Development of selenization/sulfurization-free $\text{CuIn}(\text{S},\text{Se})_2$ for thin film solar cells applications

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**Development of selenization/sulfurization-free
 $\text{CuIn}(\text{S},\text{Se})_2$ for thin film solar cells
applications**

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School of Materials Science and Engineering

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Abstract

To meet the growing demand for energy and to reduce the depletion of fossil resources, technology for the harnessing of renewable energy is urgently needed. Among all the renewable energies, solar energy is one of the most clean, abundant and sustainable energy sources that can help to solve the world energy consumption problem. Harvesting and conversion of solar energy to electrical energy required the use of solar cells. Of all the different solar cell technology, copper-indium-gallium sulfide/selenide (CIGS) solar cell is one of the most promising thin film solar cells because of its high optical absorption coefficient, suitable band gap for harvesting a wide range of visible light from the sun as well as some unique electrical and optical properties. Compared to conventional vacuum-based synthesis, there is strong push towards the use of solution-based methods to prepare these CIGS films so that the processing cost can be reduced significantly. In this thesis, the solution-based synthesis of $\text{CuIn}(\text{S,Se})_2$ thin films as well as crystals and their application in the solar energy harvesting will be presented. Generally, for the solution-based synthesis routes, selenization/sulfurization process is usually needed to incorporate Se/S, to increase the crystallinity and to encourage grain growth. However, selenization/sulfurization is toxic and requires special processing system to cater for safety. Therefore this thesis sets out to investigate methods to synthesized absorber films without any selenization/sulfurization process and also ways to increase grains size.

CuInS₂, CuInSe₂ and CuInSSe thin films were successfully synthesized without any selenization/sulfurization process. In this work, the thin films were prepared using a vulcanization process and then annealed. The vulcanization process occurred between the molecular precursors, when cross-links are formed between metal acetylacetonates and sulfur/selenium powder even before annealing. Using this method, CuInS₂/CuInSe₂/CuInSSe thin films could be formed at a relatively low temperature of about 350°C. It was found that crystallinity and morphologies of CuInS₂/ CuInSe₂/ CuInSSe could be improved by increasing the annealing temperature and annealing time. Raman characterization confirmed that no secondary phase was formed. CuInS₂ was selected for the demonstration of solar cell because its film forming ability is better compared to CuInSe₂ and CuInSSe. This is because the poor solubility of Se in pyridine compared to S. However, since there is no high temperature selenization/sulfurization involved, the grain size of CuInS₂ is still relatively small compared to those highly efficient Cu(InGa)(S,Se)₂ solar cells. The solar cell efficiency for these CuInS₂ is comparable to those Cu(InGa)(S,Se)₂ solar cells without selenization/sulfurization and can be further improved by moderating the composition and also increasing the grain size.

As mentioned earlier, large CIGS grains will result in films that showed better solar cell performance and one of the reasons is that they have fewer defect sites and recombination centers. As a route to larger grain size, nanoparticles is first synthesized and by encouraging growth in these individual CIGS nanoparticles, micron sized grains can be achieved.

CuInSe₂ nanoparticles were synthesized by solvothermal reaction at 180°C for 24hrs/48hrs. The effects of precursor concentration and type of solvents on the composition and morphology were investigated. Three different solvents were chosen: ethanol-DMF mixture, methanol-DMF mixture and water-DMF mixture. It was found that CuInSe₂ nanoparticles could be obtained from both methanol-DMF mixture and water-DMF mixture but methanol-DMF mixture will result in higher purity CuInSe₂ nanoparticles. Size and morphology of the nanoparticles could be tuned by precursor concentration. Raman spectroscopy revealed that although no secondary phases were formed, Cu-Au (CA) phase, which is believed to be harmful for device, existed in the synthesized CuInSe₂. The detrimental CA phase can be reduced by increasing the reaction time and the precursor concentration. Photocurrent measurement indicated good photoresponse from the as-synthesized CuInSe₂ and CuInSe₂ with less CA phase showed improved electrical performance.

As mentioned previously, larger grain size is preferred for good solar cells performance. Micron-sized CuIn(S,Se)₂ grains were obtained by allowing the CuInSe₂ nanoparticles to undergo a second solvothermal reaction step. TEM revealed that micron-sized plates are formed (more than 1µm) and the distribution of different elements is uniform in these plates. The mechanism for the formation of micrograin CuIn(S,Se)₂ from CuInSe₂ nanoparticles was investigated. In addition, the phases of final products after second-step solvothermal reaction with different reaction time were also studied by XRD and rietveld refinement. Photochemical studies on CuInSe₂ and CuInSSe was

carried out to investigate the electrical properties and photoresponse. CuInSSe is found to have a bandgap closer to the optimal value and larger carrier concentration. Solar cells fabricated using both CuInS₂ thin film and CuInSSe microcrystals showed a better performance compared using just CuInS₂ thin film. Our simple, environmental friendly synthesis and fabrication processes suggest a promising potential for the future solar harvesting applications.

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List of Abbreviations

CA	Cu-Au
CdS	Cadmium sulfide
CIGS	Copper indium gallium selenide (sulfide)
Cu(acac) ₂	Copper acetylacetonate
Cu _{In}	Cu substituting In defects
CZTS	Copper zinc tin sulfide
DMF	Dimethylformamide
EDX	Energy dispersive X-ray spectroscopy
E _g	Bandgap
EIS	Electrochemical Impedance Spectroscopy
FF	Fill factor
FTIR	Fourier transform infrared spectroscopy
FTO	Fluorine doped tin oxide
GWp	Giga Watt Peak
HRTEM	High resolution transmission electron microscopy
In(acac) ₃	Indium acetylacetonate
In _{Cu}	In substituting Cu defects
J _{sc}	Short circuit current density
KPI	KH ₂ PO ₄
PCE	Power conversion efficiency
PEC	Photo electrochemical
PV	Photovoltaic
SEAD	Selected area electron diffraction
SEM	Scanning electron microscope
Si	Silicon
TCO	Transparent conducting oxide
TEM	Transmission electron microscopy
TFSC	Thin film solar cells
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
UV-Vis	Ultraviolet-visible/ near infra-red
V _{Cu}	Copper vacancy
V _{oc}	Open-circuit voltage

Chapter 1 : Introduction

1.1 Background and motivations

The *World Energy Outlook 2009* published by Organisation for Economic Co-operation and Development (OECD) International Energy Agency (IEA) states that the world demand for energy is assumed to increase by about 76% from 2007-2030. To meet the growing demand and the depletion of fossil resources, technology for the harnessing of renewable energy is urgently needed. Among all the renewable energy sources, solar energy is one of the most desirable because it is clean, abundant and highly sustainable.

Solar energy harvesting and conversion relies on the use of solar cells. Solar cell, also called a Photovoltaic (PV) cell, is the smallest semiconductor element within a PV module that converts light into electrical energy. The first modern solar cell was invented in 1950s and it made use of bulk Si as the active material. Since then, the conversion efficiency of Si-based solar cells has improved tremendously and in recent years, crystalline Si-based solar cells have already achieved efficiencies above 20%[1]. However, because of its indirect band gap, a thick layer of Si is required to absorb significant amount of light from the sun. Therefore, technologies based on thin film solar cells, which use materials with direct band gap, have been developed to reduce the material consumption, manufacturing and installation cost.

Some of the leading thin film solar cells (TFSC) technology are thin film silicon solar cells (TFSi), cadmium telluride (CdTe) solar cells, dye-sensitized solar cells (DSSC), hybrid perovskite solar cells and copper indium gallium selenide (sulfide) (CIGS) solar cells. Among all these thin film solar cells, CIGS solar cells are the most promising thin film solar cells as their high optical absorption coefficient, suitable band gaps for a wide range of visible lights harvesting as well as some unique optical and electrical properties [2]. It has a theoretical maximum PCE of 33% for a solar cell of single-junction with a band gap of ~ 1.3 eV [3]. Solar cells with power conversion efficiencies close to 20% have been achieved for CuInSe₂ thin films by vacuum-based synthesis routes [4]. However, as the vacuum-based techniques, such as evaporation, sputtering, etc., always results in high fabrication cost, and hence, there is a strong push towards the use of solution-based synthesis routes to prepare these CIGS films so that the processing cost could be significantly reduced.

Solution-based synthesis of these materials are usually either by the deposition of particle precursors or from solution precursors. Preparing these thin films from solution precursors provides an advantage of easy synthetic process [5-8]. However, the difficulty in controlling the incorporation of selenium and the possibility of incorporation of impurities, such as carbon, chlorine or oxygen, from the precursors or the solvent is quite common for these solution-based approaches. The impurities are generally difficult to be removed from the CIGS system and will compromise device performance [9]. To address this issue, pre-synthesized nanocrystals can be used. The nanocrystals can be obtained via

different techniques, including hot injection [10, 11], microwave-assisted synthesis [9, 12], thermal pyrolysis [13] and solvothermal synthesis[14-17]. However, large grain size is usually desirable for polycrystalline absorber films for solar cell application since grain boundaries are potential recombination centers for photogenerated electron-hole pairs. This is due to high defect densities and impurity segregation often found at the grain boundaries [18, 19]. Selenization or sulfurization is needed to improve performance of CIS solar cells since the process will incorporate Se/S in the thin film or increase the crystallinity. However, selenization or sulfurization always involves high temperature processing as well as highly toxic H_2Se / H_2S or Se/S environment. Addressing the abovementioned limitations, this work focused on the synthesis of CIS particles with large grain size and good crystallinity as well as the understanding of growth mechanisms for better morphology and composition control, which will ultimately provide a selenization/sulfurization-free fabrication route for CISe_2 solar cells. Therefore it presents a possible solution for clean, real “low-cost” and competitive solution-based techniques for CIS manufacturing.

1.2 Objectives

In view of the above motivations, the objective of this work is to develop materials and processing steps for selenization/sulfurization-free fabrication route for $\text{CuInS}_{(1-x)}\text{Se}_x$ solar cells. The initial part of the project will focus on the synthesis of micro-grain $\text{CuInS}_{(1-x)}\text{Se}_x$. Physical and electrical characterizations will be performed. Photovoltaic devices will be developed to investigate the effects of absorber materials on the carrier dynamics. The steps carried out in this project are stated below:

1. Investigations of solution-based routes for synthesis of micro-grain $\text{CuIn}(\text{S},\text{Se})_2$

- (a) Exploration on the $\text{CuIn}(\text{S},\text{Se})_2$ products after annealing without sulfurization or selenization.

- (b) Investigation on the $\text{CuIn}(\text{S},\text{Se})_2$ nanoparticles obtained by solvothermal process.

- (c) Understanding the mechanism of chemical transformation from nanoparticles to microcrystals through effects of reaction parameters e.g. temperature and time on the product quality.

2. Fundamental studies of structure and property correlation of micro-grain $\text{CuIn}(\text{S},\text{Se})_2$

(a) Material characterizations of nano-grain and micro-grain $\text{CuIn}(\text{S},\text{Se})_2$.

(b) Investigation on the carrier dynamics and studies on the photophysics of obtained nano-grain and micro-grain $\text{CuIn}(\text{S},\text{Se})_2$.

3. Studying the effect of chemical composition and synthesis schemes on sulfurization/selenization-free solar cells

(a) Fabrication of solar cells using $\text{CuIn}(\text{S},\text{Se})_2$ thin films and crystals obtained from above approaches.

(b) Investigation on certain materials effects and the fabrication process on the solar cell performance.

Chapter 2 : Literature Reviews

2.1 Cu(In,Ga)(Se,S)₂ thin film solar cells

2.1.1 Development on Cu(In,Ga)(Se,S)₂ materials

In 1953, Si was discovered as the first material by Bell labs to directly convert sunlight into electricity for running electrical devices. Since then, several other materials have been discovered for solar energy harvesting material, e.g. GaAs, CdTe and InP with efficiency > 10%. In late 1970s, the first CuInSe₂ solar cell was also invented in the Bell labs. The first high efficiency~9% CuInSe₂ cells was demonstrated by Boeing. Boeing began to address the difficult manufacturing issues in the 1980s that related to yield and scale-up. Then they led to a much advancement in CIGS solar cell technology.

Nowadays, CIGS is one of three mainstreams in thin-film technologies together with cadmium telluride (CdTe) and amorphous silicon (aSi). High chemical stability and power conversion efficiency of CIGS makes it a very promising p-type material for thin film solar cells. So far, CIGS solar cells fabricated by three-stage co-evaporation process hold 20% energy conversion efficiency, which is the highest record for thin film polycrystalline solar cells as shown in *Figure 2.1* [20]. Although CIGS solar cells have closed the gap between the efficiencies to the Si solar cells, CIGS solar cell companies have just been developed only in the recent years. And so far only a few companies are active

in the commercial solar cell industry. Solar Frontier is the leader in CIGS industry, supplying world's largest CIGS solar plant. MiaSolé is a company, which specifies in the manufacturing process for laying CIGS to flexible stainless steel substrates. Some other CIGS companies are Solibro, Avancis and nanosolar.

Figure 2.1: Solar cell efficiency record chart published by American National Renewable Energy Lab (NREL)

The current total worldwide of PV installed capacity is just about 20GWp (Giga WattPeak), which means the contribution of these to the world energy requirement is still very small. However, as illustrated in *Figure 2.2*, the total installed PV capacity is rising very fast, therefore, research directions should have been influenced by the consideration of further expansion and

sustainability of PV. Therefore, the search for new materials becomes important of this emerging scenario [21, 22].

Figure 2.2: Total installed world PV capacity. From bottom to top: China, USA, ROW, Japan, EU. (Online version in colour.)

2.1.2 Physical and Chemical Properties

2.1.2.1 Crystallographic structure of $\text{Cu}(\text{In,Ga})\text{Se}_2$ compounds

Here, ternary CuInSe_2 will be used to demonstrate the crystallographic structure first. Chalcopyrite structure (α phase) and sphalerite structure (δ phase) can be obtained. CuInSe_2 with chalcopyrite and sphalerite structures have orientations along (112) and (111) directions respectively, which have strong (112) and (111) peaks in 2θ measurements respectively. A phase diagram of CuInSe_2 showing the transformation of chalcopyrite structure and sphalerite structure is

shown in *Figure 2.3*. Firstly, at a temperature less than 1000°C (986°C), with the composition near that of CuInSe₂, a congruent melting of solid compound can be observed. Secondly, it can be observed that a congruent solid-solid (α to δ) phase transition at lower temperature (810°C). Thirdly, it can be observed that the temperature dependent extends α phase homogeneity range to indium-rich compositions, but not towards copper-rich compositions. Lastly, it can be observed that a peritectoid decomposition of δ phase at its lowest stable temperature into α phase as well as an indium-rich defect tetragonal structure [23, 24].

For α phase of CuInSe₂, every Se atom is tetrahedrally bonded to two Cu and two In atoms, and every metal atom has four Se atoms as nearest neighbours, corresponding to a space group $I-42d$. The different chemical natures of Cu and In/Ga atoms result in different ionic characters and length between Cu-In and the bonds between their neighboring selenium, which has electronic effects of reducing bandgap energy of α phase compared to δ phase structure as the result of disordered cation sublattice of sphalerite [25].

The α phase structure can also be viewed as two interpenetrating anion and cation sub lattices with face-centered cubic structure. The chalcopyrite structure of CuIn_xGa_(1-x)Se₂ of three combinations such as CuIn_{0.25}Ga_{0.75}Se₂, CuIn_{0.5}Ga_{0.5}Se₂, and CuIn_{0.75}Ga_{0.25}Se₂ are shown in *Figure 2.4 (a-c)* respectively [26]. Different chemical natures of Cu and In atoms result in different bonds ionic characters and lengths between them as well as their

neighboring selenium atoms [27]. The alternation of bond lengths causes electronic effects of reducing bandgap energy of α phase compound in comparison with that of δ phase of same chemical composition as the result of that δ phase is of a disordered cation sublattice.

