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Solution-processed photovoltaics with advanced characterization and analysis

A dissertation submitted in partial satisfaction

of the requirements for the degree

Doctor of Philosophy in Materials Science and Engineering

by

Hsin-Sheng Duan

2014
ABSTRACT OF THE DISSERTATION
Solution-processed photovoltaics with advanced characterization and analysis

by

Hsin-Sheng Duan
Doctor of Philosophy in Materials Science and Engineering

University of California Los Angeles, 2014
Professor Yang Yang, Chair

During the last few decades, numerous promising solar cell concepts, ranging from single-crystal silicon to thin-film technologies, have been developed and are being researched intensely by a growing number of scientific groups and companies. Thin-film kesterite Cu₂ZnSn(S,Se)₄ (CZTS) photovoltaic technology, in which the indium in Cu(In,Ga)(S,Se)₂ (CIGS) is replaced with more abundant and less expensive zinc and tin, has emerged as a potential absorber material in next generation thin film solar cells. Despite the recent demonstration of solution-processed CZTS devices over 11% power conversion efficiency, the development of CZTS as an absorber material is still behind in terms of both fundamental understanding of the material system and in the capability to precisely control the material properties for device fabrication, as compared with those of CIGS and CdTe. This dissertation targets the three key areas in this field: (1) Defect characterization and understanding in order to recover $V_{oc}$ loss; (2) Phase stability and processing
control to produce a purer absorber material and (3) Solution-processing with environmentally friendly solvents for large-scale production. We start by exploring various precursor systems (hydrazine, benign organic solvents and nanoparticles) and have successfully processed CZTS from a molecular solution in a benign solvent system. A single component precursor has also been developed and proved to offer more precise phase and composition control. Lastly, using electrical and optical characterization, we have conducted detailed investigations on the bulk and the interface defects that govern the carrier recombination and the resulting device characteristics. They reveal the effects of the anions in CZTS on the defect concentration and on voltage losses of the solar cells.
The dissertation of Hsin-Sheng Duan is approved.

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2014
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Chapter 1 Introduction

1.1 Motivations of thin film photovoltaics based on earth-abundance materials

Though crystalline silicon currently accounts for more than 90% of photovoltaic units and provides module efficiencies of more than 20%, the need for thick active layers as well as the reliance on expensive wafer-based substrates and high-temperature vacuum processing currently makes this technology too expensive for cost competitiveness with conventional electricity generation.

A potential alternative approach uses thin-film absorber layers, which offer high absorptivity for solar photons due to their direct band gap, thus enabling devices with a much thinner active layer. Metal chalcogenide-based thin film solar cells are currently regarded as the most viable candidates for future cost-effective solar energy that is competitive with traditional fossil fuel sources. Cu(In,Ga)(S,Se)$_2$ (CIGS) and CdTe have reached commercial module production with stable power conversion efficiencies of over 15 percent.\(^\text{[1]}\) The potential for cost-effective energy generation by photovoltaics, however, is far higher than presently demonstrated. In order for this technology to truly reach its limits, it will be necessary to continuously develop new material systems and processing approaches that take advantage of the success of previous materials while slowly eliminating their disadvantages.

An ideal candidate PV material should have the following characteristics: direct energy gap for high absorption coefficient with proper energy gap, absence of toxic and non-earth abundant elements, and easy and low-cost processing. Kesterite Cu$_2$ZnSn(S,Se)$_4$ (CZTS) shows attractive properties as an absorber material for thin film solar cells, with an ideal energy band gap of 1.5 eV and a large optical absorption coefficient of around $10^4$ cm$^{-1}$ for much of the visible spectrum.\(^\text{[2]}\) Additionally, CZTS consists solely of earth abundant, non-toxic, and inexpensive elements, which
opens the door for both economic and ecologically friendly device production. Laboratory research on the CZTS system has progressed rapidly in the past few years, with the successful development of several new processing methods as well as a new record power conversion efficiency. For vacuum-involved deposition approaches, power conversion efficiencies around 8-9% have been reported from both evaporation and sputter deposition.\cite{3,4} For non-vacuum deposition approaches, a number of promising power conversion efficiencies between 7-9% have been reported using nanoparticle inks post-annealed under chalcogen vapor.\cite{5,6} A hybrid liquid-particle slurry approach from IBM has produced the highest reported efficiency of 11.1%.\cite{7} This method requires zinc to be dispersed in the precursor slurry as metal chalcogenide nanoparticles, which are later incorporated into the CZTS phase via post-deposition heat treatment.

Unlike CIGS, where the highest recorded laboratory efficiency has already reached 20%,\cite{8} development of CZTS as an absorber material is currently far behind in terms of both fundamental understanding of the material system and in the engineering capability to optimize the material properties for device fabrication. One challenge that must be overcome is attaining complete structural and compositional control during material processing: to favor the formation of the CZTS phase while inhibiting the growth of binary and ternary phases.\cite{9} Spatial inhomogeneities in composition and numerous impurity phases are usually found in films grown by vacuum processing methods.\cite{10} The quaternary CZTS phase, existing in a relatively small composition range in the phase diagram,\cite{11} requires careful compositional control across both time and space during deposition in order to support the fabrication of high quality devices. A second challenge is that this material system has only recently come under intense scrutiny as a potential photovoltaic material, and due to the lack of extensive fundamental studies relatively little is known about the chemical origin of its optoelectronic and defects properties.\cite{12} The inability to
correlate material properties of with an observed phase distribution and dopant distribution currently limits the ability of researchers to design and fabricate films than have been optimized to play specific roles within a given device. Yet another challenge is the presence of severe recombination losses due to electrically active defects in the bulk and at the interfaces of the absorber material, leading to a significant open-circuit voltage deficit regardless of film deposition method. This is currently one of the most important limiting factors for kesterite photovoltaic device performance. However, attempts to experimentally investigate defect properties in the kesterite family have to date remained a somewhat paltry in comparison to the well-established field of defect physics in chalcopyrite-based devices. Thus, an enhanced understanding of bulk and interface defect of CZTS is urgently needed for further improvement of cell characteristics to a level comparable with CIGS and CdTe.
1.2 Kesterite Cu$_2$ZnSn(S,Se)$_4$ material properties and devices

Kesterite materials belong to the family of chalcogenides, with a structure that can be derived from that of diamond by replacing atoms with substitutes following the rule of having an average of four valence electrons per atom. In increasing complexity, some examples of this group include diamond (C), sphalerite (ZnS), chalcopyrite (e.g. CuInS$_2$) and kesterite (e.g. Cu$_2$ZnSnS$_4$) as shown in Figure 1.1.\textsuperscript{[21]} The possibility of replacing the rare indium with readily available Zn and Sn while retaining key semiconductor properties, such as nearly identical band gap to the highly successful chalcopyrite absorbers, makes CZTSSe particularly attractive for large-scale PV production.

![Diagram of Element Group](image)

**Figure 1.1** Relationship between binary, ternary, and quaternary semiconductors to produce Cu$_2$ZnSnS$_4$, starting from a II–VI parent compound

While there are a large variety of device structures, processes and materials used in the fabrication of kesterite devices, the main features of these solar cells are similar. The substrate-based structure includes five principal layers, which for high performance devices are (Figure 1.2): (1) Substrate – Soda-lime glass
(2) Back contact – Sputtered molybdenum

(3) Light-absorbing layer

(4) Buffer layer – Cadmium sulfide

(5) Transparent conductive oxide (TCO) – Zinc oxide and Indium-doped tin oxide

**Figure 1.2** Device architecture of a Cu$_2$ZnSn(S,Se)$_4$ solar cell
1.3 Challenges of Kesterite Cu$_2$ZnSn(S,Se)$_4$ photovoltaics and dissertation organizations

A simple comparison of J-V characteristics for a world record (11.1% efficient) CZTS device and an analogous 18% CIGS device with the same band gap readily reveals the high-level limitations and strengths in the current generation of kesterite solar cells. While short circuit current, $J_{sc}$, is largely similar for the two devices, open circuit voltage, $V_{oc}$, is severely reduced for CZTS, despite similar band gap values. The fill factor is less severely impacted.

The most efficient reported CZTSSe devices have band gaps around 1.13 eV, and are thus thermodynamically limited to a PCE of about 31%.[22] The gap between the performance of existing CZTSSe solar cells and the limit of thermodynamics can be understood as arising from sub-optimal short-circuit current $J_{sc}$, open-circuit voltage $V_{oc}$ and circuit non-idealities. For example, the record 11.1% device exhibits $J_{sc} = 34.5$ mAcm$^{-2}$ and $V_{oc} = 460$ mV, whereas the ideal values are $43.4$ mAcm$^{-2}$ and $820$ mV, respectively. The efficiency gap of $(30.7 \text{–} 11.1\%) = 19.6\%$ can be quantitatively separated to non-idealities in the circuit (1.4\%), $J_{sc}$ (4.8\%) while the $V_{oc}$ (13.4\%).[22] Thus, $V_{oc}$ loss accounts for the majority of the efficiency gap between existing CZTSSe solar cells and the thermodynamic limit. Having observed this, the more important question is to identify the underlying origin of the degraded $V_{oc}$ in CZTS. Several key areas for future focus have been identified:

1. Defect characterization and passivation to recover $V_{oc}$ loss.
2. Phase stability and processing control.

The current state-of-the-art CZTS devices are made of hydrazine solution process, since hydrazine is able to dissolve several metal chalcogenides through dimensional reduction, making it a viable tool for solution processing. Despite the promising characteristics of hydrazine solutions, its toxicity and its nature of explosion make it subject to various handling limitations during film
formation. Thus, the selection of the benign processing solvents has been investigated, which lowers the handling of hazardous materials and offers the possibility for large-scale production of CZTSSe photovoltaics.

The aims of this dissertation target the three key areas mentioned earlier to attempt to resolve the hurdles encountered in this field. The dissertation starts at the hydrazine processing CZTS and the precursor development for the benign solution processing. It then proceeds to the precursor design for the precise phase and composition control. Lastly, the investigation the electrically active defects in the bulk absorber material and the interface defect at the junction interface will be discussed, leading to understanding of the effects of the defect properties on device characteristics.
1.4 References


Chapter 2 Novel solution processed \( \text{Cu}_2\text{ZnSn(S,Se)}_4 \) photovoltaics

2.1 Introduction

Kesterite copper zinc tin chalcogenide (CZTS) exhibits optical and electronic properties comparable to those of the \( \text{Cu(In,Ga)(S,Se)}_2 \) (CIGS) and CdTe material systems while consisting entirely of nontoxic constituents that avoid the scarcity and cost issues associated with indium and tellurium.\(^1\) Developing a reliable fabrication route for producing single phase kesterite material is essential for an in-depth exploration of its intrinsic materials properties and ultimately the identification of avenues toward further improvement. Such an approach must allow for the precise control and adjustment of the phase, structure, and properties of the resulting material. Conventional vacuum-based high-temperature approaches typically suffer from the high volatility of several elemental constituents as well as the narrow compositional stability window of the CZTS phase.\(^1,2\) Nonvacuum deposition techniques are able to take advantage of the increased stability of each elemental constituent at atmospheric pressure, and films deposited from hydrazine-based slurries containing both liquid and solid phases currently hold the highest reported efficiency for this material system at 11.1\%.\(^3\) Here we present a novel solution-based approach to process CZTS absorbers using fully dissolved CZTS precursor complexes in which each of the elemental constituents are mixed on a molecular scale. In contrast to particle and slurry-based processing, the solution phase molecular precursors enable very precise stoichiometric control and eliminate the need for the long range diffusion of precursors during the formation of the CZTS phase. Low processing temperatures and excellent film homogeneity make this method suitable for large-scale production, and the high performance of the resulting devices represents a chance to extend the impact of this earth-abundant material system into the next chapter of thin-film solar-cell research.
As direct bandgap semiconductors, the cost of the raw materials for most chalcogenide systems is significantly reduced, as they require less material to achieve sufficient for light absorption. The remarkable tolerance for structural defects in many of these absorber materials also leads to reduced requirements on material quality and generally reduces processing costs compared with crystalline silicon solar cells.\cite{4,5} With a highest demonstrated cell efficiency of 17.3\%, CdTe-based photovoltaic technology has achieved 0.75 $/W at GW level production.\cite{6,7} Chalcopyrite CIGS solar cells, without introducing the toxicity issues related to the use of cadmium and with an even higher demonstrated efficiency of 20.3\%, are expected to reach GW level production in the near future.\cite{8-10} The eventual cost of these technologies, and their ability to contribute to large scale PV power markets are inexorably tied to availability of indium, which is almost exclusively produced as a by-product of zinc mining and purification.\cite{11} With indium effectively replaced by zinc and tin, kesterite CZTS consists solely of earth-abundant, nontoxic, and inexpensive elements. As an absorber material, CZTS has an absorption coefficient of $\approx 10^4$ cm$^{-1}$ throughout much of the visible region, and an adjustable bandgap that can be varied from 1 to 1.5 eV to favorably match the solar spectrum.\cite{11} Significant research attention has already been focused on the CZTS material family, and a number of successful devices have been demonstrated using a number of processing approaches. For vacuum-involved deposition approaches, 9.1\% power conversion efficiencies of CZTSe have been achieved using coevaporation which allows real-time control of the sample composition and reaction path,\cite{12} efficiencies between $\approx 8$–9\% have been reported by several groups through the selenization or sulfurization of precursor materials evaporated at low temperatures,\cite{13-15} sputtered CZTS devices have reached 9.3\% from the co-sputtering of binary compound targets and post sulfurization.\cite{16} For solution-based approaches, a number of promising power conversion efficiencies have been reported using nanoparticle inks post-annealed under
chalcogen vapor: 7.2% using a CZTS nanocrystal ink,[17] 8.4% from inks containing CZTS nanocrystals incorporated with Ge nanocrystals,[18] and 8.5% (9.6% active area) from inks composed of binary and ternary chalcogenide nanocrystals.[19] The annealing of electrodeposited precursors has also produced devices with efficiencies around 7.3%.[20] Finally, hydrazine-based slurries containing both soluble and particulate precursors have deposited the absorber materials that currently hold the highest reported efficiency for this material system beyond 10%.[3, 21-23]

The advantages of the kesterite material system come at a price: consisting of a minimum of four distinct elements, kesterite materials are I$_2$-II-IV-VI$_4$ compounds, a fact that dramatically increases the complexity of their phase diagrams and introduces the possibility of forming a variety of electronically active defect structures.[24, 25] The rich defect chemistry of the CZTS material system ultimately brings about a number of difficulties that must be addressed during any deposition procedure. Perhaps the most challenging aspect of kesterite deposition, especially when compared with CIGS materials, is that single-phase kesterite exists within a much smaller stoichiometry range, and thus sophisticated compositional control is a prerequisite to achieving single-phase CZTS.[2] Careful control of the chemical potential of each reactant, which is effected by a variety of parameters including precursor concentration, processing conditions, etc., is very important in growing good-quality crystals with no secondary phase formation and low-defect density.[25] A second challenge is presented by the volatile nature of tin chalcogenide compounds and the continuous changes in film composition that take place during the course of deposition and material formation. The potential decomposition of the CZTS phase induced by the loss of tin is a source of additional difficulties for composition and phase control, especially for processing techniques involving high vacuum and elevated temperatures.[26] Based on the complexity of the kesterite material system, we can expect that the ultimate success of a specific deposition method
will come from its ability to reliably produce high-quality films with excellent uniformity over all spatial dimensions. In this report, we explore one option for highly uniform and controllable CZTS film deposition at atmospheric pressure using fully dissolved molecular precursors based on the hydrazine solvent system.
2.2 Synthesizing the precursor solution

The targeted processing method is based on a homogeneous CZTS precursor solution, similar to the hydrazine-based solution-processable precursors that have been demonstrated to produce high-quality CIGS films.[27-29] The chalcogenides of copper, tin, and a number of other metals (Cu$_2$S, In$_2$Se$_3$, SnS$_2$, etc.)[30-32] readily dissolve in hydrazine in the presence of excess chalcogen to form metal chalcogenide complexes coexistent with hydrazinium species. Unlike the various soluble chalcogenide compounds, zinc compounds such as ZnS and ZnSe, together with most other transition metals and metal chalcogenides typically show negligible solubility in hydrazine-based solvent systems.[33] Here we present a way to incorporate soluble zinc constituents into hydrazine in a completely dissolved form, stable in the presence of dissolved copper and tin complexes. By forming complexes using a hydrazine derivative, zinc can be efficiently incorporated into hydrazine-based precursor solutions as a soluble reactant.

