measured under a solar simulator in ambient conditions under AM 1.5G illumination (100 mW/cm^2) using a Keithley SMU 2400 source meter. The light intensity was calibrated by using an NREL calibrated silicon photodiode. The external quantum efficiency (EQE) was measured using a PVE300 (Bentham), with dual Xenon/quartz halogen light source.

Chapter 4. Absorber layer prepared via electrochemical deposition

4.1 One-step Electrodeposition of single phase CuInSe₂

4.1.1 Background

Conventional deposition bath for one step electrodeposition of CIS thin film comprises of Cu^{2+} , H_2SeO_3 and In^{3+} precursors in a strong acidic environment of pH 1.5-2[74, 75]. The acidic environment is usually created by the addition of strong acids. The conventional bath has a major problem. Significant difference in reduction potential of Cu^{2+}/Cu ($E^\circ=+0.34\text{V}$ vs. NHE), and In^{3+}/In ($E^\circ=-0.34\text{V}$ vs. NHE) redox couples in the bath results in drastic higher deposition rate of Cu^0 compared with that of In^0 . As a consequence, the excess deposition of Cu^0 causes the formation of Cu_{2-x}Se impurity in the CIS film[76]. This Cu_{2-x}Se secondary phase is the path of low electrical resistance [35, 74] which decreases the power conversion efficiency of the CIS solar cells. The production of the undesired Cu_{2-x}Se secondary phase can be reduced by lowering down the electrochemical activities of Cu^{2+} precursor, thus by shifting the reduction potential of the Cu^{2+}/Cu couple to more negative potential [75]. That can be done by adding Cu^{2+} chelating agents [34] such as sodium citrate[41], tartaric acid[42], potassium thiocyanate [43], triethanolamine [44] and sodium dodecyl sulfate[75]. It is worth noting that together with chelating agents, adding of additional strong acids was required to maintain the pH around 1.5-2.

In this current study, we present a novel and direct way to employ simple organic acids as the chelating agent. This eliminates the need for addition of acids into the deposition bath since the acidic environment is already provided by the chelating agents. We investigated the ability of oxalic acid, acetic acid and hydrochloric acid for this dual role function. Oxalic and acetic acids are weak acids that chelate with Cu^{2+} . In contrast, hydrochloric acid is a strong acid which doesn't chelate with Cu^{2+} ion. We investigate the contribution of oxalic acid and acetic acid to prevent production of Cu_{2-x}Se secondary phase during the CIS film deposition. HCl serves as a control in the experiment. We analyzed photoelectrochemical properties of CIS films to link their performance with their chemical compositions, morphologies etc., which are governed by the nature of acid additives.

4.1.2 Film growth and characterization

Figure 4.1 Linear sweep voltammograms (LSV) recorded on FTO electrode for CIS deposition bath at pH 2 adjusted by different acids with scan rate: $10\text{mV}\cdot\text{s}^{-1}$. A, B, C, D

represent the conversion of $\text{Cu}^{2+}/\text{Cu}^+$, Cu^+/Cu^0 , $\text{H}_2\text{SeO}_3/\text{Se}$ and In^{3+}/In for oxalic acid(1), acetic acid(2), and HCl(3) respectively.

Linear sweep voltammetry was employed to investigate the electrochemical properties of the CIS deposition baths with different acid additives. For the HCl case, four reduction peaks were observed at -0.05V, -0.2V, -0.4V and -0.7 V (marked as A3, B3, C3 and D3 respectively) vs. Ag/AgCl (**Figure 4.1**, green curve) when HCl is used to adjust the pH in the deposition bath. The first two peaks (A3 & B3) can be attributed to one electron reduction of Cu^{2+} into Cu^+ and subsequently Cu^+ into Cu^0 . The peak around ca. -0.4V vs. Ag/AgCl is attributed to the reduction of H_2SeO_3 into Se (peak C3) and the most negative peak at -0.7V (peak D3) is attributed to the reduction of In^{3+} into In (Four rectangular boxes in **Figure 4.1** represent the four different reduction windows of $\text{Cu}^{2+}/\text{Cu}^+$, Cu^+/Cu^0 , In^{3+}/In and $\text{H}_2\text{SeO}_3/\text{Se}$ respectively). The use of weak organic acids (acetic or oxalic acid) as chelating agents in the bath resulted in a cathodic shift in the reduction potential of $\text{Cu}^{2+}/\text{Cu}^+$ and Cu^+/Cu^0 couples. This phenomenon was similar to the observation that has been reported for triethanolamine additive [44]. The reason for this cathodic shift is likely due to the chelating of Cu^{2+} with acetic or oxalic acid which reduces the electrochemical activities of Cu^{2+} . Of these two weak acids, acetic acid additive induced a larger cathodic shift for the reduction potential of the Cu^{2+}/Cu couple. The presence of acetic acid in the deposition bath also resulted in the cathodic shift for reduction of H_2SeO_3 and In^{3+} .

The exact mechanism of the electrodeposition of CIS thin film still remains debatable. However, currently, it is widely accepted that the deposition mechanism is a result of the combination of electrochemical and chemical reactions as described in the following equations 4.1-4.5 [77, 78]. The precursors (Cu^{2+} , In^{3+} and SeO_3^{2-}) are first individually

reduced into their elemental forms. The elements then react, most likely via a solid-state chemical reaction, to yield the final product. The combination of products formed from the chemical reactions depends on the amount of Cu^{2+} which is reduced to Cu (equation1). In particular, when the amount of Cu^{2+} reduced is much more than that of In^{3+} reduced, a mixture of ternary phase CIS and binary phase Cu_{2-x}Se may be formed.

Total reaction:

The difference in reduction potential between Cu^{2+}/Cu and In^{3+}/In couples dictates the composition of deposited CIS film [13]. Narrower difference in potential results in the formation of CIS film which contains less secondary Cu_{2-x}Se phase. Such structure is desirable for solar cell applications. From **Figure 4.1**, the difference in reduction potential between $\text{Cu}^{2+}/\text{Cu}^0$ and $\text{In}^{3+}/\text{In}^0$ is 520 mV for HCl, 460mV for acetic acid, but only 370 mV for the oxalic acid additive. This indicates that oxalic acid is better than HCl and acetic acid for single phase CIS film deposition.

The shifts in the reduction potential may have resulted from different dissociation properties of the three acids. **Table 4.1** [79] shows the acidic dissociation constant of these three acids which were used as chelating agents in our CIS electrodeposition study. The pKa value of acetic acid is 4.79, which is much higher than the pH of the reaction (pH 2). The pKa value indicates that majority of acetic acid is in protonated form when added into deposition bath. In protonated forms, acetic acid does not have good chelating properties. On the other hand, oxalic acid has pKa₁ of 1.38. It means that in the CIS deposition bath (pH 2), oxalic acid exists predominantly in the monoanionic form COOH⁻COO⁻. This form of oxalic acid has strong chelating properties. While HCl is a strong acid that dissociates fully and exists completely in the protonated form, it has no chelating properties and is used as a control in this experiment.

Table 4-1 Structure and pKa value of different additives[79].

Chelating agents	Structure	pKa
oxalic acid		pKa ₁ = 1.38, pKa ₂ = 4.28
acetic acid		pKa= 4.79
HCl	H ⁺ Cl ⁻	Strong acid, no pKa

Figure 4.2a shows the XRD patterns of CIS deposited at -0.7V vs. Ag/AgCl for 20mins using different additives after annealing. From the XRD analysis, we observed oxalic acid additive

resulted in single phase CIS (JCPDS 00-040-1487) film, while HCl and acetic acid additives resulted in the formation of CIS film with Cu_7Se_4 (JCPDS 00-026-0557) secondary phase. At $2\theta=44^\circ$ (204) crystallographic plane of CIS, a “hump”, corresponding to a secondary phase was observed. Normalization of the data allows the comparison of the “hump” intensity as shown in **Figure 4.2b** and **Figure 4.2c**.

Figure 4.2 (a) XRD patterns of electrodeposited CIS films after annealing in N_2 at 350°C for 1.5 hours (Stars indicate the peaks from substrate); (b) magnification of the humps around (204) peak; (c) XRD data refinement according to the hump around (204) peak.

Rietveld refinement revealed that highly pure CIS film was achieved using oxalic acid while Cu_7Se_4 secondary phase was found to be 14.20% for the HCl case and up to 34.60% for the acetic acid case.

Figure 4.3 Raman spectra of CIS thin films added with three different acids.

We further investigate the chemical composition of the deposited CIS films by Raman spectroscopy. Raman spectroscopy can reveal vibration signatures which indicate the presence of amorphous phases in CIS films. These amorphous phases cannot be detected by thin film XRD analysis. The Raman spectrum of the CIS film with oxalic acid in **Figure 4.3** (olive colour) shows chalcopyrite CIS A1 and E vibration modes at 180cm^{-1} and 210 cm^{-1} [80]. Raman spectrums for CIS films deposited with HCl or acetic acids in the deposition bath revealed another strong peak at 262cm^{-1} , characteristic for A1 vibration mode of Cu-Se compound. This further confirms the presence of Cu-Se impurities in these films [80]. In addition, the intensity of the 262cm^{-1} peak is higher for the film deposited with HCl film as compared with the one deposited with acetic acid. This is consistent with the theory that acetic acid has better chelating properties compared to HCl.

Both Raman spectroscopy and XRD analysis reveal the absence of Cu-Se impurities in CIS films deposited when oxalic acid was used as precursor. There seems to be some discrepancy between the Raman and XRD data when comparing between acetic acid and HCl precursors. Raman spectroscopy revealed that Cu-Se impurities in CIS film deposited with HCl in the deposition bath is more than that deposited with acetic acid; while XRD data analysis showed that Cu-Se in film deposited with acetic acid is more than that obtained with HCl. This discrepancy between Cu-Se detected by the two analyses could be explained by the theory that XRD detects only the crystalline Cu-Se while Raman spectroscopy detects both the amorphous and crystalline Cu-Se. Hence, presence of HCl in the deposition bath results in lower amount of crystalline Cu-Se, but a higher amount of total Cu-Se (amorphous + crystalline) as compared to having acetic acid in the deposition bath. In summary, the film deposited with HCl acid has the highest percentage of Cu-Se impurities compared with that obtained with acetic acid, and the film obtained with oxalic acid is a single phase CIS and does not contain any Cu-Se. This result is consistent with our LSV data (difference in reduction potential (D_v) between $\text{Cu}^{2+}/\text{Cu}^0$ and $\text{In}^{3+}/\text{In}^0$ for deposition bath added with three acids: D_v for HCl is greater than the D_v for acetic acid, and D_v for acetic is greater than the D_v for oxalic acid) in **Figure 4.1**.

Figure 4.4 SEM images of annealed CIS films deposited at -0.7V vs. Ag/AgCl : (a) with acetic acid; (b) with HCl acid; (c) with oxalic acid.

As shown in the **Figure 4.4a**, the addition of acetic acid yields plate-like morphology dispersed in granular background. EDS analysis shows that these plates are Cu-Se and the background matrix is CIS. These plate-like structures appear to be elongated in the horizontal axis compared to CIS. The film obtained with HCl additive (**Figure 4.4b**) seems to be very rough. Using oxalic acid as the additive resulted in deposition of denser film which contains larger CIS grain size (**Figure 4.4c**). While the stoichiometry ($\text{Cu}:\text{In}:\text{Se}$) for sample c (**Figure 4.4c**) 1.15:1:2, is the closest to 1:1:2 (**Table 4.2**).

Table 4-2 Atomic ratio of Cu: In: Se for the CIS films deposited with different acidic additives

Sample with different acids	Cu:In:Se	Spectrum
Oxalic acid	1.15:1:2
Acetic acid	1.23:1:1.96
HCl	1.71:1:2.3

Finally, photoelectrochemical current measurements were carried out to compare the photon harvesting ability of the films deposited with different acids. **Figure 4.5** shows that all obtained CIS films are p-type semiconductor which yields cathodic photocurrent under light excitation. The dark current of the CIS film obtained with HCl additive was found to increase with time, indicating the chemical instability of the film. That might be due to the chemical and/or photochemical corrosion of Cu-Se amorphous phase. The photocurrent measured for

the film deposited using oxalic acid additive ($60\mu\text{A}/\text{cm}^2$) is slightly higher than that obtained for the film grown with acetic acid additive in the deposition bath ($50\mu\text{A}/\text{cm}^2$). Both films are stable under illumination condition. Therefore, in terms of photoelectrochemical properties, single phase CIS film obtained with oxalic acid additive in the deposition bath displays the best performance. We assume this CIS film is the most appropriate material for fabrication of CIS solar cell.