2.1.2.2 Metastable crystallographic structures-CuAu ordering

Other than chalcopyrite structure, CuAu (CA) ordered structure of CIGS could also exist. CA ordering was first detected in CuInS₂ by TEM [28] and it has been also detected in CuInSe₂ with both Cu- and In-rich materials grown by Migration-Enhanced Epitaxy (MEE), which have been also detected by XRD and Raman techniques. [29] CA ordered structure is an alternative ordering with a composition within equilibrium range of chalcopyrite Cu(In,Ga)Se₂. Take CuInSe₂ as an example, Wei et al. studied the formation energy of CA crystallographic structure and found out that the difference is only 0.2 meV/atom compared to chalcopyrite (CH) at T=0 [30]. The equilibrium CH-CuInSe crystallographic structure consists of (201) planes of copper and indium atoms on the cation sublattices, whereas the CuAu-CuInSe structure consists of the alternating of (111) planes (both are in cubic notation), which is shown in *Figure 2.5*. [31] According to Rudigier, the XRD spectra of Cu-Au ordering and chalcopyrite are similar. *Figure 2.6* shows the calculated XRD spectra of Cu-Au ordered and chalcopyrite structure in two-theta angle ranges of 15°-19° and 36°-38° by using software POWDEREDCELL, which can be used to distinguish both structures [32].

Unlike CuInSe_2 , CuInS_2 forms naturally as the mineral roquesite. Binsma et al. found that there are four phases at room temperature, two of them corresponds to terminal binaries. Another two are compounds $\text{CuInS}_2(\gamma)$ and $\text{CuIn}_5\text{S}_8(\epsilon)$. They also found that the homogeneity range of $\gamma\text{-CuInS}_2$ are extended to Cu rich compositions, which is different from the ternary phases with CuInSe_2 . At 1045°C , which is just below the congruent melting temperature, a third solid-phase transition of sphalerite structure can also be detected. [33]. Another study extended ternary phase of Cu-In-S to CuS-InS tie. It was confirmed that $\text{Cu}_2\text{S-in}_2\text{S}_3$ pseudobinary is the equilibrium line and they found that room temperature homogeneity domain of roquesite $\gamma\text{-CuInS}_2$ phase is limited to 52 mol% of In_2S_3 but can be extended to CuS enrichment to 6 mol% [34].

2.1.2.3 Defect Structure of chalcopyrite $\text{Cu}(\text{In,Ga})\text{Se}_2$

It is known that, for CIGS solar cells to achieve high efficiency, Cu-poor composition is necessary as copper vacancies (V_{Cu}) are the most prominent defects in CIGS materials. The optimal Cu/In composition for high efficiency CIGS solar cells is 0.8 [35]. In the Cu-poor CIGS materials, the defects concentration ($\sim 10^{20} - 10^{21} \text{ cm}^{-3}$) is much higher than hole concentration ($\sim 10^{17} \text{ cm}^{-3}$). Besides Cu vacancies, there are some other defects for the Cu-poor CIGS materials, for example, Cu substituting In defects (Cu_{In}) and In substituting Cu defects (In_{Cu}). In addition, there are also neutral defect complexes, for example, $(\text{In}_{\text{Cu}} + 2V_{\text{Cu}})$ and $(\text{Cu}_{\text{In}} + \text{In}_{\text{Cu}})$. These neutral defect complexes have relatively low formation energies. Studies revealed the

importance of neutral defect complexes, anti-site defects Cu_{In} and In_{Cu} to affect the bandgap energy as well as device performance [36-38].

Figure 2.3: Phase diagram of Cu_2Se – In_2Se_3 pseudo-binary section of Cu–In–Se system

Figure 2.4: Crystal structure of chalcopyrite $\text{CuIn}_{0.25}\text{Ga}_{0.75}\text{Se}_2$, $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$, and $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$

Figure 2.5: Crystal structure of chalcopyrite and Cu-Au ordered CuInS₂

Figure 2.6: Calculated X-ray diffraction spectra of chalcopyrite and Cu-Au ordered CuInS₂

2.1.3 Optical and electrical properties

Compared to CdTe, aSi and GaAs, CuInSe₂ materials have higher absorption coefficient in the main solar spectrum $\sim 10^5 \text{ cm}^{-1}$, as shown in *Figure 2.7* [2]. A

layer with 1 μm thickness is sufficient to absorb 99% of sunlight. In addition, diffusion length of carriers $\sim 1 \mu\text{m}$ is sufficient, which means higher absorption coefficient leads to small thickness of absorber layer needed, therefore small amounts of materials and energy are required. Also the energy pay back time (EPBT) is shorter. EPBT is the time needed for a solar cell to regain the energy used in the production and the “module cost vs. efficiency” of different PV technologies are shown in *Figure 2.8* [39].

Figure 2.7: absorption coefficient of several semiconducting materials in the main solar spectrum

Figure 2.8: module cost vs. efficiency of different PV technologies

Shockley–Queisser limit or detailed balance limit was established based on the loss mechanism in single junction solar cells. The losses are typically separated as intrinsic or extrinsic. Undesired recombinations are caused because of series resistance, impurities as well as absorption from window layer. These are examples of extrinsic losses and they can be eliminated in principle. From thermodynamic origins, solar cell can be considered as a heat engine. Assume there is no new entropy generated in doing work, the power conversion efficiency will then come from a Carnot engine which operates with the sun as a heat source with the earth's surface as the heat sink [40]. The solar cell can be considered as an absorber as well as an emitter. Recombinations of electron–hole pair decreases the total number of carriers that could be collected then

reduce the overall solar cell efficiency. Further losses can be caused by inequality angle of incident and emitted radiations. When the sunlights reach the earth, they are essentially parallel, but the reemits lights are isotropic. This angle mismatch is called angular entropy or Boltzmann loss that can lower the cell efficiency by ~9%. Transparency of the solar cell absorber to photon energies below the band gap and thermalization losses where photons with energy greater than E_g are the two largest loss channels. All of these losses lead to Shockley–Queisser limit of conversion efficiency from solar to electrical power [41]. It is calculated as a function of the band gap of the semiconductor in solar cells [3]. The maximum efficiency is around 30% under AM1.5 conditions for single solar cells with bandgaps of 1.2–1.4eV. As such, the bandgap of CuInSe₂ is too low (~1.02eV), therefore Ga is usually added to form a material (Cu(In,Ga)Se₂) with a higher bandgap closer to the optimum value as shown in *Figure 2.9* [21]. As shown in the Figure, we can see that single crystal Si solar cells have achieved efficiencies quite close to Shockley–Queisser limit already, whereas those thin film solar cells have some room for further improvements.

Figure 2.9: Maximum theoretical efficiency (Shockley–Queisser limit) for solar cells under AM1.5 illumination without concentration. The bandgaps of absorber materials (c-Si, CdTe, CIGS, CZTS) and window materials (CdS, ZnO) are shown for comparison. Note that the bandgap of the CIGS system can be tuned by controlling the In/Ga ratio

The band gap of $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ is 1.04 eV-1.70eV, depending on the In/Ga and Se/S ratio. Therefore, band gap engineering can be achieved for $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ solar cells. For example, the band gap of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ is

$$E_{g,\text{CIGS}}(x) = (1 - x)E_{g,\text{CIS}} + xE_{g,\text{CGS}} - bx(1 - x)$$

Where $x = [\text{Ga}]/[\text{In}+\text{Ga}]$ represents the Ga content of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ $b = 0.15$ - 0.24 eV is the bowing parameter describing the deviation from a linear relationship [42]. Generally, polycrystalline CIGS with slightly Cu deficient is

a p-type material. However both n-type and p-type of the CIGS can be obtained while varying the stoichiometry. Typical carrier concentrations of absorber films are of the order of 10^{15} to 10^{17} cm^{-3} and it can be increased by about one order of magnitude by the presence of Na in CIGS [43].

Cu rich $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ is always p type semiconductor, while Cu poor $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ can be both p-type or n-type. By heating n-type Cu-poor $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ in Se overpressure can convert it to p-type, while when heating p-type $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ in a Se free or Se low-pressure environment, it can be converted to n-type. The effect is believed to be originated from the Se vacancy, which acts as a donor [43, 44].

2.1.4 Typical Device Structure

The performance of the CIGS solar cells has significantly improved over the past few years. Efficiencies higher than 15% have been achieved by several groups of lab-scale devices [4]. A typical structure of CIGS solar cell is shown in *Figure 2.10* [45]. The soda-lime glass is coated with Mo, which acts as back contact. CIGS absorber layer is deposited on the Mo coated substrate. Subsequently an n-type CdS layer is deposited by chemical bath deposition (CBD). The junction is formed between p-type CIGS film and n-type CdS layer. It is stated that CBD process can also clean the CIGS surface, which can improve the epitaxial growth of CdS on CIGS. Intrinsic ZnO layer with thickness around 70nm is then sputtered on top of CdS. Finally an ITO layer

with Ni/Al on top will complete the device fabrication. This structure described above has been used in almost all top-performing CIGS-based solar cells.

Figure 2.10: Schematic image of CIGS device structure

Figure 2.11 shows the band structure of a CIGS solar cell. Within the space-charge region lies the i-ZnO band and there is a discontinuity of $\sim 0.4\text{eV}$ in conduction band that closes to i-ZnO/CdS interface. On the other hand, depending on the concentration of Ga, the discontinuity in conduction band from CdS to CIGS varies from -0.4eV for CuInSe_2 to $+0.3\text{eV}$ for CuGaSe_2 . [46].

Figure 2.11: Band structure of a CIGS-based solar cell

2.2 Synthesis of CIGS solar cells

2.2.1 Vacuum-based synthesis of CIGS solar cells

Vacuum-based methods have consistently yielded the highest performance CIGS device in many laboratories around the world. Among the vacuum-based methods, evaporation and sputtering are the mostly studied over the years.

2.2.1.1 Evaporation

Evaporation can be co-evaporation or sequential evaporation. For co-evaporation, Cu, In, Ga, and Se, can be simultaneously deposited to a substrate at 400° C to 600° C. The CIGS film is formed in a single growing process as shown in *Figure 2.12 (a)*) [47-50]. Up to date, the champion CIGS solar cell with the efficiency as high as 20.3% was achieved by co-evaporation in ZSW (Zentrum für Sonnenenergie und Wasserstoff Forschung) lab [20]. In ZSW lab, the co-evaporation process is applicable to manufacturing inline where In, Ga and Se are first co-evaporated, followed by the co-evaporation of copper and selenium, and finally, co-evaporation of indium, gallium and selenium. Besides ZSW, National Renewable Energy Lab (NREL) has also achieved CIGS solar cell efficiency ~20% [4]. *Figure 2.13* shows the cross section of the Cu(In,Ga)Se₂ absorber layer achieved from NREL. For co-evaporation, control of elements with different reaction rates in one single process is essential to achieve excellent composition homogeneity. Evaporation rates and substrate temperature are varied during the deposition time of the CuInSe₂ layer [51].

Figure 2.12: Co-evaporation process for CIGS

Figure 2.13: Cross section for CIGS absorber layer from NREL

Besides co-evaporation, sequential evaporation has also been studied by many researchers. In sequential evaporation, elements sources can be evaporated layer by layer to form CIGS. In sequential evaporation, besides high substrate temperature, post-annealing process is generally needed (*Figure 2.14(a)*) [52-54].

In this process, a metallic precursor which is slightly Cu-poor is used because of the difficulty to pass through Cu-rich phase [55]. K.G. Deepa et al. synthesized CuInSe₂ solar cell by sequential evaporation without selenization and at relatively low substrate temperature. The In layer was first evaporated at 100°C, followed by coating of Se layer at 50°C and finally Cu layer at room temperature. The resulting film is then annealed at 400°C to form CInSe₂ [53]. Besides elemental sources, alloy compounds can also be applied in sequential evaporation. S.C. Park et al. fabricated CuInSe₂ films by using CuSe and InSe binary compounds. Cu₂Se and In₂Se₃ layers are sequentially evaporated at room temperature followed by selenization at 550°C (*Figure 2.14(b)*) [52].

Figure 2.14: Sequential evaporation of (a) CInSe₂ from elements and (b) from alloys

2.2.1.2 Sputtering

Normal reactive sputtering was abandoned for preparing CIGS solar cells as when depositing, target is insulating, which does not conduct negative charges of positive-charged ions bombarding it. The problem can be solved by using magnetron sputtering [56]. Sputtering for the CIGS solar cells can be both

sequential as shown in *Figure 2.15(a)* and simultaneous (*Figure 2.15(b)*). T. Pisarkiewicz and H. Jankowski used two separate targets of Cu and In. Adjusting the layer deposition time altered the elemental ratio. Two steps of selenization were taken for formation of CuInSe₂. First step of heating at low temperature (250°C) aimed to enhance the Se saturation in alloy. Crystallization happened in the second step high temperature heating (550°C). It was observed that with the increasing concentration of Cu, the secondary phase of Cu_xIn increased [57]. Besides sequential sputtering, simultaneous sputtering is also investigated by some research groups. H.L.Hwang et al. prepared the CuInS₂ power as the direct target for sputtering. CuInS₂ powder was synthesized by direct combination of stoichiometric amounts of the constituent elements and heated at 600°C for 1 day and 1000°C for another 2 days. The synthesized powder was then pressed in a disc at pressure of 60 000 lbf in⁻² to form the target. In this study, it is claimed that varying the sulfur vapor pressure during the sputtering, the crystallinity of resulting CuInS₂ film could be changed [58].

Similar result was observed by Y.B.He et al., in which study, the target for simultaneous is Cu-In alloy with Cu/In=11/9. They observed the secondary phase of Cu₁₁In₉ with insufficient vapor pressure of H₂S [59].

Figure 2.15: (a) sequential sputtering and (b) simultaneous sputtering

Compared to evaporation, it is harder to control the precise stoichiometry for sputtering process, which also results in the impurities and secondary phases for the sputtered CIGS film. This can also explain why the efficiency for sputtered CIGS solar cell is far less than the ones produced by evaporation. Besides the efficiency, sputtering also has higher material costs with lower materials utilization rate. In addition, it requires processing equipment and additional manufacturing steps, which increase the capital expense.

2.2.2 Solution based synthesis of CIGS solar cells

Although both evaporation and sputtering process have proved them for high efficiency CIGS solar cells, due to the high fabrication cost involved in vacuum-based processes, there is a strong push towards the use of solution-based methods in order to reduce the processing cost significantly. Generally, solution-based synthesis for preparing CIGS involves either the deposition of particle precursors or the deposition of solution precursors.

2.2.2.1 Thin film based approach

Non-vacuum synthesis of CIGS by thin film based approach is depicted *Figure 2.16*. Using solution precursors to prepare thin films provides an advantage of easy synthetic processing. For example, metal salts dissolve in solvent and the solution is then deposited onto the substrate by drop-casting, spin-coating, doctor-blading, spray-pyrolysis or injet-printing [7, 8, 60, 61]. D.Y. Lee, J. Kim et al. used solutions containing CuCl_2 , InCl_3 , and $\text{SC}(\text{NH}_2)_2$ with mole ratios of (0.8–1.6):1:5. The solution was sprayed onto substrate at temperature of 460°C with transfer rate at 1.5 ml/min followed by a sulfurization at 660°C for 20 min [62].

