High Resolution Characterization of Grain Boundaries in $\text{Cu}_2\text{ZnSnSe}_4$ Solar Cells Synthesized by Nanoparticle Selenization

Mingjie Xu,¹ Bing Liu,² George Graham,¹ Xiaoqing Pan^{1, 3, *}

¹ Department of Materials Science and Engineering, University of Michigan, 2300 Hayward Street, Ann Arbor, Michigan 48109, USA;

² IMRA America, Inc., 1044 Woodridge Avenue, Ann Arbor, Michigan 48105, USA;

³ Department of Chemical Engineering and Materials Science and department of Physics and Astronomy, University of California, Irvine, 916 Engineering Tower, Irvine, California 92697, USA.

*Corresponding author E-mail: xiaoqing.pan@uci.edu

Abstract

We report a novel fabrication and multiple high resolution characterizations of $\text{Cu}_2\text{ZnSnSe}_4$ solar cells. The fabrication is based on nanoparticle precursor production by liquid-phase pulsed laser ablation(LP-PLA), electrophoretic deposition of precursor thin film under ambient condition, and selenization. Columnar grain boundaries are studied using spatially mapped Raman spectroscopy and scanning probe microscopy for their compositional and electrical properties. We observe high electrical conductivity near columnar grain boundaries, and propose poor Cu composition as the cause of the enhancement of the collection of minority carriers. We

also study horizontal grain boundaries using cross-sectional scanning transmission electron microscopy(STEM). Combining with the device I-V and quantum efficiency, we suggest that the horizontal grain boundaries act as barriers to the transportation of minority carriers. CZTSe cells with efficiencies of 4.77% and 2.20% are compared.

Keywords: CZTSe; Transmission electron microscopy; Grain boundary; Raman mapping; photo-current mapping; conductive atomic force microscopy

1. Introduction

Copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$ or CZTS), copper zinc tin selenide ($\text{Cu}_2\text{ZnSnSe}_4$ or CZTSe), and their alloys ($\text{Cu}_2\text{ZnSnS}_{4-x}\text{Se}_x$ or CZTSSe) have received increasing interest as promising absorber layer materials for low-cost thin film solar cell technology because they have the potential to achieve a similar power conversion efficiency (PCE) to $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS), but with an absorber layer made from earth abundant elements such as Cu, Zn, Sn, S and Se. Up until now, researchers have improved CZTSSe lab-scale solar cell efficiencies to 12%.[1] Such success has stimulated further interest and rapid progress in CZTSSe solar cell processing research. In addition to the traditional vacuum-based thin film deposition processes such as thermal co-evaporation,[2-4] co-sputtering,[5, 6] and hybrid electron beam evaporation,[7] various non-vacuum approaches have been developed to fabricate CZTSSe, including hydrazine-based[8-11] or other organic solution based[12] spin coating processes, synthesis of nanocrystals,[13-15] and electroplating.[16, 17] These non-vacuum approaches have generally demonstrated higher lab-scale efficiencies (5%-11%) than contemporary vacuum deposition methods. In addition, these non-vacuum based technologies have potential to be applicable to roll-to-roll mass production on light-weight and/or flexible substrates. The fact that an efficient

CZTSSe converter layer does not rely on vacuum-based fabrication opens the possibility of realizing a truly low-cost and high-throughput thin film PV technology that is competitive with the Si-based technology.

In contrast to vacuum deposition processes, use of nanoparticle precursors and electrophoretic deposition (EPD) provides a non-vacuum technology that is energy efficient while producing minimal material waste. The nanoparticles are stabilized with electric charge acquired in the laser-induced plasma, and thus additional stabilization agents are not needed, ensuring a high purity colloid into which dopants may precisely be added when desired. Precursor Cu_2ZnSn (CZT) thin films are fabricated using EPD.[18] The deposition is facilitated by the electro-kinetic mobility acquired by the electrically charged nanoparticles under an external electric field applied in the solvent. The particular advantage of EPD is the high deposition rate, in the micron/min range. Our previous work showed that CIGS fabricated by the same method can have energy conversion efficiency up to 7.37%.[19] In this paper, we demonstrate a CZTSe thin film solar cell fabricated directly on a Mo sheet substrate with PCE of 4.77%.

