Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2011, Article ID 801292, 10 pages
doi:10.1155/2011/801292

Review Article

Progress in Thin Film Solar Cells Based on Cu_2ZnSnS_4

Hongxia Wang

School of Engineering System, Queensland University of Technology, Brisbane, QLD 4001, Australia

Correspondence should be addressed to Hongxia Wang, hxwang04@yahoo.com.cn

Received 1 June 2011; Accepted 1 July 2011

Academic Editor: Leonardo Palmisano

The research in thin film solar cells has been dominated by light absorber materials based on CdTe and $Cu(In,Ga)Se_2$ (CIGS) in the last several decades. The concerns of environment impact of cadmium and the limited availability of indium in those materials have driven the research towards developing new substitute light absorbers made from earth abundant, environment benign materials. Cu_2ZnSnS_4 (CZTS) semiconductor material has emerged as one of the most promising candidates for this aim and has attracted considerable interest recently. Significant progress in this relatively new research area has been achieved in the last three years. Over 130 papers on CZTS have been published since 2007, and the majority of them are on the preparation of CZTS thin films by different methods. This paper, will review the wide range of techniques that have been used to deposit CZTS semiconductor thin films. The performance of the thin film solar cells using the CZTS material will also be discussed.

1. Introduction

Thin film solar cells based on polycrystalline cadmium telluride (CdTe), copper indium diselenide (CIS), and copper indium (gallium) diselenide (CIGS) have reached the commercialization stage; however, restrictions on heavy metal usage for Cd and limitations in supply for In and Te have raised concern about limitations on production capacity of the PV devices. To solve this issue, it is necessary to develop alternative light absorber materials that are both nontoxic and easily available. In this context, Cu_2ZnSnS_4 (CZTS) quaternary semiconductor compound has emerged as one of the promising candidates. All the constitute elements in CZTS are earth abundant and environment benign. Figure 1 illustrates the earth crust content and the current world trading price of the elements used in CZTS and CIS as well as CdTe light absorbers (logarithmic scale is used for clarity). It is found that the abundance of Zn and Sn in earth's crust is 1500 times and 45 times greater than that of In, respectively, and the price of In is almost two orders of magnitude higher than that of Zn and Sn.

2. Basic Information on CZTS Compound and Solar Cells

CZTS is a mineral which has been found in nature [1]. It shares similar structure with the chalcopyrite material $CuInS_2$ except that half of the In is replaced with Zn and another half with Sn. Crystallographically speaking, CZTS has two principal structures known as stannite-type (space group $I\bar{4}2$ m) and kesterite-type (space type $I\bar{4}$). The two structures are similar except the different arrangement of Cu and Zn atoms [2]. However, CZTS material usually appears in kesterite phase because it is more stable thermodynamically compared to the stannite-type [2]. CZTS can be synthesized through solid state chemical reactions between ZnS, Cu_2S, and SnS_2. The investigation on the phase diagram of the system has shown that a single-phase CZTS material can be formed only in a very small region (Figure 2) [3]. Impurities including ternary and quaternary compounds are easier to form than CZTS. Therefore, it is very challenging to make pure CZTS crystals.

Limited reports on the assessment of the photovoltaic performance of CZTS-based thin film solar cells normally

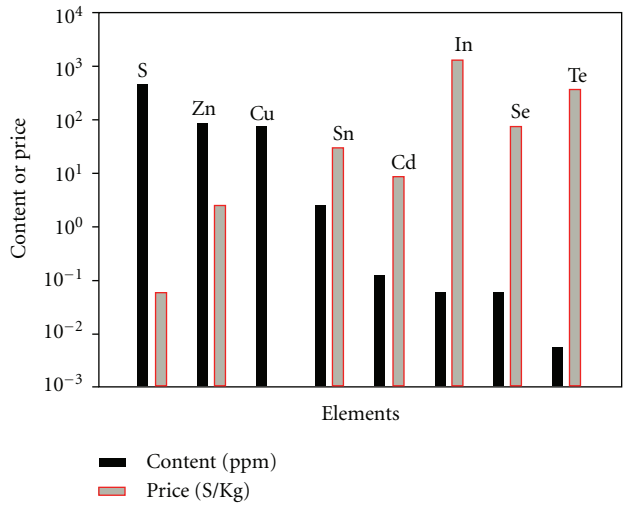

Figure 1: Content and the world trading price of the elements used in light absorbers CdTe, Cu_2ZnSnS_4, $CuInSe_2$ for thin film solar cells.

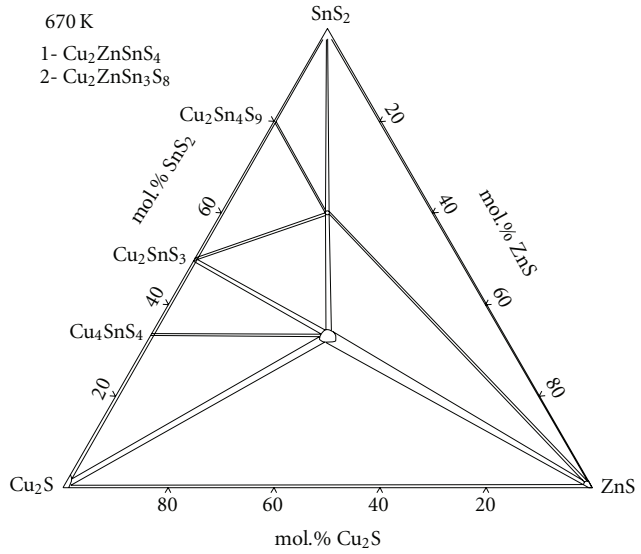

Figure 2: Phase diagram of SnS-Cu_2S-ZnS solar cells (taken from [3]).

adopt the device structure shown in Figure 3. It consists of a molybdenum- (Mo-) coated soda lime glass (SLG) as the electrical contact, a thin CZTS light absorber layer which is in contact with an n-type CdS layer to create a p-n junction, and a thin i-ZnO/Al : ZnO layer on top of the CdS layer playing the role of a window layer and electrical contact.

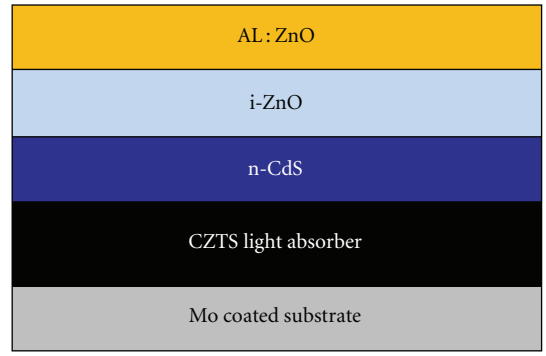

Figure 3: Schematics of the structure of CZTS solar cells.