Figure 2.16: Schematic diagrams showing the non-vacuum CIGS synthesis steps by thin film based approach[63]

M. Kaelin et al. prepared the precursor pastes by dissolving appropriate quantities of $\text{Cu}(\text{NO}_3)_2$, InCl_3 and $\text{Ga}(\text{NO}_3)_2$ in methanol. Ethylcellulose dissolved in 1-pentanol was added into the precursor to adjust with suitable viscosity for doctor blade coating. Selenium was introduced by selenization process at 560°C for 10mins. The solar cell by using this absorber layer yielded 6.7% efficiency as shown in *Figure 2.17*. The inset is the cross section of the

CIS film after selenization. There was a residue carbon layer probably due to the adding of organic materials into the system [64].

Figure 2.17: Current-voltage characteristic of a 6.7% efficient solar cell under simulated AM1.5 (Air Mass 1.5) conditions with inset of cross section of absorber layer after selenization

2.2.2.2 Crystals based approach

Figure 2.18 shows non-vacuum synthesis of CIGS by crystal-based approach. In comparison to the solution precursors, crystal-based precursors contain the pre-synthesized CIGS crystals before the precursor deposition, then the crystals are deposited followed by post-treatment of films. The preparation of crystals, especially nanocrystals that only requires some common organic solvents and precursors. Moreover, the capability of large-scale production of nanocrystals and their compatibility with high throughput deposition techniques, for example, well established industrial procedures like printing and casting. These all enable the nanocrystal-based techniques suitable for mass production.[63]

Figure 2.18: Schematic diagrams showing the non-vacuum CIGS synthesis steps by crystal based approach.[63]

More importantly, using nanocrystals enables phase formation to happen prior to film deposition. Other solution-based approaches that include particle slurries, molecular and mixed solutions, generally require more reactions after the film is dried for phase formation. As the result of the difficulty of diffusion, the film could experience larger chances to decompose into binary, ternary, or quaternary phases as the result of compositional non-uniformities of the films. The nanocrystal approach, on the other hand, the phase formation happens in liquid phase within controlled environment. This will allow each constituent with better diffusivity to overcome activation energy barriers for reaching thermodynamically stability. Moreover, other solution-phase techniques may cause some unexpected residues left in the deposited films, which is believed to influence device performance [65].

Crystals can be obtained by various approaches, such as hot injection [10, 11, 66, 67], microwave-assisted synthesis [12, 68], thermal pyrolysis [13] and solvothermal synthesis [14-17]. In a typical approach, J.Tang et al. synthesized

CuGaSe₂, CuInSe₂, and Cu(InGa)Se₂ nanoparticles by hot-injection by using CuAc, Cu(acac)₂, In(acac)₃, InCl₃ and oleylamine. The principles guiding their approach are as following [59]:

- (a) In mixtures of precursors with Se in liquid form, rapid formation of chalcopyrite compounds is observed.
- (b) Metal salts and selenium powders are dissolved in oleyamine at high temperatures that enables the formation of chalcopyrite nanoparticles.
- (c) Precursors must have the reactivities that can favor ternary and/or quaternary compounds formation, but at the same time can avoid binary compounds in a synthesis.

Figure 2.19A shows TEM images of CuGaSe₂ nanoparticles of platelike morphology with average size of 11 nm. CuInSe₂ nanoparticles (*Figure 2.19B*), on the other hand, were a mixture of round, hexagonal and triangular nanoparticles of platelike with average size of 16 nm. In addition, most of the CuInGaSe₂ nanoparticles had triangular morphology with average diameter of 15 nm. [59]

Figure 2.19: TEM images of chalcopyrite nanoparticles synthesized herein and their corresponding SAED pattern: (A) CuGaSe₂, (B) CuInSe₂, and (C) CuInGaSe₂

A synthesis was performed by Christian K. et al. to use proper amount of CuCl₂·2H₂O, InCl₃·4H₂O, and sodium citrate dihydrate were dissolved in diethylene glycol, then the solvent was heated to 100 °C under stirring. Meanwhile, NaBH₄ was dissolved in DI water. When NaBH₄ was completely dissolved. This solution was injected to the Cu(II)–In(III)–citrate solution. The whole mixture was stirred for 15 min at 100 °C. Cu₁₁In₉ nanoparticles were collected by centrifuging the mixture and ink was prepared by dissolving the as prepared nanoparticles in the ethanol and the suspensions were deposited on the substrate by doctor –blading followed by the selenization. The final CIS device had 7% efficiency. *Figure 2.20* shows the cross section of absorber before and after selenization as well as the cross section of the final device [60].

Figure 2.20: Assembly of a CuInS_2 solar cell shown with SEM cross sections: (a) $\text{Cu}_{11}\text{In}_9$ precursor layer on sputtered Molybdenum double layer; (b) $\text{Cu}_{11}\text{In}_9$ thin-film after selenization; (c) completed CuInS_2 solar cell with buffer layers (i-ZnO and CdS) and front contact (ZnO:Al) on top

2.2.3 selenization/sulfurization

Thermal annealing processes at high temperature are always employed for as-fabricated nanocrystals films. Grain growth is also required to avoid

recombinations from boundaries between those nanocrystals. Based on the experience with Cu(In,Ga)(S,Se)_2 , only films with micron-sized grains are able to produce high efficiencies solar cells. Current progresses in nanocrystal-based solar cells have proved that without a thermal annealing process to promote grain growth, solar cells are difficult to reach 1% efficiency.

Selenization/sulfurization are high temperature annealing processes that are believed to help the large grain growth and to improve crystallinity of Cu(In,Ga)(S,Se)_2 materials. Selenization is a complicated process that needs to be optimized. Most of the studies optimize the selenization by varying temperature and time. H.F.Liang et.al optimized their selenization by optimizing the temperature profile. Cross sections SEM of the absorber layer selenized at 450°C and 575°C are shown in *Figure 2.21*, *Figure 2.22* shows the XRD spectra of the (112) peak of these two absorber layers. By increasing the selenization temperature, the little impurity peak at 27.01° disappeared and (112) peak is higher and the FWHM of the (112) peak becomes narrower, indicating better crystallinity and improved compositional homogeneity [69].

Selenization of nanocrystal films sometimes also produces bi-layer structures, which have a large-grained layer on the top and a fine-grained layer at the bottom [60, 70], like what is shown in previous *Figure 2.20*. They revealed that during the selenization of nanocrystal films, recrystallization process initiates on the surface of the film and sometimes also on the molybdenum/film interface. The thermal activation barrier of recrystallization is the smallest and

interfacial energy is the largest at these surfaces. These recrystallizations can produce grains more than one micron in diameter. The reason of this unique bi-layer morphology is suspected as the involvement of carbon residues that are left behind from organic ligands [60].

Figure 2.21: cross section SEM of CIGS on Mo/glass with absorber selenized at (a) 450°C and (b) 575°C

Figure 2.22: XRD spectra of CIGS selenized at (a) 450°C and (b) 575°C

However, there are some concerns regarding the general selenization process. Selenization environment is very important to determine the quality and

properties of the film from precursors. At high temperatures, Se is supplied in the gas phase, e.g. H_2Se or elemental Se and then Se will be incorporated into the film by absorption and diffusion. This step is called chalcogenization, when chalcogenides are formed from complex interactions. The interactions include the formation of intermetallic alloys (Cu-In-Ga), the formation of intermediate binary compounds as well as phase separation CIGS compounds with various stoichiometric. As the result of the complexity and variety of the reactions, it is difficult to control properties of the CIGS film [24]. In addition, different Se sources result in differences in formed films. By using H_2Se , the Se incorporation into the absorber is the fastest and only at 400 °C, full incorporation of Se can be incorporated in films. On the other hand, by using elemental Se, the temperature needed is 500 °C and above. In this case, Se deficient and multiple phases including metal selenides and various alloys may occur in the films when the temperature is below 500 °C. In addition, use of H_2Se also provides the advantage of better compositional uniformity and larger grain sizes.

Moreover, device performance depends strongly on absorber stoichiometry. For crystal-based solar cell, the composition of as-synthesized nanocrystals is an important factor that determines the composition of final absorber layer. However, the selenization process often alters the composition of pre-synthesized nanocrystals and causes a non-uniform composition distribution. Therefore, the stoichiometry of as-synthesized nanocrystals needs to be adjusted accordingly in order to get a desired post-selenization stoichiometry.

Chapter 3 : CuInS₂/ CuInSe₂/ CuInSSe thin films from annealing of precursor

3.1 Introduction

Thin film approach to synthesis CIGS thin film involves two steps: first is the formation of a homogeneous solution, which is then followed by the deposition on the substrate and a subsequent thermal treatment. For the preparation of the precursor solution, most of the time, the most important component is the solvent, as it determines whether the metal precursor can be stabilized in the solution at room temperature. The most important consideration in the selection of deposition technique is whether or not the technique will result in a device quality thin film free of voids, cracks, defects and binary phases upon the thermal treatment [63]. Low boiling point solvent, such as alcohol and amines, are mostly used as the solvent [64, 71-78]. However, sulfur and selenium would not be able to dissolve in most of these low boiling point solvents, meaning sulfurization or/and selenization process has to be applied after the deposition. In order for a non-sulfurization/ selenization process, it is important to introduce the sulfur or selenium during the reaction and hence it is critical to find a solvent that can dissolve sulfur/ selenium source.

In order to achieve a good film quality after deposition, a precursor with a suitable viscosity for a good coverage on the substrate should be selected. To

achieve this, most of the current works choose to add in some polymer binders. However, these binders may leave carbon residues after sulfurization/selenization as reported [61, 64, 71]. To address the problems of the current work, we prepare the precursor by the application of the concept of vulcanization process. Vulcanization is a chemical cross-linking process between elemental sulfur with polymers. This sulfur chemical crosslinking has been studied in many fields [79-82]. Vulcanized polymeric ink provides the advantage of being easily to decompose and because of the viscosity, it can be applied in different deposition techniques, such as a rolling process [74]. This work was first demonstrated by Weil et al. as they used $\text{Cu}(\text{acac})_2$, $\text{In}(\text{acac})_3$ and elemental S dissolved in pyridine as the ink and the ink is deposited on the substrate using a rolling process. The film is then baked in air at 370°C resulting in Cu-In-O layer as shown in *Figure 3.1*. The Cu-In-O layer is then converted to CuInS_2 layer by heating in a sulfur environment at 525°C (sulfurization) [74].

Figure 3.1: The process of CuInS_2 formation, including ink deposition by a roller bar, formation of Cu-In-O layer and CuInS_2 film after sulfurization

The issue with this process is that sulfurization is still required to form the CuInS_2 , therefore in this work, we proposed the synthesis of $\text{CuIn}(\text{S,Se})_2$ thin film by converting Cu-In-S/Se precursor directly to $\text{CuIn}(\text{S,Se})_2$ thin film without the intermediate formation of Cu-In-O and hence without toxic sulfurization/selenization. Instead of the rolling process, which required the complicated adjustment of solution viscosity, the cross-linked precursors is drop cast to be heated to form $\text{CuIn}(\text{S,Se})_2$ thin film. The crosslinking within the precursor solution increased the viscosity and this help with the uniform film formation without the formation of clusters. Therefore, this deposition is simpler and can result in a smooth and dense thin film comparable to rolling deposition.

3.2 Experiment Details

3.2.1 Materials

Copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$, 99.99%), indium(III) acetylacetonate ($\text{In}(\text{acac})_3$, 99.99%), sulfur (powder, 99.98%), selenium (powder, 99.99%) and pyridine (anhydrous, 99.8%), were all purchased from Sigma-Aldrich. All the chemicals were used as received without any further purification.

3.2.2 Synthesis Process

The Cu-In-S precursor mixtures was prepared by dissolving 16.4mg $\text{Cu}(\text{acac})_2$ and 25.75mg $\text{In}(\text{acac})_3$ powder into 1.5 ml of pyridine. 0.25mol of sulfur power was then added into the above solution. Cu-In-Se precursor was prepared similarly by adding in Se powder into the pyridine solution with $\text{Cu}(\text{acac})_2$ and $\text{In}(\text{acac})_3$. The mixture solution was ultrosonicated until the color changed from blue to dark brown. Sulfur or selenium acts as “curatives” for acetylacetonate polymers, providing crosslinks between polymer chains. Because of this “vulcanization” process, sulfur or selenium provides the mixture solution with rheological properties suiTable for coating. After depositing the vulcanized precursor ink onto the glass substrates, the film was annealed in furnace with continuing purged Ar gas at different temperatures from 350°C to 450°C for one and half an hour.

3.2.3 Materials Characterizations

Fourier transform infrared spectroscopy (FTIR) (PerkinElmer spectrum GX) was used to obtain the infrared absorption and transmission spectrum of the

precursors. FTIR samples were prepared by grinding 10mg sample with 100mg potassium bromide (KBr). Differential scanning calorimetry (DSC) measurements and thermal gravimetric analysis (TGA) were carried out using TGA_Q500 and DSC-Q100 respectively to study the thermal stability of precursor. The phase and crystallographic structure of the synthesized CuInS₂/CuInSe₂ and CuInSSe thin films were characterized and confirmed using X-ray diffraction (XRD). The XRD patterns were recorded using a Bruker D8 Advance with graphite monochromated CuK α radiation ($\lambda=1.54\text{\AA}$) and operating at 40 kV and 40 mA. The diffraction patterns were collected at a fixed θ of 2° and for 2 θ angles ranging from 20 to 70°, scanning at a rate of 0.5° min⁻¹ and with a step size of 0.03°. The morphologies of the samples were characterized using scanning electron microscope (SEM) (JEOL JSM-7800). Horiba-JY T64000 with an excitation wavelength of 633 nm at 110 mW was used for Raman spectra to investigate the vibrational modes in the materials in order to identify any secondary compounds not distinguishable using other characterization techniques. The current density-voltage (J-V) characteristics of devices were measured under a solar simulator illumination in ambient conditions under AM 1.5G illumination (100 mW/cm²) using a Keithley SMU 2400 source meter. The light intensity was calibrated by using an NREL calibrated silicon photodiode. Pump probe measurement was performed on CuInS₂ thin film deposited on a glass substrate. Second harmonic generation of fundamental 800 nm (400 nm) wavelength was used as pump; and beam from

optical parametric amplifier was used as probe. Differential probe signals were collected using photodiode and lock-in amplifier, with respect to pump delay.

3.3 Results and discussions

As discussed in the introduction, this work essentially makes use of vulcanization as a starting point for the formation of the thin film. Therefore, to understand how the precursors can be converted to $\text{CuIn}(\text{S,Se})_2$, studies were carried out on the precursors for characterizing the vulcanization process.

3.3.1 Precursors Characterization - Decomposition and Vulcanization Studies

In this vulcanization process, crosslinks between the acetylacetonate salts are formed by either sulfur or selenium. The crosslinking process is evident by the color change in the precursor solution from blue to dark brown after 10 mins of ultrasonication, which indicate the disappearance of free Cu^{2+} in the solution. This is because that a sulfur atom tends to have a process called “sulfur curing”, which refers to the cross-linking caused by a reaction of sulfur chains with the polymer chains [83]. The elemental sulfur is made of S_8 rings, which can be converted to a linear polymeric molecules [82] and carbon can be chemically crosslinked by reaction with elemental sulfur [84].

The solutions before and after cross-links were formed are shown in *Figure 3.2*. To show that cross-links indeed occurred between the precursor molecules and sulfur, the individual components and the cross-linked precursor were studied using FTIR. *Figure 3.3* shows the comparison of the FTIR spectrum of the cross-linked precursor and $\text{Cu}(\text{acac})_2$ and $\text{In}(\text{acac})_3$. There is a slightly shift of ν CH peak of “acac” group as well as the disappearance of ν In_2O_3 , ν CuO , ν C-

CH₃ peaks, which indicate possible linkages between S and Cu and In, as well as the breakage of double bond and the linkage between S and C/CH as shown in *Figure 3.4*.