Despite the encouraging success in CZTSSe solar cell research, fundamental studies on the CZTSSe material and devices, especially structural and chemical characterization at the atomic scale, are lacking due to the material complexity. One of the fundamental issues of CZTSSe is the effect of the grain boundaries (GBs). Some reports studying grain boundary-dependence of solar cell output parameters point out that the influence of grain boundaries can be destructive to device performance when neutral grain boundaries are located within the depletion region and are parallel to the junction direction.[20, 21] However, theoretical studies have also suggested non-classical benign effects of GBs in polycrystalline CIGS, unlike traditional Si wafer based solar cells.

Although still under debate, first principles modeling suggests that grain boundaries in polycrystalline CIGS may act as hole barriers (and electron sinks) to prevent electron-hole recombination,[22] or they may act as charge-neutral defects to be electrically inactive to carrier transport.[22-25] Such benign grain boundary behavior is contrary to classic grain boundary theory, but is supported by experimental observations in CIGS films using scanning Kelvin probe microscopy,[23, 26-29] Auger electron spectroscopy,[30] and current imaging tunneling spectroscopy.[31] This grain boundary behavior provides a reasonable explanation for the high performance of fine-grained polycrystalline CIGS solar cells.[32] The recent development of instruments combining scanning probe microscopy (SPM) with chemically sensitive spectroscopies such as Raman provides a way to characterize thin film solar cells by combining spatially resolved mapping of surface topography, electrical properties and chemistry variation.

Using SPM with integrated laser Raman spectroscopy, the conductivity and even photocurrent can be mapped with high spatial resolution and correlated with structure and composition near the GBs. The Raman spectra mapping thus resolves chemistry variation and secondary phases and provides better understanding on the GB effects and optimization of the cell structure.

2. Experimental Methods

Figure 1a schematically illustrates the process of fabrication of nanoparticle precursor by LP-PLA and coating of precursor film on Mo sheet metal substrate by EPD. Colloidal precursor nanoparticles are synthesized with LP-PLA in acetone. The nanoparticles are stabilized with the electric charge acquired in laser-induced plasma and additional stabilization agents are not needed, ensuring a high purity colloid, and precise control of chemistry. Precursor CZT thin films were grown on a Mo substrate using EPD process. The EPD equipment consists of a Pt mesh and a Mo

sheet as positive and negative electrodes, respectively. Under a DC field intensity of $100\text{V}/\text{cm}^2$, the coating speed can reach a few $\mu\text{m}/\text{min}$. Selenization is performed in a sealed quartz tube in a furnace where the precursor films are placed in a graphite box together with Se pellets as a source to generate Se vapor. The furnace is fast ramped to $540\text{ }^\circ\text{C}$ at a rate of $60\text{ }^\circ\text{C}/\text{min}$, soaked for 20 min, and fast cooled to room temperature. Ar is sealed in the selenization environment during the process to prevent reaction with oxygen in air. During this process, CZT nanoparticles react with Se vapor to form CZTSe grains. These grains sinter further and form the polycrystalline CZTSe absorber layer. The solar cells are finished after deposition of a 50 nm thick CdS window layer by chemical bath deposition, a 100 nm thick intrinsic ZnO layer and a 300 nm thick indium-tin oxide (ITO) layer by RF sputtering, and a Ni/Au top contact is added by thermal evaporation.

Individual 3 mm by 3 mm cells were cut using mechanical scribing. I-V characteristics of the cells were measured under standard AM1.5G illumination at $1000\text{ W}/\text{m}^2$ intensity using a Newport Oriel IV-station. External Quantum Efficiency (EQE) was measured between 300 nm and 1100 nm using an Oriel QE measurement system. Precursor nanoparticles were observed using high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) to check the size distribution and the phase composition. Scanning electron microscopy (SEM) was used to study the surface morphology and thickness of each layer of both precursor and selenized film. Conductive AFM (C-AFM) with 1 V of bias was used to map the conductivity distribution; C-AFM with both tip and substrate grounded and under illumination of a 532 nm laser with a power density of $1\text{ mW}/\mu\text{m}^2$ was performed for photocurrent mapping. Raman mapping was performed on both front and back surface of the CZTSe film using NT-MDT NTEGRA Spectra system (Figure 1b). The positions and relative intensities of specified peaks were filtered and mapped to reveal the chemistry variation and phase changes.