To synthesize the zinc precursor, the complexing agent hydrazinocarboxylic acid (NH$_2$NHCOOH) was prepared by adding hydrazine to a vial containing excess solid-state carbon dioxide:

$$\text{CO}_2 + \text{N}_2\text{H}_4 \rightarrow \text{NH}_2\text{NHCOOH}$$

Note: The reaction between carbon dioxide and hydrazine is highly exothermic; the synthesized product is capable of corrosive action on stainless steel. 2 mmol zinc nanopowder was then added into 1 mL of H$_2$NHCOOH saturated hydrazine solution and subjected to stirring for several hours to enable the full reaction of zinc powder with the complexing agent. The completed CZTS precursor solution is then prepared by mixing hydrazine-based copper and tin precursor solutions, prepared through previously reported methods,[27,28,30] with the newly formed zinc precursor keeping an appropriate ratio between the metals, as shown in Figure 2.1. After continued stirring,
the result is a clear solution consisting of soluble copper, zinc, and tin precursor complexes. Detailed study of the structure and dissolution mechanism of the zinc complex will be described elsewhere. The molecular-scale homogeneity of the precursor solution enables: i) the freedom to independently adjust and precisely control the ratio of Zn/Sn, Cu/(Zn+Sn), and S/Se by simply varying the ratio of each type of precursor, ii) enhanced spatial uniformity in subsequently deposited films, and iii) the capacity to form a homogeneous kesterite CZTS phase without the need for long range diffusion between different precursor phases, as might be expected in a slurry system, layered precursor films, or other initially inhomogeneous precursor systems.

![CZTS precursor solution preparation schematic and photograph](image)

**Figure 2.1** CZTS precursor solution preparation schematic and photograph of a solution with the target ratio of Zn/Sn = 1.2, and Cu/(Zn+Sn) = 0.8. The zinc precursor was synthesized through the reaction of metallic zinc and hydrazinocarboxylic acid (HD).

The unique hydrazinocarboxylic acid ligand system leads to the formation of high-purity kesterite films. The solution-phase processing of metal chalcogenides using a hydrazine-based solvent system has the unique advantages of avoiding potential impurities such as C, O, or Cl, as are commonly encountered when using organic solvents or metal salt precursors. As a result, high-
quality semiconducting films and electronic devices can be achieved such as high-mobility transistors based on SnS$_2$ or In$_2$Se$_3$ and high-performance CISS and CIGS solar cells with efficiencies up to 15.2%.\textsuperscript{[30,32,34]} Although the undesirable elements of carbon and oxygen were introduced into the precursor solution in order to induce the formation of the zinc precursor, the chosen hydrazinocarboxylic acid complexing agent yields a comparatively pure absorber film without significant amounts of impurities elements. Similar to the weakly coordinating hydrazinium complexes formed in typical hydrazine precursor solutions,\textsuperscript{[35]} the volatile hydrazinocarboxylic acid species is able to easily decompose back into to gaseous species after moderate thermal treatment without leaving behind carbon and oxygen impurities in the deposited film. In its coordinated form, where hydrazinocarboxylic acid acts as a bidentate ligand,\textsuperscript{[36]} chelated metal complexes yield metal powder upon annealing, without leaving behind any impurity elements such as carbon, oxygen, or nitrogen. Reported examples of hydrazinocarboxylic acid complexes that decompose to produce pure metal upon annealing include chelated compounds of copper, zinc, nickel, and cobalt.\textsuperscript{[37-39]}

In this study, X-ray photoelectron spectroscopy (XPS) characterization was employed to check the concentrations of impurity elements within the CZTS film after heat treatment at 500 °C. The main peaks of Cu (2p$_{3/2}$), Zn (2p$_{3/2}$), Sn (3d$_{5/2}$), and S (2p$_{3/2}$) are labeled in Figure 2.2A, no evidence of other elements was detected (all remaining unlabeled peaks represent other electron transitions associated with the four elemental film constituents). A high-resolution scan (Figure 2.2B) around the O (1s) peak detected no trace of oxygen (the detection limit of XPS is <0.1%), while the intensity of C (1s) is about three orders lower than that of Cu(2p$_{3/2}$), suggesting a low impurity concentration of less than 0.5 at%. Rutherford backscattering spectroscopy (RBS) analysis on annealed thin-film samples indicates that the carbon composition throughout the entire depth of
the film is below the system detection limit. Compared with other CZTS deposition approaches utilizing organic solvents and ligands, which normally leave behind a carbon-rich layer at the backside of device, the additive introduced here has the advantages of achieving a chemically cleaner film. With appropriate additives and complexing agents, the capacity for hydrazine solution processing could be effectively be extended to new materials of interest beyond the current realm of metal chalcogenides that are currently soluble in the hydrazine-chalcogen system.\textsuperscript{[35]}
Figure 2.2 X-ray photoelectron spectroscopy (XPS) analysis on solution-deposited CZTS films after heat treatment at 400 °C. Prior to the analysis, a sputter cleaning step was applied using Ar$^+$ ions (3 keV) to remove adsorbed oxygen and carbon from the air. (a) Fast scan of the CZTS surface showing the main peaks of Cu, Zn, Sn, S. (b) Isolated signal from possible impurities
(C/O) compared with signal from a main element (Cu) obtained from a high-resolution scan using the same set of parameters.

2.3 Structural characterization

The formation of the kesterite phase from CZTS precursor solutions takes place at low temperatures, suggesting a kinetically viable transformation that does not rely on the long-range motion of precursor constituents. Figure 2.3A shows the thermogravimetric analysis (TGA) data for dried CZTS precursor preheated to 100 °C to evaporate any excess hydrazine solvent. The low-temperature weight-loss regime (below 200 °C) corresponds to the dissociation of hydrazine and other volatile complexing agents present in the film. Figure 2.3C shows the XRD pattern of the sample after 250 °C annealing, exhibiting the main diffraction peaks (112) (220) (312) of kesterite CZTS. The broad peak width indicates a relatively small grain size on the order of tens of nanometers. Due to the strong overlap between the main diffraction peaks of CZTS, ZnS, and Cu₂SnS₃ and the low signal arising from the characteristic (110) peak of CZTS at this level of crystallinity, Raman spectroscopy was used to further investigate the formation and purity of the CZTS phase. The Raman spectrum shown in Figure 2.3B more concretely verifies the formation of the kesterite CZTS phase, with the characteristic peak at 338 cm⁻¹ corresponding to the primary vibration mode of CZTS. The rapid phase evolution even at relatively low temperatures suggests a small activation energy for the decomposition of the original precursor complex. The observed low reaction temperatures can be correlated to the unique chemistry of hydrazine and its derivatives: weakly co-ordinating and highly volatile hydrazine and hydrazinium complexes spontaneously decompose into gaseous species after only a gentle heat treatment, leading to the direct formation of the chalcogenide products. These results agree well with the decomposition of
other hydrazinium precursor systems: the CISS phase has been previously reported to form from dried Cu-In-S-N₂H₄ precursor films upon annealing at temperatures as low as 100 °C.²⁸

**Figure 2.3** Thermal analysis and phase evolution of the CZTS precursor materials. (a) Thermogravimetric analysis of a powder sample at a heating rate of 2 °C/min in flowing argon. The sample was preannealed at 100°C in an inert atmosphere from the precursor solution in Figure 2.1 to evaporate excess solvent. Raman spectrum (b) and X-ray diffraction pattern (c) of the sample after going through the first main step of weight loss at 250 °C under an inert atmosphere. (d) XRD pattern of powder with a maximum annealing temperature of 450°C in an inert atmosphere, identified as kesterite Cu₂ZnSnS₄, JCPDF 00-026-0575
After the first stage of weight loss centered around 150 °C in the TGA data, further annealing up to 450 °C does not lead to significant structural variations in the material, but induces a general increase in grain size throughout the film. Based on the analogous transformation in hydrazine processed CuIn(S,Se)$_2$, the weight loss transition between 300 and 350 °C likely corresponds to the loss of extra sulfur loosely held within the film, but not actually incorporated into the CZTS lattice.$^{[41]}$ The diffraction spectrum of the final product (Figure 2.3D), annealed at 450 °C, shows good crystallinity in the desired kesterite phase (JCPDF 00-026-0575), with the lattice constants $a = b = 5.4270$ Å and $c = 10.8480$ Å. There are neither unidentified peaks nor peaks from secondary phases such as tin sulfide or copper sulfide in the spectrum. The single phase product indicates the capability of the current approach to obtain the CZTS phase while maintaining the flexibility for facile compositional adjustment. The gradual weight loss visible in the final stage of the TGA data at temperatures beyond 500 °C corresponds to the slow decomposition of the kesterite CZTS phase at high temperatures, resulting in the formation of volatile species likely related to Sn(II) compounds.$^{[26]}$ The addition of excess chalcogen vapor and optionally small amounts of tin is recommended during high-temperature annealing in order to promote grain growth while minimizing the presence of detrimental impurity phases associated with the decomposition of kesterite at high temperatures.

CZTS film deposition for device fabrication was conducted using spin coating in a nitrogen-filled glove box. Thermal treatment with peak processing temperatures between 400 and 540 °C for each deposited film was performed on a hotplate in the presence of chalcogen vapor. Figure 2.4A shows the XRD patterns of CZTS thin films deposited onto Mo-coated glass after heat treatment with added selenium vapor. The diffraction peaks from molybdenum and
MoSe$_2$ are detectable from the substrate and interfacial layers directly under the CZTS film. The structure is identifiable as JCPDF 00-052-0868, $a = b = 5.6930$ Å, $c = 11.3330$ Å, with a preferred orientation in the (112) direction. Replacement of S atoms by Se leads to a unit cell volume expansion around 15% from 319 Å$^3$ for the pure sulfide to 367 Å$^3$ for pure selenide. The grain expansion effectively shrinks the inner voids normally formed after liquid-phase deposition and post annealing, resulting in a morphology composed of close-packed large grains. Cross-sectional SEM imaging, as shown in Figure 2.4B, indicates that the CZTSe film consists of large crystallites with diameters beyond the layer thickness, with no obvious voids between. The detected MoSe$_2$ phase in the diffraction pattern corresponds to the interlayer between the molybdenum and CZTSe showing a slightly different columnar morphology from the molybdenum substrate in the SEM image. Note that the presence of a carbon layer frequently found in films prepared from organic solvents based precursor is not observed in this case at the back side of the device between the CZTS absorber and Mo back contact. The capability for the current approach to obtain a film free of non-volatile impurities is a benefit of the unique chemistry of hydrazine and its derivatives and agrees well with the previously shown compositional analysis.
Figure 2.4 (a) XRD pattern of a CZTS film on Mo/glass substrate after heat treatment at 500 °C under selenium vapor, identified as kesterite Cu$_2$ZnSnSe$_4$ (CZTSe) (JCPDF 00-052-0868) with the tetragonal lattice constants $a = b = 5.6930$ Å, $c = 11.3330$ Å. Peaks arising from the Mo substrate and the MoSe$_2$ interlayer are noted. (b) Cross-sectional SEM images of a typical Cu$_2$ZnSn(S,Se)$_4$ (CZTSS) device, with the structure Mo/CZTSS/CdS/ZnO/ITO. A layer of MoSe$_2$ showing a slightly different morphology with the underlying Mo is noted at the interface between the CZTSS and Mo layers.

The ability to tune the properties of the absorber material, especially the bandgap, to a target value is critical in achieving high-efficiency photovoltaic devices. Based on theoretical calculations, roughly 1.5 eV can be considered an optimal bandgap value for single-junction solar cells.$^{[42]}$ Experimentally, large-bandgap chalcopyrite materials (typically gallium-rich or sulfur-rich CIGS) show deteriorated performance due to increasingly active deep level recombination centers as the position of the conduction band minimum increases.$^{[43]}$ In the kesterite materials system, large-bandgap CZTS similarly shows reduced performance compared with selenium-rich material. Here we demonstrate the capability to control the S/Se ratio and resulting electronic-bandgap value by employing different chalcogen vapor compositions during the annealing process.
Type-I absorbers are pure CZTSe material formed by annealing under selenium vapor, type-II absorbers are formed under combined sulfur and selenium vapor, and type-III CZTS films are annealed under only sulfur vapor.

The (112) diffraction peaks of the three types of film are shown in Figure 2.5A. The diffraction peak shifts to smaller $2\theta$ values as the selenium content increases, indicating an increase in lattice constant due to the replacement of sulfur with selenium. Raman spectroscopy (Figure 2.5B) on the films shows the same trend with varying S/Se ratio. For the sulfide film, the major peaks appear at 338 cm$^{-1}$, 287 cm$^{-1}$, and 368 cm$^{-1}$, consistent with previously reported CZTS values.$^{[44]}$ For selenide films, the main peaks shift to 196 cm$^{-1}$, 172 cm$^{-1}$, and 238 cm$^{-1}$, agreeing well with the reported values for CZTSe.$^{[45]}$ For films with intermediate S/Se content, the main peaks from both sulfide and selenide are present, and shift toward one other, following the same trend as previously reported for CZTSS with an intermediate S/Se ratio.$^{[2]}$ The major peaks in each Raman spectra arise from the vibrational modes where chalcogen atoms oscillate while other atoms remain fixed.$^{[40]}$ Raman spectroscopy is also able to detect possible secondary phases such as ZnS and Cu$_2$SnS$_3$ that cannot be distinguished by diffraction techniques due to their similar structure to kesterite. No evidence of other possible binary phases (Cu$_2$S, Cu$_2$Se, ZnS, ZnSe) appears in the Raman spectrum for films under any of the previously mentioned heat treatments. The bandgap values calculated from external quantum efficiency (EQE) measurements of photovoltaic devices fabricated using type-I, II, and III absorbers are 1.02 eV, 1.2 eV, and 1.5 eV respectively, as shown in Figure 2.5C. These results agree well with bandgap values determined using other approaches,$^{[2]}$ and demonstrate that by judiciously adjusting the chalcogen vapor supply during post-annealing, the resulting bandgap value can be adjusted controllably throughout the range of 1.02 to 1.5 eV.

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Figure 2.5 Structural and optoelectronic properties of solution-deposited Cu$_2$ZnSnS$_{4-x}$Se$_x$ absorber layers with varying S/Se content incorporated from an annealing step at 500 °C under different chalcogen vapor compositions. (a) Shifts in the (112) diffraction peak with increasing Se content in absorber layer. The small peaks visible around 28.5° and 29° in the selenium-rich films belong to the (103) diffraction peaks of CZTSe and CZTSS. (b) Raman spectra of CZTSS films with varying S/Se ratio and appropriately shifted vibration modes. (c) Bandgap values calculated from the EQE measurements of devices with the varying S/Se content.
2.4 Device characteristics

The final test of any film-formation method is the fabrication of a completed device. Precursor solutions with the target ratios Zn/Sn = 1.2 and Cu/(Zn + Sn) = 0.8 were used for photovoltaic device fabrication. Copper-poor and zinc-rich stoichiometry has been reported to be beneficial in both vacuum-based and solution-processed approaches for the CZTS material system.\textsuperscript{[1,21]} The cross-sectional SEM of a completed device with the commonly employed structure of glass/Mo/CZTS(Se)/CdS/i-ZnO/ITO is shown in Figure 2.4 B. Illuminated current–voltage (I–V) characteristics for one of the best devices achieved to date are shown in Figure 2.6A, with a 120 nm-thick MgF\textsubscript{2} antireflection layer. Under simulated AM1.5 light, the device produces a short-circuit current density (J\textsubscript{SC}), open-circuit voltage (V\textsubscript{OC}), fill factor, and power conversion efficiency of 32.3 mA/cm\textsuperscript{2}, 409 mV, 61.0\%, and 8.08\% respectively. The device area of 0.12 cm\textsuperscript{2} is determined by mechanically scribing the finished device in order to separate the upper layers from the rest of the 1.5 × 1.5 cm\textsuperscript{2} substrate. Besides the best-performing device shown in Figure 2.6A, a number of other devices fabricated under slightly differing conditions have also been demonstrated with efficiencies above 7\%. The continued refinement of compositional and phase control may allow this method to compare competitively with vacuum-based approaches as a platform for both large scale film production and for the exploration of materials properties in order to further advance our understanding of this material system.
**Figure 2.6** Device electrical characterization. (a) Current–voltage (I–V) characteristics of one of the best CZTSS device achieved to date using the solution-processing approach under Air Mass 1.5 illumination, 100 mW/cm$^2$. (b) External quantum efficiency (EQE) spectrum of the device without any applied bias.