Figure 3.2: Color change of the precursor before and after vulcanization

Figure 3.3: FTIR of precursor compared with Cu(acac)₂ and In(acac)₃

Figure 3.4: Crosslinking of precursor

The variation in viscosity provides a way to monitor the progress of the vulcanization process. *Figure 3.5* shows the dependence of viscosity of the Cu-In-S precursor solution on time under constant heating at 50°C. The viscosity curve for Cu-In-S precursor shows an increase in viscosity for the first 400s and then the viscosity saturates. This curve is very similar to a “vulcanization curve” where the viscosity of polymeric materials increased with time until saturation is reached and the gradient of the curve can be varied by many factors such as temperature and additives. Hence the viscosity curve can be made use of to determine the vulcanization time. The viscosity reached a limiting value after 400 s suggesting that the number of cross-links do not change with time after 400 s. The inset in *Figure 3.5* shows the paste like consistency of the precursor after vulcanization. For all the samples, vulcanization was carried out for about 10 min since full cross-linking would have occurred after 10 min.

Figure 3.5: Variation in the viscosity of precursor with time measured at 50°C

In order to study the thermal transitions of the precursors, both thermogravimetric analysis and differential scanning calorimetry (DSC) analysis were carried out. Thermogravimetric analysis (TGA) was done for the precursor in Ar atmosphere up to 900°C. The TG curve (in red) for CuInS₂ precursor with its derivative (in green) is shown in *Figure 3.6*. According to the derivative curve, there are three major weight losses. The weight lost at 50°C, the weight loss may be due to physisorbed moisture. The weight loss between 50°C to 150°C is related to the pyridine evaporation. From 150°C to 550°C, there was about another 60% weight loss that probably due to the decompositions of metal acetylacetonates, [85] some sulfur because of its volatility, as well as the remaining pyridine in the precursor paste. The

formation of CuInS_2 most probably took place in this temperature range. At temperatures higher than 550°C , the decomposition of some CuInS_2 contributed to an additional 15% weight loss [86].

DSC curve of the precursor is shown in *Figure 3.7*. DSC curve of the precursor showed an exothermic peak at about 70°C , which probably corresponds to the crosslinking formed within the precursor. Besides of shift in peak position, the peak area also increases compared to pure pyridine. This indicates that with crosslinking within precursor, the potential barrier for the elimination temperature of solvent is reduced.

Figure 3.6: TGA curve of precursor heating up to 900°C

Figure 3.7: DSC curve of precursor and pure pyridine

3.3.2 Effect of Processing Conditions on the Synthesis of $\text{CuIn}(\text{S,Se})_2$ thin film

Once the vulcanization conditions are established, it is then possible to look into the structure evolution of the thin films as a function of both temperature and time. The vulcanized precursor was drop casted onto a glass substrate and heated to different temperatures for one and a half hours in Ar environment. From the previous TGA and DSC analysis, the transformation of the cross-linked precursors to CuInS_2 is found to take place between 200°C to 600°C. Hence different annealing temperatures within this temperature range were investigated.

Figure 3.8 shows the XRD spectrums for the various samples annealed at 200°C, 350°C and 530°C. For all the temperatures tested, the XRD peaks could be indexed with CuInS_2 , indicating pure CuInS_2 can be obtained by annealing

the precursor in Ar environment. Annealing at 200°C resulted in XRD peaks (indicated with stars) that shifted from the peaks that obtained at 350°C and 530°C. This is because that CuInS₂ obtained at 200°C is relatively amorphous compared to that obtained at 350°C and 530°C. With the increase in the annealing temperature, the crystallinity of CuInS₂ is improved as seen from the increase in the intensity of the reflections.

Figure 3.9 shows the SEM images of CuInS₂ annealed at 200°C, 350°C and 530°C. At 200°C, the CuInS₂ particles are about 100 nm in size, spherical in shape and embedded under the organic layer. At 350°C, the particles become more obvious. When annealing temperature increases to 530°C, all the small CuInS₂ nanoparticles form big clusters. This is in agreement with the XRD study that grain size increases with annealing temperature as the decrease of full width at half maximum (FWHM) (calculated from origin software as shown in *Table 3.1*). However, the film at 530°C looks more porous due to more degradation and evaporation of organics in the precursor above 350°C. In addition, the effect of time in the annealing process has also been investigated with the temperatures kept at 530°C as shown in *Figure 3.10*. When heated at 530°C, CuInS₂ was formed after 30mins and the crystallinity did not seem to improve with increase in reaction time. From the SEM images shown in *Figure 11*, the morphology also changes with reaction time. After 30mins, the reaction is still incomplete and not all the precursors were converted to CuInS₂ crystals. When reaction time reached 1 hr, more CuInS₂ crystals were formed based on

the increase in intensity of the diffraction peaks. However the morphology did not change with even longer reaction time.

Figure 3.8: XRD spectrums of CuInS_2 after annealing at 200°C, 350°C and 530°C for 1hr with CuInS_2 (JCPDS 47-1372) as the reference.

Figure 3.9: SEM images of CuInS_2 after annealing at 200°C, 350°C and 530°C for 1hr

	350°C	530°C
FWHM	1.507	0.941
Error	0.02868	0.01924

Table 3.1: FWHM for XRD (112) peaks for CuInS₂ from different reaction temperature

Figure 3.10: XRD spectrums of CuInS₂ after annealing at 530°C for 0.5hr,1hr and 2hrs with CuInS₂ (JCPDS 47-1372) as the reference.

Figure 3.11: SEM images of CuInS₂ after annealing at 530°C for 0.5hr, 1hr and 2hrs

Similar to CuInS₂, CuInSe₂ could also be obtained by the same synthesis route with Se powder in the precursor instead of S powder. From XRD spectra in *Figure 3.12*, it can be observed that unlike CuInS₂, pure CuInSe₂ were not obtained at 200°C. Instead, besides CuInSe₂ (XRD peaks labeled as oval), there are lots of unreacted Se remained. This may due to the lower solubility of Se in pyridine and the higher boiling point of selenium compared to sulfur. When temperature increases to 350°C and 530°C, pure CuInSe₂ could be obtained and the crystallinity increases with temperature. Similar time study was performed for CuInSe₂ at the same condition as CuInS₂ at 530°C. The same trend was found, i.e. CuInSe₂ could be obtained for longer reaction time (more than 30mins) and the morphologies remain constant over the reaction time as shown in *Figure 3.13*.

Figure 3.12: XRD spectra of CuInSe_2 after annealing at 200°C, 350°C and 530°C for 1hr with CuInSe_2 (JCPDS 40-1487) as the reference.

Figure 3.13: SEM images of CuInSe_2 after annealing at 530°C for 0.5hr, 1hr and 2hrs

Figure 3.14: XRD spectra of CuInS₂, CuInSe₂ and CuInSSe after annealing at 530°C for 1hr with CuInS₂ (JCPDS 47-1372) and CuInSe₂ (JCPDS 40-1487) as the references.

Besides CuInS₂ and CuInSe₂, CuInSSe can also be obtained from similar process using Cu-In-S-Se precursor. The XRD and Raman patterns of CuInS₂, CuInSe₂ and CuInSSe are shown in *Figure 3.14* and *Figure 3.15*. All the XRD peaks of CuInS₂ shift to smaller 2θ angle with the incorporation of Se as the atomic size of Se is larger than S. Raman pattern of CuInS₂ and CuInSe₂ both showed the peak corresponding to the dominant A₁ mode indicating the formation of single-phase chalcopyrite with enhanced crystalline ordering. The pattern of CuInSe₂ also shows other minor peaks corresponding to E³ TO mode, E¹ and B₂¹ LO mode [87].

On the other hand, the Raman pattern of CuInSSe shows A₁ modes of both CuInS₂ and CuInSe₂, which matched well with literature [88]. For all three

Raman patterns, all the peaks shown are related to either CuInS_2 or CuInSe_2 and no secondary phase is observed.

Figure 3.15: Raman patterns of CuInS_2 , CuInSe_2 and CuInSSe annealed at 530°C for 1hr

3.3.3 Demonstration of CuInS_2 solar cell

For the demonstration of the materials in solar cells, we made use of a structure similar to that of CIGS thin film solar cells, which is described in Chapter 2. As stated in the previous chapter, selenization/ sulfurization is usually needed to induce the grain growth. In our case, our absorber layer of $\text{CuIn}(\text{S},\text{Se})_2$ thin

films were obtained from the normal annealing process free of selenization/sulfurization process.

It is believed that device performances strongly depend on the absorber stoichiometry as that determines the amount of defect species and existence of secondary phases [89]. From the literature, the optimal composition for CIGS thin film solar cells is Cu poor with Cu/In ratio ~ 0.8 to 0.9 [90]. Therefore, in order to achieve this optimal composition, different composition ratios of the precursors before and after annealing were investigated. Composition of the films were determined using SEM EDX. The EDX results are shown in *Table 3.2*. The Table showed the Cu/In ratio after annealing at 120°C and 530°C . At 120°C , the crosslinks would have been formed but the compound is only formed at 530°C . It can be observed that there is very little indium or copper losses during the annealing process as expected, which is probably due to the presence of crosslinks within the precursor and this reduce the chances of changes to the stoichiometry as discussed in previous section, and therefore, the starting Cu/In ratio of $\sim 0.8:1$ was used to prepare the film for solar cell fabrication.

	Cu:In=0.5:1		Cu:In=0.7:1		Cu:In=0.9:1	
	120C	530C	120C	530C	120C	530C
Cu	8.87	14.7	13.83	17.91	14.72	18.25
In	17.14	24.69	20.34	24.21	16.55	19.84
S	73.98	60.6	65.82	57.88	68.73	61.91
Cu:In	0.51:1	0.59:1	0.68:1	0.74:1	0.89:1	0.92:1

Table 3.2: Composition of precursors before and after annealing

To fabricate a solar cell device using the synthesized thin films, a device-quality CuInSSe absorber layer is needed. Although CuInS₂, CuInSe₂ and CuInSSe could all be obtained by our proposed synthesis method, it is difficult to get smooth and dense CuInSe₂ and CuInSSe thin films because of the poorer solubility of selenium compared to sulfur powder in the pyridine. Hence the solvent needs to be replaced and further optimization is required. Hence as a demonstration, CuInS₂ thin films were chosen for the fabrication of sulfurization/selenization-free solar cell.

For our device fabrication, the absorber layer of CuInS₂ was deposited by drop casting the precursor solution on a Mo sputtered glass substrate, and following that, the film is annealed at 530°C for 1hr. A layer of CdS was subsequently deposited by chemical bath deposition on top of the annealed CuInS₂ thin film forming the p-n junction. On top of CdS layer is a layer of TCO is coated as the window layer. Finally the Au electrode was deposited on TCO to complete the device, as illustrated in *Figure 3.16*.

Figure 3.16: Device structure of CuInS₂ thin film solar cell

In *Figure 3.17*, the cross section of our CuInS₂ device shows that a smooth and dense absorber layer was obtained but with no obvious grain growth, just as we discussed in the previous section.

The current-voltage characteristic curve of this device is shown in *Figure 3.18*. The efficiency of this solar cell is 0.6% with short circuit current, $J_{sc}=6.42\text{mA/cm}^2$, open circuit voltage, $V_{oc}=0.18\text{V}$, fill factor, $FF=33.85\%$, shunt resistance, $R_{sh}=465.59\ \Omega$ and series resistance, $R_s=235.21\Omega$. In general, the J_{sc} , V_{oc} and FF are quite low compared to typical high efficiency CIGS solar cells that undergo selenization/sulfurization [4, 91, 92].

Figure 3.17: Cross section of CuInS₂ solar cell

Figure 3.18: I-V performance of CuInS₂ solar cell

Low V_{oc} obtained for the device may be due to high series resistance. This is an intrinsic problem as there is no MoS_2 interlayer as lack of sulfurization process. Therefore this may result in a Schottky barrier - an imperfect ohmic contact at $Mo/CuInS_2$ interface that can affect the current flow, poor band alignment at the $CdS/CuInS_2$ interface or poor charge transport at the grain boundaries. V_{oc} can also be affected by the minority carrier lifetime, which can be reduced when the grains are small (more recombination) and S vacancy (trap minority carriers). All these can be studied by looking at the transient properties.

Figure 3.19: Pump probe measurement of $CuInS_2$ thin film

The samples for the pump probe measurement were prepared by depositing $CuInS_2$ thin film on a glass substrate to eliminate effects of the layer on top of the semiconductor absorber layer [93]. As shown in *Figure 3.19*, the red curve

is the exponential fit for the transmitted probe pulse energy with time and the lifetime of the charges can be extracted from this fitting. The curve can be fitted with two exponential curves, $I_{PL}(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, which yields lifetime $\tau_1 \sim 1\text{ps}$ and $\tau_2 \sim 12\text{ps}$, where τ_1 and τ_2 are the fast and the slow decay times respectively. τ_1 is related to the decay of the charge species because of the presence defect sites and τ_2 is related to the radiative recombination. Although it has been known that the lifetime of the carriers in CIGS films are shorter than the lifetime in CdS/CIGS and CIGS device [94], the lifetime we obtained is still too low compared to the published data [95, 96], which could result from the recombination due to defects, grain boundaries and interfaces as our grain sizes are small, and this most probably resulted in low V_{oc} .

Although this device performance is not as good as those high performance CIGS devices, but when compared to CIGS solar cells without selenization/sulfurization process, this efficiency is comparable or even better than those published in literature [11, 97, 98] The device performance could be further improved by increasing the grain size of the absorber materials. To achieve this, the solar cells will be fabricated using pre-synthesized large size particles incorporated into the absorber thin film and this will be discussed in subsequent chapters.

3.4 Conclusions

In this work, a selenization/sulfurization free process was proposed for the preparation of $\text{CuInS}_2/\text{CuInSe}_2/\text{CuInSSe}$ thin films. The reactants were first vulcanized. Cross-links between Cu/In and S/Se were formed in the precursor. Next, the precursor can be deposited on substrates and then annealed at a relatively low temperature of around 350°C to form the $\text{CuInS}_2/\text{CuInSe}_2/\text{CuInSSe}$ thin films.. Studies on the effects of annealing temperature and time revealed that crystallinity and morphologies of $\text{CuInS}_2/\text{CuInSe}_2/\text{CuInSSe}$ could be improved by increasing the annealing temperature and the annealing time. No secondary phase was formed in the $\text{CuInS}_2/\text{CuInSe}_2/\text{CuInSSe}$ films and this was evident from the Raman spectra collected for these samples. For a simple demonstration of solar cell, CuInS_2 thin film was selected as a smooth thin film could be obtained compared to CuInSe_2 and CuInSSe . This is probably related to the poor solubility of Se compared to S in pyridine. However, the grain size of CuInS_2 is relatively small compared to that of good performance $\text{Cu}(\text{InGa})(\text{S,Se})_2$ solar cells. Therefore, although it is comparable to those $\text{Cu}(\text{InGa})(\text{S,Se})_2$ solar cells without selenization/sulfurization, the solar cell efficiency can be improved if the grains can be grown to larger sizes.

