

3.6%-CZTSS Device Fabricated From Ionic Liquid Electrodeposited Sn Layer

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Abstract: Cu/Sn/Zn stacked layers were electrodeposited and subsequently annealed in a tube furnace in elemental sulfur and selenium at 570°C. Cyclic voltammogram of Sn-salt in ionic liquid was recorded. Thin films were characterized by inductively coupled plasma-mass spectrometry (ICP-MS), Auger electron spectroscopy (AES) and scanning electron microscopy (SEM). The device was characterized by current-voltage (I-V) and quantum efficiency (QE). The device fabricated using electrodeposited precursor film resulted in efficiencies of 3.6%.

Keywords: Cu-Zn-Sn-S-Se, Cu/Sn/Zn stacked layer, ionic liquid, electrodeposited.

1. INTRODUCTION

Photovoltaic (PV) solar electric technology will be a significant contributor to world energy supplies when reliable, efficient PV power products are manufactured in large volumes at low cost. A promising pathway to reduce PV cost is the use of thin-film technologies in which thin layers of photoactive materials are deposited inexpensively on large-area substrates. The primary chalcogenide semiconductor absorber materials currently used for thin-film PV device applications are Cu(In,Ga)Se₂ and CdTe. Despite the promise of these technologies, the toxicity of Cd and supply limitations for In and Te are projected to limit the production capacity of these existing chalcogen-based technologies to <100 GWp per year. This represents a small fraction of the world's growing energy needs, which are expected to double to 27 TW by 2050. Therefore, a lot of efforts have been made recently to explore new absorber materials with nontoxic and earth-abundant elements. One prominent example of the alternative solar cell materials is Cu₂ZnSn(SSe)₄ (CZTSS). CZTSS has a direct band gap of 1.45 – 1.6 eV and an optical absorption coefficient of around 10⁵cm⁻¹ [1, 2]. Recently several groups reported CZTSS thin-films prepared by variety of fabrication methods, namely sputtering [2-5], physical vapor deposition [6-11], solution-particle approach [12-14], photochemical deposition [15], sol-gel method [16], screen-printing [17], and electroplating [18-26]. The best conversion efficiency of the CZTS solar cell is reported to be 11.1% using ink-based solution-particle approach [27]. The electroplated CZTS solar cell also demonstrated a respectable 7.3%-efficient device [26].

Electroplating is a potentially suitable preparation method to obtain low-cost precursor films. The electrodeposition process could provide: (a) high-quality film with very low capital investment; (b) a low-cost, high-rate process;

(c) use of very low-cost starting materials (e.g., low-purity salts or solvents), based on automatic purification of the deposited materials during plating; (d) a large-area, continuous, multi-component, low-temperature deposition method; (e) deposition of films on a variety of shapes and forms (wires, tapes, coils, and cylinders); (f) controlled deposition rates and effective material use (as high as 98%); and (g) minimum waste generation (i.e., the solution can be recycled) [28].

Most of the electrodeposited CZTSS precursor films reported are prepared from aqueous electrolyte solutions. The electrodeposition of an element (e. g., Sn) that has a standard reduction potential more negative than the water reduction potential becomes very difficult due to the competition between electroplating the desired element and water electrolysis. To avoid the water reduction issue, electrodeposition needs to be done using non-aqueous solvents with a large electrochemical window, like ionic liquids (ILs).

In this study, CZTSS thin films have been prepared by electrodeposition of multilayered Cu-Sn-Zn metal films on Mo/glass substrates. Cu and Zn thin films were prepared from aqueous solution and Sn was prepared from ionic liquid solvent. The electrodeposited thin-film precursor films were subsequently annealed in a tube furnace in an elemental sulfur and selenium environment.

2. EXPERIMENTAL PROCEDURE:

In general, electrodeposition of Cu-Sn-Zn was performed sequentially from a Cu-plating solution, Sn-plating solution, and Zn-plating solution, respectively. First, a Cu layer was electrodeposited on a Mo/glass substrate from an aqueous Cu-plating solution [28], the second Sn layer was electrodeposited from an ionic liquid Sn-plating solution, and the third Zn layer was electrodeposited from an aqueous Zn-plating solution. The ionic liquid solution was prepared by dissolving 313gm choline chloride in 500 ml ethylene glycol. Fisher Scientific (FB300) and VWR (300V) power supplies were used to electrodeposit Cu-Sn-Zn thin films. All films were electrodeposited by applying constant current.