Figure 4.5 Photoelectrochemical current generated under white light illumination employing CIS films which were deposited with different acids, hold at -0.4V vs. Ag/AgCl in a pH 7 phosphate buffer solution.

Figure 4.6 shows the cross section image of CIS film obtained with oxalic acid after selenization at 520°C . The grain size was quite small and didn't grow much even after selenization. It forms vertical columns and there was large gap between columns. The whole

structure was very porous and not dense, which was bad for the charge transportation. It still needs further optimization to fabricate CIS solar cell.

Figure 4.6 Cross section of CIS film obtained with oxalic acid after selenization

4.1.3 Summary

Crystalline, single phase p-type CIS thin films have been successfully deposited by one-step electrodeposition at -0.7V vs Ag/AgCl using conventional deposition bath containing Cu^{2+} , H_2SeO_3 , In^{3+} precursors and oxalic acid as chelating agent. The use of acetic and hydrochloric acid as chelating agent in the deposition bath resulted in the CIS films with amorphous Cu-Se secondary phases, which is detrimental to the electrical behavior of CIS solar cell devices. This study demonstrated that the use of oxalic acid as a chelating agent in the deposition bath is the most effective to eliminate Cu-Se secondary phase from electrodeposited CIS film and also resulted in the most compact and uniform morphology. It exhibits the best photo-response among all of the films under time dependent photocurrent measurement. Finally, this study

suggests that oxalic acid has great potential to be an effective chelating agent in the deposition of single phase p-type CIS thin film for solar energy harvesting.

4.2 Stacked elemental layer deposition followed by selenization

4.2.1 Background

Electrochemical deposition could potentially be used to fabricate low cost CIGS solar cells. The process of electrochemical deposition yields high quality films using a high throughput process with low capital investment. As stated earlier, Cu-excess CIS or CIGS film is not desired and Cu-poor CIGS film is preferred for optimal solar cell performance. Technically, it is difficult to obtain desired stoichiometric CIGS film without Cu excess just by employing single step electrodeposition. It can be done by employing appropriate Cu^{2+} chelating agent as described in section 4.1. Alternatively excess Cu can be chemically etched out by treating the CIGS/CIS with KCN [49-51]. However, KCN is highly toxic and banned in many countries. Thereby there is increasing demand for alternative methods to deal with the Cu excess issue.

Actually, depositing sequential metal layers followed by selenization can be a judicious alternative preparation of desired stoichiometric CIS/CIGS absorber layers. Adopting this strategy, the best device with power conversion efficiency of 15.4% [81] has been recorded. Indeed, this stacked layer approach has several advantages:

- (i) First, and most significant advantage is that this method allows to easily vary the composition of the metal precursors just by varying the thickness of each layer [82].
- (ii) Second, since a different electrolyte is used for each metal layer deposition, the electrolyte pH and additive composition can be tailored individually to achieve the desired deposit quality (e.g. film morphology, deposition rates, light harvesting properties etc.).

Thus, in this study, we aim to explore this method to prepare our CIS absorber for subsequent investigation of Cd-free buffer.

4.2.2 Electrodeposition of stacked Cu&In bilayer

In this approach, Cu and In are deposited through the following reduction reactions

There are some limitations on the possible stacking orders when using the electrodeposition method to produce a layered precursor. At the potential required to electrodeposit Cu, the In film may be oxidized and stripped from the substrate. Therefore a sensible deposition sequence for the stack would be in order of increasingly negative standard reduction potential, which is first deposition of Cu then followed by In. Altering this order may result in dissolution of the In upon deposition of Cu, which would make control of

composition and uniformity difficult. **Figure 4.7a** shows the optical images of Cu and In stack layer after optimization. As shown in the image, Cu was first deposited onto a plasma cleaned Mo substrate, followed by the deposition of In layer on top of the Cu layer. **Figure 4.7b** and **4.7c** show the planar SEM images of Cu and In layer, respectively. The grain size of Cu film was quite small and the film has uniform and good coverage. The uniformity of the In film is not as good as Cu, but this problem can be solved during subsequent preheating process when the In starts to melt to form alloy with Cu. These two layers are stacked very nicely and compact (**Figure 4.7d**). The thickness of each layer is very uniform and can be easily controlled by varying the deposition time of each layer. In our study, we control the thickness of each layer by monitoring the total reduction charge for each metal to keep Cu/In ratio in the range of 0.7~0.9, which is required for optimum solar cell performance.

Figure 4.7 (a)optical images of the as-deposited Cu(left) and Indium on top of Cu(right) film; (b-d)FE-SEM images of (b) Cu film on Mo; (c) In film on Cu/Mo; (d) cross section of In/Cu layer on Mo substrate.

4.2.3 Conversion of stacked Cu/In metallic layer into CIS

Conversion of stacked Cu/In metallic layer into CIS films by selenization in the presence of selenium in the tube furnace includes three stages as illustrated in chapter 3.1.2.

1. Preheating---alloying of the metallic layer to form metal alloy
2. Low temperature selenization---incorporation of selenium to form metal selenide
3. High temperature selenization---reaction of metal selenide and recrystallization of CIS[83]

These three stages occur quickly and in this chapter, the formation of CIS from these three stages will be discussed in detail and a model will be proposed for the observed sequence of phase formation.

Alloying of stacked metallic layer

The melting point of In is very low (157°C), and most of In would be evaporated if the stacked metallic layer is directly selenized at elevated temperature. This In loss results in non-uniform composition of Cu/In. Preheating before selenization could help to mitigate the problem by alloying the metal to form homogenous alloy phases which are more resistant against the In evaporation

The Cu-In alloy is then used as the precursor for CIS production in the subsequent selenization process. The alloy film quality such as roughness and uniformity has great impact on the quality of the final CIS film. Therefore, the control of preheating temperature is critical. One possible undesirable effect of alloying could be lateral segregation of elements into islands of stable phases, leading to a non-uniform composition at small length scales. **Figure 4.8** shows the optical microscopic image of Cu/In double layer film annealed at different temperature and duration. Film annealed at 180°C in Ar atmosphere for 30mins has a few small humps (**Figure 4.8a**). The film quality was significantly improved and quite uniform at reduced temperature 150°C (**Figure 4.8b**). However, the humps were again present when the duration of annealing at lower temperature (150°C) was extended from 30 min to 60 min (**Figure 4.8c**). In summary, annealing at 150°C for 30mins was found to be the optimized conditions for the first step preheating treatment.

Figure 4.8 Optical microscopic images of Cu/In film anneal at (a) 180°C for 30mins, (b) 150°C for 30mins and (c) 150°C for 60mins

Figure 4.9 shows the X-Ray diffraction pattern of Cu-In alloy after annealing at 150°C for 30mins. The Cu/In atomic ratio for this film was determined to be around 0.85. The pattern shows reflections from $\text{Cu}_{11}\text{In}_9$ (312), (11-2), (313) and (622). There is another smaller peak, which is assigned to (002) CuIn_2 . The rest of small peaks with very low intensity are referred to small amount of liquid In phases. No peak from Cu is detected from the XRD spectrum. So the possible reaction taking place in the preheating stage is

$\text{Cu}_{11}\text{In}_9$ alloy[84] is much more stable than In at elevated temperature. As can be seen from the phase diagram of Cu-In system in **Figure 4.10**, the purpose of the preheating step at 150°C is to promote the complete conversion of stacked metals to $\text{Cu}_{11}\text{In}_9$ and some In-rich phases[24]. $\text{Cu}_{11}\text{In}_9$ is the most stable phase in thin films of Cu/In alloys at high temperatures, and in general any other unstable Cu/In phase observed in the films tends to

be transformed into $\text{Cu}_{11}\text{In}_9$ [85]. This kind of slightly Cu-rich precursors was found to be optimal for Se-vapor selenization[86].

Figure 4.9 XRD of Cu-In alloy after annealing at 150°C for 30mins

Figure 4.10 Phase diagram[87] of the Cu-In binary system in terms of atomic In/(Cu+In)%

Low temperature selenization

After preheating process to form Cu-In alloy, the temperature is raised to around 300°C as Se evaporates at this elevated temperature. Se vapor reacts with Cu-In alloy producing a series of binary compounds.

During the selenization process of Cu-In alloy, the incorporation of Se element into the film results in elongation of the lattice and volume expansion of the film. Direct selenization of the Cu-In alloy at high temperature (around 500°C) would result in very fast volume expansion, generating a lot of internal stress inside the film. It may also cause high degree of roughness on the CIS surface, cracks inside the CIS films and delamination of CIS from the Mo substrate. Hence direct selenization at 500°C is not recommended.

In this study, an intermediate step was introduced to incorporate the Se slowly at lower temperature to form metal selenides and CIS with small grain size and to release part of the internal stress. This is then followed by higher temperature selenization whereby the metal selenides can react to form CIS and the grain size of CIS can be improved as compared to direct selenization. Most of the internal stress caused by selenization comes from the initial step of the Se incorporation. Therefore, the reaction in this step should be controlled at as slow as possible to minimize the disadvantages resulting from the stress expansion. In our selenization process, we use solid Se powder as the Se source and since the melting temperature of Se is around 240°C, the reaction temperature for this low temperature selenization process should be slightly higher than 240°C to activate the Se powder. **Figure 4.11** shows the Cu-In alloy with Cu/In ratio 0.85 annealed at different temperatures during this low temperature selenization step. After selenization at 260°C, there appears a lot of big plates, which could be Cu-Se secondary phase (**Figure 4.11 a&d**). This secondary phase will react and subsequently disappear during the following high temperature selenization process. But these big plates have similar disadvantages with the humps appearing in the preheating process as discussed earlier, which will also cause non-uniform composition at small length scales. At higher temperature (280°C), with higher Se activity, the plates are reduced (**Figure 4.11 b&e**). Finally when the temperature is increased to 300°C, there are no obvious big plates on the surface (**Figure 4.11 c&f**). Therefore, selenization at 300°C for 20mins at low temperature selenization step is better for further film growth.

Figure 4.11 Planar(top) and cross section(bottom) FE- SEM images of Cu-In alloy annealed at (a,d)260°C, (b,e) 280°C and (c,f) 300°C for 20mins.

High temperature selenization

During high temperature selenization, metal selenides and small grain CIS will react and recrystallize to form big grain CIS. The temperature applied in this step will directly affect the final grain size of CIS film. Typically, it is easy to grow bigger grains at higher temperature. It is noted that the reported high efficiency CIGS/CIS solar cells by metallic precursor approach coincides with big grain CIS [1, 33] suggesting that big grains may be preferred for higher efficiency. Bearing this in mind, the high temperature selenization temperature should be as high as possible. However, higher temperature will cause the formation of thicker MoSe_2 layer and poor adhesion between CIS and Mo, which are both detrimental to the device performance [88-90]. Therefore, the optimal selenization temperature should be compromised

taking into account the above factors. After several iterations of optimization, selenization at 520°C was found to produce the best quality of CIS film as shown in **Figure 4.12 a&b**. The film has compact structure, large grain size around 800nm-1µm and good adhesion to Mo.

In CuInSe₂ solar cell, the atomic ratio of Cu and In is very important. After high temperature selenization, Cu-rich film normally contains Cu_{2-x}Se, which is highly conductive and will cause short circuit of the cell [35, 74] as discussed in section 4.1.1. Therefore, it is desirable to keep the film always Cu-poor. We have systematically varied the Cu/In ratio from 0.7 to 1.1 and found that the Cu/In ratio affects the grain growth and grain size. **Figure 4.12** shows the FE-SEM top morphology (**a &c**) and cross section (**b&d**) of the selenized films with Cu/In (a) 0.85 (c) and Cu/In 1.1. It is obvious that when the Cu/In ratio is 0.85, the grain size is around 800nm-1µm. When the ratio increases to 1.1, the grain size grows to 1-3 µm. It is also apparent that there is formation of some big plates (denoted by red circles), which likely corresponds to the more conductive Cu_{2-x}Se. This is because the films with higher Cu/In ratio form more Cu-Se during the selenization process. In turn, Cu-Se can promote the crystal growth during the selenization process[23], that's why the grain size of the film with higher Cu/In ratio is much bigger than the one with lower ratio. However for such films, there is a high possibility that excess Cu-Se could be left behind in the film after selenization.

Figure 4.12 FE-SEM cross section of selenized CuInSe_2 with different Cu/In ratio (a-b) Cu/In 0.85 and (c-d) Cu/In 1.1

Figure 4.13 shows the XRD spectra of Cu-In at different stages of selenization. After low T selenization of preheated Cu-In alloy, there is formation of highly polycrystalline CIS. At 40.6° , there is a small peak, which may correspond to Cu-Se. Since Cu-Se or In-Se are amorphous, the peak intensity is very low or even cannot be detected from XRD. After high T selenization, this small peak disappears.