Chapter 4 : CuInSe₂ synthesized by

solvothermal reaction

4.1 Introduction

In recent years, both ternary and quaternary chalcogenides have drawn increasing attention because of their good optical and electrical properties that make them highly suitable to be used in solar cells, optoelectronic devices and biomedical devices. Other than the conventional vacuum-based synthesis of these chalcogenide thin films, a variety of other synthesis routes have also been well developed for these ternary and quaternary chalcogenides nanoparticles and they include the hot injection method [59, 61, 99], the solvothermal method [12, 14, 100, 101], the microwave-assisted method [68, 102, 103] and the thermal pyrolysis method [13, 104]. Hot injection usually requires expensive chemicals and limited to only small size nanoparticles [105]. Microwave-assisted synthesis usually involves high investment cost, some safety concerns as well as uncertainty about the reaction conditions such as the reaction temperature [106]. Thermal pyrolysis needs a selective precursor, which is normally obtained via a complicated synthesis route [13, 104]. Solvothermal reactions have shown to have the advantage of being a greener technology since they consume less energy due to moderate reaction temperature and at the same

time, this method also allows the use of some common and inexpensive solvents [107].

In solvothermal synthesis, the precursor solutions are subjected to high temperature and pressure thereby producing structures that have some degree of crystallinity. The synthesis is carried out in a stainless steel autoclave. Solvothermal synthesis has been used to synthesize various chalcogenide materials [108-111] and CuInSe₂ is one such chalcogenides.

As mentioned previously, CuInSe₂ has been shown to perform well as solar energy harvesting materials due to their high light absorption coefficient and suitable bandgap (1.0eV~1.5eV), complementary to the visible solar spectrum. In order for these CuInSe₂ nanoparticles to be used effectively in solar cells, the stoichiometry, shape and size of these particles has to be well controlled. These properties are in turn strongly influenced by the precursors and the synthesis conditions. Several research groups have synthesised CuInSe₂ nanoparticles by using the solvothermal method. For their synthesis of CuInSe₂ nanoparticles, organic ligands are commonly used to control the dispersion and growth [108-111]. Ligands can often cause undesirable carbonaceous impurities in the final products as well as inhibit the formation of large crystalline grains because of surface stabilization. On top of this, as Se powder is usually used as the Se source, excess Se is always needed because of the poor solubility of the Se powder in most of solvents. This makes it difficult to control the composition to produce high quality CuInSe₂ with pure phase. Therefore, we propose a

solvothermal synthetic route which used dimethylformamide (DMF) as both the solvent and the reducing agent, hence no ligand was used in the synthesis. Low-toxicity, low-cost metal selenite salts (CuSeO_3 , $\text{In}_2(\text{SeO}_3)_3$) were used as the both metal and the selenium source. The cations (Cu or In) and Se was provided by a single precursor and the problem relating to the use of excess Se in the synthetic route using conventional precursors can be overcome. To the best of our knowledge, this is the first report on the use of selenite salts as Se source for CuInSe_2 nanoparticle synthesis.

4.2 Experiment Details

4.2.1 Materials

Copper(II) nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, 99.999%), indium(III) chloride ($\text{InCl}_3 \cdot x\text{H}_2\text{O}$, 99.99%), selenium dioxide (SeO_2 , 99.8%), sodium hydroxide (NaOH), dimethylformamide (DMF, >99%) were purchased from Sigma-Aldrich. Methanol was obtained from J.T.Baker (analytical grade). All the chemicals were used as received without any further purification.

4.2.2 Synthesis Process

CuInSe_2 was prepared by reacting CuSeO_3 and $\text{In}_2(\text{SeO}_3)_3$ in DMF. CuSeO_3 was obtained by mixing $\text{Cu}(\text{NO}_3)_2$, SeO_2 and NaOH (1:1:2 mol/mol/mol) in DI water until green CuSeO_3 precipitated out. Similarly, white $\text{In}_2(\text{SeO}_3)_3$ precipitates were obtained when InCl_3 was mixed with SeO_2 and NaOH (2:3:6 mol/mol/mol) in aqueous solution. The CuSeO_3 and $\text{In}_2(\text{SeO}_3)_3$ was filtered and washed with water several times before dried.

CuInSe_2 was prepared by following procedures: 0.02M(C1) /0.04M(C2) /0.08M(C3) solution were prepared by adding in suitable amount of CuSeO_3 and $\text{In}_2(\text{SeO}_3)_3$ (1:1 mol ratio) to 20ml DMF or 20ml mixture of Me-DMF/ H_2O -DMF(1:1 v/v), the solution was stirred for about 30min then was transferred to a 50ml teflon-lined stainless steel autoclave. The autoclave was then heated in an air-oven at 180°C for 24hrs/48hrs. When the reaction was finished, the oven

was cooled to room temperature and black precipitates in the solution were collected, washed with methanol for several times and then dried.

4.2.3 Materials Characterization

The phase and crystallographic structure of the synthesized CuInSe₂ crystals were characterized and confirmed by X-ray diffraction (XRD) studies using a Bruker D8 Advance with graphite monochromated CuK α radiation ($\lambda=1.54\text{\AA}$) and operating at 40 kV and 40 mA. The diffraction patterns were collected at a fixed θ of 0.5° and for 2θ angles ranging from 20 to 70° , scanning at a rate of $0.5^\circ \text{ min}^{-1}$ and with a step size of 0.03° . Raman spectra were measured using a Horiba-JY T64000 with an excitation wavelength of 633 nm at 110 mW for identifying molecules as well as investigating the vibration and symmetry of the molecule. The morphologies of the products were characterized using scanning electron microscope (SEM) (JEOL JSM-7800) and transmission electron microscopy (TEM) (JEOL 2010). The compositions of the as-prepared CuInSe₂ crystals were quantitatively determined using energy dispersive X-ray spectroscopy (EDX) attached to SEM with working voltage of 20eV. Samples for SEM and TEM were prepared by dropping CuInSe₂ crystals dispersed in methanol onto carbon tape and onto lacey carbon-coated copper grids respectively. Photoelectrochemical measurement was carried out for the study of electrical properties by using a three-electrode configuration with a Pt-gauze as the counter electrode and an Ag/AgCl reference electrode in KH₂PO₄ (KPI) electrolyte solution (PH=7). The sample was prepared by depositing CuInSe₂ crystals crystals dispersed in methanol onto FTO substrate.

4.3 Results and Discussions

CuInSe₂ nanoparticles were synthesized by reducing CuSeO₃ and In₂(SeO₃)₃ with the help of DMF. Here DMF acted as reducing agent and solvent. Prior to this both CuSeO₃ and In₂(SeO₃)₃ have to be synthesized and the chemical equations describing the synthesis is shown below.

The as-synthesized CuSeO₃ and In₂(SeO₃)₃ were amorphous based on the XRD patterns collected. It can be observed that the size of Cu(SeO₃)₂ nanoparticles were about 70-120nm and the In₂(SeO₃)₃ particles were several hundreds of nanometers in size (*Figure 4.1*). With these starting precursors, CuInSe₂ can be synthesized via simultaneous reduction of both compounds by DMF.

Figure 4.1: FESEM images of (a) CuSeO_3 and (b) $\text{In}_2(\text{SeO}_3)_3$

Figure 4.2: XRD spectra (a) and FESEM image (b) of products synthesized in DMF at 180°C for 24hr.

The reduction strength of DMF in a solvothermal condition is not strong enough to produce pure CuInSe_2 . The XRD pattern shows that the final products contained a large amount of CuSe along with the CuInSe_2 (Figure 4.2) and amorphous products from $\text{In}_2(\text{SeO}_3)_3$ and some remaining $\text{In}_2(\text{SeO}_3)_3$. Based on this XRD results, it can deduce that CuSeO_3 is easier to reduced by

DMF compared to $\text{In}_2(\text{SeO}_3)_3$. There is a strong possibility that some $\text{In}_2(\text{SeO}_3)_3$ may still be present. As pure CuInSe_2 cannot be obtained by only using DMF as the solvent, other co-solvents were used to improve the quality of the final product.

4.3.1 CuInSe_2 synthesized in Water-N,N-Dimethylformamide (H_2O -DMF) solution

In order to obtain pure CuInSe_2 phase, solvent which can promotes higher ionic activity is needed. For some ions, it is believed that the ionic activity can be improved by using mixed solvents rather than pure solvents, and this can be seen from the modified Debye-Huckel equation shown below:

$$\log \gamma = - \frac{AZ_1Z_2\sqrt{S}}{1 + Br_{\text{solv}}\sqrt{S}}$$

where $A = 1.825 \times 10^6 / (T \cdot \epsilon)^{\frac{1}{2}}$, $B = 50.29 \times 10^8 (T \cdot \epsilon)^{\frac{1}{2}}$, Z_1 and Z_2 are charges of cation and anion, S is the molar solubility and ϵ is the dielectric constant of the solvent and r_{solv} is the solvated ions radius [112]. As the reactivity γ increases with the dielectric constant ϵ , we proposed to use a mixed solvent system so as to achieve a high dielectric. Since water has a higher dielectric constant, a mixture of water and DMF is chosen and the reason for not using pure water is because there are solubility issues for the precursors. As $\epsilon_{\text{H}_2\text{O}} > \epsilon_{\text{DMF}}$ and $\epsilon_{(\text{H}_2\text{O}-\text{DMF})} = \epsilon_{\text{H}_2\text{O}} \cdot X_{\text{H}_2\text{O}} + \epsilon_{\text{DMF}} \cdot X_{\text{DMF}}$, where X_{DMF} and $X_{\text{H}_2\text{O}}$ is the mole fraction of DMF and H_2O respectively, and the dielectric constant for the mixed solvents is larger than pure DMF. Hence, a H_2O and DMF mixture (1:1) is used

as the solvent and reducing agent. Using this solvent mixture, the effect of both reaction temperature and reaction time on the synthesis process is studied.

Figure 4.3 (a) and (b) show the XRD patterns of CuInSe₂ synthesized in H₂O-DMF system at different precursor solution concentrations (C1: 0.02M, C2: 0.04M, C3: 0.08M) after 24 hr and 48 hr. After 24 hr, CuInSe₂ particles with good crystallinity were formed for all concentrations studied. Peaks can be indexed to the standard chalcopyrite phase of CuInSe₂ (JCPDS 40-1487). Existence of a small shoulder at the (112) peak and the asymmetry of (220)/(204) peaks indicate the possible coexistence of other impurity phases which are commonly observed in nanoparticles synthesis for these materials. For the 48 hr reaction, the major peaks still matched well with CuInSe₂, but impurity phases are still present for the reactions using concentrations C1 and C2. For C1 reaction, the impurity peak labeled as star is related to InSe. For C2 reaction, the impurity peaks labeled as ovals relate to Cu₇Se₄. For the higher concentration reaction - C3, the XRD pattern also shows the formation of some metastable wurtzite phase of CuInSe₂ [113]. The reason for the impurities may be the result of the hydrolysis effect of the H₂O, and with different precursor concentrations, different impurities were formed.

Figure 4.3: XRD patterns of CuInSe₂ particles synthesized in H₂O-DMF for (a) 24hr and (b) 48hr with varying precursor concentrations. The XRD spectrum of CuInSe₂ (JCPDS 40-1487) is shown for reference

The morphology of the final product was investigated using FESEM. The morphologies of the CuInSe₂ products for different reaction conditions are shown in *Figure 4.4*. At low reaction concentration C1, the CuInSe₂ particles are spherical in shape and form large aggregates. At higher reactants concentration (C2 and C3), the morphology of CuInSe₂ particles become more plate-like and the size of the plates can reach 1 μm .

The morphology obtained is determined by the diffusion-limited aggregation (DLA) model[114]. At lower concentration - C1, both the nucleation and growth rate are very slow and the ions perform a “random walking” before aggregation, the thickness of diffusion layer is thick and the ions in the solution take long time to reach the reaction surface. Once ions reach the reaction surface, they will react immediately even though crystal may have different

reactivity along different planes, therefore the growth of the nanoparticles is uniform in all directions and the particles do not grow in any preferred direction. The final morphology is spherical. When the concentration increases above a certain level C2, both nucleation rate and growth rate increase and the thickness of diffusion layer near reaction surface decreases, more ions can diffuse to the reaction surface, when more ions reach the reaction surface than required in the reaction, the growth rates are different at planes with different reactivity, therefore aggregation can occur in preferred directions. Hence, CuInSe₂ particles can grow into two dimensional plate structures at higher concentrations.

Figure 4.4: morphologies of CuInSe₂ for 24hr reactions at different precursor concentrations

(a): C1; (b): C2 and (c): C3

Figure 4.5: Raman spectra for 24 hr reaction with different precursor concentrations (C1, C2 and C3) in H₂O-DMF

The as-synthesized particles were characterized by Raman spectroscopy to analyze the phase obtained and the purity of the phase observed. The spectra are shown in *Figure 4.5*. Raman spectra of the particles synthesized in H₂O-DMF for each precursor concentrations after 24 hr showed a major peak around 175 cm⁻¹ corresponds to the A1 mode of chalcopyrite (CH) CuInSe₂ as well as a broad peak at 225 cm⁻¹, which is attributed to the B2 mode and there are no peaks related to any impurity phases are shown.

4.3.2 CuInSe₂ synthesized in Methanol-N,N-Dimethylformamide (Me-DMF) solution

To study the effects of different solvents, methanol was used to replace water in the synthesis CuInSe₂. The synthesis route is similar to that described for H₂O-DMF system, and *Figure 4.6* shows the XRD patterns of the particles obtained

in the Me-DMF system after 24 hr and 48 hr reactions using the same precursor concentrations as in the H₂O-DMF system. All the peaks can be indexed to standard chalcopyrite phase of CuInSe₂ and the XRD patterns of the products synthesized using different reaction conditions are very similar.

Figure 4.6: XRD patterns of CuInSe₂ particles synthesized in Me-DMF for (a) 24 hr and (b) 48 hr with different precursor concentrations. The XRD spectrum of CuInSe₂ (JCPDS 40-1487) is shown for reference

Raman spectra of the samples obtained using different concentrations and after different reaction times are shown in *Figure 4.7*. Intense peak at 175 cm⁻¹ corresponds to the A1 mode of chalcopyrite (CH) CuInSe₂ and this can be seen for all the samples. The small peaks at about 213 cm⁻¹ and 225 cm⁻¹ are attributed to the B2 and E vibration mode. There are also small peaks around 260 cm⁻¹, which are responsible for the secondary Cu_{2-x}-Se phase [115]. Besides CH phase, a metastable Cu-Au (CA) phase is also easily formed. There are slightly differences of Cu-Se and In-Se bond lengths in CA phase as

compared to the CH phase, which results in the slight shift in the A1 mode to $\sim 185 \text{ cm}^{-1}$ and metasTable Cu-Au (CA) phase will affect the carrier transport and the resultant device performance [116]. When the concentration of the precursor solution increases from C1 to C3, the fraction of CA ordered phase decreases. For the 48 hr reactions, the amount of CA phase is less than that of the CH phase obtained when the reaction that has been carried out for 24 hr, indicating the transformation of metasTable CA phase to sTable CH phase at longer reaction time.

Figure 4.7: Raman spectra of as-synthesized particles using different precursor concentrations (C1, C2 and C3) in Me-DMF (a) 24 hr reaction, (b) 48 hr reaction

The B2 and E modes are less pronounced compared to the spectra from the particles synthesized in H₂O-DMF (*Figure 4.5*). This is probably due to the Raman scattering symmetry difference between CuInSe₂ crystals synthesized by Me-DMF or H₂O-DMF. In Raman, the scattering process is viewed as the

creation and annihilation of vibrational excitations by photons, so different scattering symmetry causes different vibration modes. For CuInSe₂ synthesized in Me-DMF, the intense peak is at 175 cm⁻¹ corresponding to A₁ vibration mode while a broad peak is observed at 225 cm⁻¹ for CuInSe₂ synthesized in H₂O-DMF solution, B₂ mode is more pronounced. A₁ and B₂ mode vibrations can be related to vibrational directions of the atoms (*Table 4.1*). Γ_1 and Γ_3 refers to the vibrational system of Cu^I, In^{III} and Se^{VI} atoms in the A₁ mode and B₂ mode respectively. A₁ mode relates to the vibration of Se sublattice. A pair of Se²⁻ vibrates oppositely on (100) plane. One is along the -x₃ axis and another one is along +x₄. Another pair of Se²⁻ vibrates on the opposite y₁ and -y₂. Similarly, in B₂ mode, the vibrations of cations and anions follow the resonance directions +z₁-z₂; -z₁+z₂ and +y₁ -y₂-x₃+x₄ on face (001) [117, 118].