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Cu was plated at -6.5 mA/cm^2 for 3 minutes, Sn was plated at -0.45 mA/cm^2 for 30 minutes and Zn was plated at -1.8 mA/cm^2 for 4 minutes. The desired film composition can be obtained by adjusting the film thickness of Cu, Sn and Zn. The films were electrodeposited in a vertical cell in which the electrodes (both working and counter) were suspended vertically from the top of the cell. Precursor films were prepared by employing a two-electrode cell in which the counter electrode was Pt gauze and the working electrode (substrate) was glass/Mo. The Mo film was about $1 \mu\text{m}$ thick and was deposited by direct current (dc) sputtering. All chemicals were of Analar- or Puratronic-grade purity and were used as received. The precursor electrodeposited Cu/Sn/Zn stacked layers were annealed in a tube furnace at 570°C in the presence of 2gm Se and 0.5gm S for 60 minutes. The film compositions were analyzed using Agilent Technologies 7700 Series ICP-MS system. PV devices were completed by chemical-bath deposition of about 50 nm CdS, followed by radio frequency (RF) sputtering of 50 nm of intrinsic ZnO and 350 nm of Al_2O_3 -doped conducting ZnO. Bilayer Ni/Al top contacts were deposited in an e-beam system. The final step in the fabrication sequence was the deposition of an antireflection coating (100 nm of MgF_2).

3. RESULTS AND DISCUSSION

Cyclic voltammograms (CVs) were obtained at 53°C with a scan rate of 50 mV/s , using a 3-electrode system potentiostat (Princeton, VCM-4). The electrodes used for CV measurements were Pt-working, Pt-counter, and Pt-quasi reference electrodes [29]. The measurements were performed after the open circuit voltage of the electrochemical cell was stabilized (usually 1 hour). Fig. (1a) shows a CV curve of the choline chloride-based ionic liquid used in this study. The water reduction peak at $V \approx 0.9 \text{ V vs Pt}$, indicates a trace amount of water present in the ionic liquid solvent. Fig. (1b) shows the CV curve of $0.1 \text{ M SnCl}_2 \cdot \text{H}_2\text{O}$ in choline chloride-based ionic liquid solution. The CV curve shows reduction ($\text{Sn}^{2+} + 2e^- \Rightarrow \text{Sn}$) peak of Sn at -0.89 V in ionic liquid solvent when a Pt-quasi reference electrode is used. The standard reduction potential of Sn(II) [$\text{Sn}^{2+} + 2e^- \Rightarrow \text{Sn}$] is -0.14 V vs. SHE in 1 M aqueous solution at 25°C [30].

The precursor film composition as analyzed by ICP-MS was $\text{Cu}_2\text{Zn}_{1.57}\text{Sn}_{0.99}$. The composition of the annealed film analyzed by ICP-MS was $\text{Cu}_2\text{Zn}_{1.89}\text{Sn}_{0.94}\text{Se}_{1.95}\text{S}_{1.41}$. The compositions of the films were normalized to $\text{Cu} = 2$. The compositions of the precursor and processed films were not ideal for high efficiency devices. The annealed film was Zn rich which could lead to the formation of ZnS and ZnSe impurity phases. Fig. (2) shows the X-ray diffraction (XRD) patterns of the absorber layer (annealed in Se and S). The measured peaks correspond to kesterite CZTS structure [joint committee on powder diffraction standards (JCPDS) # 26-0575]. The molybdenum (Mo) substrate peak is labeled as Mo (110). The XRD diffraction analysis does not show ZnS/ZnSe phases, even though the film is Zn-rich. The surface morphology and cross-sectional view (SEM) of the annealed film are shown in Fig. (3a, b) respectively. The SEM as shown in Fig. (3a, b), indicate that films are crack-free and have a compact dense morphology. The surface morphology (Fig. 3a) indicates secondary phases on melted large grain CZTSS thin film. The cross-sectional view