3. Evolution of the Conversion Efficiency of CZTS-Based Thin Film Solar Cells

The recognition of the photovoltaic effect of CZTS material was reported by Ito and Nakazawa in 1988 [4]. They fabricated a heterodiode that consisted of a transparent cadmium-tin-oxide thin film and a CZTS thin film on a stainless steel substrate. An open-circuit voltage of 165 mV was obtained with the device. In 1997, Friedlmeier et al. fabricated thin film solar cells using a CZTS layer as the light absorber in contact with an n-CdS/ZnO window layer. The best energy conversion efficiency produced by the cells was 2.3% [5]. This record was later broken by Katagiri's group in 1999 who produced a CZTS solar cell with 2.63% power conversion efficiency. In this cell, the CZTS film was deposited on a Mo-coated soda lime glass (SLG) substrate [6]. By optimization of the sulfurization process, the efficiency of the solar cells was increased to 5.45% in 2003 [7], and then to 6.7% in 2008 [8]. Two review papers regarding the efficiency milestones achieved in CZTS-based thin film solar cells were reported by Katagiri in 2005 and in 2009, respectively [9, 10]. The current world record efficiency of CZTS-based thin film solar cells is 9.6%, which was reported by Todorov et al. in 2010. In this cell, the CZTS thin film was partly selenized to have a broader spectral photonresponse [11]. The evolution of the power conversion efficiency of CZTS-based solar cells is summarized in Figure 4.

Since majority of the publications in this area have been devoted to the synthesis and characterizations of CZTS thin films, therefore this paper will review the most recent research activities of employing variable techniques for deposition of CZTS thin films. The main electrical and optical properties of the synthesized materials will be briefly discussed as well.

The techniques for synthesis of CZTS thin films can be classified into two categories: vacuum, and nonvacuum-based method. According to the nature of the approach used for the deposition of the thin films, each category has a few subclassifications, the details of which will be shown in the following.

4. Vacuum-Based Deposition Method

Vacuum-based fabrication techniques normally involve deposition of the constitute atoms of the CZTS compound on a substrate by sputtering or evaporation/coevaporation of the target sources under a certain pressure and temperature. These techniques have the advantage of easily controlling the chemical composition and phase profile in the thin films and normally have good reproducibility.

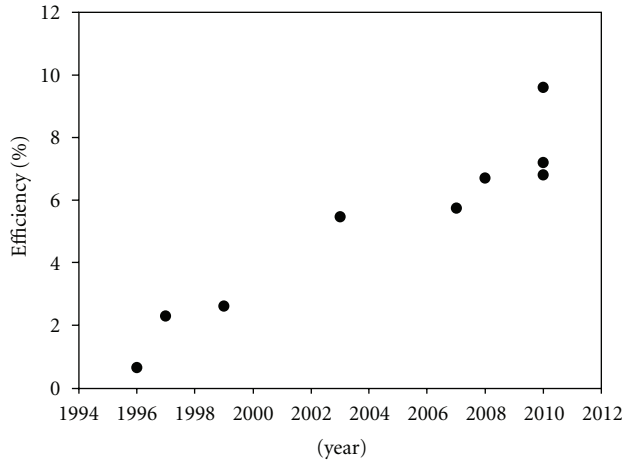

Figure 4: Evolution of the conversion efficiency of thin film solar cells using CZTS as light absorber layer.

4.1. Vacuum-Based Sputtering Deposition Technique. An atomic beam sputtering technique was employed by Ito and Nakazawa to deposit CZTS thin films in 1988. The band gap energy of the films was determined to be 1.45 eV [4]. In 2003, Seol et al. used Cu_2S, ZnS, and SnS_2 as target sources to deposit CZTS precursor thin films onto a glass substrate at room temperature by a RF magnetron sputtering technique. The as-deposited films were amorphous. After annealing in Ar + S_2(g) atmosphere, a stoichiometric ratio of Cu/Zn/Sn was achieved with the films, but S was deficient. This problem was solved by further annealing the films in a sulphur vapour atmosphere at temperature above 200°C. It was found that the composition of the thin film materials was affected by the RF power in the sputtering [12].

An integrated vacuum apparatus which combined the RF sputtering technique with the sulfurization process was employed to reduce the effect of moisture from ambient air on the property of CZTS films. Target sources were based on ZnS, and SnS and Cu. Both the quality and reproducibility of the CZTS films were significantly improved by this method. A 5.7% conversion efficiency with the CZTS-based thin film solar cells was achieved [13]. By eliminating the metal oxide impurity in the CZTS films using deionized water, the efficiency of the solar cells was further improved to 6.7% [8].

Tanaka et al. used a vacuum-based hybrid sputtering approach to deposit the constitute elements Cu, Zn, Sn on a quartz substrate. Specifically, Sn and Zn metal layers were deposited by DC-sputtering and Cu by RF-sputtering. Stoichiometry CZTS thin films were formed at the substrate temperature above 400°C. However, substantial Zn losses were observed when the temperature was above 450°C [14]. Yoo and Kim studied the influence of Cu content on the structure and morphology of CZTS films. Their results indicated that Cu-rich or a stoichiometric Cu content would lead to the formation of $Cu_{2-x}S$ in the films, whereas a Cu-poor composition favoured the formation of a smooth film surface [15]. Liu et al. reported CZTS films with a high light absorption coefficient (>10^5 cm^{-1}). The films were synthesized by a DC reactive magnetron sputtering method using a source target consisting of Cu/Zn/Sn metal mixture with stoichiometric composition (Cu : Zn : Sn = 2 : 1 : 1, molar ratio). Therefore, the precursor films could be made in one step. The CZTS compound was formed after sulfurization of the precursors. However, besides the desired CZTS materials, secondary phases $Cu_{2-x}S$ and Cu_3SnS_4 were also observed in the materials. And further characterization showed that the carrier concentration of the films was in the order of 10^{18} cm^{-3} [16]. Similar approach was also explored by Momose et al. for the fabrication of CZTS thin films. Cu, Zn, and Sn metals were simultaneously deposited on a SLG substrate by sputtering to form CZTS precursor films. After a rapid sulfurization (7 min) of the precursor at 590°C, the CZTS films were formed. An efficiency of 3.7% was obtained with the best thin film solar cell [17]. Most synthesized CZTS material is kesterite-type due to a better stability thermodynamically compared to the stannite-type. Nevertheless, stannite phase CZTS films which showed a very low sheet resistivity (0.156 Ohm cm) were synthesized by an ion-beam sputtering technique. The band gap energy of the material was determined to be 1.51 eV [18].

4.2. Vacuum-Based Evaporation Deposition. The synthesis of CZTS thin films by a thermal evaporation approach was firstly reported by Friedlmeier et al. in 1997. The elements and binary chalcogenides compounds were deposited onto a substrate in high vacuum. They found that the film composition and grain size were largely dependent on the substrate temperature [5]. Moreover, they observed that the electrical resistivity of the films could be varied between 1 and 100 ohm cm by treating the films with a KCN solution [19]. Katagiri et al. used an electron beam evaporation method to deposit a Cu/Sn/Zn stack layer sequentially on a SLG substrate at 150°C in high vacuum. The precursor film was subsequently annealed in a sulphur-containing atmosphere (N_2 + 5% H_2S) at 500°C to form the CZTS compound. The characterization of the optical and electrical properties of the film showed that the optical band gap energy was 1.45 eV and the light absorption coefficient was in the order of 10^4 cm^{-1}. The corresponding CZTS thin film solar cells with an architecture of Al/ZnO/CdS/CZTS/Mo/SLG provided an efficiency of 0.66% [20]. The same group later reported that using ZnS to replace Zn as the target source could dramatically enhance the adhesion of CZTS film to the Mo/SLG substrate [21]. An approach based on one-step synthesis of CZTS thin films by coevaporation of precursor sources Cu, Zn, Sn, S simultaneously was reported by Tanaka et al. The CZTS material showed a preferential orientation along [112] plane. The grain size of the film depended on the substrate temperature. Larger grains were obtained at higher substrate temperature [22]. In addition, growth of CZTS crystals on Si (100) wafers using a high vacuum multisource evaporation technique was reported by Oishi et al. A temperature-induced orientation growth was observed in the films [23].