3. Results and Discussion

Figure 2 shows SEM images of a CZT precursor film and TEM images of the precursor CZT nanoparticles. After the EPD process, the precursor film consists of densely packed nanoparticles with various sizes (Fig. 2a). This structure allows the Se vapor to penetrate into the precursor film through the interstitials of the nanoparticles stack, which contributes to the fast and uniform annealing process. However, it can also cause problems such as inhomogeneity and pin holes. The cause of inhomogeneity can be linked to the CZT alloy target composition and the selenization process of CZT nanoparticles. The final composition will be different from precursor depending on the synthesis method and other factors. For example, the target used for LP-PLA consists of Cu_5Zn_8 , Cu_6Sn_5 and Sn to achieve the $\text{Cu}/(\text{Zn}+\text{Sn})$ ratio of 0.9 and Zn/Sn ratio of 1.2 at a macroscopic level, which is common for high efficient cells. The EDS data indicated that the actual $\text{Cu}/(\text{Zn}+\text{Sn})$ ratio of the target is 0.82 and the Zn/Sn ratio is 1.2. Surface roughness of the alloy target may affect the ablation speed of different metal phases resulting in composition variation of colloidal suspension. SAED ring pattern indicated that these nanoparticles have the same phases as the target (Figure 2b, c). But the SAED pattern of an individual particle shows that it only consists one of the three phases (Figure 2d, e). Hence it is likely for a large precursor particle to create a local composition variation and lead to a non-uniform precursor film. The different deposition speed of each alloy nanoparticle may also contribute to the composition variation with respect the depth of the film. Due to the rapid annealing and the instability of the CZTSe phase, it is difficult for the selenization process to homogenize the film before the formation of secondary phases start to take place. The formation of highly volatile SnSe may also cause the composition to change. Details of a study of precursor nanoparticles and films causing

local chemical variation of the CZTSe film are included in the Supplementary Materials (Figures S1-S4).

In order to spatially resolve the secondary phases that may form after the selenization process, we performed Raman spectra mapping on our top view samples. Figure 3 shows the Raman mapping study of two different secondary phases on the same 10 by 20 micron area of a top view CZTSe sample. Figure 3a and 3b are the mappings of the relative intensity of a ZnSe 250 cm^{-1} peak and a CuSe 263 cm^{-1} peak. In these two mappings, brighter regions have higher peak values. Hence, the two highlighted spots (marked as 1 and 2) indicate that ZnSe and CuSe precipitates are present in these regions. The three Raman spectra in Figure 3c represent three different points of the film. Among these spectra, the two peaks at 172 and 195 cm^{-1} belong to CZTSe, and they can be observed throughout the entire region of the film. The second spectrum, taken at point 1 in Figure 3a, shows an additional peak at 263 cm^{-1} . This peak belongs to CuSe, a degenerate semiconductor, one of the major secondary phases that can hinder cell performance. CuSe can be observed both on top and bottom surfaces of the film, indicating that the formation of CuSe during selenization can not only occur at the top surface but also at the interface between the CZTSe film and the Mo substrate. Unlike material forming on the top surface, which can be etched away using KCN, CuSe at the bottom surface will remain inside the film even after the etching process. These regions can form shunting paths that reduce the fill factor of the cell. They can also increase recombination at rear surface and thus lower the EQE at long wavelength. The third spectrum has a peak at 250 cm^{-1} . It belongs to ZnSe and can also be found both on top and bottom surfaces of the film. Due to the large bandgap of ZnSe compared to CZTSe, it will create an inactive region that doesn't respond to illumination from the solar spectrum, leading to a reduction of the total effective area of the device. Such inhomogeneity in

composition can cause the Cu content to vary throughout the film. In general, a Cu-poor environment is preferred for the formation of $[V_{Cu}^- + Zn_{Cu}^+]$. [33] The Cu-rich environment can reduce the hole barrier so that the enhanced collection of carriers near GBs will be overcome by recombination. Such Cu-rich GBs can reduce the V_{OC} [34] and may be the main cause of low cell efficiency. Raman mapping can be used to study such variation of the Cu content along the film.

Recent studies have observed a change of symmetry in the CZTS system from ordered kesterite ($I\bar{4}$) to disordered stannite ($I\bar{4}2m$) if the material is Cu-poor. In Raman spectroscopy, this appears as a peak shift from 337cm^{-1} for the $I\bar{4}$ symmetry to 331cm^{-1} for the $I\bar{4}2m$ structure [35]. Figure 4 shows a CZTSe main peak position mapping of a 50 by 50 micron top area. The blue region (region 1) has peak position around 192cm^{-1} , which represents the disordered $I\bar{4}2m$ structure, while the red region (region 2) has peak position around 198cm^{-1} , which corresponds to ordered $I\bar{4}$ symmetry. Because in the Cu-poor condition the high population of V_{Cu}^- and Zn_{Cu}^+ can generate a slight widening of the peak, it is clear that the area in Figure 4 has coexisting Cu-poor and Cu-rich structures.