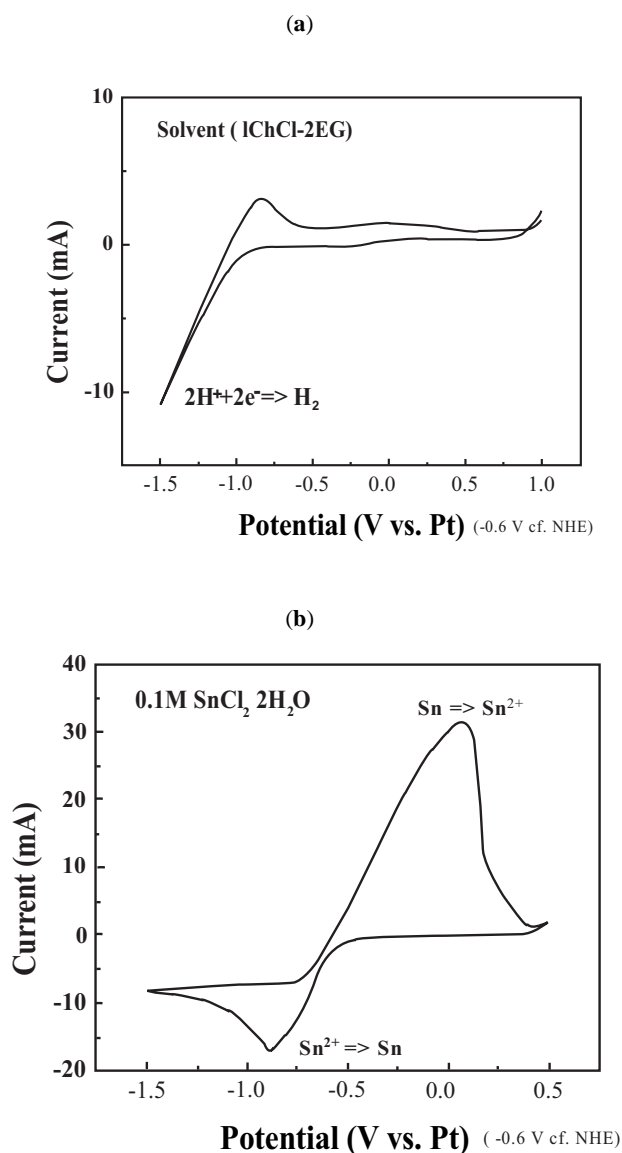


Fig. (1). (a) Cyclic Voltammogram (CV) of the ionic liquid and (b) CV of 0.1 M SnCl_2 in ionic liquid. All CVs were performed at 53°C .

(Fig. 3b) of the film shows the film thickness is about $3 \mu\text{m}$ and it has a very rough surface morphology. The grain size estimated from the top-view and cross-sectional images ranged from about 1 to $2 \mu\text{m}$ and the grains exhibit sharp facets. The compositional depth profile of the annealed film was analyzed using an Auger electron spectroscopy (AES). The profiles of the annealed film (Fig. 4) also show high concentration of Zn in the film. AES analysis data does not show any oxygen or other impurities in the film. Solar cell devices were fabricated from these absorber materials. The device efficiency of the electrodeposited CZTSS thin film without MgF_2 (Fig. 5a) was 3.4% with a $V_{oc} = 0.53 \text{ V}$, $J_{sc} = 16.1 \text{ mA/cm}^2$ and fill factor = 40. The device efficiency with MgF_2 (Fig. 5a) was 3.6% with a $V_{oc} = 0.54 \text{ V}$, $J_{sc} = 16.9 \text{ mA/cm}^2$ and fill factor = 40. Very poor fill factor and J_{sc} are probably due to poor film morphology and presence of secondary phases. Fig. (5b) displays the absolute external quantum efficiency (QE) spectrum of the device. The

maximum quantum efficiency is as high as 70% at 610-750 nm. This QE spectrum also reveals that the optical band gap of the CZTSS thin film is ~ 1.33 eV.

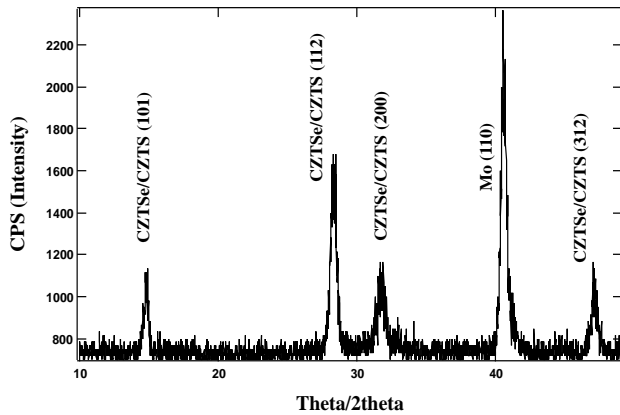


Fig. (2). X-ray diffraction (XRD) pattern of annealed CZTSS thin film (identified as kesterite, JCPDS 26-0575).