From commercial application point of view, it is necessary to develop a process by which high-quality CZTS thin films can be produced rapidly and reproducibly. Such

process has been explored recently. Wang et al. reported the deposition of Cu, Zn, Sn, and S elements on a SLG substrate simultaneously by a rapid thermal evaporation method. The thickness of the light absorber layer was less than 1.0 μm and the annealing time was only a few minutes. Thin film solar cells with 6.8% conversion efficiency were fabricated. The analysis of the electrical property of the PV device indicated that the performance of the cell was limited by the high series resistance and the high charge recombination [24]. A similar method based on rapid deposition (16 min) of CZTS thin films on Mo/SLG substrate was also reported by Schubert et al. ZnS, Sn, Cu, and S target sources were coevaporated simultaneously onto the substrate at 550°C in vacuum. The composition of the precursor films was copperrich, which resulted in the formation of secondary phases $Cu_{2-x}S$. Nevertheless, stoichiometry CZTS films were obtained by posttreating the films with KCN aqueous solution. An energy conversion efficiency of 4.1% was achieved with the thin film solar cells [25].

Moriya et al. employed a vacuum-based pulsed laser deposition technique to fabricate CZTS light absorber layer for thin film solar cells and an efficiency of 1.74% was obtained with the devices [26, 27]. The effect of the laser incident energy on the structural, morphological, and optical properties of the CZTS thin films was investigated by Pawar et al. The study revealed that the crystallinity of the films increased with the increase of the laser energy until certain value (e.g., 2.5 J/cm^2) [28]. Moreover, the pulsed laser deposition technique can also be used to grow CZTS crystals on a GaP substrate. Well-crystallized CZTS crystals were obtained at substrate temperature of 400°C and the crystals showed a preferential orientation along [112], [29].

4.3. Influence of the Stacking Order of the Metallic Layer on the Performance CZTS Solar Cell. Araki et al. studied the effect of the stacking order of Cu, Zn, Sn metal layer on the properties of CZTS thin films and the corresponding solar cell performance. It was found that the films made from the precursor with a stacking order of Mo/Cu/Zn/Sn showed larger grain sizes than that with Mo/Cu/Sn/Zn. The direct contact of Cu and Zn layers should be responsible for the formation of large grains (Figure 5). However, the best cell efficiency (1.79%) was obtained with the precursor where Zn is the bottom layer and Sn is the top layer (stacking order: Mo/Zn/Cu/Sn). This phenomenon was explained by avoiding the formation of voids between Mo and CZTS if Cu layer were in direct contact with the Mo conductive layer [30].

The properties of CZTS films made from precursors with the stacking order of Mo/Zn/Cu/Sn and Mo/Zn/Sn/Cu deposited by a DC magnetron sputtering was also investigated by Fernandes et al. In contrary to Araki et al.'s conclusion, They concluded that the later stacking sequence was in favour of the CZTS crystal growth because Cu layer on top reduced the loss of Zn and Sn in the annealing process, thus leading to a better composition control and crystallinity. However, Cu_xS may be formed on the surface of the film when Cu is the top layer [31]. Obviously, a deep understanding of the crystal growth mechanism of this quaternary compound is needed to explain these phenomena.

Weber et al. studied the loss of Sn in CZTS during the annealing process. It was found that desorption of SnS from the CZTS at temperature above 350°C led to the losses of Sn in vacuum. The decomposition process of CZTS could be reduced by addition of an inert gas in the chamber where the sintering was carried out [32]. This issue has been addressed by Redinger et al. as well. They suggested to add extra SnS and S material in the precursor to prevent the decomposition of CZTS at high temperature [33].

5. Nonvacuum Deposition Method

The vacuum-based deposition techniques generally suffer from relatively slow throughput, low material utilization, and considerable energy consumption. Therefore, nonvacuum based deposition methods have been developed to reduce the production cost. These methods including spray pyrolysis, electrochemical deposition, and spin coating of precursor solutions, have been widely investigated for preparation of semiconductor thin films such as CIGS and CdTe [34]. They have been attempted to synthesize CZTS thin films as well.

5.1. Spray Pyrolysis Deposition. The synthesis of CZTS thin films by deposition of precursor solutions using spray pyrolysis technique in ambient environment was reported by Nakayama and Ito in 1997. A precursor solution consisting of CuCl, $ZnCl_2$, $SnCl_4$, and thiourea at suitable concentrations in deionized water/ethanol solvent mixture was sprayed onto a heated SLG substrate. The as-deposited films were stannite-type [35]. Since then, similar approach has been used by other researchers for the fabrication of CZTS thin films using different precursor solutions. Kamoun et al. studied the effect of the substrate temperature and the spray duration on the crystallinity of the CZTS films. The best crystallinity was obtained at the substrate temperature 613 K and a preferential orientation along [112] plane was observed with the films [36]. The effect of the substrate temperature and the pH value as well as the compositions of the precursor solution on the crystallinity and the morphology of the CZTS material were also investigated by Kumar et al. Their results showed that the CZTS material with good crystallinity was obtained at the substrate temperature in the range of 643–683 K with the precursor solution pH = 4.5. But impurities such as ZnS were observed besides the CZTS compound [37, 38]. Prabhakar and Nagaraju used ultrasonic spray pyrolysis technique to deposit CZTS thin films on a SLG substrate. The films with kesterite structure were obtained at 613 K, consistent with the results reported by others [39].

5.2. Spin-Coating of CZTS Precursor Solution. It normally involves three steps to prepare a CZTS thin film by spin-coating technique. (1) Preparation of a precursor solution which contains the ions of interest; (2) Spin-coating the precursor solution on a SLG substrate to make the thin film; (3) annealing the thin film at suitable atmosphere to form CZTS materials.