Such local variation of Cu content can result in different electrical properties of the GBs. Figure 5 is a dark current mapping of a 10 by 10 micron region on a top CZTSe film on Mo substrate. With a positive sample bias voltage of 1 V, a brighter area in the spreading resistance image represents a higher conductivity. From Figure 5b, despite the uniform conductivity within the GBs, higher conductivity regions are found mostly near the GBs. This indicates that the carrier concentrations are increased near these GBs.

The classic Seto model [36] of polycrystalline Si and simulations [21] of CIS and CGS solar cell systems predict a down shift of both valance and conduction band energy for columnar GBs.

In the CGS system, a reduced VBM of as high as 0.55V can occur under Cu poor conditions[37]. The origin of this phenomenon is that the polarization at the cation-terminated 112 GBs can cause Cu-vacancy surface reconstruction, reduce the p-d repulsion and lower the VBM.[22, 37] This will drive the Cu ion at GBs towards the grain interiors (GIs) so that the GBs are occupied by V_{Cu}^- , and the less the symmetry at the GBs, the larger the offset will be.[38] The electrons are attracted towards the reconstructed GB cores and start accumulating near them to form depletion regions. These depletion regions, or even inverted regions, are responsible of high carrier concentration and high conductivity near the GBs. Furthermore, it should be noticed in Figure 5 that one side of the GB is always more conductive than the other side, especially for the steps and twin boundaries within the GI (top region of the mapping in Fig. 5b). Theoretical calculations concluded that the valance band offset for Se terminated 112 surface is significantly smaller than the cation terminated one.[37] Therefore, only one side of the GB can have enhanced carrier collection. This effect is more pronounced when the symmetry of the GBs goes up, as a cation-terminated facet is more likely to pair with a Se-terminated facet. Such enhanced carrier collection near these GBs is reported to be the major cause of the benign effect of GBs for CIGS.[25, 30, 39] It is therefore likely for the CZTSe system, belonging to the same chalcopyrite family as CIGS, to have a similar effect of enhanced carrier collection near some of the GBs. However, such benign effects of GBs can be influenced by the Cu-rich environment, which explains why some of the GB are less conductive than others in Figure 5b. These GBs have less VBM offset and less ability to attract electrons and repel holes. Instead, they are dominated by recombination. The VBM offset caused by V_{Cu}^- surface reconstruction requires an overall Cu poor condition. So if the GBs are initially Cu-rich, for example CuSe or Cu_2SnSe_3 is formed at the GB, the VBM offset will thus be less pronounced.[37]

These GBs with different electrical properties will therefore affect the photovoltaic properties of CZTSe solar cells. Figure 6 shows an optoelectrical analysis of a CZTSe device using C-AFM mapping. A defocused 532 nm continuous wave laser with total power of 1 mW was used as illumination surrounding the conductive diamond coated AFM tip to excite photocurrent. In Figure 6b, the zero current regions are replaced by the grey scale topography. Under zero bias, a photocurrent of as high as 350 pA can be detected near some of the GBs. This result clearly indicates that for CZTSe devices, the carrier collection is enhanced at these GBs. However, for the rest of the GBs, no photocurrent is collected near them, suggesting recombination-dominant behavior of these GBs.

Unlike the columnar GBs, planar GBs are always detrimental to the electrical behavior of the CZTSe solar cells. Figure 7 shows planer SEM images, cross sectional ABE images, the corresponding J-V curves and the EQE of two CZTSe devices (sample 1 and sample 2) with different average grain sizes. Sample 1 has an average grain size of 1 μm and an efficiency of 4.77% while sample 2 has an average grain size of 300 nm and an efficiency of 2.20%.

According to the J-V curves (Fig. 7e), sample 1 and 2 have similar V_{OC} values (0.315V and 0.325V). They also have similar long wavelength “absorption” edges (Fig. 7f). Such similar behaviors indicate that the bandgaps of the two samples are close to each other. They also have similar but low values of R_{Sh} (463 Ω and 424 Ω). Such low shunting resistances are determined by the defective device structure. The quality of the EPD grown precursor film under non-vacuum condition can cause pinholes to form near the back interface during the selenization process, which leads to loose adhesion and creates shunting paths that can result in reduced shunting resistances for both samples.