	Cu ^I	In ^{III}	Se ^{VI}
Γ_1	0	0	+y ₁ -y ₂ -x ₃ +x ₄
Γ_3	+z ₁ -z ₂	-z ₁ +z ₂	+y ₁ -y ₂ -x ₃ +x ₄

Table 4.1: Symmetry coordinates of A₁ and B₂, Atomic positions are given as Cu^I(1)(0,0,0), Cu^I(2)(0,1/2,1/4), In^{III}(1)(0,0,-1/2), In^{III}(2)(0,1/2, -1/4), Se^{VI}(1)(-1/4,x,-1/8), Se^{VI}(2)(1/4,-x,-1/8), Se^{VI}(3)(-x,-1/4, 1/8), and Se^{VI}(4)(x,1/4, 1/8).

SEM images of the particles synthesized in Met-DMF at different precursor concentrations are shown in *Figure 4.8*. Similar to those synthesized in H₂O-DMF system, we observed that at low precursor concentration (C1), the particles are mostly spherical and the size increased for longer reactions (comparison between (a) and (d)). At higher concentration (C2), plates with dimensions up to about 500 nm began to form (*Figure 4.8 (b) and (e)*). (c) and (f) revealed that at even higher concentration (C3), large plates with diameter up to about 1 μm can be obtained. At higher concentrations - C2 and C3, the morphologies remain constant even at longer reaction time. A TEM image of CuInSe₂ sample in *Figure 4.8 (a)* is shown in *Figure 4.9 (a)*. It showed that the small particles and nanoplates are less than 100 nm in size. Lattice fringes can be observed in the HRTEM images (*Figure 4.9 (b)*) and the interplanar spacing was found to be 0.37nm which corresponds to the (112) planes of chalcopyrite CuInSe₂.

Figure 4.8: : Morphologies of CuInSe_2 synthesized using different precursor concentrations after (a)-(c): 24 hrs reaction, (d)-(f): after 48 hrs reaction. (a) & (d): C1; (b) & (e): C2 and (c) & (f): C3

Figure 4.9: (a) TEM and (b) HRTEM images of the CuInSe₂ synthesized with precursor concentration C1 in Me-DMF solution for 24hr. Inset of (b) is a fast Fourier transformation (FFT) pattern of the HRTEM image

4.3.3 Comparison between the effect of the different Solvents

As seen in the results obtained so far, the choice of solvents can affect the morphology and crystallinity of the final products. Pure CuInSe₂ particles cannot be obtained in pure DMF solvent but can be obtained in Me-DMF/H₂O-DMF mixture. Ethanol-DMF system has also been studied for the same syntheses route. However, crystalline CuInSe₂ particles cannot be synthesized using ethanol-DMF. From the thermodynamic point of view, the excess molar enthalpies (H^E) for the reaction in H₂O-DMF and Me-DMF are negative whereas it is positive in ethanol-DMF [119] [120]. Hence the reaction environment is not favorable in ethanol-DMF. Comparing *Figure 4.3* and *Figure 4.6*, CuInSe₂ particles synthesized in Me-DMF solution has less impurities and better crystallinity than CuInSe₂ particles synthesized in H₂O-DMF. Negative value of excess volumes (V^E) of Me-DMF (0.393 cm³mol⁻¹) [121, 122] is smaller than H₂O-DMF (1.063cm³ mol⁻¹) [123, 124], which means Me-DMF has a stronger miscibility than H₂O-DMF. In summary, the coordinating ability and reducing ability of Me-DMF is better than H₂O-DMF, which results in better crystallinity of the product synthesized in Me-DMF.

4.3.4 Photoresponse properties of the Nanoparticles

To understand the potential of these materials for solar energy harvesting the photoelectro-chemical property of the CuInSe₂ particles was also studied. The photocurrent measurement was carried out under 100 mWcm⁻² visible light irradiation at -0.3 V vs Ag/AgCl in a 0.1 M KPI (KH₂PO₄) aqueous solution (pH =7). *Figure 4.10* showed the photo response of CuInSe₂ particles synthesized in Me-DMF after 24 hrs of reaction at different precursor concentrations. They all show good photosensitivity and the amount of photocurrent generated is about 0.04 mAcm⁻². When the concentration increases from C1 to C3, the time needed for the current to reach saturation decreases, which may be due to the decrease of the conducting metasTable Cu-Au phase of CuInSe₂ from C1 to C3, as studied in Raman measurement. Therefore, higher precursor concentration in Me-DMF presents a better reaction condition for CuInSe₂ to be used solar energy conversion.

Figure 4.10: Photocurrent measurement for CuInSe₂ nanocrystals with different precursor concentrations(C1, C2 and C3) synthesized in Me-DMF for 24 hr

4.4 Conclusions

In this study, we have synthesized highly crystalline CuInSe₂ from selenite salts by solvothermal reactions. CuInSe₂ particles with large grain sizes can be obtained without toxic selenization process. The nature of the solvent used in the reaction can affect the crystallinity. Both Me-DMF and H₂O-DMF mixture systems are shown to promote the CuInSe₂ formation and Me-DMF system is better for getting purer CuInSe₂ products with higher crystallinity. Morphologies of the particles can be tuned by adjusting precursor concentration and reaction time. Low-cost precursors, simple processing technique and good initial photocurrent response of the particles suggested the potential in the proposed synthetic route for materials to be used in thin film solar cells.

Chapter 5 : Synthesis of $\text{CuIn}(\text{S},\text{Se})_2$

microcrystals from CuInSe_2 nanoparticles

using a two-step solvothermal reaction

5.1 Introduction

Quaternary semiconducting material, $\text{CuIn}(\text{S},\text{Se})_2$, is very similar to the ternary I-III-VI₂ compound - CuInSe_2 , with some of the Se anions replaced by S. $\text{CuIn}(\text{S},\text{Se})_2$ thin film have been synthesized by electrodeposition[125]chemical solution growth technique[126] or selenization and sulfurization of Cu and In precursor [127-130]. For the synthesis of $\text{CuIn}(\text{S},\text{Se})_2$ thin film, it is difficult to control the composition of the film as selenization and sulfurization processes cannot be done at the same time. Compared to $\text{CuIn}(\text{S},\text{Se})_2$ thin films, reports on $\text{CuIn}(\text{S},\text{Se})_2$ crystals are relatively rare. $\text{CuIn}(\text{S},\text{Se})_2$ crystals offers the advantage of being able to process using low cost solution deposition techniques, hence the study on the synthesis of these crystals is very useful. These nanocrystals have been synthesized by a range of different methods such as colloidal[131, 132], solvothermal [133] and microwave routes[134]. However, so far most of the work in this area focused on the synthesis of $\text{CuIn}(\text{S},\text{Se})_2$ nanocrystals and the electrical properties of these nanocrystals

were less explored. It is believed that physical properties of nanocrystals should be tuned accurately to improve the energy conversion efficiency of nanocrystal solar cells, and $\text{CuIn}(\text{S},\text{Se})_2$ nanocrystals may be more suitable than pure CuInS_2 or pure CuInSe_2 nanocrystals for photovoltaic application [131]. In addition, although thin film solar cells based on CuInSe_2 have been reported to achieve high efficiency up to 17%, for the cells to achieve such high efficiency, the composition has to be well tuned and there should be minimum electrical and optical losses [135]. As the optimum value of E_g is around 1.35 eV at air mass one (AM1.5), the utilization of larger bandgap of $\text{CuIn}(\text{S},\text{Se})_2$ may further improve the solar cell efficiency [136, 137]. Motivated by this advantage, $\text{CuIn}(\text{S},\text{Se})_2$ will be investigated.

As mentioned above, toxic selenization and sulfurization have to be applied for $\text{CuIn}(\text{S},\text{Se})_2$ thin film and it is difficult to control composition using both selenization and sulfurization process. On top of this, larger crystals of $\text{CuIn}(\text{S},\text{Se})_2$ is desirable as this will reduce the grain boundaries when fabricated into thin films and hence improve charge transport in such films [138]. Since currently most crystals synthesized are nanosized, synthesis methods to obtain larger size particles is very attractive. In addition, the reported work on $\text{CuIn}(\text{S},\text{Se})_2$ crystals so far make use of different sources for Cu, In, Se and S and the reaction is essentially a one pot reaction [131-134], which means that the stoichiometry control of quaternary nanocrystals is more challenging as compared to that of ternary nanocrystals as reactions can be easily suffered from some unwanted side-reactions and will yield products

containing a number of compositional phases. To address this problem, a possible way is by using the pre-synthesized ternary nanocrystals as the template to react with the selected elements to form quaternary compounds. Therefore, by using the pre-synthesized CuInSe_2 nanostructures, microcrystalline CuInSSe could be obtained. In addition, it is possible to tune the composition of these crystals and also to adjust the morphology to improve the light harvesting and charge transport properties.

5.2 Experiment Details

5.2.1 Materials

Copper(II) nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, 99.999%), indium(III) chloride ($\text{InCl}_3 \cdot x\text{H}_2\text{O}$, 99.99%), selenium dioxide (SeO_2 , 99.8%), Thioacetamide (TAA, 99.5%), sodium hydroxide (NaOH), dimethylformamide (DMF, >99%) were purchased from Sigma-Aldrich. Methanol was obtained from J.T.Baker (analytical grade). All the chemicals were used as received without any further purification.

5.2.2 Synthesis Process

$\text{CuIn}(\text{S},\text{Se})_2$ was prepared by using synthesized CuInSe_2 nanocrystals (the synthesis process was described in Chapter 4 and is considered as the first solvothermal reaction step) as precursor. Suitable amount of CuInSe_2 nanocrystals precursors from the first solvothermal reaction were dispersed in 10 ml DMF and 10 ml methanol mixture together with the addition of suitable amount of $\text{Cu}(\text{NO}_3)_2$, InCl_3 and thioacetamide (TAA) (1:1:1:2 or 1:3:3:6 mol/mol/mol/mol). Similar to the synthesis of CuInSe_2 nanocrystals, the solution was ultrasonicated for 30 mins and transferred into a 50 ml Teflon-lined stainless steel autoclave followed by the second solvothermal reaction step at 180 °C for different reaction times (2 hr, 6 hr, 18 hr and 24 hr) in an air-oven. The oven was cooled down to room temperature when the reaction finished. The solution were centrifuged and then black precipitates were

collected, washed with methanol for several times, dried and kept as the final product for further characterization.

5.2.3 Materials Characterizations

The phases and crystallographic structures of the synthesized CuInSe₂ crystals were characterized and confirmed using X-ray diffraction (XRD) and Raman spectroscopy as described in Chapter 4. The morphologies of the synthesized particles were characterized using scanning electron microscope (SEM) (JEOL JSM-7800) and transmission electron microscopy (TEM) (JEOL 2010). Samples for SEM and TEM studies were prepared by drop casting CuIn(S,Se)₂ crystals dispersed in methanol onto carbon tape for SEM study and lacey carbon-coated copper grids for TEM study. Energy dispersive X-ray spectroscopy (EDX) attached to SEM with working voltage of 20 eV was used to record the relative compositions of the as-prepared CuIn(S,Se)₂ crystals. The ultraviolet-visible/ near infra-red (UV- Vis/NIR) absorption spectrum of the CuInSe₂ and CuInSSe were obtained using a UV-Vis/NIR spectrophotometer (Shimadzu 3600). The measurement was carried out at room temperature and under ambient conditions with wavelengths ranging from 300 to 1000 nm. Photoelectrochemical measurements including electrochemical impedance spectroscopy (EIS) and photocurrent measurements were carried out to study the electrical properties of CuInSe₂ and CuIn(S,Se)₂. These measurements were done using the three-electrode electrochemical cell configuration as described in Chapter 4. Pt-gauze was used as the counter electrode and the reference electrode was Ag/AgCl. The electrolyte was 0.5M H₂SO₄ (pH=0) for EIS

measurement and KPI for the photocurrent measurement is the same as that described in Chapter 4. Working electrode was prepared by drop casting CuInSe₂ and CuIn(S,Se)₂ crystals dispersed in methanol onto FTO substrate. The exposure area of the working electrode was *ca.* 0.5 cm². The devices were illuminated by using a lamp and the flux on the device was ~ 100 mW/cm².

5.3 Results and Discussions

5.3.1 Synthesis of $\text{CuIn}(\text{S,Se})_2$ microcrystals

The synthesis route for the $\text{CuIn}(\text{S,Se})_2$ microcrystals involves a two-step method. CuInSe_2 nanocrystals are first synthesized using solvothermal method. Next, the $\text{CuIn}(\text{S,Se})_2$ microcrystals were obtained by using the synthesized CuInSe_2 nanocrystals as the “growing seeds” and $\text{Cu}(\text{NO}_3)_2$, $\text{In}_2(\text{NO}_3)_3$ and thioacetic acid (TAA) (1:1:1:2 mol/mol/mol/mol) as the precursor sources. The mixture is allowed to react in an autoclave for different times.

Figure 5.1 shows the XRD patterns collected for CuInSe_2 nanoparticles synthesized in the first solvothermal step at 180 °C and $\text{CuIn}(\text{S,Se})_2$ microcrystals from the second step solvothermal reaction at 180°C. They are compared to the standards for CuInSe_2 (JCPDS 40-1487) and CuInS_2 (JCPDS 47-1372). Comparing the diffraction patterns for samples obtained in the first and second step synthesis, all the peaks for the sample obtained after the second-step solvothermal reaction were shifted to higher 2θ angles due the replacement of the larger selenium atoms with smaller sulfur atoms. The peaks of the final products lie between that for chalcopyrite CuInSe_2 (JCPDS 40-1487) and CuInS_2 (JCPDS 47-1372), confirming that the particles obtained after the second solvothermal process correspond to chalcopyrite phase of $\text{CuIn}(\text{S,Se})_2$.

Figure 5.1: XRD patterns of CuInSe₂ and CuInSSe after first and second step of solvothermal reaction and also the standard for CuInS₂ (JCPDS 40-1487) and CuInSe₂ (JCPDS 40-1372).

To elucidate the morphology of the particles obtained after the second solvothermal reaction, the particles were studied using TEM. From *Figure 5.2(a)*, it can be observed that the particles are essentially thin microsheets of CuIn(S,Se)₂ with size larger than 1 μm . The HRTEM image is shown in *Figure 5.2b* and the lattice fringes can be observed with spacings of 0.34 nm that correspond to the (112) planes of CuIn(S,Se)₂. The select area electron diffraction pattern (SAED) (inset of *Figure 5.2b*) of the nanocrystals shows a single set of diffraction spots indexed to the (112) planes, indicating the synthesized CuIn(S,Se)₂ microsheets were single crystals. SEM image of CuIn(S,Se)₂ is shown in *Figure 5.3(a)*, showing the microsheets stacked together and appear as microplates. STEM EDX maps of the particles are

shown in *Figure 5.3(e)-(f)* for the microcrystal shown in *Figure 5.3(b)*, proving that all the elements are uniformly distributed within one $\text{CuIn}(\text{S,Se})_2$ microcrystal.