Figure 4.13 XRD spectra of Cu-In during different selenization stage

However, XRD cannot detect the amorphous phases of the metal selenide. Hence, in order to study and investigate the reaction mechanisms at each stage, Raman spectroscopy measurement was carried out. **Figure 4.14** shows the Raman spectra of the CIS film at different selenization stages. It is observed that after low T selenization (150°C 30mins + 300°C 20mins), there exists E mode CIS (207, 228 cm^{-1}), A1 mode Cu_{2-x}Se (258 cm^{-1}) and InSe (175 cm^{-1} , inset). After high T selenization (full selenization), the Cu_{2-x}Se and InSe peaks disappear and the peak intensity of CIS is much enhanced. Besides, there arises another new peak at 152 cm^{-1} , which corresponds to the ordered vacancy compound of CIS (CuIn_3Se_5 or CuIn_5Se_8).

Figure 4.14 Raman spectra of the CIS after low T selenization and high T selenization

From the XRD and Raman study, the possible formation mechanism of CIS is hypothesized as follows: during the first stage preheating process, Cu and In reacts to form $\text{Cu}_{11}\text{In}_9$ alloy and liquid phase Indium; then at the second stage-low T selenization, the CuIn alloy and liquid In react with selenium to form polycrystalline CuInSe_2 and amorphous Cu_{2-x}Se and InSe ; at the last stage-high T selenization, all the selenides react to form single phase CIS and the grain size of CIS grows during this stage. If the film is Cu rich, the final film after high T selenization will still contain some Cu_{2-x}Se . This highly conductive Cu_{2-x}Se will cause the shunting problem to the CIS solar cell. Therefore, the Cu/In ratio has to be kept in a proper range, which is around 0.85.

4.2.4 CIS device with CdS buffer

The CIS solar cell is fabricated through the processes described in chapter 3.3. The cross section of the CIS solar cell is shown in **Figure 4.15(a)**. On top of $1.35\mu\text{m}$ selenized CIS with Cu/In ratio 0.85, 50nm CdS was deposited by CBD process as described in chapter 3.2.1, followed by i-ZnO and Al:ZnO through sputtering and lastly Ni: Al electrode by thermal evaporation to complete the solar cell structure.

Figure 4.15 (a) Cross section of CIS solar cell with CdS buffer, (b) J-V curve of the measured CIS device, (c) external quantum efficiency of CIS device, and (d) band gap of CIS obtained from the EQE measurement.

The PCE of CIS solar cell is 3.25% ($V_{oc}=0.28$ V, $J_{sc}=30.25$ mA/cm² and FF=38.2%). From the EQE measurement, the calculated J_{sc} is 31.2mA/cm², which is very close to the J_{sc} from the J-V measurement. The band gap of CIS is obtained by plotting $[h\nu \ln (1-EQE)]^2$ vs $h\nu$ and by extrapolating the slope to the x-axis. The intercept at x-axis represents the energy band gap of CIS, which is 1.06 eV. It is very close to the theoretical value of pure CuInSe₂.

4.2.5 Summary

Electrodeposition of stacked elemental layer of Cu and In allows easier control of Cu/In ratio and thickness of each layer. The selenization process of Cu/In mainly includes three steps: preheating to convert Cu/In stacked layer to Cu₁₁In₉ alloy and liquid In, then low temperature selenization to incorporate Se to convert the metallic alloy to Cu-Se, In-Se and small grain CIS, then lastly high temperature selenization to promote Cu-Se to react with In-Se to form CIS and recrystallize small grain CIS to form bigger grain CIS. After a series of optimization, device quality CIS is fabricated with Cu/In ratio 0.85 through preheating at 150°C for 30mins, then followed by 300°C selenization for 20mins and last 520°C for 10mins. The as-selenized CIS film, with band gap 1.06 eV, has grain size around 800nm-1μm and achieved 3.25% with CdS as buffer layer.

Chapter 5. Cd-free Zn(O,S) buffer layer properties and application in CIS device

5.1 Effect of thickness of Zn(O,S) layer on the CIS solar cell performance

5.1.1 Background

Many alternative materials have been tried in the past decade for a Cd-free buffer layer in CIGS solar cells. ZnS-based buffer layer has emerged to be one of the most promising candidates for this purpose. It was reported that CIGS cells fabricated with chemical bath deposited (CBD) Zn-S buffer layer yielded 19.1% efficiency[91], comparable to the efficiency of CIGS cell with CdS buffer which was used as a control in that study. Nakada group and Showa Shell[64] are two notable groups that have successfully established the CBD Zn (O, S) as alternative buffer layers with compromised efficiency. Nakada et al.[18, 64] employed 120nm Zn(O,S) achieved by 3 CBD deposition cycles. Conversely, Showa Shell[64] deposited a Zn(O,S) buffer which had thickness around 50nm. While there were differences in the deposition methods used by the various groups, it is noted that most of the research groups used a Zn(O,S) buffer of about 50-100nm [17-19]. Recently, there have been proponents for a thinner buffer layer. Nakada group reported that very thin buffer (10nm) was highly promising [20]. This result was also echoed by reports from other research group [21] who compared the 15nm CBD-Zn(O,S) with the control 50nm CdS buffer layer for CIGS solar cell applications. The excellent performance of ultra-thin Zn(O,S) buffers were reported either by CBD method or the atomic layer deposition (ALD) method[22]. For ALD Zn (O, S), in some cases, ultra-thin films worked even better than the thicker one[22]. However, the

results are largely empirical and the fundamental science to explain the reasons for the equivalent or better performance of the ultra-thin buffer layer compared to the thicker one is still unclear.

Here we aim to understand the effect of thickness of Zn(O,S) buffer layer on CIS solar cell. The optical properties and cell efficiencies of CIS cells with different thickness of Zn(O,S) buffer layers are investigated. We find that 20nm Zn(O,S) has higher band gap and cells fabricated with the 20nm Zn(O,S) buffer layer generates double the PCE compared with cells fabricated using 50nm Zn(O,S) buffer layer. While the conduction band offset (CBO) of the Zn(O,S)/CIS interface is almost identical for different thicknesses in this study, the carrier lifetime of the 20nm Zn(O,S)/CIS cells are measured to be higher than the 50nm one. This offers a possible explanation to understand the reason why the 20nm Zn(O,S)/CIS cell results in a higher measured J_{sc} than the cell with 50nm buffer. Although there were previous reports on the utilization of Zn(O,S) buffer layer for CIGS solar cell, this study is the first to correlate device data to charge carrier dynamics and investigate the effect of thickness of the buffer layer by optical probing.

5.1.2 Growth kinetics

The chemical bath solution comprised of 0.08M Zn(Ac)₂, 5M Thiourea (TU) and 7M NH₄OH in deionized (DI) water. The aqueous NH₃ liberated from NH₄OH functioned as a complexing agent to form complex with Zn²⁺ ions and limit the growth of ZnS, through the following reactions[92].

Complexation process:

ZnS film growth

Since solution is basic, $\text{Zn}(\text{OH})_2$ will also form through the reaction in equation (5.3)

Annealing the deposited films at 200°C for 20mins causes $\text{Zn}(\text{OH})_2$ within the Zn(O,S) film to be converted to ZnO.

Figure 5.1 shows the time duration for the CBD solution to turn milky at various ammonia concentrations. This time duration is defined to be the milky solution (MS) time. It is observed that in CBD Zn(O,S) process, the MS time is dependent on the ammonia concentration when the other two precursors' concentrations are fixed. We found that a higher ammonia concentration corresponds to a longer MS time. When the ammonia concentration is increased from 2M to 7M, the MS time increases from 15mins to 25mins. **Figure 5.2** shows the SEM images of the surface of the Zn(O,S) at the instance where the solution just starts to turn milky. The images using different ammonia concentration as precursors are shown in **Figure 5.2**. At 2M ammonia, the coverage of Zn(O,S) on CIS was quite poor. There were many pin holes and some of the CIS was even totally exposed without any coverage of Zn(O,S). Increasing ammonia concentration to 5M leads to significant improvement of Zn(O,S) coverage on the CIS surface. However, at this concentration of ammonia, there were numerous clusters of

large Zn(O,S) particles on the surface. When the ammonia concentration further increased to 7M, the coverage of Zn(O,S) was uniform and there were few large clusters of Zn(O,S). The SEM images revealed that concentration of ammonia precursor have an impact on the surface morphology of the deposited film. We believe that the main reason for the difference in MS time and morphology is highly related to the function of ammonia as complexing agent.

Figure 5.1 The duration before the CBD solution turned milky at different ammonia concentration (milky solution time)

Figure 5.2 SEM images of surface morphology of Zn(O,S) deposited on CIS with different ammonia concentration (a) 2M, (b) 5M and (c) 7M.

The solubility of ZnS ($K_{sp}=1.0 \times 10^{-25}$)[93] is lower than that of $Zn(OH)_2$ ($K_{sp}=1.0 \times 10^{-16}$). Therefore, when the concentration of Zn^{2+} in the bath is low, ZnS growth is relatively favorable compared to $Zn(OH)_2$ growth[91]. At the early stage of deposition, the ammonia concentration is high. Most of the Zn^{2+} ions are complexed by NH_3 , leaving a low Zn^{2+} in the bath. The complexed $Zn(NH_3)_4^{2+}$ then slowly releases the Zn^{2+} into the deposition bath. Since total $[Zn^{2+}]$ is quite low in the solution, Zn^{2+} will preferentially react with Thiourea to form ZnS, instead of reacting with OH^- to form $Zn(OH)_2$. At this early stage of the reaction, ZnS growth is favorable and well controlled, while $Zn(OH)_2$ growth is suppressed. At this point of time, there is heterogeneous growth of ZnS on the CIS surface, slowly covering the CIS surface with small ZnS particles. At this stage, the solution is still clear. As the reaction time increases, the concentration of Thiourea decreases to a point that it is favorable for large clusters of $Zn(OH)_2$ to be formed. Such $Zn(S,O,OH)$ film typically has a poor adhesion to the CIS and easily detaches. The large clusters also cause the solution to turn milky at this stage of the reaction. This process is called homogeneous growth.

The differences in ammonia concentration could also be explained in the following paragraph. At high ammonia concentration levels, Zn^{2+} ions are highly complexed and binded in the form of $\text{Zn}(\text{NH}_3)_4^{2+}$. This helps to keep the concentration Zn^{2+} ions low which favors the formation of ZnS as opposed to ZnO. This preferential formation of ZnS continues even after the TU concentration is depleted because Zn^{2+} ions are continually kept low by ammonias complexing activity. In contrast, at lower ammonia concentration, the complexing activity is largely inferior and only sufficient to keep Zn^{2+} ions level low at the initial part of the reaction to suppress formation of $\text{Zn}(\text{OH})_2$. As the reaction progress, the TU concentration is reduced and there are more free Zn^{2+} in the solution. $\text{Zn}(\text{OH})_2$ growth is no longer suppressed and clusters of $\text{Zn}(\text{OH})_2$ are formed easily at an increased rate. This explains the reason for the longer MS time of the solution with higher ammonia concentration.

In summary, the reaction kinetics of the CBD Zn(O,S) deposition start with heterogeneous growth, followed by homogeneous growth. The MS time could be used as a measure for the duration of heterogeneous growth. Fixing the concentration of TU, it was found that a higher concentration ammonia can form more complex with Zn^{2+} and release Zn^{2+} more slowly, consequently extending the duration of the heterogeneous growth to cover the CIS more uniformly. At a higher ammonia concentration, the growth of Zn(O,S) is slower, more uniform, and milky solution time is also extended.

5.1.3 Zn (O, S) /CIS with varied Zn (O, S) thickness

Figure 5.3a shows the top-view FE-SEM images of Zn(O,S) grown on selenized CIS. The Zn(O,S) film provided excellent coverage for the CIS without pinholes. The film morphology

revealed a fine grain structure. **Figure 5.3b** shows the XPS surface scan of the Zn(O,S)/CIS surface with different Zn(O,S) thickness. For the 20nm and 50nm Zn(O,S)/CIS samples that all the peaks from Zn, S and O were present but there are no peaks corresponding to Cu, In and Se. This is further proof that the coverage of the Zn(O,S) on CIS film is very uniform and dense.

The cross section analysis of Zn(O,S)/CIS interface was done for two different CBD conditions. In our deposition process, 12mins deposition time resulted in around 20-25 nm Zn(O,S) (**Figure 5.3c**), and 25mins deposition produced a layer of 50 nm Zn(O,S) (**Figure 5.3d**).