However, unlike V_{OC} and R_{sh} , the differences of J_{SC} and R_s between the two samples are more pronounced. Sample 1 has a J_{SC} value of 34.7 mA/cm^2 and a R_s value of 41Ω , while for sample 2 these values are 21.0 mA/cm^2 and 118Ω . The EQE data (Fig 7f) also shows an overall reduction of quantum efficiency for sample 2, especially at the long wavelength region. The loss of photocurrent in sample 2, which has a smaller average grain size, can be explained by the effect of horizontal GBs. Generally, the GBs are full of defects and dangling bonds that can be modeled as thin amorphous layers that have a larger bandgap than crystalline CZTSe. The Fermi level is thus pinned near the midgap at GBs and forms a barrier to prevent carriers from traversing GBs.[40] The density of such barriers is higher if the grain size of the polycrystalline CZTSe films is smaller, such as in sample 2. This results in an increased value of serial resistance and a reduction of photo current density, which agrees with our experimental results. Therefore, for the CZTSe system, a device with grain sizes that are too small will have a significant amount of GBs spreading across the film (horizontal GB), creating more barriers against the transportation of the carriers. A grain size of more than the thickness of the film is preferred to eliminate the majority of the horizontal GBs.

At this point, we can predict an optimized structure for the CZTSe thin film absorber based on the detrimental horizontal GBs and beneficial columnar GBs. The film should consist of a series of columnar CZTS nanorods with average diameters at the same order of the average distance a minority carrier can travel before it recombines. In this case, the electrons moving along the film can easily reach the depletion region near the columnar GBs and move toward the CdS and be collected; the electrons moving across the film will not be blocked by any horizontal GB barriers and will have more chances to be collected before recombination takes place.

4. Summary

With regards of the interest in fast and low-cost synthesis of earth abundant CZTSe solar cells, we report a unique method for fabrication involving LP-PLA and EPD, which provides a non-vacuum technology that is energy efficient while producing minimal material waste. These advantages are achieved by fast processing due to the non-vacuum synthesis of high purity nanoparticles and high-speed deposition of precursor thin films. Our CZTSe device fabricated using this technology has achieved a PCE of 4.77%. The C-AFM mapping shows differences in photocurrent and conductivity along GBs. As confirmed by Raman mapping, such variation is caused by different Cu concentration at the GBs, since Cu-poor GBs can induce downward band bending and increase valance band offset to increase the carrier concentration and reduce recombination. The Cu-rich GBs can act as recombination centers that limited the device performance. The CZTSe film structure and quality need to be further optimized, and we propose that a columnar polycrystalline film structure is preferred for best carrier collection.