The integrated short-circuit current density extracted from the EQE measurements, shown in Figure 2.6B for a CZTSSe device, agrees well with that obtained under simulated sunlight. The incomplete current collection in the IR region, especially beyond 800 nm, indicates the need for a thicker absorber with enhanced minority-carrier transport. Perhaps the largest room for improvement compared with chalcopyrite devices with similar bandgap values is in open-circuit voltage. Possibilities include the existence of charge-transportation barriers either at the back contact arising from interfacial MoSe$_2$, or parasitic recombination at the interface between the absorber and buffer layers. With further optimization of the device components, we believe the CZTS photovoltaic devices based on the current processing approach could reach power conversion efficiencies well above 10%.
2.5 Conclusion

By introducing hydrazine derivatives, zinc compounds have been successfully incorporated into hydrazine solution to enable the formation of a CZTS precursor solution that is homogeneous on the molecular scale. Solutions produced in this manner provide a robust way to tune the metallic stoichiometry, allowing for films to fall within the relatively narrow window for the formation of the CZTS phase with minimal secondary phases present. High-quality single-phase films can be achieved using this approach, with the capacity for the continuous adjustment of the material's bandgap from 1.0 to 1.5 eV through the use of annealing treatments in chalcogen vapor of varying composition. The rapid decomposition of the employed precursor species is able to favorably form kesterite CZTS at low temperatures, which circumvents one of the challenges faced by vacuum-based approaches involving the loss of volatile components such as tin and tin(II) sulfide. The homogeneous nature of this processing approach enables potentially scalable high-throughput film production, compatible with the terawatt (TW) target provided by the earth-abundant raw materials of this absorber system. Furthermore, the chemical and structural purity of the final product, formed by incorporating hydrazine derivatives into the solvent, expands the metal chalcogenide materials that can be incorporated into hydrazine-based precursor solutions that are homogeneous on a molecular level for use in semiconducting thin-film deposition.
2.6 Experimental details

Solution Preparation: All of the hydrazine-based solutions were prepared in a nitrogen-filled glove box where the oxygen and moisture levels were both below 1 ppm. Note: Hydrazine is highly toxic, and appropriate protective equipment should be used to prevent direct contact with the liquid or vapor. To form the copper precursor solution, Cu$_2$S (1 mmol) and sulfur (2 mmol) were combined with N$_2$H$_4$ (1 mL), following procedures described elsewhere.$^{[28]}$ Similarly, the tin precursor solution was prepared in a separate vessel, by mixing and stirring SnS$_2$ (1 mmol) and excess sulfur (2 mmol) in N$_2$H$_4$ (1 mL).$^{[30]}$ To synthesize the chelated zinc precursor, the complexing agent hydrazinocarboxylic acid (NH$_2$NHCOOH) was first prepared by adding hydrazine to a vial containing solid-state carbon dioxide. It was observed that the viscosity of the solution increased significantly as the NH$_2$NHCOOH was gradually formed in the system. Note: the reaction between carbon dioxide and hydrazine is highly exothermic and the synthesized product has a corrosive effect on stainless steel. Zinc nanopowder (2 mmol) was added into a H$_2$NHCOOH saturated hydrazine solution (1 mL), producing a moderately vigorous reaction with the continuous generation of fine bubbles in the mixture. This reaction was typically conducted on the scale of several tens of milliliters in one iteration. The solution was stirred for several hours to enable the full reaction of zinc powder with the complexing agent. The final CZTS precursor solution was prepared by mixing each constituent solution with a final ratio of Zn/Sn = 1.2 and Cu/(Zn+Sn) = 0.8.

Device Fabrication and Characterization: CZTS-based photovoltaic devices were fabricated with the structure of glass/Mo/CZTSSe/CdS/ZnO/indium tin oxide (ITO). The p-type CZTS films were deposited via spin-coating from the as-prepared precursor solution in a glove box on molybdenum-coated soda-lime glass substrates. To reach the targeted thickness of the absorption
layer, several successive layers were coated following an intermediate heat treatment between 250–350 °C. A final annealing was conducted on a ceramic hot plate at 500 °C, verified by an IR thermometer under different chalcogen vapor supply including pure selenium vapor, pure sulfur vapor, combined sulfur and selenium vapor treatment. The n-type layer CdS was deposited via a standard chemical-bath deposition method described previously.\textsuperscript{[28]} Intrinsic ZnO and ITO were deposited using radio frequency (RF)-sputtering with argon flow as the transparent electrode. The current–voltage ($I–V$) performance was measured under an AM1.5G filter at 100 mW/cm\textsuperscript{2} using a Newport Oriel 92192 solar simulator. The external quantum efficiency (EQE) was measured using a system designed by Enli Tech.

**Materials Characterization:** For XPS, XRD, and Raman analysis, films were deposited via spin-coating onto molybdenum-coated glass, while powder was prepared by evaporating the solvent from the precursor solution itself. Both the films and powder samples were annealed at the desired temperature on a hot plate with the temperature verified by an IR thermometer. The XPS measurements were performed using an Omicron XPS/UPS system, with a base pressure lower than $10^{-9}$ mBar. A monochromatic Al K\textsubscript{a} (1486.6 eV) X-ray source was used for excitation and the spectra were collected with a pass energy of 50 eV. To exclude the influence from surface-absorbed oxygen and carbon, Ar\textsuperscript{+} ion (3 keV) etching for 3 min was performed before collecting the X-ray generated electrons. RBS analysis was conducted by the Evans Analytical Group, with the spectra acquired at a backscattering angle of 160° and a grazing angle at 110°, using a He$^{++}$ ion beam with an energy of 2.275 MeV. XRD patterns were collected on a PANalytical X'Pert Pro X-ray powder diffractometer using Cu K\textsubscript{a} radiation ($\lambda = 1.54060 \text{ Å}$). Raman shift spectroscopy was carried out using a Renishaw inVia Raman Microscope using an excitation laser with a wavelength
of 514 nm. The cross-sectional scanning electron microscope (SEM) images were taken using a JEOL JSM-6700F instrument.
2.7 References


[16] V. Chawla, B. Clemens, presented at the 38th IEEE Photovoltaics Specialists Conference (PVSC38), Austin, Texas, June 3-8, 2012.


Chapter 3 Benign solution processed Cu$_2$ZnSn(S,Se)$_4$ photovoltaics

3.1 Introduction

Nowadays, renewable energy is a widely discussed topic that focuses on the replacement of fossil fuel energy, and a low-cost substitute for fossil fuels is thin-film photovoltaics due to the excellent light-absorbing abilities of their material components. One of these materials is kesterite, Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe), which not only consists of earth-abundant and non-toxic elements, but also features an absorption coefficient of $10^5$ cm$^{-1}$. Various deposition methods for the CZTSSe absorber layer have yielded a range of efficiency levels. The National Renewable Energy Laboratory demonstrated a 9.2% device efficiency using high vacuum co-evaporation;[1] the IBM Watson Research Center attained a world record efficiency of 11.1% using particle-based hydrazine slurries;[2] UCLA yielded a 8.1% efficiency through homogeneous hydrazine solution processing.[3] However, despite the high efficiencies of vacuum processing and electrodeposition, these processes are limited by scaling issues and high intrinsic costs. Hydrazine, on the other hand, is able to dissolve several metal chalcogenides through dimensional reduction,[4] making it a viable tool for solution processing. Despite the promising characteristics of hydrazine solutions, several material and device issues limit the prospective application of this approach for commercial device fabrication. Because hydrazine is toxic and explosive, it is subject to various handling limitations during film formation. To circumvent these hazards, we have synthesized a hydrazinium metal chalcogenide complex solute that is compatible with commonly used organic solvent systems.

Another solution process available to thin film devices is the application of colloidal nanocrystals. The University of Washington presented 8.4% efficiency for a selenized device fabricated in this manner.[5] However, regardless of whether the nanocrystals were composed of binary, tertiary or quaternary metal chalcogenides, the colloidal system is inhomogeneous and
impure.\textsuperscript{[6,7]} Hot injection of surfactant at elevated temperatures during nanocrystal synthesis also constrains the uniformity and mass production of the resulting inks. In contrast to colloidal systems, our CZTSSe precursor is a viable solution which allows for the intermixing of the constituents at a molecular level with all solute preparation and dissolution steps performed at room temperature. Our solution of metal constituents is stable, and the use of separate Cu- and Zn/Sn- constituents facilitates simple compositional adjustments. These are each useful advantages for the scalable and safe manufacture of low-cost and high efficiency photovoltaics.

We also propose a sequential annealing method to transform the deposited precursor films into the final CZTSSe phase. Thermal annealing at a high temperature (e.g. 500\degreeC) is essential for CZTSSe device fabrication, and is usually carried out in the presence of chalcogen (e.g. selenium or sulfur) vapor to prevent the possible decomposition of the kesterite absorber. In the chalcopyrite or kesterite device structure, sputtered molybdenum (Mo) serves as the back contact for various historical and scientific reasons.\textsuperscript{[8]} Mo can form a low-resistance contact with the metal chalcogenide film. As temperatures rise, Mo does not easily diffuse into the absorber layer: this provides a large window for high temperature film treatments.\textsuperscript{[8]} Nevertheless, during this thermal process, Mo shows significant reactivity with selenium or sulfur, leading to the formation of an interfacial Mo(S, Se)\textsubscript{2} layer.\textsuperscript{[9]} The formation of a thick interfacial MoSe\textsubscript{2} is undesirable, since it adversely affects solar cell performance.\textsuperscript{[10,11]} Although it has been claimed that the interface of CuInGaS\textsubscript{2} (CIGS)/MoSe\textsubscript{2} provides an ohmic contact,\textsuperscript{[12]} the generation of a thick Mo(S,Se)\textsubscript{2} layer affects the ultimate adhesion of the absorber layer. Preserving sufficient Mo as the back contact is crucial for successful device fabrication. In our design, a thin layer of MoS\textsubscript{2} present between CZTS and Mo by a brief annealing in the presence of sulfur vapor can efficiently inhibit Mo(S,Se)\textsubscript{2} formation during a subsequent heat treatment with selenium vapor. From the point of view of grain
growth, the precursor film on the Mo-coated substrate becomes a continuous layer of fine grains after sulfurization. These fine grains serve as feedstock for further large grain growth by a later selenization treatment. This prevents the formation of voids between grains, which act as shunting paths in devices. Overall, during the annealing process, both sulfur and selenium vapors are employed in sequence, and it is shown that this modified annealing method not only effectively reduces the consumption of the molybdenum back contact, but is also able to assist with grain growth and obtain a desirable grain structure.

Currently, the benign solution system accompanied by the sequential annealing process has produced devices with 7.5\% power conversion efficiency. This unique fabrication lowers the handling of hazardous materials and offers the possibility for large-scale production of CZTSSe photovoltaics. In this paper, we will illustrate the solution preparation, film formation, and device fabrication. We will also present the material and electrical study based on several characterization techniques, and will conclude by briefly summarizing our results.
3.2 Precursor solution design

At the beginning of this experiment, our first challenge was to avoid impurities in the precursor solution. We realized that by using hydrazine, we could easily eliminate unwanted oxygen, chlorine, and long-chain ligands from the metal chalcogenide precursors. Developing an environmentally benign final solvent system for the metal chalcogenide solution was our next target. Dimethylsulfoxide (DMSO), ethanolamine (EA), and formamide (FA) were chosen as solvents for several reasons. According to the HSAB theory, the sulfur atom in DMSO serves as a soft acid, which is able to react with the soft base Cu⁺. The interaction between metal and organic compound can then bring the solute into liquid phase. From a structure-conformation point of view, EA was chosen because the -NH₂ and -OH groups provide strong intramolecular interactions and reducing capabilities, allowing for good stabilization. FA was similarly chosen; it has a simple amide group with high polarity, and provides reducing capabilities as well. Although the carbonyl group is more reactive due to its electrophilic tendencies, the high-resonance stabilization between the N-C and C=O bonds allows amides to become the most stable carbonyl coupling compounds.

The details of how the EA-DMSO mixture solvent dissolves Cu₂S has been reported in previous studies.\[13\]

The Zn/Sn hydrazine solution does not follow the dimensional reduction of a metal chalcogenide framework. Thus, solvent choices differed for this solution than the previous ones. By introducing carbon dioxide into hydrazine, hydrazinocarboxylic acid was formed. The metallic Zn lattice was dismantled and combined with hydrazinocarboxylate in a slurry form. A fully dissolved molecular solution was made with the aid of a tin sulfide (SnS₂) hydrazinium complex and surplus chalcogen.\[14\] Zn, SnS₂ hydrazinium and additional chalcogen moieties kept the solution stabilized, and the dissolved species were able to survive the physical evacuation of the
excess hydrazine. The Zn/Sn hydrazinium constituent was then dissolved by EA at room temperature. In our metal chalcogenide system, it was the first time an organic compound served as a solvent solely to dissolve the binary metal chalcogen hydrazinium component. EA is a relatively non-toxic alkaline substance. It has been used in the formation of the metal salt CZTS precursor solutions.\cite{15} Furthermore, both the solubility and stability of the metal salt increases with an amine-containing complexing agent. However, the solubility of the Zn/Sn hydrazinium complex in FA was only half the value we attained using EA. We also found the saturated FA solution to be unstable at room temperature, with a white precipitate forming after a few days. As shown in the X-ray Photoelectron Spectroscopy (XPS) spectrum depicted in Figure 3.1, the white precipitation was composed of insoluble Zn, Sn and S compounds.

![Figure 3.1 X-ray photoelectron spectroscopy (XPS) of white precipitation in Zn/Sn FA solution](image)
When mixing the Cu- and Zn/Sn- constituents together, DMSO ($\varepsilon=46.7$) and EA ($\varepsilon=37$) formed a stable and homogeneous solution, as expected due to their similar polarities. With Zn/Sn EA solution and Cu DMSO/EA solution, the polarity of final precursor is not affected during intermixing. On the other hand, since FA is a highly polar solvent ($\varepsilon=109.5$), the polarity of the overall solution changes when mixing the Cu and Zn/Sn constituents. In addition, the solution stability and homogeneity were also less desirable than the EA-DMSO system.

The surface tension and boiling point of EA and FA influenced film deposition. Both of DMSO and EA possess low surface tension (DMSO: $\gamma=43$ dynes/cm; EA: $\gamma=48.3$ dyne/cm), and the solution could easily spread out during spin-coating. With FA ($\gamma=59.1$ dyne/cm) in the precursor, the as-deposited film showed streaks or partial coverage, resulting in non-uniformities within the deposited film. The boiling point of the solvents played a key role in film morphology during the pre-baking process; the boiling points of DMSO and EA are 189°C and 171°C, respectively. Under the pre-baking temperature of 350°C, both solvents evaporated easily. FA has a higher boiling point (210°C), which hindered solvent removal. Furthermore, during pre-baking, the low vapor pressure of FA created an uneven pattern on Mo, which can be seen in Figure 3.2.

![Figure 3.2 As deposited CZTS films made by (a) FA, and (b) EA](image)
Thermogravimetric analysis (TGA) of the CZTS precursor is shown in Figure 3.3. The weight loss began at 170°C, which corresponds to the boiling point of EA. Two major stages of weight loss appear at approximately 200 to 250°C and 250 to 350°C. The lower temperature transition—below 250°C—consists of the loss of solvents. The amount of weight lost was equal to the expected neutral EA and DMSO content in the precursor solution. The higher temperature transition—above 250°C—represents the loss of excess chalcogen. Another significant difference between EA and FA is viscosity. From a film formation point of view, thicker precursor films speed up film formation. EA has a higher viscosity (μ=19.37cp) than FA (μ=3.30cp), and consequently, the Zn/Sn- constituent in EA solution had higher viscosity and produced thick, smooth films. As a result of the low quality films formed from FA-containing solutions, we took the CZTS precursor deposited using EA and DMSO for further device fabrication.

![Figure 3.3 TGA result for CZTS precursors using Zn/Sn solution made by (a) EA and (b) FA](image_url)
3.3 Sequential annealing

The crystalline phase of CZTS was obtained using an annealing temperature of 350°C with very fine grains under an inert atmosphere. To get larger CZTSe grains, most fabrication procedures require high temperature annealing in a sulfur or selenium atmosphere. However, those methods usually generate issues in regards to a thick Mo(S,Se)₂ layer and grain size control. To solve such problems, we developed a sequential annealing process. It assisted the absorber in (1) achieving a smooth and continuous CZTSSe film, and (2) inhibiting the growth of Mo(S,Se)₂. The first step—sulfurization on a hotplate for five minutes at 500°C—generated a continuous CZTS layer consisting of densely packed small grains, which became seeds to facilitate later grain growth. The second step—selenization in a tube furnace for 20 minutes at 500°C—expedited the CZTSSe grains to grow continuously and apart from the seed layer toward the substrate.