Figure 5.3 (a) Planar FE-SEM image of annealed Zn(O,S) on top of CIS, (b) XPS survey scan

for the surface of Zn(O,S)/CIS/Mo, and cross section of Zn(O,S)/CIS interface with (c) 20nm Zn(O,S)/CIS,(d) 50nm Zn(O,S)/CIS

Figure 5.4 (a) optical transmittance of Zn(O,S) film grown on quartz substrate for different time with annealing treatment at 200°C for 20mins ,inset: energy band gap plot of the Zn(O,S) films on quartz; (b) XPS depth profile for a sputtered 50nm Zn(O,S)/CIS layer

Figure 5.4a shows the optical absorption spectra of the Zn(O,S) layer deposited on UV-transparent quartz after annealing at 200°C for 20mins. The Zn(O,S) film was characterized using UV-Vis spectroscopy at a wavelength range of 300-800nm. We observed that the transmittance of 50nm film was slightly lower than that of 20nm film in the 300-600nm range. The band gap of the 20nm Zn(O,S) was 3.75 eV (**Figure 5.4a inset**). Increasing the CBD deposition time not only increased the film thickness to 50 nm, but also reduced the E_g to 3.4 eV. The reason for this decrease is due to the dependence of the E_g of Zn(O,S) on the S/(S+O) ratio[67, 68]. M.bar.et al reported that when the CBD method was used for buffer layer deposition, ZnS/(ZnS+ZnO) formation is thickness dependent[94]. At the initial growth stage, a very thin ZnS film is formed and in the later growth stage, more O is incorporated in the ZnS film, resulting in a decreased S/(S+O) ratio. **Figure 5.4b** shows the XPS depth profile of 50nm Zn(O,S)/CIS from the Zn(O,S) surface to the Zn(O,S)/CIS interface with increasing

sputtering time. It is observed that at the surface of Zn(O,S) (0s sputtering), the S/(S+O) ratio is around 0.5, this ratio increases gradually towards the Zn(O, S)/CIS interface (400s sputtering) till 0.7. As discussed earlier, due to the characteristic growth process of CBD-Zn(O, S), we can assume that the composition profile from 240s sputtering onwards actually is quite similar to that of 20nm Zn(O, S), provided constant sputtering rate and Zn(O, S) growth rate. Since the S/(S+O) has a direct impact on E_g , it can be inferred that for the CBD deposited Zn(O, S) film, the band gap is thickness dependent. The 20nm Zn (O, S) is sulfur rich and has a band gap of 3.75 eV. This band gap value is close to that of pure ZnS film (3.8 eV); while for the 50nm film, the presence of more oxygen or ZnO reduces the band gap to be closer to the theoretical band gap of ZnO (3.2eV).

Figure 5.5 shows the J-V curves and EQE spectra of the typical CIS solar cells fabricated with 20nm and 50nm Zn(O, S) after post treatment at 200°C in air for 20 mins. As shown in **Figure 5.5a**, the cell with 20nm Zn(O, S) has a power conversion efficiency of 3.9%. When the buffer thickness increased to 50nm, there was little effect to V_{oc} and FF values. However, J_{sc} decreased sharply from 38.8mA/cm² to 16.6mA/cm², resulting in a decline in cell performance to 1.53%. **Figure 5.5b** shows the external quantum conversion efficiency of these two cells. The EQE of 50nm cell was only about half of the EQE of 20nm cell for the entire wavelength range measured. The integrated photocurrent measured by EQE is consistent with J_{sc} whereby the J_{sc} of 50nm cell was also about half of that of 20nm cell. A possible reason for the sharp decrease of J_{sc} measurements may be due to the high series resistance of thicker Zn(O,S) film[95]. There is slight difference on the onset of the absorbance of the device in EQE curve on higher wavelength region. Probably,

different degrees of selenization in the different position of selenization tube developed slightly different band gap of the absorbers.

Figure 5.5 (a) J-V curve and (b) EQE spectra of CIS solar cell fabricated with 20nm and 50nm Zn(O,S) annealed at 200°C for 20 mins.

Table 5-1 Parameter for J-V characteristics of photovoltaic device with 20nm and 50nm thick Zn(O,S) buffer layer:

Buffer Layer Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill Factor (%)	Efficiency (%)
20nm	0.285±0.017	34.25±7.44	33.14±3.91	3.20±0.60
50nm	0.233±0.035	20.39±3.05	32.03±1.51	1.50±0.04

The band alignment of the heterojunction is determined from depth profiling XPS of shallow core levels and the valence band edge as shown in **Figure 5.6a**[96]. During the depth profiling

towards the interface, the shallow core levels of Zn 3d and In 4d of the Zn(O,S) and CIS, respectively, are monitored. When the relative contribution of the shallow core levels are similar in intensities, the level of depth profile is taken to indicate the Zn(O,S)/CIS interface where the VBO measurement is obtained. However, since this interface spectrum contains overlapping valence band contribution from each material, they have to be deconvoluted to avoid errors associated with overlap of valence band signals[97]. In this approach, we use the bulk valence band spectra of sputter clean Zn(O,S) and CIS at the interface, as shown in **Figure 5.6b** respectively, to achieve the deconvolution. The shallow core levels of the bulk materials are scaled to match both the intensity and the binding energies as measured from the interface spectrum. This will account for both electrostatic and intensity variations. The scaled bulk spectra were subsequently summed to check the agreement with the interface spectra and this is shown in **Figure 5.6c**, where a good agreement was observed. The VBO can then be determined from the individual bulk valence band edges after the scaling and alignment as shown in **Figure 5.6a**. A VBO value of 1.2 eV is obtained for the Zn (O, S)/CIS interface. The corresponding CBO can be derived from the equation

$$\text{CBO} = E_{g \text{ Zn (O, S)}} - E_{g \text{ CIS}} - \text{VBO} \quad [96, 98] \quad (5.4)$$

Figure 5.6d shows the XPS survey spectrum of the bare CIS surface with the individual elements. The composition of the film is determined from quantitative analysis of the fitted core levels from the individual elements. This yields a material composition of $\text{CuIn}_{2.9}\text{Se}_{4.8}$. This stoichiometry is close to that reported for surface composition of CIS (CuIn_3Se_5), where an ordered vacancy compound (OVC) exists and this yields a band gap of 1.23 eV and this is the value we use for our CBO calculation [99]. As discussed earlier, the composition of 50nm

Zn(O,S) is quite similar to that of 20nm Zn(O,S) at the Zn(O,S)/CIS interface, hence we have used the band gap value (3.75eV) of 20nm Zn(O,S) for CBO calculations. According to equation (4), the calculated CBO value is 1.32 eV, which is very close to the reported value by Nakada group [96].

Importantly, it is shown from this work that CBO value for the 20nm Zn(O,S)/CIS would be very similar to the CBO of 50 nm Zn(O,S)/CIS through the similar determined VBOs and compositions of the material. This also agrees with the identical V_{oc} of the devices since there is a direct correlation between the CBO and V_{oc} values[100, 101]. This serves as a further proof for our CBO determination method. We therefore conclude from our studies that the CBO in our devices is not the dominant factor that gives rise to the drastic performance differences as observed. This is similar to the proposition put forward by the Nakada group[96].

Figure 5.6 (a) XPS depth profile of 50nm Zn(O,S)/CIS interface, (b) XPS bulk profile of CIS and Zn(O,S), (c) interface spectra matching with scaled bulk spectra and (d) XPS surface scan of selenized CIS

In order to further investigate the fundamental reasons of the superior performance of 20nm Zn(O,S)/CIS cell compared to the 50nm Zn(O,S)/CIS cell, the carrier (electron) relaxation dynamics of CIS at the Zn(O,S)/CIS interface is investigated by femtosecond optical pump-optical probe (OPOP). The Zn(O,S)/CIS was pumped at 800nm, and then probed at 900nm. The decay curves of bare CIS and CIS/Zn(O,S) samples are shown in **Figure 5.7a**. As the probe is at 900nm, this decay represents the decay of the carriers from CIS to the Zn(O,S) layer. It is observed that there is a delay in the excitation of 20nm Zn (O, S)/CIS and 50nm

Zn (O, S)/CIS compared to bare CIS. This correlates to the rise time of these three different samples (**Table 5.2**). The rise time of 20nm Zn (O, S)/CIS and 50nm Zn(O,S)/CIS has both increased from 2ps (bare CIS) to 9ps (Zn(O,S)/CIS). Longer rise time indicates that the electrons take more time to saturate the conduction band of CIS. The delay in the saturation of CIS electrons in conduction band is evidence of charge transfer from CIS conduction band to the conduction band or defect states of Zn(O,S), which confirms that there is a charge transfer process between CIS and Zn(O,S) as shown in **Figure 5.8**(process 2 &3). The electron decay time of these two samples is both higher than that of bare CIS sample. Compared to the 50nm Zn(O,S)/CIS, the electron decay time of CIS in the 20nm Zn(O,S)/CIS sample is much higher(43ps compared to 25.8ps), indicating that the recombination rate of 20nm Zn(O,S)/CIS in the depletion region is much slower than that of 50 nm Zn(O,S)/CIS. This is probably due to lower defect density in the 20nm Zn(O, S) film than the 50nm Zn(O,S) film. During the second half growth of 50nm Zn(O,S), more Zn(OH)₂ is formed. After heat treatment, Zn(OH)₂ is converted to ZnO, leaving behind a lot of dangling bonds. These dangling bonds are source of traps for the recombination of electrons and holes. Therefore, the charge relaxation time of 20nm Zn(O,S), is higher than that of 50nm Zn(O,S)/CIS. In other words, the recombination rate of 20nm Zn(O,S)/CIS is much lower than that of 50nm Zn(O,S)/CIS, which support the higher J_{sc} value for the 20nm Zn(O,S)/CIS solar cell than that of 50nm Zn(O,S)/CIS solar cell.

Femtosecond laser excited time-resolved photoluminescence (TRPL) decay curves of the Zn(O,S)/CIS/glass samples collected at defect states emission (550 nm) of Zn(O,S) are shown in **Figure 5.7b**. Best fits to the decay curves are achieved with double exponential decays. Decay times and their coefficients are tabulated in **Table 5. 3**. The first decay was found to

be not much affected by changes in thickness of Zn(O,S) film, but second decay is longer for thinner Zn(O,S). The lower PL intensity for the 20 nm film than 50 nm proves that there are fewer defects in 20nm Zn(O,S)/CIS sample.

The reason for the slightly faster decay time τ_1 could be due to surface defects at the Zn(O,S) surface. Surface defects results in a higher recombination rate of electrons and holes. After the CIS solar cell is irradiated under light, the holes will be transported to CIS side and conducted to circuit through Mo back electrode and the electrons from CIS will transport to buffer Zn(O,S) side then to TCO and conducted to circuit. Compared to the τ_2 life time of the 20nm Zn(O,S)/CIS (2294 ps) the τ_2 life time for the 50nm Zn(O,S) is much shorter (1570 ps). This is because the fewer defects inside 20nm Zn(O,S) as discussed earlier. A higher rate of recombination is also another reason to explain why the life time for the 50nm Zn(O,S) is much reduced compared to 20nm Zn(O,S)/CIS and to explain why J_{sc} for the 50nm Zn(O,S)/CIS cell is only half of the J_{sc} of 20nm Zn(O,S)/CIS cell.

Figure 5.7 (a) pump probe transient for the Zn(O,S)/CIS/glass samples with 20nm and 50nm Zn(O,S) after heat treatment at 200°C for 20mins. (b) Time-resolved luminescence decay curve. Excitation wavelength was 325nm.

Table 5-2 Luminescence decay parameters obtained with an excitation wavelength at 325 nm and τ the lifetime and A the corresponding amplitude

samples	A_1	$\tau_1(\text{ps})$	A_2	$\tau_2(\text{ps})$
20nmZn(O,S)/CIS	0.72 ± 0.02	192 ± 50	0.3 ± 0.02	2300 ± 150
50nmZn(O,S)/CIS	0.72 ± 0.02	170 ± 40	0.3 ± 0.02	1600 ± 100

Table 5-3 OPOP decay parameters and τ the lifetime and t the corresponding rise time

samples	Decay τ 1(ps)	Rise t (ps)
CIS	12 $\pm$ 3	2 $\pm$ 1
20nm Zn(O,S)/CIS	43 $\pm$ 5	9 $\pm$ 2
50nm Zn(O,S)/CIS	26 $\pm$ 5	9 $\pm$ 2

Figure 5.8 Band diagram of Zn (O, S)/CIS/glass sample.