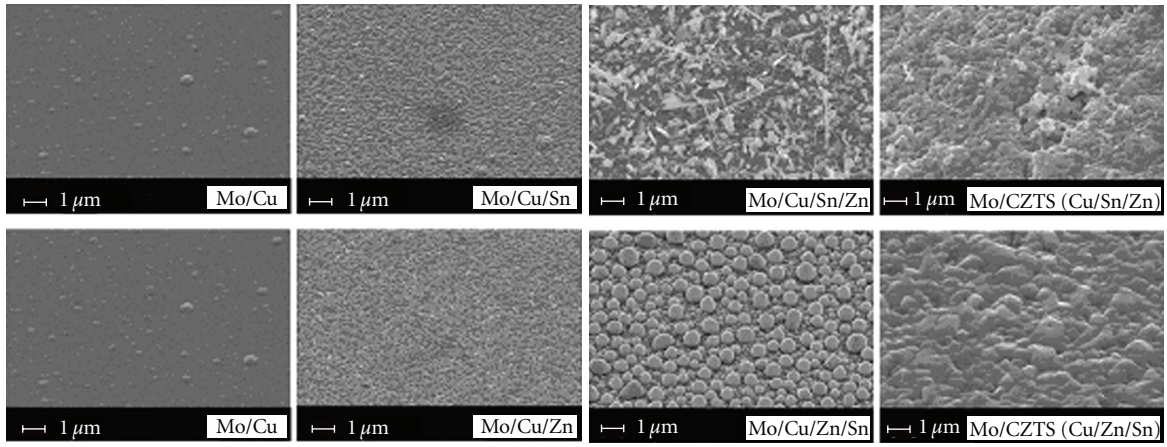

Figure 5: SEM pictures of precursor and CZTS films with different stacking order of metal layers (taken from [30]).

Tanaka et al. synthesized CZTS films by spin-coating a sol-gel precursor solution. The precursor solution contained acetate salts of copper (II) and zinc (II) as well as tin (II) chloride in 2-methoxyethanol solvent. Monoethanolamine was added to the solution to prevent the formation of precipitations. CZTS thin films were formed by annealing the precursor films in H_2S containing atmosphere at 500°C [40]. They later reported using non-vacuum methods to fabricate all the other components of thin film solar cells besides the CZTS layer. Specifically, the Zn/ZnO : Al window layer was made by a spin-coating method and the CdS buffer layer was made by a chemical bath deposition approach. The CZTS solar cells fabricated by the non-vacuum methods showed an efficiency of 1.01% (J_{sc} = 7.8 mA/cm^2, V_{oc} = 390 mV) [41]. The effect of the chemical composition of the precursor solution on the morphology and the optical properties of the CZTS thin films were investigated. Large grains were found in the films made from the precursor solution with copper poor (Cu/(Zn+Sn) < 0.8, molar ratio). The band gap energy of the copper-deficient films was larger compared to that of the copper-rich films. The best solar cell showed an efficiency of 2.03% [42].

Pawar et al. studied the effect of the complexing agent trisodium citrate in the precursor solution on the structure, morphology and composition of the CZTS thin films. The results showed that the crystallinity of the films was improved by using the complexing agent. However, the surface of the precursor films were uneven compared to the films deposited from the electrolyte without the complexing agent. Such effect was reduced by postsulfurization treatment of the films [43]. Similarly, Liu et al. employed additive such as ethylxanthate molecule to facilitate the formation of a homogeneous CZTS precursor solution which was used to deposit CZTS films [44].

Fischereder et al. deposited CZTS films by spin coating a precursor solution consisting of metal salts of copper (I), tin (IV), and zinc (II) and thioacetamide in pyridine. They found that the formation of CZTS compound occurred at temperature at low as 105°C in vacuum. The band gap energy of the films varied between 1.41 and 1.81 eV by changing the annealing temperature point [45]. This is probably due to the coexistence of secondary phases in the film under low annealing temperature.

Todorov et al. prepared a CZTS precursor which was based on a hydrazine-based particle-solution slurry consisting of Cu, Zn, Sn, and S elements. The CZTS films or partly selenized CZTS (CZTSSe) thin films were obtained by annealing the precursor films in sulphur or sulfoselenide containing atmosphere at 540°C. The films showed large grains and uniform composition (Figure 6(a)). The best cell efficiency was 9.66% which was obtained with the CZTSSe-based solar cells. The onset of the photon response in the IPCE spectrum of the thin film solar cells was close to 1200 nm (Figure 6(b)), indicating a lower band gap energy of the materials [11].

5.3. Electrochemical Deposition. Electrochemical deposition is considered to be a promising technique for the low-cost preparation of semiconductor thin films and has been employed by BP and CISEL for the commercial deposition of CdTe and CIGS thin film PV modules [46, 47]. The key for using this method is to find suitable electrochemical potential at which the metal cations can be reduced efficiently while unwanted reactions will not occur. CZTS films made by an electrodeposition method were firstly reported by Scragg et al. A stacking metal layer of Cu/Sn/Zn was deposited sequentially on a Mo/SLG substrate using a three-electrode configuration where Ag/AgCl was used as reference electrode. Cu and Sn was deposited at −1.14 V and −1.21 V, respectively using suitable alkaline solutions, and Zn was deposited at −1.20 V in an acidic environment (pH = 3). CZTS thin films were formed after annealing the precursor in a sulphur atmosphere at 500°C. The doping density of the films was in the order of 10^{16} cm^{-3} [48]. Further investigation of the photovoltaic performance of the corresponding thin film solar cells indicated that the device performed better under low illumination intensity. At high illumination intensity (equivalent to 1 sun), the recombination in the space charge region was increased, leading to the decrease of the performance [49]. An energy conversion efficiency of 3.2%

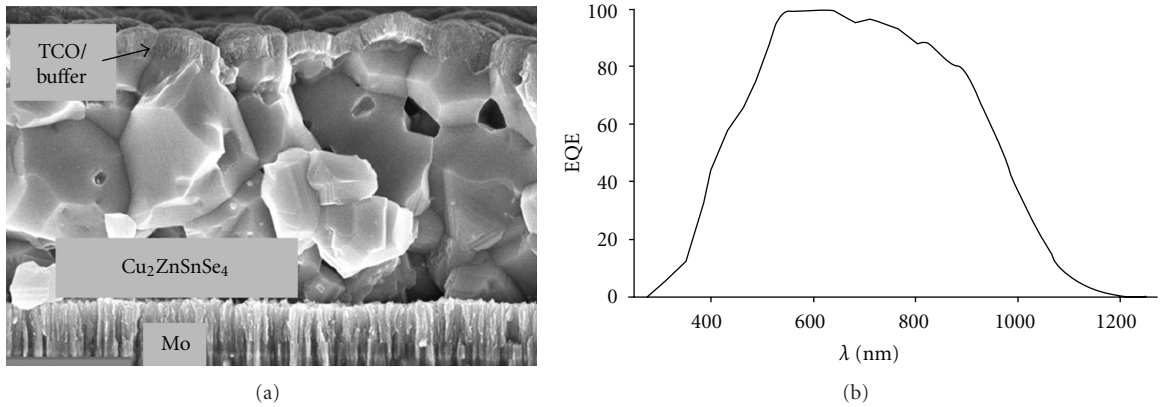

Figure 6: SEM of cross section and EQE of thin film solar cells based on CZTSSe light absorber (taken from [11]).

was obtained with a full-structured thin film solar cell. In this cell, the morphology and uniformity of the CZTS thin films were optimized through modification of the stacking order of the electrodeposited metallic layers [50]. Ennaoui et al. electrodeposited Cu-Zn-Sn precursor thin films on a Mo/SLG substrate using an electrolyte containing copper (II), zinc (II), and tin (IV) cations together with complexing agents and additives. The best thin film solar cell showed an efficiency of 3.4% (J_{sc} = 14.8 mA/cm^2, V_{oc} = 563 mV, FF = 41%) which was Cu-poor in the CZTS material. Their study also revealed that secondary phases such as ZnS for the Zn-rich material and Cu_2SnS_3 for the Zn-poor film existed at the interface of CZTS/Mo-SLG [51]. Scragg et al. also compared the morphology of the electrodeposited CZTS films which were annealed in different gaseous atmosphere. They found that H_2S containing atmosphere benefited the enhanced crystallinity of the films compared to the sulphur containing environment [52]. Zhang et al. used electrochemical method to grow the atomic layer of Cu, Zn, Sn, and S layer by layer on a Ag substrate. A [112] preferential orientation was observed with the as-deposited CZTS thin film [53].