- [1] M.T. Winkler, W. Wang, O. Gunawan, H.J. Hovel, T.K. Todorov, D.B. Mitzi, Optical designs that improve the efficiency of $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ solar cells, *Energy & Environmental Science*, 7 (2014) 1029-1036.
- [2] K. Wang, O. Gunawan, T. Todorov, B. Shin, S.J. Chey, N.A. Bojarczuk, D. Mitzi, S. Guha, Thermally evaporated $\text{Cu}_2\text{ZnSnS}_4$ solar cells, *Appl. Phys. Lett.*, 97 (2010) 143508.
- [3] A. Redinger, K. Hoenes, X. Fontane, V. Izquierdo-Roca, E. Saucedo, N. Valle, A. Perez-Rodriguez, S. Siebentritt, Detection of a ZnSe secondary phase in coevaporated $\text{Cu}_2\text{ZnSnSe}_4$ thin films, *Appl. Phys. Lett.*, 98 (2011) 101907.
- [4] B. Shin, O. Gunawan, Y. Zhu, N.A. Bojarczuk, S.J. Chey, S. Guha, Thin film solar cell with 8.4% power conversion efficiency using an earth-abundant $\text{Cu}_2\text{ZnSnS}_4$ absorber, *Prog. Photovoltaics*, 21 (2013) 72-76.
- [5] K. Jimbo, R. Kimura, T. Kamimura, S. Yamada, W.S. Maw, H. Araki, K. Oishi, H. Katagiri, $\text{Cu}_2\text{ZnSnS}_4$ -type thin film solar cells using abundant materials, *Thin Solid Films*, 515 (2007) 5997-5999.
- [6] H. Katagiri, K. Jimbo, S. Yamada, T. Kamimura, W.S. Maw, T. Fukano, T. Ito, T. Motohiro, Enhanced conversion efficiencies of $\text{Cu}_2\text{ZnSnS}_4$ -based thin film solar cells by using preferential etching technique, *Appl. Phys. Express*, 1 (2008) 41201.
- [7] L. Grenet, S. Bernardi, D. Kohen, C. Lepoittevin, S. Noël, N. Karst, A. Brioude, S. Perraud, H. Mariette, $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ based solar cell produced by selenization of vacuum deposited precursors, *Sol. Energy Mater. Sol. Cells*, 101 (2012) 11-14.
- [8] T.K. Todorov, K.B. Reuter, D.B. Mitzi, High-efficiency solar cell with earth-abundant liquid-processed absorber, *Adv. Mater.*, 22 (2010) E156-E159.
- [9] D.A.R. Barkhouse, O. Gunawan, T. Gokmen, T.K. Todorov, D.B. Mitzi, Device characteristics of a 10.1% hydrazine-processed $\text{Cu}_2\text{ZnSn}(\text{Se}, \text{S})_4$ solar cell, *Prog. Photovoltaics*, 20 (2012) 6-11.
- [10] S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, T.K. Todorov, D.B. Mitzi, Low band gap liquid-processed CZTSe solar cell with 10.1% efficiency, *Energy & Environmental Science*, 5 (2012) 7060-7065.
- [11] T.K. Todorov, J. Tang, S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, D.B. Mitzi, Beyond 11% efficiency: Characteristics of state-of-the-art $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ solar cells, *Adv. Energy Mater.*, (2012) doi: 10.1002/aenm.201200348.
- [12] G. Wang, W. Zhao, Y. Cui, Q. Tian, S. Gao, L. Huang, D. Pan, Fabrication of a $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ Photovoltaic Device by a Low-Toxicity Ethanol Solution Process, *ACS applied materials & interfaces*, 5 (2013) 10042-10047.
- [13] G.M. Ford, Q.J. Guo, R. Agrawal, H.W. Hillhouse, Earth abundant element $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{S}_4$ nanocrystals for tunable band gap solar cells: 6.8% efficient device fabrication, *Chem. Mat.*, 23 (2011) 2626-2629.
- [14] Q. Guo, G.M. Ford, W.-C. Yang, C.J. Hages, H.W. Hillhouse, R. Agrawal, Enhancing the performance of CZTSSe solar cells with Ge alloying, *Sol. Energy Mater. Sol. Cells*, 105 (2012) 132-136.
- [15] Q. Guo, G.M. Ford, W.C. Yang, B.C. Walker, E.A. Stach, H.W. Hillhouse, R. Agrawal, Fabrication of 7.2% efficient CZTSSe solar cells using CZTS nanocrystals, *J. Am. Chem. Soc.*, 132 (2010) 17384-17386.
- [16] A. Ennaoui, M. Lux-Steiner, A. Weber, D. Abou-Ras, I. Kotschau, H.W. Schock, R. Schurr, A. Holzing, S. Jost, R. Hock, T. Voss, J. Schulze, A. Kirbs, $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cells from electroplated precursors: Novel low-cost perspective, *Thin Solid Films*, 517 (2009) 2511-2514.
- [17] M. Ganchev, J. Iljina, L. Kaupmees, T. Raadik, O. Volobujeva, A. Mere, M. Altosaar, J. Raudoja, E. Mellikov, Phase composition of selenized $\text{Cu}_2\text{ZnSnSe}_4$ thin films determined by X-ray diffraction and Raman spectroscopy, *Thin Solid Films*, 519 (2011) 7394-7398.
- [18] J.H. Dickerson, A.R. Boccaccini, *Electrophoretic Deposition of Nanomaterials*, Springer, New York, 2012.
- [19] W. Guo, B. Liu, Liquid-Phase Pulsed Laser Ablation and Electrophoretic Deposition for Chalcopyrite Thin-Film Solar Cell Application, *ACS applied materials & interfaces*, 4 (2012) 7035-7041.