Figure 3.4a and Figure 3.4b show the XRD patterns and Raman spectra of deposited film after each step of the sequential annealing process, respectively. Peaks corresponding to the CZTS phase were observed at 289, 335 and 373 cm⁻¹, which compare well with published Raman data for CZTS. [16] The appearance of the CZTS phase after the first step of the sequential annealing process was also consistent with the XRD results. After the second annealing step in a selenium atmosphere, the CZTS to CZTSSe transformation is clearly observed in the second Raman spectrum. Moreover, the characteristic peaks of CZTSSe were located at 172, 195, and 238 cm⁻¹. [3][17] No obvious secondary phases was observed by either Raman or XRD measurements. The composition analysis of the as-deposited film was obtained by using an X-ray fluorescence spectrometer (XRF). One advantage of XRF is that it avoids the overlapping of XRD signals from the binary, tertiary, and quaternary phases composed of copper, zinc, tin, sulfur or selenium due to similarities of crystalline structure. The atomic ratios between the metal elements were close to
the target ratio: Zn/Sn=1.18 and Cu/(Zn+Sn)=0.78. In addition, S/(S+Se) was 0.99 as deposited and after the sulfurization (the first step annealing), and it became less than 0.1 after selenization (the second step annealing), consistent with their corresponding structural characteristics discussed previously. As shown in the SEM top view of Figure 3.4c, the closely packed CZTS grains were obtained after sulfurization. In Figure 3.4d, due to the substitution of larger Se atoms for smaller S atoms, the unit cell volume expansion gave support for further CZTSSe grain growth during the selenization process. If no sulfurization is performed beforehand, voids are frequently found in the selenized film (see the inset in Figure 3.4d or Figure 3.5), which can become shunting paths between the electrodes and increase the leakage current in the devices.

In addition, Figure 3.6 shows the cross sectional SEM images for CZTSSe devices processed in different annealing conditions: (a) selenization for 20 minutes (b) sulfurization 5 minutes followed by selenization 20 minutes and (c) sulfurization 12 minutes followed by selenization 20 minutes. Note that the original thickness of molybdenum is around 350 nm, determined by Dektak 150 surface profiler. The thickness of remaining molybdenum in CZTSSe devices with annealing recipes (a), (b) and (c) are roughly 155 nm, 230 nm, and 181 nm, respectively. It suggests that with use of the sequential annealing, MoS$_2$ interface formed in the first step annealing likely prohibited selenium to diffuse for further reacting with molybdenum, yielding a thinner interfacial layer between CZTSSe and Mo.
Figure 3.4 CZTS/CZTSSe film characterization: (a) XRD profiles for as-deposited film (350°C pre-baking) (black), after 1st step 500°C sulfurization (red), and 2nd step 500°C selenization (blue); (b) Raman spectrum of sequential annealing films; (c) SEM top view image of CZTS, and (d) CZTSSe; the inset is CZTSSe without pre-sulfurization.
Figure 3.5 SEM top view image of a CZTSSe film without pre-sulfurization

Figure 3.6 SEM cross-section of Mo(S,Se)₂/Mo interface for different sequential annealing times
3.4 Device performance and characterization

Figure 3.7a depicts results from the scanning electron microscopy (SEM), which reveals the internal microstructure of the film. We found the CZTSSe layer to be composed of large grains (~600–700nm) on top of a small grain (~300–400nm) layer. The densely packed large grains were formed after sequential annealing. Some voids were observed within the small grain layer, and an amorphous carbon signal could be observed by Raman profiling. The columnar bottom contact structure is typical of Mo, and a Mo(S,Se)₂ layer was formed between the absorber layer and Mo with its accompanying volume expansion. The current-voltage (J-V) characteristics for the best device we attained are shown in Figure 3.7b. With 110nm MgF₂ antireflection coating, the dark J-V curve demonstrates the rectifying properties of the p-n junction of CZTSSe and CdS; the light J-V curve yields short-circuit current (Jₘₖ), open-circuit voltage (Vₙₖ), fill factor (FF), power conversion efficiency as 37.3 mA/cm², 0.39 V, 49.0%, 7.2% respectively under AM1.5G conditions. The device area was 0.12cm², defined by mechanical scribing of a 1.5 x 1.5 cm² substrate. Note that the cell without the sequential annealing process (i.e. without sulfurization before selenization) shows relative lower open-circuit voltage, compared to the one with sequential annealing (Figure 3.8), possibly related to the observed voids in the absorber (Figure 3.5) leading to the shunting paths between the electrodes.
**Figure 3.7** (a) SEM cross-section of the stack of CZTSSe device after sequential annealing. (b) J-V characteristics of CZTSSe device; (c) Corresponding IPCE measurement at zero bias without light-soaking effect. The dotted line represents the dark J-V, the black solid lines represent the light performance without light-soaking, and the red solid lines represent with light-soaking.

**Figure 3.8** J-V characteristics of CZTSSe devices with (blue, pre-sulfurization and selenization) and without (black, only selenization) sequential annealing. Solid lines and dot lines represents light and dark J-V, respectively.
We observed light-soaking effects during J-V measurement. The light-soaking effect increases the device performance, which has also been found for other chalcogenide devices, such as CdTe and CIGS.\cite{18} After Xenon (Xe) lamp illumination, the FF had a 5\% improvement, and the efficiency improved to 7.5\%. However, since the light-soaking effect is a reversible process, the FF relaxed back to the original value when the device was removed from exposure. It could also possibly be caused by the metastable of photoconductivity within the absorber layer, similar to what has been observed in CIGS films.\cite{19} The high mobility of copper migration might play a role in the device performance as well.\cite{20} The black line in Figure 3b represents the J-V character without light-soaking, and the red line shows the J-V character after Xe lamp illumination.

The IPCE measurement in Figure 3.7 depicts the external quantum efficiency from 300nm to 1300nm with MgF$_2$ anti-reflection coating. The slope from 700 to 1100nm indicates a loss of deeply absorbed photons from within the absorber layer.\cite{21} It implies a thickness adjustment of the absorber might be required to improve the collection of minority carriers. Furthermore, IPCE measurements revealed the material band gap, which corresponds roughly to the wavelength at 25\% maximum QE.\cite{21} In our case, the band gap was about 1.04 eV. With different applied biases, there were no substantial differences in QE, which implies that recombination induced by defects might be negligible.\cite{22} Yet, compared with other CZTSSe fabrication reports with similar bandgap, the open circuit voltage still needs substantial improvements. Possibly due to the charge transport in the carbon-rich layer of the absorber, recombination occurs at the unavoidable Mo(S,Se)$_2$ interface, or at the top contact. We believe with device optimization, this benign solution system could reach higher efficiency and be widely applied.
To further investigate the defects of our device, we used capacitance-based characterization methods, such as admittance spectroscopy (AS) and drive-level capacitance profiling (DLCP).\[^{23}\]

By measuring the junction capacitance as a function of frequency at different temperatures, the energy level of defects within the bandgap can be extracted. Figure 3.9a shows the capacitance-frequency (C-F) scans taken over the range of 120K to 300K in the dark, and with a frequency range of $10^2$ to $10^6$ Hz. An AC voltage of 30mV was applied and the DC bias was kept at zero during the measurement. Using the inflection point of each AS spectrum at different temperatures from 120K to 300K, an Arrhenius plot was drawn, and can be seen in Figure 3.9b. The fitting curve followed the equation:

$$\omega_0 = 2\pi v_0 T^2 \exp\left(\frac{-E_a}{kT}\right)$$  \hspace{1cm} (1)

where $\omega_0$ was the step frequency; $E_a$ was the energetic depth of the defect relative to the corresponding band edge; and $v_0$ was the pre-exponential factor comprising all temperature-independent terms, such as the defect capture cross section for holes ($\sigma_p$), the effective density of states in the valence band ($N_v$), and the thermal velocity ($v_{th}$).\[^{24}\] According to Kimerling’s model,\[^{25}\] the capacitance at high frequency represents the response of the free carrier density, while the capacitance at low frequency represents the response of the sum of free carriers and deep traps. In Figure 3.9a, the C-F curve at room temperature (300K) indicates defect levels in the bandgap dominating the device capacitance. The lowering of temperature leads to reduced capacitance, which indicates that the deep traps and free carriers were gradually frozen out.\[^{26}\] The moderate frequency dependence of the capacitance in this high Se content device is consistent with other solution-processed CZTSSe devices.\[^{24,27}\] However, compared to previous cases,\[^{24}\] the smaller capacitance over the same frequency range could be explained by the carbon-rich layer in the CZTSSe film. As with other non-hydrazine processed CZTSSe devices, the use of organic
solvents was the main carbon contribution.\cite{28} The conductive amorphous carbon layer between the CZTSSe film and the molybdenum back contact is generally considered detrimental to device performance. From the slope of the fitting curve derived from the temperature-dependent AS spectrum, the Arrhenius plot (Figure 4b) allows for the extraction of the activation energy ($E_a$), which is approximately the average value of the energy difference between defect level and the valance band edge. The $E_a$ of our device was 117 meV, and the pre-exponential factor was around the order of $10^3$. This demonstrates a relatively shallow defect distribution in our system.

**Figure 3.9** Device characterization: (a) Admittance spectra (AS) measured at temperature between 120K and 300K with increments of 10K. (b) Arrhenius plot of the inflection frequencies resolved from the derivative of the AS. (c) Deep-level responses at 300K (solid circle) and 190K
(hollow circle) show free carrier density as a function of depletion distance from junction. The measurement frequency is 10kHz with the dc bias ranging from 0.3 to -0.3V; (d) Photoluminescence (inset) and Photoluminescence decay at room temperature

Drive-level capacitance profiling (DLCP) was also applied to this new system. DLCP provides the density of defects within the band gap of the absorber as a function of both energy and spatial position by measuring the junction capacitance over a range of AC voltages and DC biases. In our case, the DLCP measurement was performed with DC bias ranging from 0.3 to -0.3V, and AC amplitude varying from 0.01V to 0.05V at room temperature with a frequency of 10 kHz. At room temperature (300K), the DLCP signal corresponds to the response of both free carriers and deep level acceptors, which was measured to be approximately $1.4 \times 10^{15}$ cm$^{-3}$, as shown in Figure 3.9c. At a reduced temperature (190K), the DLCP response corresponds to the free carrier density of $5.1 \times 10^{14}$ cm$^{-3}$. The difference between the high- and low-temperature DLCP responses was $9 \times 10^{14}$ cm$^{-3}$, which is commonly assigned as the density of deep traps. These deep traps are expected to serve as the most active recombination centers within the device.\textsuperscript{[1]}

Time-resolved photoluminescence (TR-PL) measurements were performed on the finished cell at room temperature. Fitting the spectra in Figure 3.9d, the minority carrier lifetime was around 2-3 ns, which is consistent with other reports on CZTSSe. Possible explanations for the PL peak ($E = 0.97$ eV) shift from $E_g$ (determined from the IPCE measurement) include the following: (1) the impurity recombination dominates the PL emission,\textsuperscript{[30]} and/or (2) localized luminescence from low band gap regions dominates the PL emission in an inhomogeneous absorber film.\textsuperscript{[31]}
3.5 Conclusion

We have created a homogeneous molecular CZTS precursor solution by using metal chalcogenide hydrazinium complexes as the solute. This largely diminished the risks during film deposition. The EA-DMSO combination provides an excellent platform to dissolve the Cu-hydrazinium constituent. The EA solution with the Zn/Sn-hydrazinium constituent is very stable and easily prepared. The other benefit of this individual metal constituent is that it offers flexibility when adjusting the metal composition of the deposited films. The sequential annealing process provides a close-packed CZTS seed layer for further CZTSSe grain growth. It also contributes to the preservation of the Mo back contact against Mo(S,Se)$_2$ formation. The final device achieves 7.5% efficiency, assisted by mild light-soaking effects. With thermogravimetric, Raman, and XRD analysis, we can confirm it is a valid way to transform the molecular metal precursor to CZTS/CZTSSe bulk film with the right phase. AS and DLCP characterizations further demonstrate the electronic properties of this new system. This work discovers the possibility of a homogeneous molecular solution based route. It potentially can achieve comparable performance in large-scale photovoltaic devices.
3.6 Experimental Section

Zn-, Sn- and Cu- constituents are first reacted with hydrazine to form hydrazinium complexes in the presence of excess dissolved chalcogen. The hydrazinium metal chalcogenides were used as the solutes; Formamide (FA), ethanolamine (EA), and mixtures of EA and dimethylsulfoxide (DMSO) were used as solvents. The dissolution process was performed in a nitrogen-filled dry box where oxygen and moisture levels were both below 0.1 ppm. The excess chalcogen species dramatically increased the solubility of the solute in the final solution.

For Cu- constituent preparation, 1 mmol of copper sulfide (Cu$_2$S) and 2 mmol sulfur (S) were combined with 1 mL hydrazine. After physically evacuating the liquid hydrazine, the yellow Cu$_2$S solution transformed into black powder, which was then dissolved in the EA-DMSO mixture; the EA-DMSO volume ratio was set as 3:5. Then, excess sulfur was added. Several hours of stirring at 65°C produced a dark brown solution. For Zn-constituent solution, the hydrazinocarboxylic acid (NH$_2$NHC$_2$OOH) was used to fully dissolve zinc powder in hydrazine. Hydrazinocarboxylic acid was prepared by adding hydrazine to a vial containing solid-state carbon dioxide. Zinc nanopowder (2 mmol) was added into a NH$_2$NHC$_2$OOH saturated hydrazine solution (1 mL), producing a white Zn-paste after continuous stirring. Sn- constituent solution was prepared in a separate vessel, by mixing and stirring 2 mmol of tin sulfide (SnS$_2$) and 4 mmol sulfur (S) in 1 mL hydrazine. Zn/Sn solution is formed by combining 1.2 ml Zn-paste ([Zn] = 2M) with 1 ml Sn-constituent ([Sn] = 2M) with 1.2 mmol sulfur, with a 1.2:1 target ratio of Zn to Sn. After stirring for several hours, the Zn/Sn mixture turns from brown into a colorless and transparent solution. Different from the Cu- constituent, 1 mL of the Zn/Sn mixture hydrazine solution became a transparent gel after physical evacuation. The addition of 1 mL EA into the Zn/Sn gel with moderate stirring at room temperature transformed the gel to a transparent solution. The Zn/Sn EA solution remained stable for several
months. Besides EA, Formamide (FA) was also tested as a solvent. 2 mL of FA were added to the Zn/Sn gel, and the mixture was heated to 100°C with moderate stirring. The final solution was also colorless and transparent, however the Zn/Sn FA solution is less stable than the EA solution, with white precipitation visible after two days. Figure 3.10 shows the images of Cu- and Zn/Sn solutions. After both solutions were prepared, the Zn/Sn precursor in EA or FA was then mixed with a Cu precursor in EA-DMSO solution to form a target Cu/(Zn+Sn) ratio of 0.8.

![Figure 3.10](image_url)

**Figure 3.10** Precursor solutions: (a) Zn/Sn FA solution, (b) Cu EA/DMSO solution, and (c) Zn/Sn EA solution

The CZTSSe precursor solution was evaluated by thermal gravimetric analysis (TGA). TGA powder samples were prepared by heating the precursor solution at 100°C for one hour to evaporate the solvent; the TGA ramping profile is 5°C/min from 50°C to 550°C, and was then held at 550°C for 20 minutes. TGA profiles were collected on a TA instrument Q600 with a horizontal balance and furnace.

The film formation process followed the flow diagram shown in Figure 3.11. After mixing the Cu- and Zn/Sn- constituents, the liquid precursor was converted to a 2-D network on the substrate by spin-coating. To achieve a certain thickness of the absorber, we repeated the spin coating, pre-baking, and cooling process several times. The pre-baking temperature was set to be 350°C. For
the final annealing, there were two steps: (1) sulfurization for five minutes on the hotplate at peak processing temperatures between 480°C and 520°C, and (2) selenization for 20 minutes at 500°C within a graphite box.

CZTSSe thin films were characterized by X-Ray Diffraction (XRD), Raman spectroscopy, and X-Ray Fluorescence (XRF). XRD, Raman and XRF samples were prepared as CZTS films deposited via spin coating on Mo-coated soda lime glass (SLG). XRD patterns were collected on a PANalytical X’Pert Pro X-ray Powder Diffractometer using Cu-Kα radiation (λ=1.54060Å).
Raman spectroscopy analysis was performed in a backscattering configuration with a confocal microscope at room temperature using a Renishaw inVia Raman system equipped with a 514.5 nm Ar laser. XRF elemental analysis was performed using a Rigaku Supermini sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometer.

Devices were fabricated with a SLG/Mo(350nm)/CZTS(1.2um)/CdS(50nm)/ZnO(25nm)/ITO(120nm) structure. Mo was deposited on the SLG by DC sputtering. Before spin-coating the absorber, surface treatment with O₂/Ar plasma was required. The n-type material, cadmium sulfide (CdS), was formed via chemical bath deposition. Intrinsic ZnO and ITO were deposited using RF-sputtering with Ar flow as the top window layer. A 110-nm-thick MgF₂ antireflection coating was deposited on top of the device by thermal evaporation. The cell area was 0.12 cm², and the current versus voltage (J-V) performance was measured under an AM1.5G filter at 100 mW/cm², using a Newport Oriel 92192 solar simulator. The IPCE measurement was collected by using a system designed by EnliTech.