Besides the conventional electrodeposition approach, a method based on photoelectrochemical deposition was reported by Moriya et al. for the fabrication of CZTS films using an aqueous solution containing the sulphate of Cu^{2+}, Zn^{2+}, and Sn^{2+} as well as sodium thiosulfate. They reported that the pH value of the precursor solution had little influence on the composition of the film [54].

5.4. CZTS Nanocrystal by Hot-Injection Method. Hot injection solution chemical method is an established approach for the synthesis of materials with well-defined size and shape (nanocrystals). It has been widely used in preparation of semiconductor nanocrystals. In 2009, three papers on synthesis of CZTS nanocrystals by hot-injection method appeared in *Journal of the American Chemical Society*. The sizes of the synthesized nanocrystal were less 20 nm. The band gap energy of the nanocrystals was around 1.5 eV, which is comparable to that of the bulk material [55–57]. Kameyama et al. studied the effect of the reaction temperature in the hot-injection process on the formation of CZTS nanocrystals. They found that a single-phase CZTS were formed at temperature over 240°C whereas secondary phase such as CuS was formed at low reaction temperature. The valence band and the conduction band of the as-synthesized films was 0.3 eV and −1.2 eV versus Ag/AgCl, respectively [58]. By tuning the composition of the hot chemical solution, the band gap energy of the nanocrystals was adjusted from 3.48 eV (ZnS) to 1.23 eV (CZTS, sphalerite type). The application of the CZTS nanocrystals in dye-sensitized solar cells was investigated, but the efficiency was very low (0.03%) [59]. In contrast, CZTS nanocrystals which was annealed in Se vapour at 500°C for 15 min showed an enhanced grain growth. The thin film solar cells using the CZTSSe light absorber showed an energy conversion efficiency of 7.2%, and the cell did not show significant degradation in a one-month light soaking test [60].

Traditionally, CZTS appears in either kesterite or stannite phase with tetragonal structure. Recently, CZTS nanocrystals with wurtzite phase were synthesized by Lu et al. using hot-injection method. The new structure has a hexagonal structure and showed a band gap energy of 1.4 eV [61].

5.5. Other Nonvacuum Synthesis Methods. Wangperawong et al. reported a novel synthesis method for CZTS precursor films. Firstly, SnS and ZnS materials were coated on a Mo/SLG substrate by chemical bath deposition, and Cu ion was then incorporated into the precursor films via ion exchange mechanism. CZTS films with good crystallinity were formed by annealing the precursor films in a H_2S containing atmosphere at 500°C [62]. Another chemical solution-based non-vacuum method for the synthesis CZTS nanocrystals was based on a dissolution-reprecipitation process which involved the use of KSCN as molten salt to finely tune the supersaturation condition of the precursor solution. The successful preparation of the discrete nanocrystals relied on the precursor properties such as ultrafine size of the aggregates and a high short-range order in the nanocrystals according to the authors [63].

Hydrothermal method has been widely employed for synthesis of nanomaterials. It is thought very difficult to synthesize single-phase CZTS material, however, owing to

Table 1: Characteristic parameters of the current best efficiency CZTS-based thin film solar cells with light absorber made by various methods.

Method	Material	η (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	Ref
RF magnetron sputtering	CZTS	6.77	0.61	17.9	0.62	[8]
Thermal evaporation	CZTS	6.8	0.587	17.8	0.65	[24]
Electrodeposition	CZTS	3.4	0.563	14.8	0.41	[51]
Hot injection	CZTSSe	7.2	0.42	30.4	0.527	[60]
Hydrazine	CZTSSe	9.67	0.516	28.6	0.65	[11]

the complexity of the compound and the narrow stable thermodynamic region where the material can exist. Cao and Shen reported the synthesis of CZTS materials at 150°C in an autoclave using a precursor solution containing $CuCl_2$, $(C_2H_3O_2)_2Zn$, $SnCl_4$, and S in ethylenediamine. Though CZTS target material was obtained, ZnS impurity was also formed [64].

Zhou et al. reported using a wet ball milling combin-ed with screen-printing technique for the preparation of CZTS thin films. Primary elements copper, zinc, tin, and sul-phur were homogeneously mixed under vigorous milling. CZTS powder was formed by sintering the precursor material in an inert gas at 500°C. A screen printable paste made from the CZTS powder was deposited on a Mo-coated polyimide substrate for fabrication of thin film solar cells. The sheet resistance of the thin film was 2.42×10^3 ohm and the carrier density was 3.8×10^{18} cm^{-3}. Hall mobility of the CZTS material was 12.61 cm^2 V^{-1} S^{-s}. The best conversion efficiency of the thin film solar cells was 0.49% [65].

6. Defect Physics/Chemistry of CZTS

Defect plays an important role in determining the electrical property of semiconductor materials. Chen et al. have studied the defect mechanism of CZTS material. They employed DFT-based first principal calculation to study the thermodynamic stability of the quaternary compound. The results have revealed that the stable chemical potential region for the formation of a stoichiometry CZTS is very narrow, consistent with the previous experimental observations. Theoretical calculation has also predicted that Cu-rich/Zn-poor conditions are necessary for the growth of a single-phase CZTS crystal. The intrinsic defect in CZTS material is p-type Cu_{Zn} antisite (Cu at Zn site) under such growth condition. Nevertheless, the authors have argued that Cu_{Zn} defect is not optimal for solar cell applications due to the relatively deep acceptor levels. Instead, copper vacancy V_{Cu} is preferred for high efficiency solar cells. Moreover, there are self-compensated defect pair complexes such as $[Cu_{Zn}^{-} + Zn_{Cu}^{+}]$ for Cu-rich/Zn-poor growth condition and $[V_{Cu}^{-} + Zn_{Cu}^{+}]$ for Cu-poor/Zn-rich condition in CZTS [66]. These electrically neutral defect complexes can remarkably passivate the deep levels in the band gap, reducing the recombination in the PV devices [67]. Similar results have also been reported by Nagoya et al. and Maeda et al. [68, 69]. These authors have claimed that ZnS should be the main competing phase under the prevalent Cu-poor and Zn-rich growth condition, and Cu at Zn sites Cu_{Zn} is the most stable defect in the entire stability range of CZTS [67]. Chory et al. have used electron spin resonance (ESR) measur-ement to investigate the defects of CZTS materials made by a sol-gel method. The study has indicated the exist-ence of Cu(II) in the compound. This phenomenon was explained due to the charge transfer between Sn(IV) and Cu(I), leading to the formation of Sn(II) and Cu(II) [70].