- [20] K. Taretto, U. Rau, J.H. Werner, Numerical simulation of grain boundary effects in Cu(In,Ga)Se₂ thin-film solar cells, *Thin Solid Films*, 480 (2005) 8-12.
- [21] M. Gloeckler, J.R. Sites, W.K. Metzger, Grain-boundary recombination in Cu(In,Ga)Se₂ solar cells, *J. Appl. Phys.*, 98 (2005) 113704.
- [22] C. Persson, A. Zunger, Anomalous Grain Boundary Physics in Polycrystalline CuInSe₂: The Existence of a Hole Barrier, *Physical review letters*, 91 (2003) 266401.
- [23] Y. Yan, C.S. Jiang, R. Noufi, S.H. Wei, H.R. Moutinho, M.M. Al-Jassim, Electrically benign behavior of grain boundaries in polycrystalline CuInSe₂ films, *Physical Review Letters*, 99 (2007) 235504.
- [24] S.H. Wei, S.B. Zhang, A. Zunger, Effects of Na on the electrical and structural properties of CuInSe₂, *J. Appl. Phys.*, 85 (1999) 7214-7218.
- [25] Y. Yan, R. Noufi, M. Al-Jassim, Grain-boundary physics in polycrystalline CuInSe₂ revisited: experiment and theory, *Physical review letters*, 96 (2006) 205501.
- [26] S. Siebentritt, S. Sadewasser, M. Wimmer, C. Leendertz, T. Eisenbarth, M.C. Lux-Steiner, Evidence for a neutral grain-boundary barrier in chalcopyrites, *Physical Review Letters*, 97 (2006) 146601.
- [27] C.S. Jiang, R. Noufi, J.A. AbuShama, K. Ramanathan, H.R. Moutinho, J. Pankow, M.M. Al-Jassim, Local built-in potential on grain boundary of Cu(In,Ga)Se₂ thin films, *Appl. Phys. Lett.*, 84 (2004) 3477-3479.
- [28] C.S. Jiang, R. Noufi, K. Ramanathan, J.A. AbuShama, H.R. Moutinho, M.M. Al-Jassim, Does the local built-in potential on grain boundaries of Cu(In,Ga)Se₂ thin films benefit photovoltaic performance of the device?, *Appl. Phys. Lett.*, 85 (2004) 2625-2627.
- [29] S. Sadewasser, T. Glatzel, S. Schuler, S. Nishiwaki, R. Kaigawa, M.C. Lux-Steiner, Kelvin probe force microscopy for the nano scale characterization of chalcopyrite solar cell materials and devices, *Thin Solid Films*, 431 (2003) 257-261.
- [30] M.J. Hetzer, Y.M. Strzhemechny, M. Gao, M.A. Contreras, A. Zunger, L.J. Brillson, Direct observation of copper depletion and potential changes at copper indium gallium diselenide grain boundaries, *Appl. Phys. Lett.*, 86 (2005) 162105.
- [31] H. Monig, Y. Smith, R. Caballero, C.A. Kaufmann, I. Lauermann, M.C. Lux-Steiner, S. Sadewasser, Direct evidence for a reduced density of deep level defects at grain boundaries of Cu(In, Ga)Se₂ thin films, *Physical Review Letters*, 105 (2010) 116802.
- [32] U. Rau, K. Taretto, S. Siebentritt, Grain boundaries in Cu(In, Ga)(Se, S)₂ thin-film solar cells, *Appl. Phys. A-Mater. Sci. Process.*, 96 (2009) 221-234.
- [33] S.Y. Chen, X.G. Gong, A. Walsh, S.H. Wei, Defect physics of the kesterite thin-film solar cell absorber Cu₂ZnSnS₄, *Appl. Phys. Lett.*, 96 (2010) 21902.
- [34] S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, T.K. Todorov, D.B. Mitzi, Low band gap liquid-processed CZTSe solar cell with 10.1% efficiency, *Energy Environ. Sci.*, 5 (2012) 7060-7065.
- [35] M.Y. Valakh, O. Kolomys, S. Ponomaryov, V. Yukhymchuk, I. Babichuk, V. Izquierdo-Roca, E. Saucedo, A. Perez-Rodriguez, J. Morante, S. Schorr, Raman scattering and disorder effect in Cu₂ZnSnS₄, *physica status solidi (RRL)-Rapid Research Letters*, 7 (2013) 258-261.
- [36] J.Y. Seto, The electrical properties of polycrystalline silicon films, *J. Appl. Phys.*, 46 (1975) 5247-5254.
- [37] C. Persson, A. Zunger, Compositionally induced valence-band offset at the grain boundary of polycrystalline chalcopyrites creates a hole barrier, *Appl. Phys. Lett.*, 87 (2005) 211904-211904-211903.
- [38] S.S. Schmidt, Microscopic properties of grain boundaries in Cu(In,Ga)₂ and CuInS₂ thin-film solar cells studied by transmission electron microscopy, in, 2011.
- [39] M. Hetzer, Y. Strzhemechny, M. Gao, S. Goss, M. Contreras, A. Zunger, L. Brillson, On microscopic compositional and electrostatic properties of grain boundaries in polycrystalline CuIn_{1-x}Ga_xSe₂, *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures*, 24 (2006) 1739-1745.