5.1.4 Effect of post-deposition annealing

Annealing treatment of the CBD Zn(O,S) is normally done for CIS thin film solar cell fabrication to convert the Zn(OH)_2 to ZnO at elevated temperature and also improve the crystallinity of the buffer [19]. Research groups have found that 200°C annealing is the

optimal heat treatment temperature for the Zn(O,S)/CIS system[102]. Annealing also increases the electron injection efficiency but too high annealing temperature will cause the quantum efficiency loss in the long wavelength region (800-1100nm) [102]. In order to further investigate the effect of annealing on the optical, electronic properties of Zn(O,S) and also on the device performance, a comparison study on the Zn(O,S) buffer and CIS devices with Zn(O,S) buffer without and with annealing at 200°C was carried out. **Figure 5.10a** shows the band gap of 20nm Zn(O,S) with and without annealing. The band gap of as-deposited Zn(O,S) is around 4.2 eV, much higher than the typical value of bulk ZnS (3.6 eV). This is due to the quantum confinement effects of the small particle size (around 5nm) of the polycrystalline Zn(O,S) films[19]. Other groups also have the similar findings [103, 104]. After annealing treatment, the grain size grows slightly bigger, which is confirmed by the higher XRD peak intensity in **Figure 5.9**. The increased crystallite size causes weaker quantum confinement effect and band gap will be slightly reduced. Some other research group also found that after annealing the conduction band of Zn(O,S) was lowered down because of the conversion of Zn-OH to Zn-O and thus the band gap of annealed Zn(O,S) is reduced[105].

Figure 5.9 XRD of 50nm Zn(O,S) before and after annealing

Figure 5.10b compares the device performance of solar cell with 20nm Zn(O,S) before and after annealing. After annealing, the PCE increases from 1.3% to 3.9%, with V_{oc} increment from 0.185V to 0.29V, J_{sc} from 27.37mA/cm² to 38.8mA/cm² and fill factor from 25.6 to 34.5. After heat treatment, the PCE has increased almost three times compared to the one without annealing. Transient properties of the 20nm Zn(O,S)/CIS film with and without annealing were investigated by OPOP (**Figure 5.11**) to understand the fundamental carrier dynamics of the system.

Figure 5.10 (a) UV-Vis energy band gap plot of 20nm CBD Zn(O,S) and (b) J-V curve of CIS solar cell fabricated with 20nm Zn(O,S) with and without annealing at 200°C for 20mins

Figure 5.11 shows that the decay curve has a right shift after heat treatment, which implies that the charge transfer between Zn(O,S) and CIS is much enhanced by the heat treatment. OPOP decay parameters were summarized in **Table 5.4**. The rise time for pure CIS thin film was 2ps, and 20nm Zn(O,S)/CIS without annealing was 3ps. The improved rise time means that there is charge transfer from CIS to Zn(O,S). However, this process was quite weak between the CIS and as-deposited Zn(O,S) without annealing. After annealing at 200°C for 20mins, this conversion process was much enhanced and rise time increased to 9ps, much higher than 3ps for the one without treatment, indicating charge injection rate from CIS to Zn(O,S) is much enhanced after annealing. This probably because heat treatment induced increase of band bending in the CIS absorber illustrated in **Figure 5.12** could result in lower CBO, which was beneficial for the charge transportation[105]. Some work also reported the formation of acceptor like Zn_{Cu}^+ states [106] at the absorber surface, as a result of heat treatment-promoted Cu-Zn intermixing at the buffer/absorber interface, enhanced downward

band bending towards the CIS surface. The downward bending resulted in the increase in open circuit voltage after heat treatment.

After heat treatment, the minority carrier lifetime also increased from 20ps to 43ps. This can be explained by the improvement of the Zn(O,S) film quality that results from the reduction of the amount of Zn-OH bonds as we have discussed previously in section 5.1.3. This improvement enhanced the electron injection efficiency[54, 92] and thus resulted in higher short circuit current.

Figure 5.11 Pump probe transient for the Zn(O,S)/CIS/glass samples with 20nm Zn(O,S) before and after heat treatment at 200°C for 20mins.

Table 5-4 OPOP decay parameters and τ the lifetime and t the corresponding rise time

samples	Decay τ 1(ps)	Rise t (ps)
CIS	12 ± 3	2 ± 1
20nmZn(O,S)/CIS without annealing	20 ± 5	3 ± 1
20nmZn(O,S)/CIS with annealing	43 ± 5	9 ± 2

Figure 5.12 Model scheme of the (Zn(S,O)/ZnS)/CIS hetero-interface before (black line) and after (red line) post-annealing[105].

In summary, heat treatment at 200°C for 20mins modifies the electronic structure between Zn(O,S) and CIS. In addition, the charge transfer process at Zn(O,S) and CIS was enhanced and minority carrier lifetime was doubled after heat treatment. All of these factors contribute

to the improved open circuit voltage, short circuit current, fill factor and thus PCE of the solar cell with 20nm Zn(O,S) after annealing.

5.1.5 Comparison between CdS/CIS and CBD-Zn (O, S)/CIS device

As mentioned previously, one of the motivations to replace CdS with Zn(O,S) is the narrow band gap of CdS. To evaluate the advantages of Zn(O,S), a comparison study was done between CIS solar cells with 20nm Zn(O,S) (best thickness for device) and 50nm CdS.

In **Figure 5.13**, the UV-Vis transmittance of both buffers show that the band gap of 20nm Zn(O,S) (3.75eV) is much higher than that of 50nm CdS (2.4 eV).

Figure 5.13 Energy band gap plot of the 50nm CBD-Zn(O,S) and CdS films on quartz

The device performances of the solar cells with these two buffer layers are compared in **Figure 5.14**. The best cell fabricated in this experiment with 50nm CdS has a PCE of 3.25% ($V_{oc}=0.28V$, $J_{sc}=30.25 \text{ mA/cm}^2$, $FF=30.2$). For 20nm Zn(O,S) buffer, the best cell reaches a

PCE of 3.9 % ($V_{oc}=0.29V$, $J_{sc}=38.8 \text{ mA/cm}^2$, $FF=34.5\%$). The higher efficiency for the cell with Zn(O,S) buffer is mainly due to the higher short circuit current. The higher short circuit current can in turn be attributed to the higher band gap of Zn(O,S). In **Figure 5.14b**, the EQE measurement clearly shows that the cell with Zn(O,S) has less absorption of blue light at 300-500nm range and thus obtained an additional current gain compared to CdS device.

Figure 5.14 (a) J-V curve and (b) EQE spectra of CIS solar cell fabricated with 20nm Zn(O,S) and 50nm CdS

5.1.6. Summary

A uniform and pinhole-free Zn(O,S) film was deposited by CBD method on electrodeposited CIS film. Heat treatment at 200°C for 20mins after CBD process enhanced the charge transfer at the CIS/Zn(O,S) buffer interface, and this annealing process also doubled the minority carrier lifetime of CIS. The PCE for the cell with 20nm buffer is higher than that of 50nm buffer. This phenomenon is attributed to the higher defect density of the 50nm Zn(O,S) as shown by the pump probe and TRPL

measurements. The carrier lifetime extracted by pump probe measurements for the electrons in 20nm Zn(O,S)/CIS is much higher than that of 50nm Zn(O,S)/CIS, which is consistent with our finding that the J_{sc} of the 20nm Zn(O,S)/CIS cell is almost double that of 50nm Zn(O,S)/CIS cell.

5.2 Effect of composition of Zn(O,S) on the film properties and application in devices

5.2.1 Back ground

Zinc sulfide compound has emerged to be one of the most promising candidates to replace CdS in CIGS chalcopyrite solar cell technology. Zn(O,S) buffer layer can be deposited by various methods, including chemical bath deposition(CBD)[107] and atomic layer deposition(ALD) [13]. As ZnS has a larger band gap than CdS, thus there is room for improvement for cell efficiency using ZnS or Zn(O,S) as buffer layer in principle. However, the challenge is that there exists a high conduction band offset between ZnS and CIS, resulting in a big spike formed at the interface. Such a spike impedes the electron transport from CIS to ZnS, thereby limits the J_{sc} . One method to control this spike is to modify the conduction band position of ZnS by dopants, such as oxygen. Reports have shown that the conduction band of Zn(O,S), and hence the spike at the CIS/Zn(O,S) interface, can be tuned through varying the S/(S+O) ratio[67]. Among various methods for Zn(O,S) deposition, the sputtering and ALD methods allows for easy control of S/(S+O) ratio, however, these two methods require the vacuum technique which increases the cost in production. In addition, the surface damage to the absorber layer will be caused during the sputtering process, and the reported

growth rate of the Zn(O,S) using ALD is quite slow. Hence, the CBD method, despite its obvious limitations in the difficulty to control the S/(S+O) ratio, has gained popularity due to the potential of a cost effective fabrication method. For a fixed condition of CBD Zn(O,S) process, the S/O ratio of the as deposited film is thickness dependent, which results in a big challenge to systematically alter the S/O ratio and study the effect on the band alignment and consequently the effect on the device performance[66]. In this systematic study, we used another solution based method-spray pyrolysis, which could allow us to control the S/O ratio in Zn (O,S) film accurately.

Recently, spray pyrolysis technique has drawn considerable interests in the CIGS solar cell field[29], due to the following reasons: low cost, fast, material-efficient, large-area scalable and simple method for growing thin film layers in which the deposition parameters can easily be varied[108, 109]. For the spray pyrolysis of Zn(O,S), there have been substantial work reported over the past few years [110-112]. In those reports, the spray temperature recorded was always found to be above 300°C [110-112]. At such a high temperature, there would be diffusion of Cu from absorber to the interface and consequently result in the quantum loss of the CIGS solar cell in the long wavelength region(800-1100nm) [102]. Thus a lower temperature based spray pyrolysis of Zn(O,S) buffer is much more desirable to avoid the efficiency loss.

In this study, we developed a low temperature based (200 -250 °C) spray pyrolysis process to fabricate the Zn(O,S) buffer layer with controllable S/(S+O)ratio by varying the composition of the precursor. We then fabricated the CIS solar cell with the low temperature sprayed Zn(O,S) to demonstrate its feasibility. The focus of this study is to investigate the ability to

control the S/(S+O) ratio and study the influence of the S/(S+O) on the properties of these films. All data in this study will show the precursor ratio of TAA over ZnCl₂ instead of the actual amounts of Zn²⁺ and S²⁻ present in the samples since it is the relative amounts and not the absolute amounts that will make the difference.

5.2.2 Growth kinetics

In the spray pyrolysis process, the choice of solvents will affect the composition and morphology of as-sprayed films. We have compared water and alcohol as solvents. Alcohol has lower boiling point than water, and evaporates faster from the substrate. The resulting film deposited is denser, but the growth rate is much slower than that with water as solvent. **Figure 5.15** shows the effect of different solvents in this study. Mixture of DI water and ethanol as solvent will generate some plates dispersed in the film (**Figure 5.15 a-c**). EDX analysis reveals that the plates are O-rich Zn(O,S). Such big plates are not ideal for device application. In summary, only pure ethanol as solvent can produce uniform Zn(O,S) with small grain size and good coverage.

Figure 5.15 Planar FE-SEM images of Zn(O,S) spray with fixed TAA/Zn ratio at 200-250°C with different solvent composition: (a) 100% DI water, (b) 75% DI water and 25% ethanol, (c) 25% DI water and 75% ethanol and (d) 100% ethanol

Figure 5.16 shows the FTIR spectra of Zn(O,S) films sprayed around 200°C-250°C at different TAA/ZnCl₂ ratios with pure ethanol as solvent. With increasing TAA/ZnCl₂ ratio, the intensity of 3498 cm⁻¹ peak (which may refer to -NH bond stretch), and 1633 cm⁻¹ peak (which may refer to NH bend) slightly increases. The absolute intensity of the peak however is very low at only around 3%. This seems to prove that there is very little organic residue left in the as-sprayed film, and that the temperature is sufficient for the decomposition or evaporation of the organic precursors and components generated during the reaction.

Figure 5.16 FTIR spectra of Zn(O,S) films deposited at 200°C with different TAA/ZnCl₂ ratios with pure ethanol as solvent

Figure 5.17 shows the XRD pattern of the Zn(O,S) films with different TAA/ZnCl₂ ratio and the phase compositions from rietveld refinement (**Figure 5.18**) were summarized in **Table 5.5**. When the ratio is 0, (which corresponds to the situation whereby no Thiourea precursor is added), the film is pure ZnO phase. When the ratio is increased to 0.1, intensity of the peaks decreases. Rietveld refinement reveals that the Zn(O,S) film is 100% Zn(O,S) solid solution in zincblende ZnO unit cell. A further increase to ratio of 0.3 results in additional peaks on the XRD pattern. The new peaks correspond to the wurtzite ZnS structure that coexists together with the cubic ZnO structure in this film. When the TAA/ZnCl₂ ratio is 0.4, cubic ZnS peaks start to appear while the peaks corresponding to cubic ZnO are largely diminished. The diminished intensity of the peaks implies that crystallinity of the film is quite poor.