Figure 5.2: TEM image of synthesized CuInSSe after second step of solvothermal reaction

Figure 5.3: (a) SEM image of synthesized CuInSSe microcrystals and (c)-(f) STEM EDX mapping of CuInSSe as shown in (b) indicating presence of Cu, In, Se and S.

Figure 5.4: Plot of $(\alpha h\nu)^2$ with photon energy ($h\nu$) for measurements of band gaps of (a) CuInSe₂ and (b) CuInSSe synthesized after first and second step solvothermal reactions respectively

UV-Vis spectroscopy was used to characterize the optical absorption properties of CuInSe₂ and CuIn(S,Se)₂ synthesized in the first and second solvothermal reactions. *Figure 5.4(a)* shows the absorption spectra of CuInSe₂ and CuIn(S,Se)₂ particles in methanol. Both samples have strong absorption in the visible range extending to the infrared range. The absorption properties can depend on crystallinity, the composition and stoichiometry of the phases [134, 139, 140]. In our study, the change in absorption spectra can be attributed to the composition changes. With the presence of sulfur, as the Cu/In-S bonds are shorter than Cu/In-Se bonds, therefore anti-bonding state of S 3s shifted to a higher energy, which results in a blue shift in the absorption spectrum and a higher bandgap [141].

The relationship between the absorption coefficient (α) near the absorption edge and the optical band gap (E_g) follows the Stern relationship [142] [143]:

$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where A is a constant, $h\nu$ is the photon energy, exponent n depends on the type of transition, and $n = 1/2$ for direct transition. Since $\text{CuIn}(\text{S,Se})_2$ are direct band gap semiconductors, the direct optical band gap of the mixture phases can be deduced from the extrapolation of the linear portion of the plots of $(\alpha h\nu)^2$ vs. $h\nu$ to $\alpha=0$.

Therefore, the band gaps of CuInSe_2 and $\text{CuIn}(\text{S,Se})_2$ were obtained by extrapolating the slope of the plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$), which is shown in *Figure 5.4(b)*. The calculated band gap of CuInSe_2 and $\text{CuIn}(\text{S,Se})_2$ are ~1.25eV and ~1.35eV respectively, which correspond to the expected band gap energy ranging from 0.99eV to 1.5eV for $\text{CuIn}(\text{S,Se})_2$ materials [144-146] making these materials suitable for thin film solar cell applications.

5.3.2 Understanding the transformation mechanism from CuInSe_2 nanocrystals to $\text{CuIn}(\text{S,Se})_2$ microcrystals

The shape, size, composition and structure of the nanocrystals play important roles in the performance of the nanocrystal-based solar cells and these properties can be controlled by the nucleation and growth processes occurring during the synthesis [147].

Nucleation can occur either homogeneously or heterogeneously. In either case, if the size of the nucleus is too small, the surface energy will render it unstable and it will dissolve rather than grow. A critical size is required before a nucleus becomes stable enough to grow. Therefore, to some extent, the probability of nucleation is strongly dependent on the nucleus ability to reach the critical size.

In the presence of a seed crystal, the growth kinetics is significantly affected by the attachment and detachment processes of molecules on the crystal surface, which is determined by the chemical bonding between molecules on the surface of the crystals, the solution environment and the reaction time. The strength of bonding is a function of temperature and solvent structure. The solvent structure can be influenced by many factors, such as solution composition, pH values and ionic strength [148].

Since the particles properties are strongly influenced by nucleation and growth processes, it is important to have a good understanding of the reaction mechanism. To understand the transformation of CuInSe₂ nanoparticles to microcrystals, different reaction times i.e. 2hrs, 6hrs, 18hrs and 24hrs were used for the second step solvothermal reaction and the development of the crystals was investigated. The samples obtained after different reaction times were collected and characterized using XRD. From the XRD patterns shown in *Figure 5.5*, it can be observed that when the reaction time is 2hrs, CuIn(S,Se)₂ peaks were barely observed. When the reaction time was increased to 6hrs, CuIn(S,Se)₂ were observed and final products were mixtures of CuInSe₂ and

$\text{CuIn}(\text{S},\text{Se})_2$ and no CuInS_2 was present. *Figure 5.6* presents the rietveld refinement of the XRD spectrum of 2hr, 6hr and 18hr reactions with mixture of CuInSe_2 and $\text{CuIn}(\text{S},\text{Se})_2$. With the further increase of reaction time (18hr), the amount of $\text{CuIn}(\text{S},\text{Se})_2$ in the final product mixture increased. Finally, a single phase of $\text{CuIn}(\text{S},\text{Se})_2$ could be obtained for the 24hrs reaction. The grey lines shown in (a), (b) and (c) represent the difference in the profiles between the measured (blue) and the calculated (red) spectrum and the phase fraction of CuInSe_2 and $\text{CuIn}(\text{S},\text{Se})_2$ can be deduced based on this fitting. With increase in reaction time, the phase fraction of $\text{CuIn}(\text{S},\text{Se})_2$ increases while the fraction of CuInSe_2 decreases.

TEM micrographs for samples obtained after 18hrs reaction are shown in *Figure 5.7*. As discussed earlier for the XRD data, the samples obtained at this time is made up of CuInSe_2 and some CuInSSe microcrystals. The HRTEM image showed two sets of spacing, which relate to CuInSSe (0.32nm~0.33nm) and CuInSe_2 (0.38~0.39nm), confirming that the sample is a mixture of $\text{CuIn}(\text{S},\text{Se})_2$ and CuInSe_2 . Energy dispersive X-ray (EDX) maps of copper (Cu), indium (In), sulfur (S) and selenium (Se) was collected for the microcrystal shown in *Figure 5.7(a)*. From *Figure 5.7(c)-(f)*, it is observed that copper, indium and selenium is distributed uniformly in the whole particle, while sulfur are mostly detected on the outside of the particle, similar to a core-shell structure. This is consistent with the HRTEM observation (*Figure 5.7(b)*) that both CuInSe_2 and $\text{CuIn}(\text{S},\text{Se})_2$ were present within one crystal. In this second-step solvothermal reaction, CuInSe_2 acts like a growing seed, CuInS_2

begins to nucleate and grow from the outside part of the CuInSe₂ with excess Cu²⁺, In³⁺ and S²⁻ around the CuInSe₂. Gradually the whole CuInSe₂ transforms to single phase CuIn(S,Se)₂ and grows into microcrystal with increase in reaction time. According to the above observations, we proposed a mechanism of the transformation from CuInSe₂ nanocrystals to CuIn(S,Se)₂ microcrystals as illustrated in *Figure 5.8* as following: .

where there are some soluble by-products inside the solvents.

Figure 5.5: XRD spectra of products synthesized with different reaction times (2hrs, 6hrs, 18hrs and 24hrs) with the reference spectra of CuInS₂ (JCPDS 47-1372) and CuInSe₂(JCPDS 40-1487)

Figure 5.6: Refinement of final products after 2hr, 6hr and 18hr of two- step solvothermal reaction for reaction I

Figure 5.7: TEM image (a), HRTEM image (b) and TEM elemental mapping (c-f) of products from 12hrs reaction

Figure 5.8: Growth of microcrystal CuInSSe from CuInSe₂ nanoparticles

5.3.3 Investigation on the photochemistry of micro-grain CuIn(S,Se)₂ crystals

5.3.3.1 Electrochemical impedance Spectroscopy (EIS) studies

Electrochemical impedance Spectroscopy (EIS) analysis provides information about the electronic properties of the materials. These properties are important to evaluate the applicability the absorber materials for the PV application. The information that can be obtained from EIS analysis are the type of carriers in

the semiconductor materials, its majority charge carrier density (n_d), space-charge capacitance (C_{sc}) and Fermi level ($E_{F,sc}$, identified as the flatband potential, V_{FB} , in the dark) from equations 1 and 2 listed in *Table 5.1*, where ϵ_0 is the vacuum permittivity and ϵ_r is the relative permittivity of CIGS (~ 11), e is electron charge and A is the surface area which is electrochemically active ($\sim 4\text{cm}^2$), k is the Boltzmann constant and T is the absolute temperature (295K) [149]. Measurements were carried out using a three-electrodes set-up as shown in *Figure 5.9*. Working electrodes were obtained by drop-casting CuInSe₂ and CuInSSe particles on FTO and then annealed at 200°C for 1hr in Ar environment. Ag/AgCl was used as the reference electrode, Pt was used as the counter electrode and the electrolyte used is 0.5M H₂SO₄ [150]. The measurements were done in the dark at room temperature. It is believed that measurements conducted at high frequencies minimized the effects of surface states which is caused by surface defects and absorbed ions from the electrolyte [149]. Hence using a high frequency scan, i.e. 30k Hz, According to *equation 1*, Mott-Schottky plots were obtained for both CuInSe₂ and CuIn(S,Se)₂, and they are shown in *Figure 5.10*. The linear region in Mott-Schottky plots determined the voltage range [151].

The negative slopes of the curves between 0.1eV to 0.5eV of both Mott-Schottky plots indicate these materials to be p-type semiconductor. Carrier concentrations are important parameter in the evaluation of device performance[138]. According to the *equation 2* listed in *Table 5.1*, carrier concentrations for CuInSe₂ and CuIn(S,Se)₂ are found to be $3.1 \times 10^{16} \text{ cm}^{-3}$ and

$5.3 \times 10^{16} \text{ cm}^{-3}$ respectively, which are calculated from the slope of straight lines at $1/C_{sc}^2$. These values are within the range for high efficiency CIGS solar cells [138, 152]. According to the intercept of the straight line at $V=0$, the flat band potentials for CuInSe₂ and CuInSSe are -0.36V vs NHE and -0.62V vs NHE respectively. As the Fermi level of the semiconductor equals to the flat band potential in the dark, the Fermi levels $E_{F,sc}$ for CuInSe₂ and CuInSSe are -4.14eV and -3.88eV respectively and these values are very close to the reported values [149, 150].

Equation 1	$C_{sc} = \frac{1}{42\pi f Z_{im} }$
Equation 2	$\frac{1}{C_{sc}^2} (F^{-2}) = \left(\frac{2}{e\epsilon_r\epsilon_0 n_d A^2} \right) \left(V - V_{fb} - \frac{kT}{e} \right)$

Table 5.1: Equations for EIS measurement

Figure 5.9: Set-up for EIS measurement

Figure 5.10: Mott-Schottky plots obtained of CuInSe_2 and Cu^{2+} , In^{3+} and S^{2-} in the precursor solution and CuInSe_2 working electrode immersed in 0.5M H_2SO_4

5.3.3.2 Photoresponse properties

To investigate the potential of these materials for solar energy harvesting, the photo-response property of synthesized $\text{CuIn}(\text{S},\text{Se})_2$ microcrystal synthesized using two-step solvothermal reaction in Me-DMF for 24 hrs was studied. The photocurrent measurement was carried out under 100 mWcm^{-2} visible light irradiation at -0.3 V vs Ag/AgCl in a 0.1 M KPI (KH_2PO_4) aqueous solution ($\text{pH}=7$). *Figure 5.11* showed the photo response of CuInSSe microcrystals and the inset showed the I-V behaviour under dark and light conditions. Good photo response was demonstrated when the light was switched on, suggesting its good photosensitivity and its potential to be applied in a solar device.

Figure 5.11: Photocurrent measurement for CuInSSe microcrystals with irradiation of 150 mW cm^{-2} visible light in 0.1 M KPI solution

5.3.4 Composition-mediated band gap tuning

For large $\text{CuInS}_{1-x}\text{Se}_x$ grains, selenization and sulfurization process are normally essential to incorporate sulfur or selenium. The main challenge for

this approach is that the sulfur to selenium ratio is difficult to control using selenization or sulfurization process. However, in our two-step solvothermal synthesis, the composition of selenium to sulfur can be controlled in the second solvothermal reaction by varying the amount of CuInSe_2 and Cu^{2+} , In^{3+} and S^{2-} in the precursor solution, so as to realize the composition-mediated band gap tuning. *Figure 5.12 (a)* shows the XRD spectra for the two different compositions of $\text{CuInS}_{1-x}\text{Se}_x$ ($x=0.5$ and $x=0.25$). Looking at the (112) diffraction peak from the two samples with different selenium to sulfur ratios, the (112) peak shows a slight shift to a higher degree of 2θ with increased amount of sulfur, which is as expected due to the smaller atomic size of sulfur relative to selenium. The Raman spectra in *Figure 5.12(b)* reveal that the vibration modes of both synthesized $\text{CuInS}_{1-x}\text{Se}_x$ ($x=0.5$ and $x=0.25$) are related to the A1 mode for CuInSe_2 and CuInS_2 as described in literature [153]. The peaks between 175cm^{-1} and 188cm^{-1} are related to the A1 optical phonon mode of CuInSe_2 , which is attributed to the symmetric vibration of Se atoms in c plane. The peaks between 290cm^{-1} and 305cm^{-1} are related to the A1 optical phonon mode of CuInS_2 , which is a vibrational mode that involves the displacement of only anions in the lattice in an anti-phase motion following the X–Y crystallographic directions of the crystal, while cations remain at rest. This feature makes this band extremely sensitive to variations in the chemical and/or physical structure of the crystal [154]. For chalcopyrite materials, the A1 symmetry mode usually gives the intense and dominant peak in the scattering spectrum and it provides the characteristics of the materials.

Using Raman spectroscopy, it is possible to carried out both qualitative (as discussed previously) and quantitative evaluations of the phases and the chemical environment of the samples. Quantitative analysis of a mixture is typically performed by measuring the relative intensities of bands that are directly proportional to the relative concentrations of the compounds. In this work, with more sulfur ($x=0.25$), the peak corresponding to the A1 mode of CuInS_2 has a higher intensity as compared to the peak corresponding to the A1 mode of CuInSe_2 , which is as expected.

The various compositions of $\text{CuInS}_{1-x}\text{Se}_x$ ($x=0.5$ and $x=0.25$) were confirmed using EDX and the EDX spectra are shown in *Figure 5.13(a)* and *(b)* for $x=0.5$ and $x=0.25$ respectively and the compositions are shown in *Figure 5.13(c)*.

UV-Vis absorption spectra for $\text{CuInS}_x\text{Se}_{(1-x)}$ with $x=0.25$ and $x=0.5$ are shown in *Figure 5.14(a)*. Both samples have strong absorption in the visible range extending to the infrared regime. Red shift is observed in the spectrum with increasing sulfur content. As discussed previously in our study, the change in absorption spectra should be attributed to the composition changes. With more presence of sulfur, the absorption spectrum shows a blue shift.

In addition, as the direct optical band gap of the mixture phases can be deduced from the extrapolation of the linear portion of the plots of $(\alpha h\nu)^2$ vs. $h\nu$ to $\alpha=0$ [143] and the band gaps of $\text{CuInS}_x\text{Se}_{(1-x)}$ with different x are obtained from plots shown in *Figure 5.14(b)*. When x changes from 0.25 to 0.5, the band gap increased from 1.35eV to 1.45eV.

Figure 5.12: Characterizations of $\text{CuInS}_x\text{Se}_{(1-x)}$ microparticles synthesized with different Se/S compositions: (a) XRD spectra with inset of an expanded view of (112) peaks and (b) Raman spectra

Figure 5.13: EDX spectrum of final $\text{CuIn}(\text{S}_{1-x}\text{Se}_x)_2$ when (a) $x=0.25$ and (b) $x=0.5$, and the compositions are shown in (c)

Figure 5.14: (a) Room temperature UV-Vis spectra and (b) Plot of $(\alpha h\nu)^2$ with photon energy ($h\nu$) for measurements of band gaps of $\text{CuInS}_x\text{Se}_{(1-x)}$ with $x=0.25$ and $x=0.5$ respectively

5.3.5 Effects of precursors on formation for $\text{CuIn}(\text{S},\text{Se})_2$

Besides using CuInSe_2 nanoparticles for the synthesis of $\text{CuIn}(\text{S},\text{Se})_2$, alternative pathways have also been pursued to evaluate the differences in the reaction. The synthesis using CuInSe_2 nanoparticles is named as reaction I for comparison. The alternative precursors are proposed in reaction II and III as shown in *Figure 5.15* and the details of reaction I, II and III are shown below:

Reaction I was the synthesis carried out for $\text{CuIn}(\text{S},\text{Se})_2$ microcrystals, in which CuInSe_2 nanoparticles were synthesized in the first step of solvothermal reaction and was used together with $\text{Cu}(\text{NO}_3)_2$, InCl_3 and TAA to form $\text{CuIn}(\text{S},\text{Se})_2$ microcrystals in a second solvothermal reaction.