[40] C. Shi, X. Liu, R. Chuai, Piezoresistive sensitivity, linearity and resistance time drift of polysilicon nanofilms with different deposition temperatures, *Sensors*, 9 (2009) 1141-1166.

Acknowledgements

The work at the University of Michigan was funded by the National Science Foundation, under grants DMR-1506535 and DMR-0723032 (TEM instrument). The authors also acknowledge the support of the Michigan Center for Materials Characterization (MC)².

The fabrication of CZTSe devices and the J-V and EQE testing was funded by IMRA America, Inc.

The SPM was funded by the University of Michigan.

Figure Captions

Figure 1. (a) A schematic of formation of the CZT precursor film by LP-PLA and EPD. (b) A schematic of the conductive AFM measurement with illumination of a 532 nm laser.

Figure 2. (a) Top surface topography SEM image of a CZT precursor film. (b) A TEM image of the precursor nanoparticles and (c) its SAED ring pattern. (d) A HRTEM image of a Cu_6Sn_5 nanoparticle and (e) its SAED pattern.

Figure 3. Raman spectra mapping of the (a) CuSe (263 cm^{-1}) peak and (b) ZnSe (250 cm^{-1}) peak from the same region. (c) Raman spectra of a pure CZTSe phase region and 2 spots with secondary phases located in (a) and (b).

Figure 4. (a) A map of the CZTSe primary Raman peak position over a region of 50 by 50 μm . The red area shows a shift to the left corresponding to Cu-rich kesterite with the $\bar{1}\bar{4}$ structure. The blue region indicates the Cu-poor $\bar{1}\bar{4}2\text{m}$ structure.

Figure 5. a) AFM surface topography of a polycrystalline CZTSe film in contact mode. b) The current mapping of the same region under +1 V bias. c) The 3d model of the superimposed mapping of a) and b). d) The line profile of the height-current relationship in the region marked in blue line in a), b) and c).

Figure 6. (a) AFM topography of the top surface of a CZTSe device. (b) Zero biased photocurrent mapping, under illumination of a defocused 532 nm continuous wave laser with total power of 1mW. The photocurrent mapping is superimposed on the topography in (a) to illustrate the correlation between the position of the photo current and that of the GBs.

Figure 7. (a), (c) Planar SEM images and (b), (d) cross-sectional STEM ABF images of CZTSe sample 1 and 2, respectively, as well as (e) their J-V curves and (f) EQE spectra.

Figures

Figure 1 (a) A schematic of formation of Cu-Zn-Sn precursor film by LP-PLA and EPD. (b) A schematic of the conductive AFM measurement with illumination of a 532 nm laser.

Figure 2 (a) Top surface topography SEM image of a CZT precursor film. (b) A TEM imaging of the precursor nanoparticles and (c) its SAED ring pattern. (d) A HRTEM imaging of a Cu₆Sn₅ nanoparticle and (e) its SAED pattern.

Figure 3 Raman spectra mapping of the (a) CuSe (263 cm^{-1}) peak and (b) ZnSe (250 cm^{-1}) peak from the same region. (c) Raman spectra of a pure CZTSe phase region and 2 spots with secondary phases located in (a) and (b).

Figure 4 (a) A map of the CZTSe primary peak position over a region of 50 by 50 μm . The red area shows a shift to the left corresponding to Cu-rich kesterite with the $I\bar{4}$ structure. The blue region indicated the Cu-poor $I\bar{4}2m$

Figure 5 a) An AFM surface topography of a polycrystalline CZTSe film in contact mode. b) The current mapping of the same region under +1 V bias. c) The 3d model of the superimposed mapping of a) and b). d) The line profile of the height-current relationship in the region marked in blue line in a), b) and c).

Figure 6 (a) AFM topography of the top surface of a CZTSe device. (b) Zero biased photocurrent mapping, under illumination of a defocused 532 nm continuous wave laser with total power of 1mW. The photocurrent mapping is superimposed on the topography in (a) to illustrate the correlation between the position of the photo current and that of the GBs.

Figure 7 (a)(c) Planer SEM images and (b)(d) cross-sectional STEM ABF images of CZTSe sample 1 and 2, respectively, as well as (e) their J-V curves and (f) EQE spectra.