Further increase of the ratio beyond 0.4 leads to increased amount of wurtzite ZnS and reduced amount of cubic ZnO in the films. It can be deduced that for ratios from 0.3 to 1.0, the film has mixture phases of Zn(O,S), ZnO and ZnS. At the ratio of 1.5, ZnO peaks do not exist. Rietveld refinement shows that when TAA/Zn is 1.5, 48.16% Zn(O,S) sits in the zincblende ZnS unit cell and 51.84% Zn(O,S) sits in the wurtzite unit cell. When the ratio increases to 2.0, only 0.14% Zn(O,S) with zincblende ZnS structure is present and 99.86% of Zn(O,S) sits in the wurtzite ZnS unit cell. The Zn(O,S) formed using this ratio is nearly pure wurtzite phase.

Figure 5.17 XRD patterns of sprayed Zn(O,S) with different TAA/ZnCl₂ ratios

Table 5-5 Phase composition of Zn(O,S) film from XRD Rietveld refinement

TAA/Zn ratio	Phase composition
0.1	100% Zn(O,S) in zincblende ZnO unit cell
1.5	48.16% Zn(O, S) in zincblende ZnS unit cell+51.84% Zn(O, S) in wurtzite ZnS unit cell
2.0	0.14% Zn(O, S) in zincblende ZnS unit cell+99.86% Zn(O,S) in wurtzite ZnS unit cell

Figure 5.18 Rietveld refinement of XRD

Figure 5.19 (a) XPS survey spectra of the Zn(O,S)/CIS samples with different TAA/ ZnCl₂ ratio and (b) high resolution XPS spectra of Zn2p in Zn(O,S) thin film deposited with different TAA/ZnCl₂ ratio.

Figure 5.19a shows the XPS survey spectra of the Zn(O,S)/CIS sample series with different TAA/ZnCl₂ ratio. For the 50ml spray, it is inferred that Zn(O,S) can fully cover CIS absorber because there is no XPS or XAES signals attributed to CIS observed. With the increased TAA/ZnCl₂ ratio, an increase of the Zn-related photoelectron and Auger electron signals is detected. Close inspection of the data shows that the S2p XPS signal at ~162 eV binding energy also undergoes a similar but far less pronounced intensity increase as the Zn-related peaks. Although the O1s XPS signal at 532eV also exhibits the little intensity increment, the oxygen signals might not be a suitable measure for the composition of the Zn(O,S) buffer. This is because Zn(O,S) buffer is deposited by wet chemical spray and exposed to air during spray, and the oxygen could come from the adsorbates. So it may be misleading to use oxygen peaks for analysis.

The binding energy of the constituent elements in the Zn(O,S) thin film was examined by XPS narrow scan. **Figure 5.19b** shows the high resolution XPS spectra of Zn2p of the Zn(O,S) films sprayed with different ratio of S/Zn. The binding energy of Zn 2p_{3/2} consisted of two binding energies positioned between 1021eV and 1022.5eV. From the previous XPS study of Zn(O,S) film, the Zn2p_{3/2} spectra are partially composed of a ZnO and ZnS contribution [16, 113]. The slightly lower binding energy corresponds to Zn2p_{3/2} in ZnO, while the higher one corresponds to the Zn2p_{3/2} in ZnS. From **Figure 5.19b**, we can observe that there is a right shift of the Zn 2p_{3/2} with gradual increase of S/Zn ratio. This is because with very low S/Zn ratio (0.5), the film has high percentage of O and less S. With increased S/Zn ratio, the S incorporated into the Zn(O,S) also increases, resulting in the right shift of the Zn 2p_{3/2} shift.

5.2.3 Optical and electronic properties

Figure 5.20a shows the S/Zn ratio inside the Zn(O,S) films sprayed at different TAA/ZnCl₂ ratio from the XPS surface scan of the films. The S/Zn ratio in the as-sprayed films is always lower than the TAA/ZnCl₂ ratio used in the precursor. The S/ Zn ratio increases with the increased precursor ratio until saturation at S/Zn 0.8(TAA/ZnCl₂=2.0). Under ambient conditions, oxygen from the solvent and air could easily be incorporated into the film. The incorporation of oxygen results in the lower S/Zn ratio and saturation of S. The band gap trend of the as-sprayed films with increased TAA/Zn ratio is shown in **Figure 5.20b**. The band gap increases drastically from 3.0 eV to 3.7eV, which is close to the band gap of ZnS, and then decreases slowly till 3.4 eV. This trend is different from the reported bowing effect of Zn(O,S) band gap[68]. We propose that the mixture phases of the as-sprayed Zn(O,S) formed at low

temperature may affect the band gap differently and result in a different band gap evolution trend.

Figure 5.20 (a) S/Zn ratio of Zn(O,S) film from XPS surface scan and (b) band gap of Zn(O,S) from UV-Vis spectroscopy measurement with different TAA/ZnCl₂ ratio

Room temperature PL spectra analysis shown in **Figure 5.21** was used to explore the optical properties of the Zn(O,S) with different TAA/Zn ratio. Only one PL band at ~534nm was observed for the film with TAA/Zn ratio of 0.0. It is generally accepted that this visible emission is attributed to the single oxygen vacancy in the ZnO, which is formed from the radiative recombination of a photo-generated hole with an electron occupying the oxygen vacancy [114, 115]. With increasing TAA/Zn ratio, there is more S doped into Zn(O,S). The increased S content changes the crystal structure and lowers the oxygen vacancy concentration. This could be detected by PL spectrum analysis, which shows a reduction in the intensity at ~534nm. This peak is also found to be slightly shifted. In addition, PL analysis shows some new features. The additional peaks at 450nm are observed for the Zn (O, S) film with TAA/Zn ratios of 0.5 and 1.5. When the ratio further increases to 2.0, this new peak disappeared. It was reported that this emissions is attributed to the ZnS defects from the sulfur

vacancies[116]. When the TAA/Zn ratio is 2.0, an excess S is used during the synthesis and sulfur vacancies are filled up.

Figure 5.21 PL spectra of as-sprayed Zn(O,S) film with different TAA/Zn ratios, with 325nm as excitation wavelength

5.2.4 Application in CIS solar cell

Figure 5.22a shows the cross section FE-SEM of 80nm-thick Zn(O,S) sprayed on CIS with TAA/ZnCl₂ ratio 2.0. The as deposited Zn(O,S) is quite uniform in small spherical particles with size around 10nm and it shows good coverage over the CIS absorber layer. Zn(O,S) buffers with different TAA/Zn ratios have been investigated for the CIS device fabrication. For the ratios we tried here, only with TAA/ZnCl₂ ratio of 2.0 resulted in decent device efficiency. The efficiency measured was 1.24% ($V_{oc}=0.29V$, $J_{sc}=14.49 \text{ mA/cm}^2$, $FF=29.44\%$) (**Figure 5.23b**). The cell efficiency of devices with other TAA/ZnCl₂ ratio was very low due to the extremely low J_{sc} . Correlating this with previous XRD spectra and discussion, we

propose that the low cell efficiency, especially low J_{sc} , with other TAA/Zn ratios except 2.0 may be due to the mixture phases of the as-sprayed Zn(O,S) at low T. There are a lot of grain boundaries between different phases of Zn(O,S), which are detrimental to the electron transport and results in very low J_{sc} . When TAA/ZnCl₂ ratio is 2.0, the Zn(O,S) is nearly single phase wurtzite structure, the cell fabricated with the buffer at this condition doesn't suffer the similar problems and thus the J_{sc} is higher than that with other ratios. Therefore, it is inferred that only single phase Zn(O,S) sprayed at low temperature can be used for CIS solar cell.

Figure 5.22 (a) cross section FE-SEM of Zn(O,S) on CIS and (b) J-V curve of the measured Zn(O,S)/CIS device with TAA/Zn 2.0

5.2.5 Summary

In summary, the optical and structural properties of Zn(O,S) thin films deposited by spray pyrolysis at 200 -250°C have been investigated. When using pure ethanol as the solvent, the as sprayed Zn(O,S) is quite uniform in particle size and has good coverage. The S/Zn ratios in the as-deposited Zn(O,S) films can be controlled by the precursor ratio of TAA/ZnCl₂. With increasing of TAA/ZnCl₂ ratio, a phase change is observed in Zn(O,S) films; for TAA/Zn

<0.3 , the Zn(O,S) films in the oxygen-rich phase are in ZnO zincblende crystal structure and when the TAA/ZnCl₂ ratio is from 0.3 to 1.5, diffraction peaks corresponding to several structural phases of Zn(O,S), ZnO and ZnS are observed. When TAA/Zn=1.5, the Zn(O,S) films consists of the sulfur-rich phase with zincblende and wurtzite structures. When TAA/Zn=2.0, pure Zn(O,S) with the wurtzite ZnS structure is observed. Due to the presence of mixture phases of Zn(O,S), the band gap of Zn(O,S) with increasing S content shows a significant difference in trend from the literature reported. PL study indicates that with increasing S content, Zn(O,S) film has different types of defects: from mainly O vacancy to S vacancy and finally almost defect free. Finally, CIS solar cell using the sprayed Zn(O,S) buffer layer was demonstrated. It has been found that only single phase Zn(O,S) with TAA/Zn ratio 2.0 works for the CIS solar cell. Hence we propose that at low T (200 -250°C) condition, only single phase Zn(O,S) can be used for device application. The presence of several phases may be harmful to the electron transport and thus results in extremely low J_{sc} .

Chapter 6. ZnSnO as alternative Cd-free buffer layer in CIS solar cells

6.1 Background

The alternatives to Cd-based buffers are either In based buffer, such as In_2S_3 and In_2Se_3 or Zn based. Zn-based buffers have the advantage of being much cheaper than In-based buffers. In addition, since the window layer is intrinsic ZnO, Zn-based buffer has more suitable band alignment and better lattice matching with the window layer than other types of Cd-free buffer layer. Besides the most widely studied Zn(O,S), there are also other kinds of Zn-based buffer layers such as ZnMgO and ZnSnO that are investigated by researchers. Very recently, ZnSnO attracts significantly more research attention because Sn is more abundant than Mg, and most importantly, contrary to CdS, Zn(O,S) and ZnMgO, which form polycrystalline structure readily at low temperature, ZnSnO is amorphous phase according to the previous buffer study for CIGS[15, 69, 70]. The amorphous nature of ZnSnO phase is interesting because such an amorphous phase can reduce the grain boundaries both within the bulk of buffer layer and at the buffer/absorber interface, and also enhance the transparency as well[70]. Reduced amount of grain boundaries will lead to less charge carrier recombination at the interface and result in higher J_{sc} . The Uppsala research group have achieved PCE of 18% with ZnSnO (V_{oc} =0.684V, J_{sc} =35.2mA/cm², FF=74.9%)[70]. In their study, ZnSnO was prepared by ALD method, which requires expensive vacuum equipment. The ALD process is also well known for its low production throughput. In our study, we aim to develop a solution based method to prepare ZnSnO buffer for CIGS/CIS solar cell application.

The conventional solution based method to deposit ZnSnO is spin coating of the solution composed of Zn precursor and Sn precursor with different ratios, and then annealing at high temperature around 400-600°C to allow the evaporation, condensation, densification and impurity removal of the solution oxide[117, 118]. However, under such a high temperature, it will cause the Cu diffusion from the bulk of absorber to the buffer/absorber interface and cause shunt problem for the CIGS solar cell device. Therefore, the high temperature annealing process is not compatible with the absorber, and it needs to be improved for ZnSnO buffer deposition. Here we have developed a low temperature solution based method for ZnSnO deposition with tunable band gap of the as deposited film by combustion method. Such a process is based on the highly exothermic redox chemical reactions between an oxidizer and a fuel. The self-generated heat of synthesis provides a localized energy supply, eliminating the need for high, externally applied processing temperatures[119] and thus achieve the energy-efficient synthesis of bulk materials. In this study, a redox-based combustion synthetic approach is applied to ZnSnO thin films, using acetylacetone as a ‘fuel’ and metal nitrates as oxidizers.