Reaction II made use of CuSeO_3 and $\text{In}_2(\text{SeO}_3)_3$, which were the materials to synthesize CuInSe_2 nanocrystals in the first step of solvothermal reaction. They

were used together with $\text{Cu}(\text{NO}_3)_2$, InCl_3 and TAA in a solvothermal reaction with the same reaction time and temperature as Reaction I.

Reaction III made use of $\text{Cu}(\text{NO}_3)_2$, InCl_3 and SeO_2 , which were the materials to synthesize CuSeO_3 and $\text{In}_2(\text{SeO}_3)_3$. They were used with TAA in a solvothermal reaction with the same reaction time and temperature as Reaction I and II.

As described above, for reaction I, II and III, the solvothermal reaction time and temperature were kept constant. The only difference was the source for “selenium”. The selenium source can determine the reaction speed and hence this comparison helped to study the nucleation and growth of CuInSe_2 nanoparticles into micro-sized $\text{CuIn}(\text{S,Se})_2$ grains.

All the characterizations for reaction I were described in the previous section 5.3.1 and *Figure 5.16 (a)* and *Figure 5.16 (b)* show the XRD and SEM of the final products from reaction II. One can see that the final products are made up of a mixture of two $\text{CuIn}(\text{S,Se})_2$ phases with different S/Se compositions and poor crystallinity. The SEM image showed that the particles are less than 500 nm in size and the shapes are similar to the starting precursors CuSeO_3 and $\text{In}_2(\text{SeO}_3)_3$, which were discussed in the previous chapter. In this synthesis route, the formation of CuInSe_2 from CuSeO_3 and $\text{In}_2(\text{SeO}_3)_3$ and the formation of CuInSSe from CuInSe_2 and S^{2-} happened at the same time, and since these two reactions have different nucleation and growth rate in the solvent, therefore different phases of $\text{CuIn}(\text{S,Se})_2$ are formed.

Figure 5.17 (a) and (b) show the XRD patterns for various reaction times and SEM images of the final products from reaction III. With the increase in reaction time, the final products change from CuInSe_2 to $\text{CuIn}(\text{S},\text{Se})_2$. This indicates that nucleation rate of selenide is faster than sulfide as only CuInSe_2 was formed with shorter reaction time. Unlike route I, there is no indication of nucleation of CuInS_2 , and that CuInSe_2 behaves like a nucleation site and reacts with S^{2-} forming $\text{CuIn}(\text{S},\text{Se})_2$. However, by synthesis route III, the morphologies of the obtained $\text{CuIn}(\text{S},\text{Se})_2$ are microsphere formed by aggregation of nanoplates. The driving force for this agglomeration of nanoplates to microsphere is still unclear at this moment, but the chemical reaction environment for both reaction I and III are quite different and the presence of sulfur can result in the formation of two dimensional nanoplates.

Figure 5.15: The proposed synthesis routes for the synthesis of CuInSSe with different selenium source

Figure 5.16: (a) XRD and (b) SEM of final products from synthesis route II with CuInS_2 (JCPDS 40-1487) and CuInSe_2 (JCPDS 40-1372) as the reference.

Figure 5.17: (a) XRD of final products from synthesis route III at different reaction times and (b) SEM of final products from synthesis route III for 24hrs with CuInS_2 (JCPDS 40-1487) and CuInSe_2 (JCPDS 40-1372) as the reference.

5.4: Development of $\text{CuIn}(\text{S},\text{Se})_2$ solar cell

As discussed above in chapter 3, low efficiency solar cell was obtained by using CuInS_2 thin film absorber, which was probably the result of poor grain growth. Therefore, large grain crystals were then favored for a better solar cell performance as discussed in chapter 4 and 5. However, solar cells with pure crystals suffer from the difficulty to obtain a dense film, especially crystals from solvothermal reaction, as they tend to have agglomerated morphologies and non-uniform size distribution, which is probably due to the non-uniform formation of nuclei upon the heating treatment, which also makes them hard to form stable crystal inks for deposition of device quality film [63, 85, 118, 119]. Therefore, we propose a solar cell to incorporate both thin film and crystals as the absorber to achieve an absorber with large grains and the prevention of shunting.

Precursor I (CuInS_2) precursor was prepared as described in chapter 3 and the precursor was deposited onto the Mo substrate by drop casting. The Cu-In-S film was then annealed in the furnace at 530°C for 1hr with the continuous flow of Ar at 10ccm, forming CuInS_2 thin film. Precursor II was prepared by dissolving 10mg CuInSSe crystals in 1ml precursor I and ultrasonic for 10min. Precursor II was then deposited onto CuInS_2 by drop casting and annealed at 50°C for 1hr in open air. Subsequently, another layer of precursor I was deposited on to it. Lastly, the whole film was again annealed in furnace at

530°C for 1hr forming the final absorber layer. The device structure is illustrated in *Figure 5.18*.

Figure 5.18: Device structure of $\text{CuIn}(\text{S},\text{Se})_2$ solar cell

The I-V curve of this device is shown in *Figure 5.19*. The efficiency of this solar cell is 1.25% with $V_{oc}=0.35\text{V}$, $\text{FF}=32.35\%$, $J_{sc}=12.42\text{mA}/\text{cm}^2$, $R_{sh}=422.87\text{ohm}$, and $R_s=481.68\text{ohm}$.

Figure 5.19: I-V performance for $\text{CuIn}(\text{S},\text{Se})_2$ solar cell

Comparing these values with the ones for CuInS₂ thin film solar cell discussed in Chapter 3, as shown in *Table 5.2*, we can see that the CuInSSe solar cell has higher Voc and Jsc, and similar FF. The increase of Voc and Jsc may due to the larger grain size of CuInSSe particles compared to CuInS₂ thin film, which can form better p-n junction and have less recombination. However, compared to CuInS₂ thin film solar cell, this CuInSSe solar cell doesn't have an improvement on FF, which may due to the much larger thickness of CuInSSe absorber, which can also affect the Rs and FF.

	V_{oc} (V)	FF(%)	J_{sc}(mA/cm²)	R_{sh}(Ω)	R_s(Ω)	Efficiency
CuInS₂	0.18	33.85	6.42	465.59	235.21	0.6
CuIn(S,Se)₂	0.35	33.25	12.42	422.87	481.68	1.25

Table 5.2: Comparison of solar cell performance made from CuInS₂ and CuIn(S,Se)₂

5.5 Conclusions

In this study, we introduced a two-step solvothermal reaction to synthesize highly crystalline $\text{CuIn}(\text{S},\text{Se})_2$ microcrystals from CuInSe_2 nanocrystals. Micron sized $\text{CuIn}(\text{S},\text{Se})_2$ particles can be obtained without toxic selenization or sulfurization process and the composition of sulfur and selenium can be easily controlled by varying the amount of precursor in separate steps of reactions. Low-cost precursors, simple and non-toxic technique, possibility to tune the composition and good initial photocurrent response suggest that this proposed synthetic route is highly promising for the preparation of thin film solar cells. This new synthetic methodology also provides a new insight into formation of microcrystals using nanocrystals as growing seeds.

Chapter 6 : Conclusions and Scientific Contributions

6.1: Overall Summary

Cu(In,Ga)(S,Se)_2 thin film solar cells have been widely studied because of their high optical absorption coefficient, suitable band gap for harvesting a wide range of visible light from the sun as well as some unique electrical and optical properties. Compared to conventional vacuum based synthesis, solution based synthesis of CuIn(S,Se)_2 have attracted much interests as the processing cost could be lowered significantly. In solution based synthesis, selenization and/or sulfurization process is usually needed for incorporation of Se/S and most importantly, to increase crystallinity and encourage grain growth as it is believed that larger grain size is better for device performance. However, selenization and sulfurization processes are toxic and special processing systems are needed for safety issues. To address such issues to increase grain size and in order to avoid toxic selenization and sulfurization process, in this thesis, we have synthesized CuIn(S,Se)_2 thin films as well as CuIn(S,Se)_2 crystals without toxic selenization or sulfurization.

In the work of CuIn(S,Se)_2 thin films synthesis, CuInS_2 , CuInSe_2 and CuInSSe thin films were successfully synthesized without any selenization/sulfurization

process. $\text{Cu}(\text{acac})_2$, $\text{In}(\text{acac})_3$ and sulfur powder were used as the precursor and they formed cross-linkings in the pyridine solvent. By studying the annealing temperature and time, it was found that CuInS_2 , CuInSe_2 and CuInSSe thin films could be formed when temperature is above 350°C and no secondary phase was founded by Raman measurement. Crystallinity and grain size of CuInS_2 , CuInSe_2 and CuInSSe thin films could be improved with the increase of annealing time and temperature. CuInS_2 thin film was used as the absorber layer for the demonstration of solar cell and 0.6% efficiency was achieved. Although the efficiency is comparable to the literature, it is still quite low compared to the solar cells with selenization/sulfurization treatment. The V_{oc} is especially low and therefore pump probe measurement was carried out to study the carrier lifetime. It was found that carrier lifetime of CuInS_2 thin film is quite low, which could result from small grain sizes that can cause recombination at the defects sites, grain boundaries, which subsequently results in low V_{oc} and bad solar cell performance.

As the grain size of $\text{CuIn}(\text{S,Se})_2$ thin films are relatively small, $\text{CuIn}(\text{S,Se})_2$ crystals were synthesized for better device performance. CuInSe_2 was first synthesized by solvothermal reaction. Metal-selenite salts were used as the precursor at the first time and two solvents mixture were used. In each solvents mixture, three different precursor concentrations were used with reaction time of either 24hr or 48hrs. For both solvent mixtures, CuInSe_2 could be formed. However, CuInSe_2 formed in Me-DMF has a better crystallinity. In addition, some impurities were also formed when H_2O -DMF is used as the solvent.

Morphologies could be tuned by varying the precursor concentrations and reaction times. The Raman spectrum of CuInSe₂ synthesized in H₂O-DMF shows A1 and B2 vibration modes and the Raman spectrum of CuInSe₂ synthesized in Me-DMF shows A1 mode as well as CA phase. The CA phase is believed to affect the solar cell performance and the amount of CA phase decreases with increase of precursor concentrations. This is in agreeing with the photocurrent measurement, that for the CuInSe₂ with less CA phase, better photocurrent performance was observed.

CuIn(S,Se)₂ microcrystals were formed in a 2-step solvothermal reaction by using synthesized CuInSe₂ nanocrystals as the growing seeds. Crystalline CuInSSe microplates with no impurities were formed with uniform composition within the crystal. The reaction mechanism of formation of CuIn(S,Se)₂ from CuInSe₂ was investigated by XRD, Rietveld refinement and TEM mapping. It was found that during the formation of CuIn(S,Se)₂, no CuInS₂ was formed, instead, CuInSe₂ nanocrystals acted like growing seeds and CuInSSe were formed around CuInSe₂ and then grow to a micro crystal. This 2-step solvothermal synthesis route also enables the composition control of S and Se could be achieved. Photochemical measurement was carried out on both CuInSe₂ nanocrystals and CuInSSe microcrystals and the CuInSSe microcrystals show better photochemical properties. A solar cell device was demonstrated by using both CuInS₂ thin films and CuInSSe microcrystals as the absorber materials and the solar cell power efficiency was much improved compared to solar cell with only CuInS₂ thin film as the absorber material. Our

selenization /sulfurization- free synthesis and fabrication process of micro-grain $\text{CuIn}(\text{S},\text{Se})_2$ suggests a promising potential for the future solar harvesting applications.

6.2 Scientific Contributions

1. Selenization/sulfurization process is usually needed for selenium and/or sulfur incorporation and increase of crystallinity and grain size. This work demonstrates growth mechanism of micro-grain $\text{CuIn}(\text{S},\text{Se})_2$ crystals without selenization/sulfurization by using CuInSe_2 nano-crystals as growing seeds.
2. Selenite salts have been used as the precursor for the first time for synthesis of $\text{CuIn}(\text{S},\text{Se})_2$ crystals in solvothermal reaction for selenium incorporation.
3. Detailed morphology and composition control of $\text{CuIn}(\text{S},\text{Se})_2$ thin films as well as $\text{CuIn}(\text{S},\text{Se})_2$ crystals by varying reaction conditions have been elaborated.
4. Carrier dynamics and photophysical nature of $\text{CuIn}(\text{S},\text{Se})_2$ thin films as well as $\text{CuIn}(\text{S},\text{Se})_2$ crystals have been investigated and the importance of micro-crystals on solar cells have been demonstrated.
5. The possibility of selenization/sulfurization-free solar cells have been elaborated by the demonstration of $\text{CuIn}(\text{S},\text{Se})_2$ solar cell using CuInS_2 thin film as well as $\text{CuIn}(\text{S},\text{Se})_2$ microcrystals as absorber materials.

6.3 Future Directions

The research findings and analysis described in this thesis led to a good understanding of reaction mechanism of micro-grain $\text{CuIn}(\text{S},\text{Se})_2$ without selenization and/or sulfurization . This work investigated crystallo-chemical properties of synthesized $\text{CuIn}(\text{S},\text{Se})_2$ thin films as well as $\text{CuIn}(\text{S},\text{Se})_2$ crystals. In addition, the work demonstrates the potential of selenization/sulfurization free $\text{CuIn}(\text{S},\text{Se})_2$ solar cells. However, there are still some questions and issues remained to be answered and further explored, such as:

1. To further understand the carrier transport mechanism of CuInSe_2 nanocrystals and $\text{CuIn}(\text{S},\text{Se})_2$ microcrystals. Further investigations could be done on the effects of the grain size as well as composition on the charge transport and optical-electrical properties. To achieve this, simulation modeling such as Monte Carlo Modeling (MCM) could be carried out.
2. To further improve efficiency of selenization/sulfurization free $\text{CuIn}(\text{S},\text{Se})_2$ solar cells by investigation on the effects of materials and fabrication process techniques on the solar cell performance.

3. Explore the possibility of single crystal solar cell by using micro-grain $\text{CuIn}(\text{S},\text{Se})_2$. The proposed works include further increasing the grain size and establishing suitable device structure.

6.4 Publications

1. Mengxi Wang, Sudip K. Batabyal, Zhenggang Li, Dehui Li, Subodh G. Mhaisalkar and Yeng Ming Lam, *Nanocrystalline Copper Indium Selenide (CuInSe_2) for Solar Energy Harvesting*, *RSC Adv.*, 2013,3, 9829-9834
2. Mengxi Wang, Sudip K. Batabyal, Zhenggang Li, Huimin Lim, Subodh G. Mhaisalkar and Yeng Ming Lam, *Formation of $\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$ microcrystals from CuInSe_2 nanoparticles by two step solvothermal method*, *J Alloys Compd* (Accepted)
3. Mengxi Wang, Sudip K. Batabyal and Yeng Ming Lam, Synthesis of CuInS_2 thin film solar cell by the application of vulcanization of precursor (In preparation)

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