7. Summary

The recent significant progress in Cu_2ZnSnS_4 has demonstrated the feasibility of developing high efficiency PV devices with low cost and low environment impact materials. A broad range of techniques including vacuum or non-vacuum approaches have been explored to deposit CZTS films. The vacuum-based sputtering method has produced CZTS films for thin film solar cells with an efficiency of 6.77%, which is comparable to the performance of the films synthesized by a rapid thermal evaporation. From application point of view, the rapid vacuum thermal evaporation approach is more promising for large scale production of the thin film materials.

Among the non-vacuum preparation methods, hydrazine-based particle-solution method has demonstrated its capability in fabrication of high quality CZTS materials. This claim is justified by the thin film solar cells with 9.66% energy conversion efficiency using hydrazine method. It seems that hot-injection method is a promising synthesis technique for CZTS material as well. The thin film solar cells with the selenized CZTS nanocrystals have showed 7.2% conversion efficiency. Though electrodeposition has been successfully applied for the deposition of CdTe and CIGS thin films commercially, this method is yet able to compete with other techniques for deposition of high quality CZTS films currently. The best solar cell with the electrodeposited CZTS film has shown 3.4% conversion efficiency. Table 1 summarizes the characteristic parameters of the state-of-the-art thin film solar cells made by different methods. Clearly, the two most high efficiency cells are based on the selenized CZTS light absorber materials (CZTSSe). The short circuit current density of the cells is nearly twofold that of the rest of the cells which are based on CZTS materials. This is attributed to the broader spectral response of the CZTSSe light absorber owing to the lower band gap energy. The open circuit voltage of all the CZTS-based solar cells is around

0.6 eV, which is much lower than the theoretical value of 1.5 eV. A high charge recombination in those devices is probably responsible for the low V_{oc}. A detailed investigation of the electrical properties and kinetics of charge transport in the device is necessary in order to disclose the exact physical reasons for the low V_{oc}.

In order to improve the efficiency of CZTS-based thin film solar cells, a deeper understanding of the fundamental properties of CZTS, particularly the nature of the defects as well as their impact on the properties of CZTS material is important. CZTS material for thin film solar cells which have produced good efficiency normally always shows Cu-poor/Zn-rich in the composition. Therefore, secondary phase(s) should exist in the light absorbers. It is necessary to identify those secondary phases and their effects in order to optimize the fabrication process to make CZTS thin films with desired properties.

Acknowledgment

H. Wang thanks Queensland University of Technology for funding this project via Vice-Chancellor Research Fellowship Scheme.

References

[1] S. A. Kissin, "A Reinvestigation of the stannite (Cu_2FeSnS_4)—kesterite (Cu_2ZnSnS_4) pseudobinary system," *Canadian Mineralogist*, vol. 27, pp. 689–697, 1989.

[2] S. Schorr, "Structural aspects of adamantine like multinary chalcogenides," *Thin Solid Films*, vol. 515, no. 15, pp. 5985–5991, 2007.

[3] I. D. Olekseyuk, I. V. Dudchak, and L. V. Piskach, "Phase equilibria in the Cu_2S-ZnS-SnS_2 system," *Journal of Alloys and Compounds*, vol. 368, no. 1-2, pp. 135–143, 2004.

[4] K. Ito and T. Nakazawa, "Electrical and optical properties of stannite-type quaternary semiconductor thin films," *Japanese Journal of Applied Physics*, vol. 27, no. 11, pp. 2094–2097, 1988.

[5] T. M. Friedlmeier, N. Wieser, T. Walter, H. Dittrich, and H. W. Schock, "Heterojuncitons based on Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ thin films," in *Proceedings of the 14th European Conference of Photovoltaic Science and Engineering and Exhibition*, p. 1242, Bedford, UK, 1997.

[6] H. Katagiri, K. Saitoh, T. Washio, H. Shinohara, T. Kurumadani, and S. Miyajima, "Development of thin film solar cell based on Cu_2ZnSnS_4 thin films," *Solar Energy Materials and Solar Cells*, vol. 65, no. 1–4, pp. 141–148, 2001.

[7] H. Katagiri, K. Jimbo, K. Moriya, and K. Tsuchida, "Solar cell without environmental pollution by using CZTS thin film," in *Proceddings of the 3rd World Conference on Photovoltaic Energy Conversion*, pp. 2874–2879, Osaka, Japan, May 2003.

[8] H. Katagiri, K. Jimbo, S. Yamada et al., "Enhanced conversion efficiencies of Cu_2ZnSnS_4-based thin film solar cells by using preferential etching technique," *Applied Physics Express*, vol. 1, no. 4, Article ID 041201, 2 pages, 2008.

[9] H. Katagiri, "Cu_2ZnSnS_4 thin film solar cells," *Thin Solid Films*, vol. 480-481, pp. 426–432, 2005.

[10] H. Katagiri, K. Jimbo, W. S. Maw et al., "Development of CZTS-based thin film solar cells," *Thin Solid Films*, vol. 517, no. 7, pp. 2455–2460, 2009.

[11] K. Todorov, K. B. Reuter, and D. B. Mitzi, "High-efficiency solar cell with earth-abundant liquid-processed absorber," *Advanced Materials*, vol. 22, no. 20, pp. E156–E159, 2010.

[12] J. S. Seol, S. Y. Lee, J. C. Lee, H. D. Nam, and K. H. Kim, "Electrical and optical properties of Cu_2ZnSnS_4 thin films prepared by rf magnetron sputtering process," *Solar Energy Materials and Solar Cells*, vol. 75, no. 1-2, pp. 155–162, 2003.

[13] K. Jimbo, R. Kimura, T. Kamimura et al., "Cu_2ZnSnS_4-type thin film solar cells using abundant materials," *Thin Solid Films*, vol. 515, no. 15, pp. 5997–5999, 2007.

[14] T. Tanaka, T. Nagatomo, D. Kawasaki et al., "Preparation of Cu_2ZnSnS_4 thin films by hybrid sputtering," *Journal of Physics and Chemistry of Solids*, vol. 66, no. 11, pp. 1978–1981, 2005.

[15] H. Yoo and J. Kim, "Growth of Cu_2ZnSnS_4 thin films using sulfurization of stacked metallic films," *Thin Solid Films*, vol. 518, no. 22, pp. 6567–6572, 2010.

[16] F. Y. Liu, K. Zhang, Y. Q. Lai, J. Li, Z. A. Zhang, and Y. X. Liu, "Growth and characterization of Cu_2ZnSnS_4 thin films by dc reactive magnetron sputtering for photovoltaic applications," *Electrochemical and Solid-State Letters*, vol. 13, no. 11, pp. H379–H381, 2010.

[17] N. Momose, M. T. Htay, T. Yudasaka et al., "Cu_2ZnSnS_4 thin film solar cells utilizing sulfurization of metallic precursor prepared by simultaneous sputtering of metal targets," *Japanese Journal of Applied Physics*, vol. 50, no. 1, part 3, Article ID 01BG09, 4 pages, 2011.

[18] J. Zhang, L. X. Shao, Y. J. Fu, and E. Q. Xie, "Cu_2ZnSnS_4 thin films prepared by sulfurization of ion beam sputtered precursor and their electrical and optical properties," *Rare Metals*, vol. 25, no. 6, pp. 315–319, 2006.