All characterizations were done on final devices as well. Time-resolved photoluminescence was measured using a NIR-sensitive photomultiplier tube (Hamamatsu H10330A-75) with Picoquant single photon counting techniques, and the excitation was provided by a picosecond diode laser at the wavelength of 640 nm. The detailed experiment setup has been described elsewhere. The admittance spectroscopy (AS) and drive-level capacitance profiling (DLCP) were measured using a Hewlett-Packard 4284A LCR Meter. Temperature dependent measurements were carried out using a Linkam temperature-controlled stage equipped with liquid nitrogen cooling. The temperature was monitored by a calibrated platinum sensor embedded close to the surface of the stage.
3.7 References


Chapter 4 Single component precursor for precise phase and composition control

4.1 Introduction

Kesterite-phase Cu$_2$ZnSnS$_4$ (CZTS) has recently been highlighted as emerging absorber material in next generation thin film solar cells, owing to its decent optical property and earth abundant nature.[1][2] The successful demonstration of CZTS processing,[3][4][5] is largely benefit from controlling the formation of the kesterite phase, a target that poses unique material challenges. Unlike its analogous Cu(In,Ga)S$_2$ (CIGS) or CdTe,[12][13][14] single-phase kesterite CZTS exists only within a narrow stoichiometry range.[15][16] The presence of volatile elemental constituents and binary phases[17][18][19] (such as zinc metal and tin chalcogenide) further complex the phase purity issue within the deposited films, particularly under high temperatures and vacuum conditions. Thus, the exquisite controllability over composition[20][21][22][23] and phase becomes the key prerequisite in any synthetic routes for the fabrication of high performance CZTS films.

Similar with other members of metal chalcogenide family, high quality CZTS films have been deposited via a cost-effective solution processing.[3][5][6] Solution processing, by taking advantages of its high precursor diffusivity and uniform precursor distribution in liquids, is capable of producing pure kesterite phase at low temperature.[4][5][19] An ideal solution precursor for high quality kesterite phase requires identical compositions in both liquid and film, absence of impurities, precise control on composition stoichiometry, free of phase segregation and small geometry reorganization during film formation. Despite the remarkable progresses, current solution processing precursors, varying from solution mixture of multiple molecules or binary/ternary nanoparticles, quarternary particles to preformed single-component quarternary nanoparticles, still hardly meet all the criteria.[7][8][9] Solution mixture of multiple molecular or binary/ternary nanoparticles enables large stoichiometry tunability, however, the local element
distribution in spin-coated films is uncertain owing to phase segregation, which may lead to an intensive kinetically ion diffusion barrier during phase formation. A single-component precursor, such as quaternary kesterite-phase CZTS nanocrystals with only one composition, enables identical local compositions in both liquid and film state, but on the cost of surface long chain hydrocarbon ligands contaminating film purity. Thus, developing a clean uniform solution precursor that exhibits controllability over composition and phase progression during film formation is highly preferable.

For the first time, a facile single-component nanoparticle precursor, Cu$_{2-x}$S nanoparticles (NPs) capped with Zn-Sn complex (Zn-Sn complex abbreviates the mixture of Zn(hyc)$_2$(N$_2$H$_4$)$_2$ (hyc: hydrazinocarboxylic), [Sn$_2$S$_7$]$^{6-}$ and [SnS$_4$]$^{4-}$), for high-quality kesterite-phase CZTS film (Figure 4.1), is reported. In this approach, Zn-Sn complex is directly capped onto the ultra-small Cu$_{2-x}$S nanoparticles surface to form homogeneous nanoparticles. Compared with quaternary kesterite-phase CZTS nanocrystals, Cu$_{2-x}$S/Zn-Sn nanoparticle (Cu$_{2-x}$S/Zn-Sn) precursor exhibits similar composition controllability, resulted from their single-component nature, but the absence of surface hydrocarbon ligands. Upon annealing, local element re-distribution produces the resulting kesterite-phase CZTS with increased film homogeneity and less impurities. Surface Zn-Sn ligands surrounding Cu$_{2-x}$S nanoparticles provide both colloidal stabilization and essential components for CZTS. The stoichiometry of CZTS is simply adjusted by the concentration of Cu$_{2-x}$S nanoparticles and Zn-Sn ligands. Film formation is investigated in detail with X-ray diffraction and Raman spectroscopy. We find that, with current single-component nanoparticle precursor, very few steps are required to produce kesterite Cu$_2$ZnSnS$_4$ phase. Using the present precursor, photovoltaic devices have been successfully demonstrated, and advanced optoelectronics are expected by precisely tuning the kesterite material properties.
4.2 Experimental details

**Chemicals:** All chemicals are purchased from Aldrich, and used without any further purification.

**Synthesis of Cu$_{2-x}$S nanoparticles:** The synthesis of Cu$_{2-x}$S nanoparticles followed the literature method.\[^{25}\] In a typical synthesis, 1.25 mmol of ammonium diethyldithiocarbamate is mixed with 10 mL of dodecanethiol and 17 mL of oleic acid in a three-neck flask. Then, the solution is heated up to 110 °C under Argon (Ar) flow and maintained at 110 °C for 30 minutes, followed by a quick injection of a suspension composed of 1 mmol of copper(II) acetylacetonate and 3 mL of oleic acid. After that, the solution is quickly heated up to 180 °C and kept at the temperature for 10 minutes. The solution containing Cu$_{2-x}$S nanoparticles is cooled down naturally to room temperature before was taken out of the flask for centrifuging at 5000 rpm for 8 minutes. The supernatant is discarded and the precipitation is first fully dissolved in 4 mL of toluene and then precipitated out by adding 30 mL of isopropanol followed by centrifuging at 5000 rpm for 8 minutes. The as-obtained precipitation is fully dissolved in toluene with mass concentration of 20 mg/mL Cu$_{2-x}$S nanoparticles for further construction of CZTS precursor.

**Preparation of Zn-Sn ligand solution:** The Zn-Sn hydrazine solution was prepared according to the previous work of our group.\[^{26}\] In brief, Zinc nanopowder (2 mmol) was mixed and stirred with H$_2$NNHCOOH saturated hydrazine solution (1 mL), which was first prepared by adding hydrazine to a vial containing solid-state carbon dioxide. The tin precursor solution was prepared in a separate vessel, through mixing SnS$_2$ (1 mmol) and excess sulfur (2 mmol) in N$_2$H$_4$ (1 mL) with stirring. The Zn-Sn hydrazine solution was made by mixing the above two solution with adjusted molar ratio of Zn/Sn = 1.2. Note: Hydrazine is highly toxic, and appropriate protective equipment should be used to prevent direct contact with the liquid or vapor. The reaction between carbon dioxide and hydrazine is highly exothermic. The hydrazine-based solutions were prepared in a nitrogen-
filled glove box where the oxygen and moisture levels were both below 1 ppm. The Zn-Sn dried precursor was prepared by evaporating Zn-Sn hydrazine solution overnight, and was re-dissolved in appropriate amount of benign solvents, such as formamide (FA), ethanolamine (EA) with continuous stirring at 100 °C for 1-2 h. The as-prepared Zn-Sn species in EA or FA are adjusted with desired concentration for the construction of CZTS precursor solution in the next step.

**Preparation of CZTS precursor:** The final CZTS precursor solution was prepared by mixing the following constituents, 0.3 mL 0.2 M Zn-Sn solution of FA, 0.5 mL 20 mg/mL Cu$_{2-x}$S colloidal solution of toluene and 0.2 mL extra FA in the glovebox. The as-formed two-phase mixture was stirred vigorously for several hours, after which toluene phase turned colorless while the FA phase turned black, indicating ligand exchange of nanocrystals. The colorless upper toluene phase was discarded and the bottom FA phase was washed three times with toluene. Then, the bottom black layer was collected by adding adequate amount of acetonitrile, followed by centrifuging at 5000 rpm for 6 min, and lastly was re-dispersed in FA solvent. The as-obtained CZTS precursor solution was stored in the glovebox for further characterization and device fabrication. For FTIR characterization, the precursor solution is dried under vacuum in order to measure its solid state behaviour. The off-stoichiometric CZTS precursor solution was prepared by mixing excessive Zn-Sn solution with Cu$_{2-x}$S nanocrystals, e.g. 0.4 mL 0.2 M Zn-Sn solution and 0.5 mL 20 mg/mL Cu$_{2-x}$S colloidal solution, and the rest of the preparation procedures remain the same.

The formation of stable CZTS precursor solution is mainly attributed by selecting the appropriate solvents and mixing the adequate amount of the ligands. In order to develop an environmentally benign and air-stable preparation, a large number of solvents have been tested to redissolve the dried Zn-Sn precursor, derived from the hydrazine precursor solution. It is found that only FA or ethanolamine (EA) provides accepted solubility, while dimethylformamide (DMF),
dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF) which are commonly used for dissolving water insoluble inorganic compound, hardly redissolve the Zn-Sn precursor. Interestingly, the combination of EA and DMSO, which showed great solubility for the Cu and In hydrazinium precursor,\textsuperscript{28} are not effective when it applies on the Zn-Sn precursor, but EA alone is capable to dissolve Zn-Sn precursor. This could be ascribed to the polarity, the reducing and the coordination ability of EA. An alternative solvent FA, shares some similar structure features as EA, which both possess an NH2 group in their molecular structures. The prepared solutions, either Zn-Sn in FA, or Zn-Sn in EA are further used to conduct the ligand exchange for the Cu2-xS nanocrystals. Experimental results indicate that FA can give a more stable CZTS precursor solution, while EA cannot stabilize the nanocrystals after ligand exchange, since Cu2-xS nanocrystals tend to precipitate after the phase transfer. This can be resulted from the different dielectric constants of EA and FA,\textsuperscript{35} where FA (\(\varepsilon = 106\)) has a much higher dielectric constant value than that of EA (\(\varepsilon = 37.7\)). Different solution stability comparisons between EA and FA suggest that the higher dielectric constant solvent likely assists to stabilize nanocrystals. In addition to the choice of solvent, the amount of Zn-Sn in the final precursor solution also plays an important role to facilitate the process of ligand exchange, since inadequate Zn-Sn amount versus Cu species would lead to the precipitation of Cu2-xS nanocrystals.

**Materials Characterization:** Both the films and powder samples were annealed at the desired temperature on a hot plate with the temperature verified by an IR thermometer. XRD patterns were collected on a PANalytical X’Pert Pro X-ray powder diffractometer using Cu K\(\alpha\) radiation (\(\lambda=1.54060\ \text{Å}\)). The scanning electron microscope (SEM) images were taken on Nova 230 with an accelerating voltage of 5 kV. Raman shift spectroscopy was carried out using a Renishaw inVia Raman microscope using an excitation laser with a wavelength of 514 nm. TEM images were
taken on an FEI CM120 microscope operating at 120 kV, and FEI Titan 80-300 kV S/TEM operating at 300 KV. FTIR spectra were obtained on a PerkinElmer Paragon 1000 FT-IR Spectrometer at a resolution of 4 cm⁻¹ with a PerkinElmer IR microscope.

**Synthesis of Cu₂ZnSnS₄ nanocrystals:** The synthesis of Cu₂ZnSnS₄ nanocrystals follows the literature method¹⁸. In a typical synthesis, 1.332 mmol of copper acetylacetonate, 0.932 mmol copper acetylacetonate, and 0.75 mmol tin acetylacetonate dichloride were mixed with 10 mL of oleylamine in a three-neck flask. Then, the solution was heated up to 130 °C under Argon (Ar) flow and maintained at 130 °C for 30 minutes, followed by a quick injection of a solution composed of 2 mmol of sulfur in 2 mL of oleylamine. After that, the solution was quickly heated up to 225 °C and kept at this temperature for 30 min. The solution containing Cu₂ZnSnS₄ nanocrystals was then cooled down naturally to room temperature and was centrifuged at 7500 rpm for 8 min with adding 50 mL ethanol. The supernatant was discarded and the precipitation was first fully dissolved in 5 mL of toluene and then precipitated out by adding 30 mL of ethanol followed by centrifuging at 7500 rpm for 8 min. The as-obtained precipitation was fully dissolved in toluene with mass concentration of 100 mg/mL for CZTS nanocrystals. The CZTS film was made by coating the as-prepared CZTS nanocrystals for multiple times, and annealed at 500 °C for 10 minutes.

**Fabrication and characterization of Cu₂ZnSn(S,Se)₄ (CZTSSe) solar cells:** CZTSSe absorber was deposited onto the molybdenum-coated glass substrate by spin-coating the precursor solution multiple times, with intermediate annealing steps of 300 °C followed by a final selenization in a graphite box at 560 °C for 20 minutes. The cadmium sulfide (CdS) layer was then deposited onto CZTSSe layer by chemical bath deposition. Finally, Ag nanowires (NW)/ITO-nanoparticles films were spin coated onto the devices as a transparent top electrode. The area of each cell was 2 mm
by 2.5 mm, defined by mechanical scribing of a 1 cm by 1 cm substrate. The current versus voltage (J-V) performance was measured under an AM 1.5G filter at 100 mW/cm², using a Newport Oriel 92192 solar simulator.
4.3 Structural characterization of the single component precursor

![Figure 4.1](image.png) A schematic illustration of the synthetic route to CZTS film. Initially, Cu$_{2-x}$S nanoparticles were capped with Zn-Sn complexes to form the single-component precursor, Cu$_{2-x}$S/Zn-Sn nanoparticles. Then Cu$_{2-x}$S/Zn-Sn nanoparticles were deposited into the precursor film, followed by thermal annealing to form the kesterite CZTS film.

The single-component precursor, Cu$_{2-x}$S/Zn-Sn, was synthesized by a two-step ligand-exchange reaction, as illustrated in Figure 4.1. In brief, Cu$_{2-x}$S nanoparticles were firstly synthesized, followed by a surface ligand exchange from oleic acid to Zn-Sn ligands. Cu$_{2-x}$S nanoparticles were firstly synthesized following a literature method,[25][27] where copper acetylacetonate and ammonium diethylthiocarbamate reacted in a mixed solvent of dodecanethiol and oleic acid. Figure 4.2a and inset show the Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) images of the as-obtained Cu$_{2-x}$S nanoparticles. The average size of the nanoparticles was measured as 5.2 ± 0.4 nm, based on TEM statistic results. Characteristic interplanar distance of 0.2 nm from the (110) planes of single-crystal hexagonal Cu$_{2-x}$S was also observed in the HRTEM image (inset of Figure 4.2a). X-ray Diffraction (XRD) further confirmed the hexagonal chalcocite Cu$_{2-x}$S (JCPDS 012-0176, Figure 4.3) phase of the as-prepared Cu$_{2-x}$S nanoparticles, which was in agreement with the TEM results. Figure 4.3 shows the X-ray diffraction pattern of as-prepared Cu$_{2-x}$S nanocrystals. It
is clear that the sample displays four main peaks at 37°, 46.3°, 48.5° and 54.3°, indicating Cu$_{2-x}$S prepared in this way are hexagonal chalcocite (JCPDS 012-0176). This is in consistent with the TEM imaging.