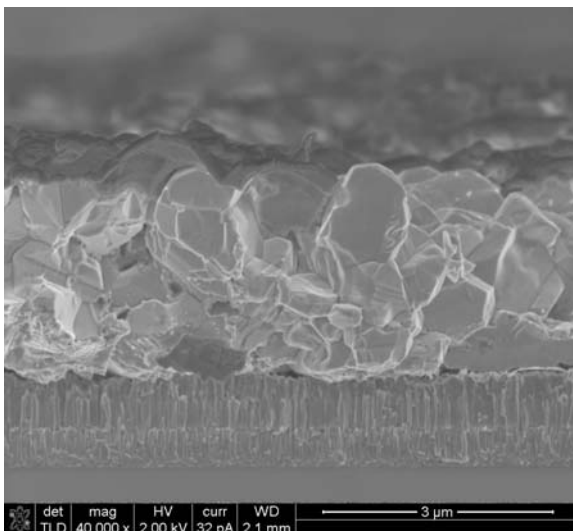
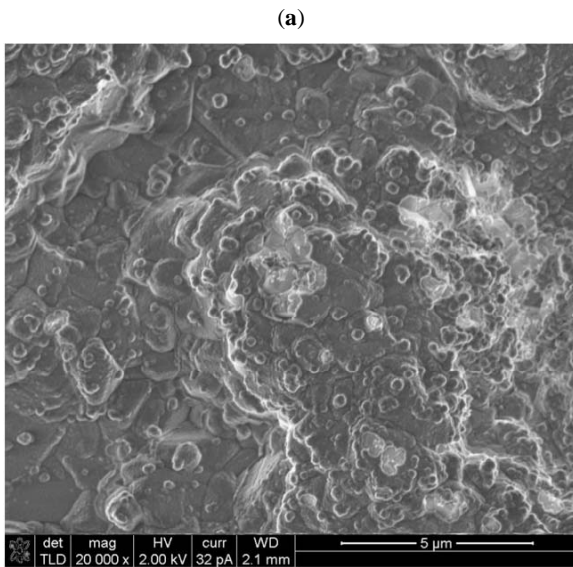


Fig. (3). (a) SEM surface morphology; (b) SEM cross-section of annealed CZTSS thin films.

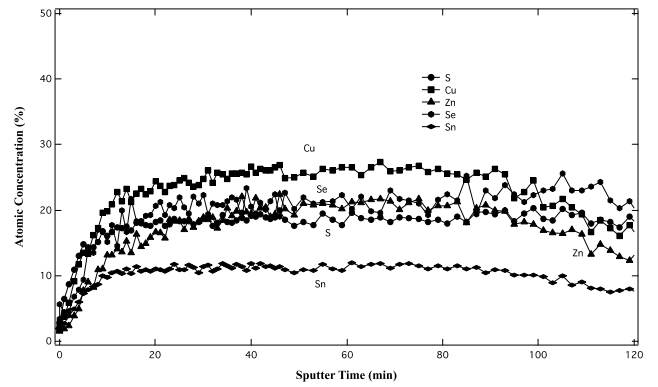


Fig. (4). Auger analysis data of the annealed electrodeposited CZTSS thin film.

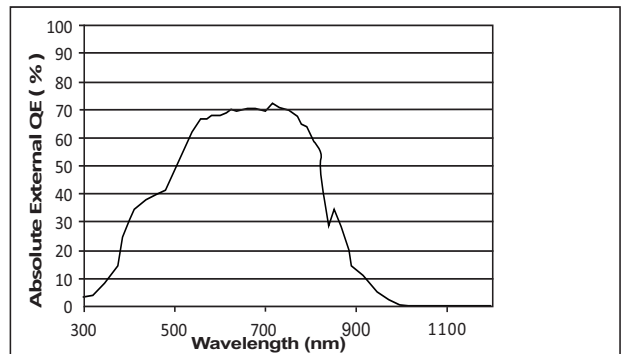
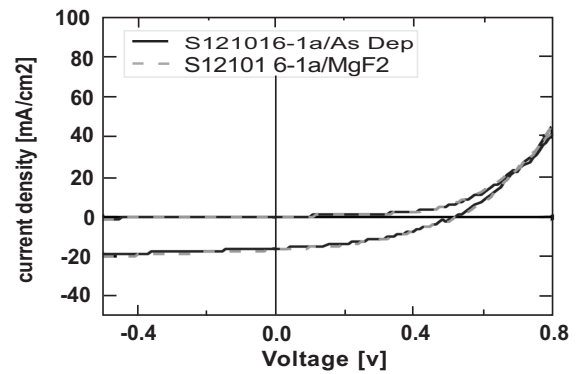