[19] T. M. Friedlmeier, H. Dittrich, and H. W. Schock, "Growth and characterization of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ thin films for photovoltaic applications," *Ternary and Multinary Compounds*, vol. 152, pp. 345–348, 1998.

[20] H. Katagiri, M. Nishimura, T. Onozawa et al., "Rare-metal free thin film solar cell," in *Proceedings of the Power Conversion Conference*, pp. 1003–1006, Nagaoka, Japan, August 1997.

[21] H. Katagiri, N. Ishigaki, T. Ishida, and K. Saito, "Characterization of Cu_2ZnSnS_4 thin films prepared by vapor phase sulfurization," *Japanese Journal of Applied Physics*, vol. 40, no. 2, pp. 500–504, 2001.

[22] T. Tanaka, D. Kawasaki, M. Nishio, Q. Guo, and H. Ogawa, "Fabrication of Cu_2ZnSnS_4 thin films by co-evaporation," *Physica Status Solidi C*, vol. 3, no. 8, pp. 2844–2847, 2006.

[23] K. Oishi, G. Saito, K. Ebina et al., "Growth of Cu_2ZnSnS_4 thin films on Si (100) substrates by multisource evaporation," *Thin Solid Films*, vol. 517, no. 4, pp. 1449–1452, 2008.

[24] K. Wang, O. Gunawan, T. Todorov et al., "Thermally evaporated Cu_2ZnSnS_4 solar cells," *Applied Physics Letters*, vol. 97, no. 14, Article ID 143508, 2010.

[25] B. A. Schubert, B. Marsen, S. Cinque et al., "Cu_2ZnSnS_4 thin film solar cells by fast coevaporation," *Progress in Photovoltaics*, vol. 19, no. 1, pp. 93–96, 2011.

[26] K. Moriya, K. Tanaka, and H. Uchiki, "Fabrication of Cu_2ZnSnS_4 thin-film solar cell prepared by pulsed laser deposition," *Japanese Journal of Applied Physics*, vol. 46, no. 9, pp. 5780–5781, 2007.

[27] K. Moriya, K. Tanaka, and H. Uchiki, "Cu_2ZnSnS_4 thin films annealed in H_2S atmosphere for solar cell absorber prepared by pulsed laser deposition," *Japanese Journal of Applied Physics*, vol. 47, no. 1, pp. 602–604, 2008.

[28] S. M. Pawar, A. V. Moholkar, I. K. Kim et al., "Effect of laser incident energy on the structural, morphological and optical properties of Cu_2ZnSnS_4 (CZTS) thin films," *Current Applied Physics*, vol. 10, no. 2, pp. 565–569, 2010.

[29] K. Sekiguchi, K. Tanaka, K. Moriya, and H. Uchiki, "Epitaxial growth of Cu_2ZnSnS_4 thin films by pulsed laser deposition," *Physica Status Solidi*, vol. 3, no. 8, pp. 2618–2621, 2006.

[30] H. Araki, A. Mikaduki, Y. Kubo et al., "Preparation of Cu_2ZnSnS_4 thin films by sulfurization of stacked metallic layers," *Thin Solid Films*, vol. 517, no. 4, pp. 1457–1460, 2008.

[31] P. A. Fernandes, P. M. P. Salomé, and A. F. da Cunha, "Precursors' order effect on the properties of sulfurized Cu_2ZnSnS_4 thin films," *Semiconductor Science and Technology*, vol. 24, no. 10, Article ID 105013, 2009.

[32] A. Weber, R. Mainz, and H. W. Schock, "On the Sn loss from thin films of the material system Cu-Zn-Sn-S in high vacuum," *Journal of Applied Physics*, vol. 107, no. 1, Article ID 013516, 2010.

[33] A. Redinger, D. M. Berg, P. J. Dale, and S. Siebentritt, "The consequences of kesterite equilibria for efficient solar cells," *Journal of the American Chemical Society*, vol. 133, no. 10, pp. 3320–3323, 2011.

[34] C. J. Hibberd, E. Chassaing, W. Liu, D. B. Mitzi, D. Lincot, and A. N. Tiwari, "Non-vacuum methods for formation of $Cu(In, Ga)(Se, S)_2$ thin film photovoltaic absorbers," *Progress in Photovoltaics*, vol. 18, no. 6, pp. 434–452, 2010.

[35] N. Nakayama and K. Ito, "Sprayed films of stannite Cu_2ZnSnS_4," *Applied Surface Science*, vol. 92, pp. 171–175, 1996.

[36] N. Kamoun, H. Bouzouita, and B. Rezig, "Fabrication and characterization of Cu_2ZnSnS_4 thin films deposited by spray pyrolysis technique," *Thin Solid Films*, vol. 515, no. 15, pp. 5949–5952, 2007.

[37] Y. B. K. Kumar, G. S. Babu, P. U. Bhaskar, and V. S. Raja, "Preparation and characterization of spray-deposited Cu_2ZnSnS_4 thin films," *Solar Energy Materials and Solar Cells*, vol. 93, no. 8, pp. 1230–1237, 2009.

[38] Y. B. K. Kumar, G. S. Babu, P. U. Bhaskar, and V. S. Raja, "Effect of starting-solution pH on the growth of Cu_2ZnSnS_4 thin films deposited by spray pyrolysis," *Physica Status Solidi A*, vol. 206, no. 7, pp. 1525–1530, 2009.

[39] T. Prabhakar and J. Nagaraju, "Ultrasonic spray pyrolysis of CZTS solar cell absorber layers and characterization studies," in *Proceedings of the 35th IEEE Photovoltaic Specialists Conference, (PVSC '10)*, pp. 1964–1969, June 2010.

[40] K. Tanaka, N. Moritake, and H. Uchiki, "Preparation of Cu_2ZnSnS_4 thin films by sulfurizing sol-gel deposited precursors," *Solar Energy Materials and Solar Cells*, vol. 91, no. 13, pp. 1199–1201, 2007.

[41] K. Tanaka, M. Oonuki, N. Moritake, and H. Uchiki, "Cu_2ZnSnS_4 thin film solar cells prepared by non-vacuum processing," *Solar Energy Materials and Solar Cells*, vol. 93, no. 5, pp. 583–587, 2009.

[42] K. Tanaka, Y. Fukui, N. Moritake, and H. Uchiki, "Chemical composition dependence of morphological and optical properties of Cu_2ZnSnS_4 thin films deposited by sol-gel sulfurization and Cu_2ZnSnS_4 thin film solar cell efficiency," *Solar Energy Materials and Solar Cells*, vol. 95, no. 3, pp. 838–842, 2011.

[43] B. S. Pawar, S. M. Pawar, S. W. Shin et al., "Effect of complexing agent on the properties of electrochemically deposited Cu_2ZnSnS_4 (CZTS) thin films," *Applied Surface Science*, vol. 257, no. 5, pp. 1786–1791, 2010.

[44] Y. F. Liu, M. Y. Ge, Y. Yue et al., "Colloidal Cu_2ZnSnS_4 nanocrystals generated by a facile route using ethylxanthate molecular precursors," *Physica Status Solidi*, vol. 5, no. 3, pp. 113–115, 2011.