**Figure 4.2** (a) TEM images of the as-prepared oleic acid capped Cu$_{2-x}$S nanoparticles; (b) Photograph of Cu$_{2-x}$S nanoparticles before and after ligand exchange of Zn-Sn ligand; (c) TEM images of Zn-Sn ligand capped Cu$_{2-x}$S nanoparticles

**Figure 4.3** XRD pattern of as-prepared Cu$_{2-x}$S nanocrystals
The Zn-Sn ligand solution was separately prepared by evaporating Zn-Sn hydrazine solution (including Zn(hyc)$_2$(N$_2$H$_4$)$_2$ (hyc: hydrazinocarboxylic), [Sn$_2$S$_7$]$^{6-}$, and [SnS$_4$]$^{4-}$) into a dried precursor, followed by re-dissolution into formamide (FA). Upon the mixing with Cu$_{2-x}$S nanoparticles solution, Zn and Sn constituents substituted the original surface oleic acid ligands. Figure 3.2b showed the sequential images before and after ligand exchange. Original Cu$_{2-x}$S nanoparticles in the toluene phase were then transferred into the Zn-Sn containing FA phase, leaving a transparent toluene layer on the top. Stable Cu$_{2-x}$S/Zn-Sn precursors were finally harvested by centrifuging and re-dispersing the bottom layer. TEM image showed similar morphology of Cu$_{2-x}$S before (Figure 4.2a) and after (Figure 4.2c) surface ligand exchange. Notably, only capped nanoparticles were stabilized in FA, preserving the surface modification uniformity at single particle scale. Also, inadequate amount of Zn-Sn complex ligands versus Cu species would lead to the precipitation of Cu$_{2-x}$S nanoparticles in formamide. Thus, successfully preparing the CZTS precursor solution in formamide without precipitate indicates the presence of single-component nanoparticles, rather than simply the mixture of Cu$_{2-x}$S nanoparticles and Zn-Sn complex ligands, in the CZTS precursor solution. In addition, to prove the homogenous distribution of Zn-Sn complex on Cu$_{2-x}$S nanoparticles, a scanning transmission electron microscopy (STEM)-energy dispersive spectrum (EDS) measurement was conducted (Figure 4.4). Because of the weak signal from a single nanoparticle (size of ~5 nm), a scanning range of ~45 nm (the inset of Figure 4.4a) that covered several nanoparticles, was selected as our measurement scope. The plots of metal composition at varied scanning positions were drawn for Cu, Zn and Sn, respectively (Figure 4.4b). The signals of Cu, Zn and Sn follow similar distribution profiles, indicating that the Zn-Sn complexes ligands likely capped on the surface of Cu$_{2-x}$S nanoparticles evenly.
The successful fabrication of single-component Cu$_{2-x}$S/Zn-Sn nanoparticle precursor was further confirmed by FTIR and Raman spectra. As shown in Figure 4.5a, solid-state FTIR studies indicated the removal of the original hydrocarbon ligands: the characteristic C–H vibrations peak at 2800–3000 cm$^{-1}$ disappeared after the ligand exchange. In Raman spectra (Figure 4.5b), after ligand exchange, the peak around 300 cm$^{-1}$ and 352 cm$^{-1}$, indicative of the bridge vibration of S$_3$Sn–S–SnS$_3$ and [SnS$_4$]$^{4-}$ stretching mode, disappeared, while two new peaks at 334 cm$^{-1}$ and 475 cm$^{-1}$ likely from Cu$_2$ZnSnS$_4$ and Cu$_2$S were observed, respectively.$^{[19][29][30]}$ Importantly, the appearance of Cu$_2$ZnSnS$_4$ vibration at 334 cm$^{-1}$ indicates the surface binding between Cu$_{2-x}$S nanoparticles and Zn and Sn species at room temperature, and the effective surface distribution of Zn and Sn around Cu$_{2-x}$S nanoparticles.

Figure 4.4 (a) a STEM image of Cu$_{2-x}$S nanoparticles capped with Zn-Sn complexes; (b) a EDS line scan of the several Cu$_{2-x}$S nanoparticles capped with Zn-Sn complexes shown in the inset of figure (a), showing the distribution of Cu (top), Zn and Sn (bottom), respectively
Figure 4.5 (a) FTIR spectra of the Cu$_{2-x}$S nanoparticles, before (red line) and after (black line) ligand exchange with Zn-Sn complex; (b) Raman spectra of Zn-Sn precursors in FA and Cu$_{2-x}$S nanoparticles with Zn-Sn complexes in FA
4.4 Reaction pathway investigation

Next we investigated the phase formation and intermediate products within the as-deposited film via temperature-dependent XRD and Raman spectrum. At each temperature, the film was incubated for 10 minutes, and then characterized by XRD and Raman, as shown in Figure 4.6. At 100 °C, strong signals from Cu$_{2-x}$S and amorphous hydrazinium frameworks were recorded in XRD. Due to the spectrum overlap, diffraction patterns from the crystalline phases of CZTS or its sub-phases were hard to be identified. Same sample exhibits one Raman peak at 470 cm$^{-1}$, in good agreement with the reported vibrational mode of Cu$_{2-x}$S phase.[31] Besides, there is a broad peak appeared at 330 cm$^{-1}$ with a shoulder at 298 cm$^{-1}$, suggesting the formation of Cu$_2$ZnSnS$_4$ or Cu$_2$SnS$_3$.[32]

When the temperature reached 175 °C (stage 1), we observed clear signs indicative of dramatic phase changes from Cu$_{2-x}$S to Cu$_2$ZnSnS$_4$ or Cu$_2$SnS$_3$. XRD diffraction from Cu$_{2-x}$S disappeared, together with the appearance of a mixture of diffraction patterns from hexagonal phase of ZnS (JCPDS 00-005-0492) and a cubic phase, from either Cu$_2$SnS$_3$ (JCPDS 01-089-2879) or Cu$_2$ZnSnS$_4$ (JCPDS 00-026-0575), appeared in XRD spectrum. The appearance of these bimetallic or trimetallic chalcogenides, clearly indicated the reaction between Cu$_{2-x}$S nanoparticles and Zn-Sn ligands at mild conditions, even though it is challenging to differentiate the close phases of Cu$_2$SnS$_3$ and Cu$_2$ZnSnS$_4$. Same phase change was also evidenced in Raman spectrum, where a strong peak at 330 cm$^{-1}$ from the dominant phase of Cu$_2$ZnSnS$_4$ or Cu$_2$SnS$_3$ appeared instead of the Cu$_2$S peak. Notably, we didn’t observe the wurtzite ZnS in Raman spectrum owing to the lack of proper laser source to excite the corresponding vibrations. The new formed phases appeared
around Cu$_{2-x}$S nanoparticles, suggesting the single-component precursor as the nucleation center for the phase formation in the film.

**Figure 4.6** (a) XRD patterns and (b) Raman spectra of Cu$_{2-x}$S nanocrystals and Zn-Sn ligand precursor annealed at various temperatures. Stage 1 (RT–175 °C): formation Cu$_2$ZnSnS$_4$ or Cu$_2$SnS$_3$ based on reaction between Cu$_{2-x}$S and Zn-Sn species; stage 2 (175 °C–540 °C): formation of pure kesterite Cu$_2$ZnSnS$_4$ from Cu$_2$SnS$_3$ and ZnS.

Further temperature increment kept triggering phase change till the complete formation of kesterite Cu$_2$ZnSnS$_4$ (stage 2). From 200 °C to 540 °C, the characteristic diffraction patterns from wurtzite ZnS, gradually decreased till final diminish; whereas diffraction intensity from crystallined kesterite Cu$_2$ZnSnS$_4$ on the contrary, was increasing, till all its characteristic peaks appearing, evidencing a pure kesterite Cu$_2$ZnSnS$_4$ in the film. In Raman, the improvement...
crystallined kesterite Cu$_2$ZnSnS$_4$ promoted the peak intensity at around 330 cm$^{-1}$ during the whole stage 2.

The complementary study based on XRD and Raman spectroscopy suggested a two-stage film formation upon annealing. Starting from the single-component precursor, Cu$_{2-x}$S/Zn-Sn nanocrystals, Cu$_{2-x}$S firstly reacts with surface Zn-Sn species to form CZTS or Cu$_2$SnS$_3$ at 175 °C (stage 1), which then gradually grows larger till final conversion to the dominant pure kesterite Cu$_2$ZnSnS$_4$ stable up to at least 540 °C (stage 2). This two-stage growth is unique compared to other deposition processes starting from pure elements or binary chalcogenides, because the Cu$_{2-x}$S nanoparticles provide not only key constituent but also nucleation centers for film growth. A homogeneous elemental distribution down to the nanoscale, as indicated in Figure 4.4, enables a uniform film (Table 4.1) from the single component precursor. Local ion diffusion within short distances of each precursor may provide a desired phase composition; in contrast, long-distance ion diffusion is often required in other deposition processes. Similar growth processes have also been reported in hydrazine based approach which starts with Cu$_2$Sn(Se,S)$_3$ and Zn(Se,S)N$_2$H$_4$, where much larger nanoparticle mixture are used.$^{[19]}$

For the first time, Cu$_{2-x}$S nanocrystals are capped with Zn-Sn complex to form the single-component nanoparticle precursor, Cu$_{2-x}$S/Zn-Sn, towards high-quality uniform kesterite CZTS films. This strategy enables quantitative, facile, and clean CZTS film controllability on both composition and phase formation. For the composition controllability, the element stoichiometry in the as-deposited film is identical to the stoichiometry of Cu$_{2-x}$S nanoparticles and Zn-Sn complex in solution. Prescribed composition of the film can be directly synthesized by controlling solution concentration and the amount. Preparing the single-component nanoparticle precursor is achieved by direct mixing of multiple constituents at room temperature, without the need to
consider incorporation discrimination of multiple elements into nanoparticle or as-deposited film. Phase segregation in molecular solution-deposited or multiple nanoparticle solution is absent with current single-component precursor, ensuring the uniform element distribution, both locally near nucleation centers and globally through the film. For the stoichiometry product fabricated with single-component precursor, no extra XRD patterns, coming from possible secondary phases, such as ZnS in slightly off-stoichiometric composition are observed, as shown in Figure 4.7a. Substituting hydrocarbon molecules with Zn-Sn complex further ensures only the desired constituents present in the film, and diminishes the carbon contamination that is observed in traditional nanoparticle precursors as shown in Figure 4.7b.

**Figure 4.7** (a) The XRD pattern of the Cu$_{2-x}$S/Zn-Sn precursor solution based film, with adjusted ratio between Cu$_{2-x}$S nanoparticles and Zn-Sn species; (b) The Raman spectra of Cu$_{2-x}$S/Zn-Sn precursor solution and CZTS nanocrystals. The CZTS nanocrystals was obtained by the procedure detailed in supporting information.
4.5 Device performance and discussion

The as-prepared single component CZTS precursors are further used to fabricate the solar cell devices. Figure 4.8a shows a cross section SEM image of a CZTSSe film after selenization and Figure 4.8b represents a typical J-V characteristics of a solar cell made from the present CZTS precursor. It is worth noting that there is an absence of carbon-rich layer in the selenized films, which is different from that based on CZTS nanoparticles capped with long chain carbon ligands. This indicates the successful ligand exchange process, leading to negligible hydrocarbon residues in the final film. In a first optimization, the device exhibits an open circuit voltage (V\text{OC}) of 0.151 V, short circuit current (J\text{SC}) of 25.3 mAcm\textsuperscript{2}, fill factor (FF) of 30.8%, and power conversion efficiency of 1.2%. Continued optimization of absorber fabrication and interface engineering is underway.

Figure 4.8 (a) Cross section SEM image of a CZTSSe film after selenization and (b) J-V characteristics of a photovoltaic device prepared from the single-componenent CZTS precursor

Cu\textsubscript{2-}\textsubscript{x}S as the nucleation center might overcome the activation energy barrier of film growth to the thermodynamically stable phase, where the stability of secondary impurity phase is largely decreased. Zn-Sn species are homogeneously distributed on Cu species, producing comparative
shorter local diffusion length for all the constituents to reach the thermodynamically equilibrium positions than that in a phase-segregated film. Different from the single-component precursor present here, an alternative approach using Sn$_2$Se$_6^{4–}$-capped Cu$_2$Se and ZnS nanocrystals,$^{[33]}$ still needs complex accurate balancing on both composition and ion diffusion among all the constituents. During film formation, significant longer ion diffusion through Sn species separated Cu and Zn nanoparticles are also observed. Hence, pre-formed small nanocrystals serve as perfect models for investigating the mediation of nucleation and growth within a solid-state film from soluble precursors. A more controllable nucleation and growth mode from liquid state to solid state will in turn benefit the development of solid state chemistry.

Using Zn-Sn species as the capping ligands of the colloidal nanocrystals enriches the inorganic ligand family, from single halogen anion or single metal-based metal chalcogenide complex (MCC) to multi-metal-based MCC ligands.$^{[33]}$–$^{[36]}$ We have noticed, the presence of multi-metal-based MCC ligands, with their high affinity to replace typical organic ligands on nanoparticle surface, solves both carbon contamination and surface surfactant barrier for ion diffusion. In particular, some inorganic species may perform as the indispensable components to improve performance of designed optoelectronic device, while Zn-Sn species as an inorganic ligand, is a promising candidate with the capability for tuning optical and electrical properties for optoelectronics development.
Figure 4.9 XRD patterns (a) and Raman spectra (b) of Cu$_{2-x}$S nanocrystal and Zn/Sn ligand precursor annealed at 500 °C

Figure 4.10 SEM image of the cross section of an as-deposited CZTS film
### Table 4.1 Energy dispersive x-ray spectroscopy data from five different spots along a CZTSSe film after selenization. The spots were separated by approximately 1 μm from one another. The composition ratio of [Cu]/([Zn]+[Sn]) and [Zn]/[Sn] remain nearly constant at around 0.73 and 1.06, respectively, thus confirming the film homogeneity. Cu, Zn and Sn atomic percentages were extracted from Cu K line, Zn K line and Sn L line, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Cu atom%</th>
<th>Zn atom%</th>
<th>Sn atom%</th>
<th>Cu/(Zn+Sn)</th>
<th>Zn/Sn</th>
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</thead>
<tbody>
<tr>
<td>spot 1</td>
<td>9.59</td>
<td>6.62</td>
<td>6.3</td>
<td>0.74</td>
<td>1.05</td>
</tr>
<tr>
<td>spot 2</td>
<td>10.47</td>
<td>7.54</td>
<td>6.83</td>
<td>0.73</td>
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</tr>
<tr>
<td>spot 3</td>
<td>7.73</td>
<td>5.6</td>
<td>5.29</td>
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<td>1.06</td>
</tr>
<tr>
<td>spot 4</td>
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<td>6.04</td>
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<td>1.10</td>
</tr>
<tr>
<td>spot 5</td>
<td>8.57</td>
<td>6.16</td>
<td>5.65</td>
<td>0.73</td>
<td>1.09</td>
</tr>
</tbody>
</table>
4.6 Conclusion

In summary, we report a facile, quantitative and clean fabrication of kesterite CZTS film from a single-component precursor, crystalline Cu$_{2-x}$S capped with multi-metal MCC ligands, Zn-Sn complex, and demonstrate its optoelectronic performance. This facile approach possesses unique controllability over CZTS composition and phase formation progression. For the first time, Zn, together with Sn chacolgenide in the form of Zn-Sn complex, are used as surface capping ligand for Cu$_{2-x}$S to provide both colloidal stability and essential components for CZTS. Kesterite CZTS film composition is thus governed by the prescribed stoichiometry between Cu$_{2-x}$S nanoparticles and the Zn-Sn complex in solution. The characteristic that Zn-Sn species homogeneously distributed on Cu$_{2-x}$S nanoparticles, enables a favorable CZTS phase formation pathway, with less than 175 ℃ formation temperature, and a minimized secondary phase growth mode. Substitution of traditional hydrocarbon capping ligands by Zn-Sn complex significantly decreases the carbon contamination in films, and photovoltaics devices have been successfully demonstrated. Current strategy, owing to its relative simple processes, clean composition against organic sacrificial groups during annealing, and low-temperature fabrication, could be further expanded to other I-II-IV-VI$_4$, I-V-VI$_2$ based electronic and optoelectronic materials. Facile processing of high-quality clean kesterite film will thus contribute to the ongoing development of optoelectronic devices into industry production of next-generation optoelectronics. The combination of pre-formed small nanocrystals and capped essential component serve as perfect models for investigating the mediation of nucleation and growth within a solid-state film from soluble precursors, which will in turn benefit the development of solid state chemistry.
4.7 References


Chapter 5 The role of anions in solution-processed Cu$_2$ZnSn(S,Se)$_4$ and its effect on defect properties

5.1 Introduction

Kesterite Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) photovoltaics are considered a potential alternative to traditional chalcogenide-based thin film solar cells (e.g. Cu(In,Ga)(S,Se)$_2$ and CdTe) because of its earth-abundant and non-toxic constituents. Since 2010, high efficiency (>8%) Cu$_2$ZnSn(S,Se)$_4$ photovoltaics have been demonstrated successfully via various approaches. Several reports include an 11.1% device made by spin-coating particle-containing hydrazine precursor slurries and annealing on a hot plate,\textsuperscript{[1]}\textsuperscript{[2]}\textsuperscript{[3]} an 8.1% device made by using molecular level homogeneous hydrazine precursor solution,\textsuperscript{[4]} an 8.4% device made by annealing colloidal nanocrystals in selenium vapor,\textsuperscript{[5]} and with the use of the coevaporation technique a 9.15%\textsuperscript{[6]} and an 8.4%\textsuperscript{[7]} device were reported. While these early-stage developments show a promising future for kesterite photovoltaics, it is also important to understand its defect physics and recombination mechanisms.\textsuperscript{[8]} This understanding is urgently needed for further improvement of the cell characteristics to a level comparable with Cu(In,Ga)(S,Se)$_2$(CIGS) and CdTe.