Fig. (5). (a) Current-voltage characteristics: $V_{oc} = 0.53$ V, $J_{sc} = 16.1$ mA/cm², fill factor = 40%, and efficiency = 3.4% without MgF₂; $V_{oc} = 0.54$ V, $J_{sc} = 16.9$ mA/cm², fill factor = 40%, and efficiency = 3.6% with MgF₂; (b) QE characteristics of the device with MgF₂.

4. CONCLUSION

Electrodeposited Sn layer was fabricated from non-aqueous ionic liquid solvent. Electrodeposited Cu and Zn layers were fabricated from aqueous solvent. The stacked Cu/Sn/Zn layers were annealed in the tube furnace in the presence of elemental sulfur and selenium to obtain CZTSS absorber layer. The absorber material used for the device fabrication is zinc rich film. It is interesting to note that 3.6%-device was fabricated from such non-stoichiometric Zn-rich thin. This is a very encouraging result. This indicates

that high efficiency devices could be obtained by hybrid electrodeposition process using both aqueous and ionic liquid solvents. At present the composition of the precursor films and processing conditions are being optimized to obtain smooth and uniform $\text{Cu}_2\text{ZnSn}(\text{SSe})_4$ thin film. We are expecting to improve the device efficiency significantly after optimizing the deposition and processing conditions.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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REFERENCES