[45] A. Fischereder, T. Rath, W. Haas et al., "Investigation of Cu_2ZnSnS_4 formation from metal salts and thioacetamide," *Chemistry of Materials*, vol. 22, no. 11, pp. 3399–3406, 2010.

[46] D. R. Johnson, "Microstructure of electrodeposited CdS/CdTe cells," *Thin Solid Films*, vol. 361, pp. 321–326, 2000.

[47] S. Taunier, J. Sicx-Kurdi, P. P. Grand et al., "$Cu(In,Ga)(S,Se)_2$ solar cells and modules by electrodeposition," *Thin Solid Films*, vol. 480-481, pp. 526–531, 2005.

[48] J. J. Scragg, P. J. Dale, and L. M. Peter, "Towards sustainable materials for solar energy conversion: preparation and photoelectrochemical characterization of Cu_2ZnSnS_4," *Electrochemistry Communications*, vol. 10, no. 4, pp. 639–642, 2008.

[49] J. J. Scragg, P. J. Dale, and L. M. Peter, "Synthesis and characterization of Cu_2ZnSnS_4 absorber layers by an electrodeposition-annealing route," *Thin Solid Films*, vol. 517, no. 7, pp. 2481–2484, 2009.

[50] J. J. Scragg, D. M. Berg, and P. J. Dale, "A 3.2% efficient Kesterite device from electrodeposited stacked elemental layers," *Journal of Electroanalytical Chemistry*, vol. 646, no. 1-2, pp. 52–59, 2010.

[51] A. Ennaoui, M. Lux-Steiner, A. Weber et al., "Cu_2ZnSnS_4 thin film solar cells from electroplated precursors: novel low-cost perspective," *Thin Solid Films*, vol. 517, no. 7, pp. 2511–2514, 2009.

[52] J. J. Scragg, P. J. Dale, L. M. Peter, G. Zoppi, and I. Forbes, "New routes to sustainable photovoltaics: evaluation of Cu_2ZnSnS_4 as an alternative absorber material," *Physica Status Solidi*, vol. 245, no. 9, pp. 1772–1778, 2008.

[53] X. Zhang, X. Z. Shi, W. C. Ye, C. L. Ma, and C. M. Wang, "Electrochemical deposition of quaternary Cu_2ZnSnS_4 thin films as potential solar cell material," *Applied Physics A*, vol. 94, no. 2, pp. 381–386, 2009.

[54] K. Moriya, K. Tanaka, and H. Uchiki, "Characterization of Cu_2ZnSnS_4 thin films prepared by photo-chemical deposition," *Japanese Journal of Applied Physics*, vol. 44, no. 1, pp. 715–717, 2005.

[55] S. C. Riha, B. A. Parkinson, and A. L. Prieto, "Solution-based synthesis and characterization of Cu_2ZnSnS_4 nanocrystals," *Journal of the American Chemical Society*, vol. 131, no. 34, pp. 12054–12055, 2009.

[56] Q. J. Guo, H. W. Hillhouse, and R. Agrawal, "Synthesis of Cu_2ZnSnS_4 nanocrystal ink and its use for solar cells," *Journal of the American Chemical Society*, vol. 131, no. 33, pp. 11672–11673, 2009.

[57] C. Steinhagen, M. G. Panthani, V. Akhavan, B. Goodfellow, B. Koo, and B. A. Korgel, "Synthesis of Cu_2ZnSnS_4 nanocrystals for use in low-cost photovoltaics," *Journal of the American Chemical Society*, vol. 131, no. 35, pp. 12554–12555, 2009.

[58] T. Kameyama, T. Osaki, K. I. Okazaki et al., "Preparation and photoelectrochemical properties of densely immobilized Cu_2ZnSnS_4 nanoparticle films," *Journal of Materials Chemistry*, vol. 20, no. 25, pp. 5319–5324, 2010.

[59] P. C. Dai, X. N. Shen, Z. J. Lin, Z. Y. Feng, H. Xu, and J. H. Zhan, "Band-gap tunable $(Cu_2Sn)x/3Zn1\text{-}xS$ nanoparticles for solar cells," *Chemical Communications*, vol. 46, no. 31, pp. 5749–5751, 2010.

[60] Q. J. Guo, G. M. Ford, W. C. Yang et al., "Fabrication of 7.2% efficient CZTSSe solar cells using CZTS nanocrystals," *Journal of the American Chemical Society*, vol. 132, no. 49, pp. 17384–17386, 2010.

[61] X. T. Lu, Z. B. Zhuang, Q. Peng, and Y. D. Li, "Wurtzite Cu_2ZnSnS_4 nanocrystals: a novel quaternary semiconductor," *Chemical Communications*, vol. 47, no. 11, pp. 3141–3143, 2011.

[62] A. Wangperawong, J. S. King, S. M. Herron, B. P. Tran, K. Pangan-Okimoto, and S. F. Bent, "Aqueous bath process for deposition of Cu_2ZnSnS_4 photovoltaic absorbers," *Thin Solid Films*, vol. 519, no. 8, pp. 2488–2492, 2011.

[63] J. Y. Chane-Ching, A. Gillorin, O. Zaberca, A. Balocchi, and X. Marie, "Highly-crystallized quaternary chalcopyrite nanocrystals via a high-temperature dissolution-reprecipitation route," *Chemical Communications*, vol. 47, no. 18, pp. 5229–5231, 2011.

[64] M. Cao and Y. Shen, "A mild solvothermal route to kesterite quaternary Cu_2ZnSnS_4 nanoparticles," *Journal of Crystal Growth*, vol. 318, no. 1, pp. 1117–1120, 2011.

[65] Z. H. Zhou, Y. Y. Wang, D. Xu, and Y. F. Zhang, "Fabrication of Cu_2ZnSnS_4 screen printed layers for solar cells," *Solar Energy Materials and Solar Cells*, vol. 94, no. 12, pp. 2042–2045, 2010.

[66] S. Y. Chen, X. G. Gong, A. Walsh, and S. H. Wei, "Defect physics of the kesterite thin-film solar cell absorber Cu_2ZnSnS_4," *Applied Physics Letters*, vol. 96, no. 2, Article ID 021902, 2010.

[67] S. Y. Chen, J. H. Yang, X. G. Gong, A. Walsh, and S. H. Wei, "Intrinsic point defects and complexes in the quaternary kesterite semiconductor Cu_2 $ZnSnS_4$," *Physical Review B*, vol. 81, no. 24, Article ID 245204, 2010.

[68] A. Nagoya, R. Asahi, R. Wahl, and G. Kresse, "Defect formation and phase stability of Cu_2ZnSnS_4 photovoltaic material," *Physical Review B*, vol. 81, no. 11, Article ID 113202, 2010.

[69] T. Maeda, S. Nakamura, and T. Wada, "First principles calculations of defect formation in in-free photovoltaic semiconductors Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$," *Japanese Journal of Applied Physics*, vol. 50, no. 4, part 2, Article ID 04DP07, 2011.

[70] C. Chory, F. Zutz, F. Witt, H. Borchert, and J. Parisi, "Synthesis and characterization of Cu_2ZnSnS_4," *Physica Status Solidi*, vol. 7, no. 6, pp. 1486–1488, 2010.