6.2 Growth kinetics and film properties

The conventional method was attempted in our study as a baseline for the combustion method. ZnSnO was deposited by the method described in section 3.2.4. The spin coating solution is composed of ZnCl₂ and SnCl₂ in acetonitrile solvent. The TGA curve of the precursor solution at 15°C/min heating rate is shown in **Figure 6.1a**. An initial weight loss below 100°C represents the evaporation of the acetonitrile solvent. The next weight loss up to 300°C indicates the decomposition of ZnCl₂. Another weight loss around 300–350°C (**Figure 6.1a**

inset) is attributed to the decomposition of SnCl_2 [120], and the thermal decomposition is completed around 450°C . These results suggest that ZnSnO precursor would be converted to ZnSnO film only when annealing temperature is higher than 450°C .

In the actual solar cell application, annealing at 450°C is not feasible. One promising approach is via a localized heating mechanism analogous to low-temperature poly-Si laser crystallization[119, 121]. In our study, ultraviolet laser was employed to irradiate the ZnSnO films annealed at low temperature. **Figure 6.1b** shows the UV-Vis transmittance of ZnSnO films annealed at different conditions. The critical transformation temperature for ZnSnO was founded to be 350°C . When comparing the UV-Vis spectra of the films annealed at 350°C and 500°C , one can see that for the film annealed at 350°C , the transmittance remains quite high through all the wavelength range, while for the film annealed at 500°C , the transmittance starts to decrease sharply from 400nm to 300nm. The differences in the transmittance spectra indicate that the ZnSnO precursor hasn't converted to ZnSnO film until 500°C anneal, and the film annealed at 350°C is mostly ZnCl_2 and SnCl_2 , instead of ZnSnO semiconductor. After ultraviolet laser irradiation, the transmittance of this film also decreases exactly the same as the one annealed at 500°C , which indicates that UV annealing can reduce the ZnSnO conversion temperature and help to form ZnSnO at lower temperature. Our further experiments have proven that this annealing temperature at 350°C cannot be further lowered down. Films annealed below 350°C cannot be converted to ZnSnO semiconductor even with the aid of UV annealing. Therefore the minimum activation temperature is about 350°C .

Figure 6.1 (a)TGA of conventional ZnSnO precursor solution at 15°C/min heating rate in air.Inset: enlarge of TGA during 200°C-500°C;(b) optical transmission spectra of ZnSnO prepared by conventional method at different annealing conditions.

Although UV-annealing can help to decrease the ZnSnO formation temperature to 350°C such process is still not ideal for CIGS solar cell application as the considerable long annealing (350°C for half an hour and plus UV for another half hour) will damage the CIGS absorber. Moreover, the UV annealing for extended period of time may also damage the CIGS/CIS absorber. Another approach is to synthesize ZnSnO by combustion process. In this study, acetylacetone was used as fuel and different ratios of oxidizers (zinc nitrate and tin nitrate) were used. Since tin nitrate is not stable, it is synthesized by mixing of SnCl_2 and NH_4NO_3 for overnight.

In **Figure 6.2**, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data of the combustion precursor system exhibit substantially lower complete conversion temperatures ($T_{\text{completion}} < 200^\circ\text{C}$) than the conventional oxide systems ($T_{\text{completion}} > 400^\circ\text{C}$). Unlike conventional systems, which exhibit broad endotherms at around 250°C for oxide lattice formation, the combustion system exhibits intense exotherm

at around 150°C in the DSC (**Figure 6.2a**) that corresponds exactly to the abrupt mass loss in the TGA also at around 150°C (**Figure 6.2b**). The energy is inferred to be sufficient to drive the reaction rapidly to completion since after 150°C, there is no further weight loss for the precursors.

It can be seen that combustion synthesis offers many advantages. Firstly, the generation of high local temperatures without a furnace enables low-cost large-scale bulk syntheses, and the high self-generated energy can convert precursors into the corresponding oxides at low process temperature[119]. Furthermore, conventional processes and precursors typically require high temperatures for oxidizing organic impurities to achieve phase-pure products, whereas in combustion reactions with balanced redox chemistry, the atomically local oxidizer supply can efficiently remove organic impurities without coke formation.

Figure 6.2 Thermal analysis(a) DSC and (b) TGA of the combustion precursors versus conventional precursors

Since ZTO precursors decompose at around 150°C and CIGS/CIS absorber can sustain heat treatment around 200°C, the spin coated ZnSnO precursors on top of selenized CIS film are

annealed between 150 -200°C for film formation. CBD-Zn(O,S)/CIS film is then placed into the oven when the oven temperature reaches 200°C and annealed for 20mins. We apply the same process to the ZnSnO combustion precursor(**Figure 6.3a**) after spin coating. However, the resulting film properties are not ideal. The film surface is rough and there were many plates in the film(**Figure 6.3b**). The abrupt high temperature may have induced the combustion reaction to take place very rapidly and generate a lot of heat in a very short time. As a result, there may not be enough time for the heat to dissipate and cause the uneven reaction rate. The dispersed plates and rough surface are quite harmful to the CIS device. To overcome this problem, a graded heat treatment process is shown in **Figure 6.3c**. The precursor was annealed from room temperature to 150°C with 12°C/min ramping rate and held at 150°C for 2mins. Subsequently, the temperature was increased to 200°C within 5mins with a ramping rate 10°C/min and held at 200°C for 10mins. The slower ramping rate allows more gentle reaction and sufficient time for heat release. The slower annealing produces ZnSnO films with smaller particles and more uniform coverage with very few plates (**Figure 6.3d**).

Figure 6.3 Different thermal annealing profile of ZnSnO precursor(left:a&c) and corresponding surface morphology of the films(right:b&d)

The X-ray diffraction (XRD) profile (**Figure 6.4**) shows a broad peak between $2\theta = 34^{\circ}$, which is characteristic of the amorphous[120, 122] nature of the ZnSnO film. This amorphous property is interesting because there are less grain boundary both within the bulk of buffer layer and at the buffer/absorber interface[70]. Less grain boundary is beneficial to charge transport in the cell.

Figure 6.4 X-ray diffraction (XRD) pattern of ZnSnO on glass

6.3 Optical and chemical properties

The as-deposited films were analyzed by XPS to confirm the composition and chemical state of the elements. **Figure 6.5** shows the narrow scans of the various prepared samples. The Zn 2p_{3/2} and the Sn 3d_{5/2}, which were at 1022.7 eV and 487.0 eV respectively, were monitored to estimate the relative composition of the films. They were consistent with the nominal compositions of the precursor solutions. Since Sn can exist in its Sn or Sn oxidation state (which can result in p-type SnO or n-type SnO₂), the oxidation state of samples prepared from SnCl₂ solutions were examined. The narrow scan for Sn 3d is shown in the **Figure 6.5b**. The 3d_{5/2} shows only one component at 487.0 eV, ruling out the coexistence of SnO and SnO₂. This binding energy proves that the Sn in ZnSnO is in the +4 state.

Figure 6.5 XPS narrow scan of (a) Zn 2p and (b) Sn 3d

Figures **6.6 a&c** show the optical transmission spectra of ZnSnO with different precursor ratios in both conventional and combustion methods. In both methods, the bandgap varies significantly as a function of the of Sn concentration (**Figure 6.6b&d**) and follows the similar trend as reported [15]. It is found that this change in the band gap mainly results from a shift in the valence band edge towards higher energies with increasing Sn concentration, whereas only a moderate shift is observed in the conduction band edge[15]. Thus it is feasible to control the band gap of ZnSnO by controlling the precursor ratio.

Figure 6.6 Optical transmission spectra of ZnSnO with different precursor Sn/(Zn+Sn)% with conventional method(a) and combustion method(c); band gap trend of ZnSnO with different Sn/(Zn+Sn)% with conventional method(b) and combustion method(d).

6.4 Device application

In order to understand the carrier dynamics between ZnSnO and CIS films, the ZnSnO /CIS films are investigated by femtosecond OPOP. The ZnSnO /CIS films were pumped at 800nm, and then probed at 900nm. The decay curves are shown in **Figure 6.7** and parameters are plotted in **Figure 6.8**. The rise time decreases with increasing Sn concentration (with one point at 50% Sn increases). This implies that the charge transfer from CIS to ZnSnO is slower at high Sn concentrations. Based on **Figure 5.8**, process 2(charge transfer from conduction band

of absorber to conduction band of buffer) and/or process 3(charge transfer from conduction band of absorber to the defects states of buffer) may affect the rise time. We would like to find out if process 2 or process 3 is the dominant factor affecting rise time. The argument is as follows; It has been reported that with increasing Sn concentration in the thin films, there is higher possibility for formation of oxygen-related defects [15]. Now, if process 3 is the dominant factor, increasing oxygen-related defects must result in increase in the rise time. However the result is contrary whereby the rise time decreases with increased Sn concentration. This leads to the reasoning that process 2 is the main factor to determine the rise time. The influence of process 2 to the rise time can be explained by the band evolution of ZnSnO shown in **Table 2.1** which shows that the conduction band of ZnSnO shifts with varied Sn concentration. The trend can be correlated with the trend of the rise time. In the electron decay time analysis, it was also observed that an increase in Sn concentration from 5% to 10% reduces the decay time significantly. This can be simply explained by the formation of oxygen-related defects with increasing Sn concentration[15]. Increasing Sn concentration in excess of 10% Sn only leads to small change in decay time. A plausible explanation for this observation is that the change is corresponding to the small change in the oxygen defect density or defects energy level. From the OPOP characterization point of view, ZnSnO with 10%-20% Sn has the better electronic properties.

Figure 6.7 Pump probe transient measurement for the ZnSnO/CIS/glass samples with varied Sn concentration.

Figure 6.8 OPOP decay parameters obtained (a) the rise time and (b) the corresponding carrier decay time.

Prior study of ALD ZnSnO for CIGS solar cell has demonstrated that ZnSnO films which contain around 20% (atomic) Sn/(Sn+Zn) perform better than the films with other Sn concentrations[15, 70]. We take heed of this optimized parameter to fabricate device with

20% Sn ZnSnO. The cell performance was shown in **Figure 6.9**. The cell with ZnSnO by combustion method achieved PCE of 1.53 % ($V_{oc}=0.22$ V, $J_{sc}=20.6$ mA/cm², FF=33.77%). Since the PCE of devices with ZnSnO by conventional method was very low, with extremely low J_{sc} , the experimental result affirms that ZnSnO prepared by high temperature process after absorber selenization is detrimental to the CIS device. An alternative will be the combustion method. The combustion method requires a lower synthesis temperature and has advantages over the conventional method for the CIS solar cell.

Figure 6.9 J-V curve of CIS solar cell fabricated with $Zn_{0.8}Sn_{0.2}O$ with 6 cycles of spin coating.

6.5 Summary

Combustion sol gel method can synthesize the ZnSnO with controllable composition and electronic properties. A limitation of the conventional method is that it requires very high

temperature (350°C+UV annealing) to convert the ZnSnO precursor into ZnSnO semiconductor. Such high temperature may damage the solar cell. Combustion method generates a lot of energy locally and can reduce the temperature within the range that CIS solar cell can sustain. Solution processed amorphous ZnSnO thin films were deposited successfully through both conventional method and combustion method. The Sn in ZnSnO is in the +4 state and the composition of the spin-coated films is consistent with the nominal compositions of the precursor solutions. The band gap of ZnSnO can be well controlled by altering the Sn/ (Sn+Zn) ratio in the precursor solution by both of the methods. A proof of concept device was demonstrated by the solar cell with 20% Sn, with a PCE of 1.53%. This study shows that the combustion sol gel ZnSnO can be used as a very promising Cd-free buffer layer for CIGS solar cell.

Chapter 7. Conclusions and recommendations for future work

7.1 Overall summary

CdS is currently the material of choice for the buffer layer of state-of-the-art CIS solar cells. However, moving forward, environmental concerns and the low band gap of CdS necessitates the need for an alternative material. Zinc based buffers are leading candidates among researchers for this application. This study focused on the application of Zn based buffer fabricated by solution methods at low temperature.

In order to study the Cd-free buffer layer, the CIS absorber layer has to be standardized. Electrodeposition is the method selected to deposit this absorber layer. Polycrystalline single-phase p-type CIS thin films were successfully deposited by electrodeposition of stacked elemental layer of Cu and In followed by selenization. This method allows for easier control of Cu/In ratio and thickness of each layer compared to the one-step electrodeposition. The as-selenized CIS film, with band gap of 1.06 eV, has grain size of around 800nm-1 μ m and achieved PCE 3.25 % with CdS as buffer layer. The CIS absorber layer is the unchanged variable in the experiments as the focus of this study is on the properties of the synthesized Cd free buffer layer.