- Jimbo K, Kimura R, Kamimura T, *et al.* $\text{Cu}_2\text{ZnSnS}_4$ -type thin film solar cells using abundant materials. *Thin Solid Films* 2007; 515: 5997-9.
- Ito K, Nakazawa T. Electrical and optical properties of stannite-type quaternary semiconductor thin films. *Jpn J Appl Phys* 1998; 27: 2094-7.
- Chalapathy RBV, Jung GS, Ahn BT. Fabrication of $\text{Cu}_2\text{ZnSnS}_4$ films by sulfurization of Cu/ZnSn/Cu precursor layers in sulfur atmosphere for solar cells. *Sol Energy Mater Sol Cells* 2011; 95: 3216-21.
- Tanaka T, Nagatomo T, Kawasaki D, *et al.* Preparation of $\text{Cu}_2\text{ZnSnS}_4$ thin films by hybrid sputtering. *J Phys Chem Solids* 2005; 66: 1978-81.
- Seol JS, Lee SY, Lee JC, Nam HD, Kim KH. Electrical and optical properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films prepared by rf-magnetron sputtering process. *Sol Energy Mater Sol Cells* 2003; 75: 155-62.
- Oishi K, Saito G, Ebina K, *et al.* Growth of $\text{Cu}_2\text{ZnSnS}_4$ thin films on Si (100) substrates by multisource evaporation. *Thin Solid Films* 2008; 517: 1449-52.
- Katagiri H, Sasaguchi N, Hando S, Hoshino S, Ohashi J, Yokota T. Preparation and evaluation of $\text{Cu}_2\text{ZnSnS}_4$ thin films by sulfurization of E-B evaporated precursors. *Sol Energy Mater Sol Cells* 1997; 49: 407-14.
- Katagiri H, Saitoh K, Washio T, Shinohara H, Kurumadani T, Miyajima S. Development of thin film solar cell based on $\text{Cu}_2\text{ZnSnS}_4$ thin films. *Sol Energy Mater Sol Cells* 2001; 65: 141-8.
- Grenet L, Bernardi S, Kohen D, *et al.* $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ based solar cell produced by selenization of vacuum deposited precursors. *Sol Energy Mater Sol Cells* 2012; 101: 11-4.
- Wang K, Gunawan O, Todorov T, Shin B, Vhey SJ, Bojarczuk NA. Structural and elemental characterization of high efficiency $\text{Cu}_2\text{ZnSnS}_4$ solar cells. *Appl Phys Lett* 2011; 98: 051912.
- Salome PMP, Malaquias J, Fernandes PA, *et al.* Growth and characterization of $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ thin films for solar cells. *Sol Energy Mater Sol Cells* 2012; 101: 147-53.
- Mitzi DB, Gunawan O, Todorov TK, Wang K, Guha S. The path towards a high-performance solution-processed kesterite solar cell. *Sol Energy Mater Sol Cells* 2011; 95: 1421-36.
- Todorov TK, Reuter KB, Mitzi DB. High-Efficiency Solar Cell with Earth-Abundant Liquid-Processed Absorber. *Adv Mater* 2010; 22: E156-9.
- Barkhouse DAR, Gunawan O, Gokmen T, Todorov TK, Mitzi DB. Device characteristics of a 10.1% hydrazine-processed $\text{Cu}_2\text{ZnSnS}_4$ solar cell. *Prog Photovoltaics Res Appl* 2012; 20: 6-11.
- Shin B, Zhu Y, Gunawan O, Bojarczuk NA, Chey SJ, Guha S. Thin film solar cell with 8.4% power conversion efficiency using an earth-abundant $\text{Cu}_2\text{ZnSnS}_4$ absorber. *Prog Photovolt: Res Appl* 2011; doi: 10.1002/pip.1174.
- Moriya K, Tanaka K, Uchiki H. Characterization of $\text{Cu}_2\text{ZnSnS}_4$ thin films prepared by photo-chemical deposition. *Jpn J Appl Phys* 2005; 44: 715-7.
- Zhou ZH, Wang Y, Xu D, Zhang Y. Fabrication of $\text{Cu}_2\text{ZnSnS}_4$ screen printed layers for solar cells. *Sol Energy Mater Sol Cells* 2010; 94: 2042-5.
- Tanaka K, Oonuki M, Moritake N, Uchiki H. $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cells prepared by non-vacuum processing. *Sol Energy Mater Sol Cells* 2009; 93: 583-7.
- Araki H, Kubo Y, Jimbo K, *et al.* Preparation of $\text{Cu}_2\text{ZnSnS}_4$ thin films by sulfurization of co-electroplated Cu-Zn-Sn precursors. *Phys Status Solidi C* 2009; 61: 1266-8.
- Kurihara M, Berg D, Fisher J, Siebentritt S, Dale PJ. Kesterite absorber layer uniformity from electrodeposited precursors. *Phys Status Solidi C* 2009; 6: 1241-4.
- Ennaoui A, Lux-Steiner M, Abou-Ras D, *et al.* $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cells from electroplated precursors: Novel low-cost perspective. *Thin Solid Films* 2009; 517: 2511-4.
- Pawar SM, Pawar BS, Moholkar AV, *et al.* Single step electro synthesis of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films for solar cell application. *Electrochim Acta* 2010; 55: 4057-61.
- Chan CP, Lam H, Surya C. Preparation of $\text{Cu}_2\text{ZnSnS}_4$ films by electrodeposition using ionic liquids. *Sol Energy Mater Sol Cells* 2010; 94: 207-11.
- Schurr R, Holzling A, Jost S, *et al.* The crystallization of $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cell absorbers from co-electroplated Cu-Zn-Sn precursors. *Thin Solid Film* 2009; 517: 2465-8.
- Deligianni H, Ahmed S, Romankiw LT. The Next Frontier: Electrodeposition for Solar Cell Fabrication. *Interface* 2011; 20: 47-53.
- Ahmed S, Reuter KB, Gunawan O, Gao L, Romankiw LT, Deligianni H. A high efficiency electrodeposited $\text{Cu}_2\text{ZnSnS}_4$ solar cell. *Adv Energy Mater* 2012; 2: 253-9.
- Todorov TK, Bag S, Gunawan O, Gokmen T, Zhu Y, Mitzi DB. Beyond 11% efficiency: characteristics of state-of-the-art $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$. *Solar Cells* 2013; 3: 34-8.
- Bhattacharya RN. CIGS-based solar cells prepared from electrodeposited stacked Cu/In/Ga layers. *Sol Energy Mater Sol Cells* 2013; 113: 96-9.
- Bhattacharya RN, Kim YJ. Cu-Zn-Sn-S thin films from electrodeposited metallic precursor layers. *Open Surface Sci J* 2012; 4: 19-24.
- CRC Handbook of Chemistry and Physics. In: David R, Ed. 74th ed. Boca Raton: CRC Press 1993-1994.

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