The majority of previous reports\textsuperscript{[1]}–\textsuperscript{[7]}\textsuperscript{[9]}–\textsuperscript{[11]} have shown that the highest-efficiency kesterite solar cells are made of CZTSSe alloys with high selenium (Se) content rather than high sulfur (S) content, despite the fact that the sulfur-rich compound has a more optimal bandgap, 1.4 eV, according to theoretical calculations.\textsuperscript{[12]} In the case of Cu(In$_x$Ga$_{1-x}$)$_2$Se$_2$, high gallium (Ga) concentration is not beneficial for the device performance since CuGaSe$_2$ is difficult to be doped as n-type,\textsuperscript{[13]}\textsuperscript{[14]} resulting in the absence of an n-type inverted layer in CuGaSe$_2$ absorbers which facilitates carrier extraction. With the use of the first-principle calculations and Density Functional Theory, Chen et al\textsuperscript{[15]} reported that CZTSSe alloys with high Se content are more easily converted
to n-type semiconductor and thus CZTSSe solar cells with high Se content are expected to have better carrier collection efficiency than CZTS. Besides, it was reported that the self p-type doping in kesterite are mainly related to Cu\textsubscript{Zn} antisite defects and \( V_{Cu} \) (Cu vacancies).\textsuperscript{16} The energy level of Cu\textsubscript{Zn} antisites becomes shallower (closer to the valence band) as sulfur concentration decreases in CZTSSe alloys because in CZTS, the stronger hybridization between the sulfur 3p and copper 3d orbitals brings the valence band lower. Based on these simulated results, high efficiency CZTSe (low S content) devices should be achievable because of more facile n-type and p-type doping than CZTS (high S content). However, attempts to experimentally investigate defect properties in the kesterite family\textsuperscript{17}\textsuperscript{18} have not yet reached the level of maturity of the well-established field of defects physics in chalcopyrite-based devices.\textsuperscript{19}\textsuperscript{22}

In this paper, we report a comparative study of solution-processed kesterite CZTSSe cells with three different bandgaps (resulting from three different Se and S concentrations in alloys). We aim at correlating the electrical defect levels of CZTSSe, observed through admittance spectroscopy and charge density profiling, with the cells’ characteristics deduced from current density-voltage and quantum efficiency measurements. Based on the experiment results, we have found that changes in the S and Se ratio significantly alters both the energy level and concentration of the dominant defects, and ultimately produces the poor carrier collection efficiency and larger losses of open circuit voltage as a result of the increasing numbers of observed recombination centers.
5.2 Current-voltage characteristics

Figure 5.1 shows the illuminated current density-voltage (J-V) characteristic curves for devices with different amounts of selenium and sulfur, with the corresponding external quantum efficiency (EQE) curves shown in the inset. The cell parameters deduced from J-V measurements, as well as the bandgap deduced from the long-wavelength cutoff of the EQE[23] are summarized in Table 5.1. The devices A, B, and C correspond to three different S contents of [S]/([S]+[Se])≈ 0.35, 0.8 and 1, respectively. CZTSSe films were deposited through hydrazine solution processing. X-ray diffraction and Raman data indicate the presence of only the kesterite phase in the films, and are discussed in detail in a separate publication.[4]

The device with high sulfur content has a higher open-circuit voltage (~0.6V), consistent with its large bandgap (~1.5eV). The device with low sulfur content has relatively small open-circuit voltage (0.406V) but has much larger short-circuit current density (J_{sc}), mainly due to improved carrier collection at longer wavelengths. Among the three devices, low sulfur content device (sample A) gives the highest power conversion efficiency of 7.4%. In EQE data measured at 0V (Figure 5.1), the high sulfur content device (sample C) has a lower peak value than the others. This reveals that the S concentration in the alloy not only changes the bandgap but also gives rise to stronger recombination losses.[24][25]
Figure 5.1 Light J-V data of CZTSSe devices with various sulfur contents. Low sulfur device (A) shows the highest efficiency ~7.4%. Inset: corresponding external quantum efficiency
Table 5.1 Device parameters for CZTSSe cells at room temperature with various [S]/([S]+[Se]) ratio.

<table>
<thead>
<tr>
<th>Device</th>
<th>Eff(%)</th>
<th>(V_{oc}(V))</th>
<th>(E_g(eV))</th>
<th>(E_g-qV_{oc})</th>
<th>(J_{sc}(mA/cm^2))</th>
<th>FF(%)</th>
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<tr>
<td>Sample A</td>
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<td>1.15</td>
<td>0.74</td>
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<td>59.55</td>
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<td>Sample B</td>
<td>5.3</td>
<td>0.541</td>
<td>1.35</td>
<td>0.81</td>
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<tr>
<td>Sample C</td>
<td>3.5</td>
<td>0.599</td>
<td>1.5</td>
<td>0.90</td>
<td>10.7</td>
<td>54.28</td>
</tr>
</tbody>
</table>
5.2 Admittance spectroscopy

Admittance spectroscopy (AS) measurements, which are commonly used to estimate the energy level of defects inside the band gap, were taken on each of the three types of samples. Capacitance-Frequency (CF) scans taken in the temperature range 160K to 300K are shown in Figure 5.2. CF scans were measured in the dark from $10^2$ to $10^6$ Hz. An AC voltage of 30mV was used and DC bias was kept at zero during the measurement.

Using the model implied by the work of Kimerling,[26] the capacitance at high frequency represents the response of the free carrier density, while the capacitance at low frequency represents the response of the sum of free carriers and deep traps. In Figure 4.2c, the capacitance of the device with high sulfur content shows a larger variation as a function of frequency, while the capacitance of the devices with low sulfur content show small changes between high and low frequencies (Figure 5.2a). The significant frequency dependence of the capacitance in the high sulfur content device indicates larger trap densities in the absorber. A similar trend of has been reported recently for devices with bandgaps falling in the range of 1.0 to 1.5eV.[18] In Figure 4.2b and 4.2c, it is visible that the capacitance data converges at high frequency and low temperature, where it is likely determined by the geometric capacitance of the devices due to carrier freeze-out.[27]
Figure 5.2 Admittance spectra of devices with various sulfur content, measured at temperature between 160K and 300K with a step of 10K. The y-axis of three plots have been scaled to be the same.

Figure 5.3 shows the Arrhenius plot for the inflection points in the three admittance spectra in Figure 5.2. The step frequency $\omega_0$ (or inflection point frequency) for each AS curve is determined by using the angular frequency point at the maximum of the $\omega^*dC/d\omega$ plot. The fitting of the Arrhenius plot is according to the equation:\[20]

$$
\omega_0 = 2\pi \nu_0 T^2 \exp\left(\frac{-E_a}{kT}\right)
$$

where $\omega_0$ is the step frequency, $E_a$ is the energetic depth of the defect relative to the corresponding band edge, and $\nu_0$ is the pre-exponential factor comprising all temperature independent terms, such as defect capture cross section for holes $\sigma_p$, effective density of states in the valence band $N_v$, and thermal velocity $\nu_{th}$.

In this case, the activation energy $E_a$ determined by the Arrhenius plot is approximately the energy difference between defect level and valence band edge. Assuming that their energy levels are within a small range, the $E_a$ value deduced from the Arrhenius plot can also represent the average value of activation energies of a band of defects in the bandgap. The activation energy $E_a$
is around 0.134 eV, 0.163 eV and 0.183 eV for devices A, B and C (from low to high sulfur content), respectively. In addition, we calculated the pre-exponential factors, which is around the order of $10^3$ for all devices.

A general increase of activation energy with increasing sulfur fraction in the absorber is clearly visible in the admittance spectroscopy data. The change of defect activation energy in three samples is possibly related to the shifts of the valence band maximum resulting from the differing sulfur concentrations in the CZTSSe absorber. As the sulfur content increases in CZTSSe alloys, the valence band moves down, potentially yielding defects with higher ionization energies.[15] A larger value of $E_a$ is generally an indicator of a slower hole emission rate, corresponding to the lower transition frequency in the AS curves, and thus it is more likely that defects with larger activation energies tend to act as more effective recombination centers. The defect response in the high sulfur content device occurred at a higher energy (0.183 eV) than in the low sulfur content device (0.134 eV). Thus, the low sulfur content device can be expected to experience relatively lower recombination rates than the high sulfur content one. This observation can also be correlated with external quantum efficiency (Figure 5.1b). The high sulfur content device exhibited much lower quantum efficiency, likely as a result of significant recombination losses due to increased defect activity.
Defect density spectra resulting from CF scans at each temperature (Figure 4.2) are superimposed in Figure 5.4. For each sample, the calculation of the rescaling factor of the y-axis, including the band-bending and built-in voltage, uses typical values reported in literature \cite{28} and the conversion of the x-axis from frequency to energy is achieved following relation (1). The dashed line is the Gaussian fit to the respective defect energy level, as described in the work of Walter et al. \cite{20} The integrated defect density of the low sulfur content device is $4.96 \times 10^{15}$ cm$^{-3}$, which is relatively smaller than the value of the high sulfur content device, $1.14 \times 10^{16}$ cm$^{-3}$. We
also noticed that these integrated defect densities are roughly proportional to the difference between the largest capacitance value and smallest capacitance value in CF scans.

In each of the three cases, the calculated activation energies are between 0.1 and 0.2 eV, so this defect level could potentially be ascribed to a structure similar to the N1 trap level commonly observed in CIGS.\textsuperscript{[29]} Similar defect levels in kesterite were also found by other groups.\textsuperscript{[17][18]} Note that the defect state at 0.3 eV above the valence band, known as the N2 defect in CIGS,\textsuperscript{[29]} was not found in our measurement. The origin of the N1 defect level remains unclear, but in chalcogenide photovoltaics it has been assigned to several possible sources, such as (In,Ga)\textsubscript{Cu} defects at the CIGS surface,\textsuperscript{[30]} defects at the CIGS/CdS interface,\textsuperscript{[29]} bulk defects inside the CIGS absorber,\textsuperscript{[31]} defects at the CIGS/Mo back contact,\textsuperscript{[32]} or surface anion vacancies $V_{Se}$ that involve interfacial donors.\textsuperscript{[33][34]} In this work, a possible source of the observed acceptor level is the Cu\textsubscript{Zn} antisite, which has the lowest formation energy and is located at 0.12 eV above the valence band, according to first principle calculations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{sample.png}
\caption{Defect spectra derived from admittance spectra. The y-axis of three plots have been scaled to be the same.}
\end{figure}
Copper vacancies, commonly assigned as the primary p-type dopants in CIGS,[35] are predicted to be a relatively shallow defect at 0.02 eV above the valence band in kesterite, but with higher formation energies than CuZn antisite.[16] However, this defect energy level was not observed in AS measurements. It is controversial whether or not copper-on-zinc antisites or copper vacancies are the dominant acceptors in kesterite.[8][36] Several photoluminescence (PL) studies of defects in kesterite alloys showed donor-acceptor (DA) pair transitions at low temperatures, indicative of a shallow acceptor level around 30meV or less, in Cu-rich samples.[37][38] A recent study films with metallic ratios of [Cu]/([Zn] + [Sn]) = 0.9 and [Zn]/[Sn] = 1.3, observed an acceptor level in the range of 29-40 meV above the valence band via the fitting of PL intensity at various temperatures.[39] Meanwhile, broad emission spectra were detected in both photoluminescence and cathodoluminescence in Cu-poor and Zn-rich films, suggesting localized potential fluctuations in the conduction band minimum and valence band maximum.[36][39] The fluctuation of energy levels was estimated to a value of 172±2 meV. With regard to the huge conduction and valence band fluctuation, it is possible that the ionization energy of acceptors deduced from the PL intensity-temperature plot is underestimated, and thus, the exact defect energy level seen in luminescence is comparable with the AS results.
5.3 Drive-Level Capacitance Profiling

Though traditional capacitance profiling data can provide the spatial defect density as deduced from capacitance-voltage (CV) scans, it is unable to distinguish between the bulk and interface defects, since both types of defects respond to this type of measurement. In order to identify different types of defects in the film (bulk defects, interface defects, and free carriers), Drive-Level Capacitance Profiling (DLCP) measurements were employed by using the technique of Heath at el,\cite{21} supplemented with CV profiling measurement (not shown here). Compared to CV measurements, DLCP gives a more accurate assessment of the free carrier density in the film, while CV measurements are more sensitive to interface states which commonly exist in chalcopyrite-based cells. In the method that Heath et al developed, the contribution of the interface states can be extracted by a subtraction of DLCP defect density from CV defect density.\cite{31} These will be discussed in detail later.

DLCP measurements were performed with DC bias from -0.5 to 0 volts with the AC amplitude varying from 0.01V to 0.1V, and temperature range from 160K to 300K. The measurement frequency of 11kHz was selected. We estimated that, in the low sulfur device (sample A), DLCP response at 160K corresponds to $E_a$ (activation energy) = 0.12 eV while DLCP response at 300K corresponds to $E_a$ = 0.25 eV, with the other devices exhibiting comparable activation energy measurement ranges. AS for all three devices indicate defects with characteristics energy between 0.1-0.2 eV; thus our range of profiling spans the energy response of these defects at all three absorber compositions. The charge density was determined by the relevant relation described in literature.\cite{21} The resulting charge density, $N_{DL}$, is shown in Figure 5.5 (the horizontal axis is $<x> = \varepsilon A/C_0$, the average location of charges response to AC signal,
where $C_0$ is from a quadratic fit of measured capacitance $dQ/dV$, $\varepsilon$ is the permittivity of the CZTSSe absorber layer,\[^{[40]}\] and $A$ is the device area).

Here, we assumed that the entire depletion region is mainly in the CZTSSe absorber layer because of the high $n$-type doping concentration of the CdS layer. Therefore $N_{DL}$ measured by DLCP, represents the charge density of the CZTSSe layer. At high temperatures, DLCP is capable of observing the response from free carrier and deep defects, but at sufficiently low temperatures only free carriers contribute to the DLCP signal. Thus, the subtraction of the low temperature $N_{DL}$ value from the high temperature $N_{DL}$ value is closely correlated to the defect density in the absorber.\[^{[21]}\] The $N_{DL}$ points at $V_{dc}=0$ were chosen to estimate the defect density (the defect density is labeled as $N_T$ in Figure 5.5). The estimated values for each condition are listed in Table 5.2. The high sulfur content device possesses a larger bulk defect density than the low sulfur content one. This trend is consistent with the AS data, where the high sulfur content device exhibited a larger capacitance variation, as a function of frequency.
Secondly, by applying the subtraction of the low temperature $N_{DL}$ from the high temperature $N_{DL}$, the high sulfur content device has approximately an order of magnitude larger free carrier concentration than the low sulfur content device. The free carrier density derived from DLCP generally corresponds to the density of fully ionized dopants, indicating the dependence of doping concentration on sulfur content as seen Table 5.2. It is known that the semiconductors with high doping concentration have greater recombination, resulting in shorter minority carrier lifetimes as well as shorter diffusion lengths. Thus, the dependence of doping concentration on...
sulfur content is consistent with previous reports showing that CZTSe (almost no sulfur content in the device) has longer carrier lifetime (10 ns) than CZTSSe (low sulfur content, 3 ns). This finding also explains the high recombination losses in the high sulfur content device as a result of its high doping concentration. While the structural origin of the high doping concentration on sulfur content is inconclusive at this point, the changes in carrier concentration observed here are possibly related to varying levels of compensation from donor defects, such as anion vacancies (V_S or V_Se) that may be dependent on the sulfur and selenium content of the absorber material. A more detailed understanding of this behavior is currently under investigation.

Thirdly, the defect concentration is expected to be a major determinant of open circuit voltage (V_oc), and the voltage shortfall, E_g−qV_oc, and defect density can be correlated in the relation:\[ E_g - qV_{oc} \propto A \ln N \] (2)

where \( E_g \) is the bandgap energy, \( q \) denotes the elementary charge, \( A \) is the diode ideal factor and \( N \) is the concentration of recombination centers in the bulk of the CZTSSe film. The defect density measured from AS (Figure 5.2) and from DLCP (Figure 5.5) both correlate with the voltage shortfall shown in Table 5.1. As the voltage deficit increases, so does defect density detected by AS and DLCP. This correlation shows that the open circuit voltage losses result from high bulk defect concentrations in absorber materials that have higher sulfur content.