In this study it was discovered that different thicknesses of compositionally graded CBD-Zn(O,S) affects the device performance. Different thicknesses results in varied defect density, which has a direct impact on device performance, in particular, thinner Zn(O,S) results in superior cell performance. The PCE for the cell with 20nm buffer is higher than that with

50nm buffer. OPOP and TRPL measurements proved that this is due to the 20nm Zn (O, S) has fewer defects than 50nm one. The carrier lifetime extracted by pump probe measurements for the electrons in 20nm Zn (O, S)/CIS is much higher than that of 50nm Zn (O, S)/CIS, which is consistent with our findings that the J_{sc} of the 20nm Zn (O, S)/CIS cell is almost double that of 50nm Zn (O, S)/CIS cell. Another finding from this study revealed that heat treatment at 200°C for 20mins after CBD process enhances the charge transfer between absorber and buffer, and that this annealing process doubles the minority carrier lifetime of CIS.

This thesis also investigates the effect of varied composition on the optical and electronic properties of Cd-free buffers: Zn(O,S) and ZnSnO. Previous work have reported the ability to control the composition and band structures of these two buffers via vacuum based methods as summarized in Table 2-1. Our study has focused on the deposition of these two Zn-based buffers via solution based methods: spray pyrolysis and spin coating.

The optical and structural properties of Zn (O, S) thin films deposited by spray pyrolysis at 200°C-250°C were investigated. Pure ethanol as the spray solvent produces small spherical Zn (O, S) nanoparticles with uniform coverage. S/Zn ratios in the Zn (O, S) films can be controlled by the precursor ratio of TAA/ZnCl₂. With increasing of TAA/ZnCl₂ ratio, a structural transformation is observed in Zn (O, S) films. Due to the presence of mixture phases of Zn (O, S), the band gap of Zn (O, S) with increasing S content shows a significant difference in trend from the literature reported. PL study indicates that with increasing S content, Zn (O, S) film has different types of defects: from mainly O vacancy to S vacancy and finally almost defect free. CIS solar cells with Zn(O,S) buffer layer were fabricated. It was discovered that

only single phase Zn(O,S) with TAA/Zn ratio 2.0 works for the CIS solar cell, hence we propose that at low T (200-250°C) condition, only single phase Zn(O,S) can be used for device application. Presence of several phases may be harmful to the electron transport and thus result in extremely low J_{sc} .

Solution processed amorphous ZnSnO thin films were fabricated by combustion sol-gel method. Combustion method generates a lot of energy locally and can reduce the temperature within the range acceptable for CIS solar cell. Thus ZnSnO can be synthesized at relatively low temperature around 200°C. The band gap of ZnSnO can be well controlled by altering the Sn/(Sn+Zn) ratio in the precursor solution. A proof of concept device using Sn/(Sn+Zn) ratio of 20% was demonstrated with a PCE of 1.53%.

This study shows that Cd-free alternatives for buffer layer are feasible. The research findings and analysis described in this thesis has led to the deep understanding of the effect of graded composition of Zn(O,S) on the carrier lifetime at the interface and thus the correlation to the CIS solar cell device performance. It also demonstrated that Cd-free buffer layer Zn(O,S) and ZnSnO with controllable composition and band gap can be applied with low temperature solution based methods. Tuning the composition of buffer layer can alter the energy level of buffer layers. Brief insight to the reaction mechanism and also proof for the feasibility of application as buffer layer for CIS solar cell has been discussed. However, much more in-depth research has to be done before the Cd-free alternative can gain mainstream acceptance.

7.2 Recommendations for future work

There are still many gaps to be addressed before Cd-free alternatives can be used in production of commercial CIS solar cells. These following future works are recommended together with my suggestions to overcome some of the inherent problems.

7.2.1 Improvement of crystallinity of Zn(O,S) prepared by spray pyrolysis

Study of Zn(O,S) in section 5.2 has shown that Zn(O,S) prepared by spray pyrolysis at low temperature has poor crystallinity and only single crystalline Zn(O,S) can be applied as buffer layer for CIS solar cell. To improve the crystallinity of sprayed Zn(O,S), ZnS nanoparticles as shown in Figure 7.1 can be synthesized first and then sprayed together with the precursor solution. ZnS can function as the nucleation site for the growth of Zn(O,S) to enhance the crystallinity of Zn(O,S).

Figure 7.1 TEM image of ZnS nanoparticles

7.2.2 Reduction of oxide formation

The solution based Cd-free buffer layers are all deposited at ambient conditions. Hence, it is easy to form a very thin layer of oxide on top of CIS before the buffer is deposited during the spray or spin coating process. This is harmful to the CIS solar cell and needs to be avoided. A plausible solution is to deposit of a very thin layer of buffer precursor solution with reducing agent such as citric acid, etc.

7.2.3 Exploration of other Zn-based buffer layer such as ZnSnOS

The band gap trend of ZnSnO and Zn(O,S) with different composition has been already studied in this study. Both ZnSnO and Zn(O,S) can be considered as a kind of doping of ZnO with another element. It is interested to know how is the trend if ZnO is doped by both Sn and S, which is ZnSnOS.

7.2.4 Surface engineering of CIS to alter the band gap

As mentioned in section 2.2.1, the incumbent problem for the Cd-free buffer in CIGS thin film solar cell is the big CBO at the interface between absorber and buffer. The performance of solar cell can be enhanced if the energy barrier is lowered. I put forward two suggestions to overcome this. Firstly, the band gap and energy level of buffer can be tuned by composition engineering or replacement of new type of buffer which is discussed in this thesis; secondly, the band gap of CIS absorber at the surface could be widened by sulfurization or Ga doping.

One disadvantage of CIS is the low band gap (1.05eV), which limits the open-circuit voltage to values below 500 mV in solar cells. Increasing the open-circuit voltage by expanding the band gap is an important key to improve the performance of CIS solar cell. However, too large band gap could reduce the J_{sc} and the cell performance. A band gap of about 1.2 –1.3 eV is considered optimal for maximizing the conversion efficiencies[123]. And to reduce the CBO at the buffer/absorber interface, band gap of absorber at the surface needs to be further increased slightly as illustrated in Figure 7.2. It requires the addition of gallium or sulfur to raise the band gap at the surface.

The band gap of CIS can be increased by incorporation of S. The E_g of CISSe follows the equation:

$$E_g = 1.05 + 0.5x - 0.167x(1-x) \quad [124] \quad (7.1)$$

Where x is the ratio of $S/(S+Se)$, and 0.167 is the so-called band gap bowing coefficient.

In order to create a larger band gap at the CISSe surface than bulk, more S needs to be incorporated at the surface. I suggest two thermal profiles to create the CISSe band profile. First, at the base of the current selenization profile as described in section 3.1.2, around 10 mol% S powder can be added into the Se powder, this step is more like selenization and sulfurization at the same time, producing CISSe, with slightly larger band gap in the bulk than the previous selenized sample; second, CISSe will be exposed to S powder for 1-2mins, sulfurization happens again. This step will further increase the band gap of CISSe at the surface and create a graded band gap from the surface to bulk (**Figure 7.2**).

Figure 7.2 Desired band gap of CISSe or CIGS after selenization and sulfurization

Similar band tuning can be also done by Ga doping[125] of CIS.

7.2.4 Measurement of the CBO with both varied buffer and absorber

In this thesis, we employ CIS as the absorber with a fixed band gap and energy level, and focus on the composition and band gap tuning of buffer layers. We try to correlate our buffer layer with varied composition to the reported band structures of buffers with specific composition. With fixed absorber energy level, the CBO can be calculated systematically as long as we know the band structure of buffer. However, with varied absorber as we recommend in 7.2.3, the calculation is not so simple anymore. Detailed characterizations at the interface are necessary to know the CBO at the interface. To investigate the band gap of CISSe film, optical transmittance and reflectance spectra can only test the average band gap of bulk material. We have to use another indirect way to measure and calculate the band gap at the different thicknesses. Depth profiling of X-ray photoelectron spectrometry (XPS) and secondary ion mass spectrometry (SIMS) can be employed to test the composition of film all along the thickness. Then according to the S/(S+Se) ratio, we can calculate the band gap at each depth, based on the equation (7.1).

To correlate the effects of different CBO on the solar cell device parameters, measurement of the CBO of these with various absorber and buffer conditions needs to be carried out. Ultraviolet photoelectron spectrometry (UPS) depth profile[126] is a very useful tool to characterize the electronic properties of interface. It is used to assess the electronic structure of the buffer/absorber interface. Photoemission spectra can be acquired at different physical levels within the buffer and absorber. Then the CBO at the buffer/absorber interface can be calculated as follows:

$$CBO_{\text{CISSe/ZnS}} = E_g^{\text{ZnS}} - E_g^{\text{CISSe}} - VBO_{\text{CISSe/ZnS}} [54] \quad (7.2)$$

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Appendix A List of Abbreviations

CIGS	Cu (In,Ga)Se ₂
CISSe	CuIn(S,Se) ₂
CuInSe ₂	CIS
ZTO	ZnSnO
CBO	Conduction band offset
VBO	Valence band offset
ALD	Atomic layer deposition
CBD	Chemical bath deposition
SEL	Stacked Elemental Layer
E _g	Energy band gap
hν	Photon energy
V _{oc}	Open circuit voltage
J _{sc}	short circuit current
FF	Fill factor
V _m	maximum voltage
I _m	maximum voltage
η	Solar cell efficiency
PCE	power conversion efficiency
EQE	External Quantum efficiency
J-V	current density-voltage
τ	carrier lifetime
SCR	Space charge region
ΔE _c	Gap between two energy level of the conduction band bottom

E°	Standard electrode potential
NHE	Normal hydrogen electrode
ED	Electrochemical deposition
LSV	Linear sweep voltammograms
Dv	Difference in reduction potential
CVD	Chemical vapour deposition
FTO	Fluorine doped tin oxide
SLG	Soda-lime glass
FESEM	Field Emission Scanning Electron Microscope
EDS	Energy dispersive spectroscopy
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
TEM	Transmission electron microscopy
UPS	Ultraviolet photoelectron spectrometry
KPFM	Kelvin probe force microscopy
TRPL	Time resolved Photoluminescence
DSC	Differential Scanning Calorimeter
TGA	Thermo gravimetric analysis
FTIR	Fourier Transform Infra-red
OPOP	Optical pump-optical probe
SIMS	Secondary ion mass spectrometry

Appendix B List of Author's Publications

Journals

1. **Juan Sun**, Cheng Sun, Sudip K. Batabyal, Phong D. Tran, Stevin.S.Pramana, Lydia H.Wong, Subodh.G.Mhaisalkar, "Morphology and stoichiometry control of hierarchical CuInSe₂/SnO₂ nanostructures by directed electrochemical assembly for solar energy harvesting," *Electrochemistry Communications*, vol.15, pp.18-21, 2012.
2. **Juan Sun**, Sudip K. Batabyal, Phong D. Tran, and Lydia H. Wong, "Electrodeposition of single phase CuInSe₂ for solar energy harvesting: Role of different acidic additives," *Journal of Alloys and Compounds*, vol. 591, pp. 127-131, 2014
3. **Juan Sun**, Venkatram Nalla, Mai Nguyen, Yi Ren, Sing Yang Chiam, Yue Wang, Handong Sun, Nikolay Zheludev, Sudip K. Batabyal and Lydia H.Wong, "Charge relaxation dynamics of compositionally- graded Zn (O, S) buffer layer for CuInSe₂ solar cell ", **accepted by Solar energy with minor revision.**
4. Rajiv, Huu Loc Nguyen, Mulmudi Kumar, Pablo P. Boix, **Juan Sun**; John, Rohit; Sudip Batabyal, Lydia Wong, " Facile Water based Spray Pyrolysis of Earth Abundant Cu₂FeSnS₄ Thin Films as an Efficient Counter Electrode in Dye-Sensitized Solar Cells" *ACS Applied Materials & Interfaces*, **Doi: 10.1021/am503888v. Epub 2014 Oct 9.**
5. **Juan Sun**, "Low Temperature combustion sol gel ZnSnO for application in chalcopyrite solar cell", **under preparation**

Conferences presentations

1. J.Sun, C.Sun, Sudip K. Batabyal, L. H. Wong, Subodh G. Mhaisalkar, A novel p-n Nanostructure Formation by Electrodeposition of CuInSe₂ on SnO₂ Nanowires for Photovoltaics Applications. European Materials Research Society (EMRS) Spring Meeting, Nice, France (2011).
2. J.Sun, Sudip K. Batabyal, L. H. Wong, Subodh G. Mhaisalkar, Morphology Control of Electrodeposited CuInSe₂ absorber layer. Materials Research Society (MRS) Spring Meeting, San Francisco, USA (2011)

3. J.Sun, Sudip K. Batabyal, L. H. Wong, Subodh G. Mhaisalkar, Morphology Control of CuInSe_2 by electrodeposition. International Conference on Materials for Advanced Technologies(ICMAT), Singapore(2011)