As mentioned earlier, the effect of interface defects can be relatively quantified based on the subtraction of DLCP-evaluated charge density at room temperature from CV-evaluated charge density at room temperature, where the points at zero DC bias were used in the calculation. While the resulting interface state response in all three samples is on the same order of magnitude, the high sulfur content device exhibits a relatively higher interface defect density, suggesting that
the interfacial defects are related the open circuit voltage losses seen in the device performance section of this study. Furthermore, as seen in the plot of $V_{oc}$ versus temperature in the recent reports,\cite{1}\cite{25} the deduced value of activation energy of recombination suggested that the deficiency in $V_{oc}$ is strongly influenced by interface recombination, possibly at the absorber/buffer interface.\cite{44} By contrast, it has been demonstrated that in CIGS space charge recombination (SCR) is dominant. Thus, it should be expected that the interface state response of CZTSSe is much stronger than the response of CIGS. However, enhanced interface defect response is not evident in CZTSSe cells, compared to CIGS data in the literature.\cite{45}

<table>
<thead>
<tr>
<th>Device</th>
<th>Free carriers density (cm$^{-3}$)</th>
<th>Trap density (cm$^{-3}$)</th>
<th>Interface state response (relative values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>$3.22 \times 10^{14}$</td>
<td>$8 \times 10^{14}$</td>
<td>$1.17 \times 10^{16}$</td>
</tr>
<tr>
<td>Sample B</td>
<td>$1.33 \times 10^{15}$</td>
<td>$9 \times 10^{14}$</td>
<td>$1.07 \times 10^{16}$</td>
</tr>
<tr>
<td>Sample C</td>
<td>$3.15 \times 10^{15}$</td>
<td>$8.22 \times 10^{15}$</td>
<td>$1.81 \times 10^{16}$</td>
</tr>
</tbody>
</table>
5.4 Conclusion

By employing admittance spectroscopy and carrier density profiling measurements at various temperatures, we have observed the influence of sulfur content in CZTSSe alloys on defect activation energy, defect density, and photovoltaic performance. The high sulfur content device showed higher defect energy level (0.183 eV) as well as high bulk defect density (8.2×10^{15} \text{cm}^{-3}), and this behavior of defects leads to the strong recombination losses as indicated by low external quantum efficiency values and a large V_{oc} deficit. In contrast, the low sulfur content absorber showed the best performance (7.4%) and highest external quantum efficiency as a result of the relatively low activation energy (0.134 eV) and the low bulk defect density (8×10^{14} \text{cm}^{-3}). Overall, when enlarging the bandgap of the absorber by increasing its sulfur content, the open-circuit voltage increases, but overall device efficiency is reduced. These findings provide a better understanding of defect properties in kesterite alloys, which are critical for the control of recombination processes, doping, and junction formation in solar cells fabricated from this material.
5.5 Experimental details

Device fabrication

CZTSSe hydrazine-based precursor solutions were prepared in a nitrogen filled glove box. Cu-constituent and Sn-constituent solutions were prepared following the procedures described elsewhere[46][47]. For Zn-constituent solution, the hydrazinocarboxylic acid (NH$_2$NHCOOH) was used to fully dissolve zinc powder in hydrazine. Final CZTS precursor solutions were prepared by mixing all constituent solutions with a final ratio of Zn/Sn=1.2, Cu/(Zn+Sn)= 0.8. Detailed procedures of CZTSSe precursor solution and film preparation can be found in a separation publication[4].

CZTSSe films were then deposited by spin-coating the precursor solution on molybdenum coated soda lime glass substrates. To prepare the absorber layers with different bandgaps, various amounts of chalcogen vapor, including pure selenium vapor, pure sulfur vapor and mixed selenium and sulfur vapor, were supplied during the annealing at 500 Celsius on a ceramic hot plate. A CdS buffer layer was completed via a standard chemical bath deposition[22], and ZnO and ITO were deposited on top with the RF sputtering system, giving a standard device structure: glass/Mo/CZTSSe/CdS/ZnO/ITO with nominal area 0.1cm$^2$, determined by mechanically scribing all layers aside from the molybdenum back contact.

Device characterization

The current density–voltage (J–V) characteristics of the photovoltaic devices were measured using a Keithley 2400 source meter. Illumination was provided by a Newport Oriel solar simulator (Model 91191-1000) with an AM 1.5G filter (Model 81088). The light intensity was stabilized at 100mW/cm$^2$ using a Newport Oriel 68945 light intensity controller. The external quantum efficiency (EQE) was measured using a system designed by EnliTech. The capacitance of the
photovoltaic device was measured using a Hewlett-Packard 4284A LCR Meter. Temperature dependent measurements were carried out using a Linkam temperature-controlled stage equipped with liquid nitrogen cooling. The temperature was monitored by a calibrated platinum sensor embedded close to the surface of the stage.
5.6 References


Chapter 6 Studies of interface properties in solution-processed photovoltaics through photoluminescence spectroscopy

6.1 Introduction

The chalcogenide-based material Cu(In,Ga)(Se,S)\textsubscript{2} (CIGS) is an attractive candidate for use as an absorber layer in thin-film photovoltaics, and has received significant research interest based on its high laboratory record efficiency.\cite{1,2} To enable the large-scale manufacturing of CIGS technology, a wide variety of solution and slurry-based deposition methods have been developed in an effort to significantly reduce the fabrication cost relative to vacuum-based approaches.\cite{3,4} Recently, a hydrazine-based solution process has been demonstrated for the deposition of several chalcopyrite materials,\cite{5,6} and to date its applications in solar cell fabrication have shown promising power conversion efficiency.\cite{7-10} Nevertheless, there is still great uncertainty about fundamental material properties essential to the device performance such as the carrier recombination in CIGS/CdS junction and the recombination lifetime in absorber materials processed in this manner. In this technology, the preferred n-type layer is cadmium sulfide (CdS), and it is generally produced by a chemical reaction in an aqueous bath, called the chemical bath deposition (CBD) process.\cite{11} It has been suggested that the copper vacancies (V\textsubscript{Cu}) at the surface of the absorber can be substituted by the Cd atoms during CBD process.\cite{12} In this report, we study the effects of the CdS layer on defect passivation in the hydrazine-processed CuIn(S,Se)\textsubscript{2} (CISSe) material and its optoelectronic properties through photoluminescence.

The CISSe films were deposited on Molybdenum-coated soda-lime glass substrates through the repeated spin-coating of a hydrazine precursor solution. The detailed solutions and the films preparation can be found elsewhere.\cite{5,8,13} The films were annealed on a hot plate at a maximum temperature of 390°C for 30 min, and the final film thickness was around 1 to 1.2μm. All of the
processes described above were completed in a nitrogen-filled drybox. The composition of CISSe films is copper-poor, Cu/In ~ 0.8, and selenium-rich, Se/(Se+S) ~ 0.98, as indicated from X-ray Fluorescence measurements. The cadmium sulfide (CdS) layer was deposited via a standard chemical bath deposition (CBD)\cite{13} procedure to yield a 30 nm CdS film, followed by a heat treatment in the air at temperature of 120°C for 30 min. The Cd-soaked CISSe films are made by soaking the finished CISSe films in a cadmium acetate (Cd(OAc)$_2$) aqueous solution at 65°C for 30 minutes. Neither thiourea nor ammonium hydroxide is added in the cadmium soaking solution. The concentration of the Cd(OAc)$_2$ solution used for soaking was about 2.7mM, which is the same as used in CdS deposition. Note that bare CISSe samples were exposed to the air just prior to measurement, to avoid possible lifetime degradation associated with excessive ambient exposure.\cite{14}
6.2 Experimental details

Energy-resolved photoluminescence spectra were measured using a steady-state diode laser (532 nm) and an NIR-sensitive photomultiplier tube (Hamamatsu R5509-72) operated at -80°C. Time-resolved photoluminescence was acquired using the time-correlated single-photon counting technique (Picoharp 300), and the excitation was provided by a picosecond diode laser at the wavelength of 640 nm with a repetition frequency in the range of 5-80 MHz (PDL 800B). The laser excitation was kept low (5.54×10¹⁰ photons/cm²) to avoid the distortion of the lifetime measurement.[¹⁵] Combining with an iterative deconvolution data analysis, the resulting temporal resolution of the system is approximately 120 ps. Temperature dependent measurements were carried out using a Linkam temperature-controlled stage equipped with liquid nitrogen cooling. The temperature was monitored by a calibrated platinum sensor embedded close to the surface of the stage.
6.3 Results and discussions

Figure 6.1 shows the PL spectra obtained at room temperature for the CISSe samples with different post-treatments after spin-coating. Since the excitation wavelength is well above the bandgap of the CISSe, it is expected the incident light is strongly absorbed in the first 400 nm of the CISSe layer. For the CISSe films coated with CdS through CBD the emission originates simply from CISSe layer, because CdS is transparent to the incident light. No emission is detected from the as-deposited CISSe, while the film after the final annealing shows a principal peak at 1 eV, corresponding to the formation of the CISSe phase in the films annealed at 390°C. Note that the peak energy of this PL spectrum is below the reported bandgap of CISSe.\textsuperscript{[7][8]} A major change in the emission profile is observed after a CdS layer is deposited on the CISSe film. The emission at 1.06 eV is enhanced and it is stronger than the dominant peak at 1 eV in the bare CISSe film. These changes in the dominant PL peaks observed at room temperature from our solution-processed CISSe films before and after CdS deposition are unique compared to the PL spectra obtained from three-stage coevaporated CIGS films.\textsuperscript{[16][17]} The differing effects of CdS deposition in our films can be at least partially explained by the average grain size of our CISSe films falling in the sub-100nm range,\textsuperscript{[8]} which relatively small compared with CISSe films prepared by vacuum processes at higher temperatures.\textsuperscript{[2]} The small grain size in our films likely provides a greater opportunity for the diffusion of Cd-ions into the CISSe films during the CBD-CdS process, allowing the effect of Cd ions to extend a longer distance into the CISSe films.\textsuperscript{[13]} The inherently Cu deficient nature of the surface of CISSe may also assist in substituting Cd ions into Cu vacancy sites.\textsuperscript{[12]} This leads us to speculate that the action of Cd ions on Cu vacancies sites reduces the overall defect concentration, and lowers the non-radiative recombination in CISSe, yielding enhanced emission in CdS-coated CISSe. As a result, the peak of the PL spectrum of annealed CISSe (at 1 eV) can be
considered to be a free-to-bound transition which mediated by an acceptor level around 60 meV above the valence band maximum, while the peak of the PL spectrum of CdS-coated CISSe (at 1.06 eV) is likely the band-to-band transition corresponded to the full band gap of the CISSe material.

![Photoluminescence spectra at room temperature. Note that the photoluminescence intensity of annealed the CISSe has been multiplied by three times for comparison. Inset: the normalized photoluminescence spectrum of the annealed CISSe and the Cd-soaked CISSe.](image)

**Figure 6.1** Photoluminescence spectra at room temperature. Note that the photoluminescence intensity of annealed the CISSe has been multiplied by three times for comparison. Inset: the normalized photoluminescence spectrum of the annealed CISSe and the Cd-soaked CISSe.

To exclude the effects of that come from the junction formation after CBD-CdS process, Cd-soaked CISSe film is prepared, and it displays the similar emission profile to that of CdS-coated CISSe (the inset of Figure 6.1). In addition, the minority carrier lifetime, extracted from TRPL data in Figure 6.2, of the Cd-soaked film (0.43 ns) is longer that of bare CISSe film (≤ 0.12 ns, 110
limited by the system response; the spike after the main peak is an artifact from the detector, possibly due to the back scattering electrons from a dynode). Such Cd-soaking treatment on solution-processed CISSe has been proved to improve the device performance.\textsuperscript{[13]} We have also checked the PL spectra of CISSe samples soaked only in the aqueous thiourea solution (with the same sulfur concentration as that is used in CBD), minimal change is observed in the steady state PL spectrum and PL decay signal. The estimated concentration of sulfur in the CBD is about 5×10\textsuperscript{-3} M and the whole CBD takes place at 65 Celsius. This relatively low sulfur concentration and the low reaction temperature should lead to very limited change on the composition of the absorber, which is in consistent with our observation. Thus, it is likely that the defects responsible for the free-to-bound transition in bare CISSe films are partially passivated by Cd ions during the Cd-soaking or the CBD-CdS process. Since the energy level of Cu vacancies are typically reported to be roughly 30 meV from the maximum of the valence band,\textsuperscript{[18]} the defects related to the enhanced PL here may be a defect complex which is comprised of Cu vacancy.\textsuperscript{[16]} The intensity of the PL peaks increases by a factor of 1.5 after CdS-covered CISSe is annealed in air at 120\textdegree{}C for 30 min. This could be interpreted as an improvement in the passivation of the CISSe/CdS interface; such post-annealing of CBD-CdS process typically gives better open-circuit voltage and fill factors in completed cells.\textsuperscript{[19]}
**Figure 6.2** Time-resolved photoluminescence of the CISSe film and the Cd-soaked CISSe film at room temperature

Figure 6.3 shows the temperature dependence of the PL spectra of bare CISSe and of a CdS-coated CISSe film. As the CISSe film is cooled down from room temperature to 100K, the PL intensity increases, the full width at half maximum of PL spectrum narrows, and the position of the peak maximum shifts toward lower energy values. The peaks of the PL spectrum of the CdS-coated CISSe film (Figure 5.3(b)) also shift to lower energy values. As is visible in the figure, both the bare and CdS-coated CISSe films exhibit only a single PL peak when the temperature is below 220 K. This implies that the free-to-bound transition dominates at low temperature, while band-to-band transition becomes present at higher temperature (T > 220K). This temperature dependence of the dominant recombination may be related the potential fluctuation in the samples. [20]
Figure 6.3 Photoluminescence spectra of (a) the CISSe film and (b) the CdS-coated CISSe film (with 120°C post-annealing) measured at various temperatures.

Figure 6.4(a) and 6.4(b) show the normalized PL spectra of the CISSe film and of the CdS-coated CISSe film measured between 100K to 150K, respectively. A transition at 0.87 eV is weak but visible in the PL spectrum of the bare CISSe film. In contrast, no such transition is found in the PL spectrum of the CdS-coated CISSe film. The 0.87 eV peak is possibly related to a defect with the ionization energy around 0.19 eV in the CISSe film, provided that it is a free-to-bound transition. Also, this peak could be originated from a donor-to-acceptor transition, since the passivation of Cu-vacancy by Cd ions forms Cd\text{Cu} donor in the surface region of CISSe.\cite{19}

Furthermore, Shirakata et al.\cite{17} reported that the termination of dangling bonds on the CdS-coated CISSe surface can produce a similar PL profile due to the significant decrease of the surface...
recombination. The origin of which is not possible to determine at this stage, and thus a more detailed understanding of this behavior is currently under investigation.

Figure 6.4 Photoluminescence spectra of (a) the CISSe film and (b) the CdS-coated CISSe film (with 120°C post-annealing) measured in the range of 100K to 150K

The integrated PL intensity (I_{PL}) of the CISSe film exhibits the temperature dependence as shown in Figure 5, where I_{PL} is plotted as a function of inverse temperature. A typical thermally activated PL transition can ideally be represented by the following expression:[21]

\[ I_{PL} = I_{PL,0} / [1 + C_{PL} \times \exp(-E_a / kT)] \]

where \( I_{PL,0} \) is the integrated PL intensity at 0K, \( C_{PL} \) is a constant fitting parameter, and \( E_a \) is the thermal activation energy of the defect taking part in the transition. Using the model implied by the work of Keyes et al.[22] the acceptor energy level and the density of the associated acceptor state can be estimated according to the relations: \( E_a = E_{acceptor} - E_v \) and \( C_{PL} = N_v / N_a \)

where \( E_v \) is the valence band energy, \( E_{acceptor} \) is the energy level of the acceptor state, \( N_v \) is the effective valence band density of states, and \( N_a \) is the total number of available holes. Fitting the temperature dependence of the integrated PL intensity results in the extraction of an acceptor

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energy level 57 meV above the valence band maximum, and an $N_a$ value of roughly $10^{15}$ cm$^{-3}$ ($10^{19}$ cm$^{-3}$ is used for the valence band density of states$^{[23]}$), which is in general agreement with the measured dopant concentration in various Cu(In,Ga)(Se,S)$_2$ films.$^{[13][22]}$ The acceptor level extracted from the temperature dependence analysis is consistent with the observed PL profile changes at room temperature.

Figure 6.5 Temperature dependence of integrated PL intensity of the annealed CISSe film. The solid line is the fitting result according equation (1)
6.4 Conclusion

In sum, the role of CBD-CdS in hydrazine-processed CISSe photovoltaics was studied carefully using PL. After a CdS layer was deposited on the CISSe film, significant changes in the emission profile of the CISSe film were observed. When the CISSe film is soaked in the cadmium aqueous solution, the similar change of the PL profile is also found. The PL lifetime of the CISSe sample becomes longer after the Cd-treatment. This behavior is likely related to Cd diffusion into the CISSe film, which is made more severe as a result of the fine grain size of our solution-processed films. This leads to the increased action of Cd ions on Cu vacancies sites, a general reduction in the concentration of acceptor defects, and a decrease in non-radiative recombination, leading to enhanced emission yields and longer carrier lifetimes. Steady state photoluminescence spectra measured at lower temperatures show that a defect-related transition at 0.87 eV is mostly passivated as the CISSe film is covered by the CdS layer, though the exact structural origin of the defect is not possible to determine at the moment. Lastly, the energy level and density of the acceptor state in the CISSe material are estimated to be 57 meV and $10^{15}$ cm$^{-3}$, respectively, from the fitting of the temperature dependence of integrated PL intensity. The information provided in this study should be valuable for the future development of the solution-based CuIn(S,Se)$_2$ photovoltaics.
6.5 References


