Compositional effects in Ag₂ZnSnSe₄ thin films and photovoltaic devices

Talia Gershon,^{1,a,b)} Kasra Sardashti,^{2,3,a)*} Yun Seog Lee,¹ Oki Gunawan,¹ Saurabh Singh,¹ Douglas Bishop,¹ Andrew C. Kummel,³ Richard Haight¹

¹ IBM TJ Watson Research Center, 1101 Kitchawan Rd, Yorktown Heights, NY 10598, USA

² Materials Science and Engineering Program, University of California, San Diego, 9500 Gilman Dr, La Jolla, CA 92093, USA

³ Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Dr, La Jolla, CA 92093, USA

a) These authors contributed equally to this work.

b) Author to whom correspondence should be addressed. E-mail: tsgercho@us.ibm.com

Abstract

Ag₂ZnSnSe₄ (AZTSe) is a relatively new n-type photovoltaic (PV) absorber material which has recently demonstrated a conversion efficiency of ~ 5% in a Schottky device architecture. To date, little is known about how the influence of composition on AZTSe material properties and the resulting PV performance. In this study, the Ag/Sn ratio is shown to be critical in the controlling grain growth, non-radiative recombination, and the bulk defect structure of the absorber. Insufficient Ag (relative to Zn and Sn) results in small grains, low photoluminescence intensities, and band gap narrowing, possibly due to an increase in the bulk defect density. Additionally, etching the AZTSe films in KCN prior to junction formation is found to be important for achieving reproducible efficiencies. Surface analysis using Auger Nanoprobe Microscopy analysis reveals that a KCN etch can selectively remove potentially harmful Ag-

rich secondary phases, therefore improving the MoO_3 / AZTSe junction quality. Moreover, grain boundaries in AZTSe are found to be enriched in Sn and O following KCN; the role this oxide plays in surface passivation and junction formation has yet to be determined.

1. Introduction

For over a decade, $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSSe) thin-film photovoltaic absorbers have been studied as earth-abundant alternatives to more conventional materials such as $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) and CdTe [1-4]. However, the performance of CZTSSe-based devices lags behind CIGS due to its limited open-circuit voltage (V_{oc})[5-8]. Materials analysis (neutron diffraction, Raman spectroscopy, photoluminescence measurements, scanning tunneling microscopy, etc.) has revealed that the CZTSSe bulk contains a large density ($> 10^{20} \text{ cm}^{-3}$) of Cu-Zn antisite pairs, resulting in almost complete disorder on the Cu-Zn atomic plane in the material[9-18]. Efforts have been made to eliminate these bulk defects but these have been met with limited success.

It is believed that the Cu-Zn disorder stems in part from a similarity in covalent radius between Cu^{+1} and Zn^{2+} cations as well as the fact that they differ in valence by only one charge, leading to a low formation enthalpy for defects due to the small strain resulting from $\text{Cu}^{+1} / \text{Zn}^{2+}$ exchange [19-21]. Therefore, one promising approach for overcoming the limitations with CZTSSe based photovoltaics is to transition to a material which has a larger barrier to I-II site exchange. Recent studies point to $\text{Ag}_2\text{ZnSnSe}_4$ (AZTSe) and the $(\text{Ag,Cu})_2\text{ZnSnSe}_4$ alloys as promising replacements for CZTSSe to mitigate the band tailing and defect problems[20, 22, 23]. While Ag is not considered to be earth-abundant, Ag use is not likely to limit the implementation of AZTSe-based PV since it is estimated to require less than 1/5 of the Ag per area (for a 1.5- μm film) compared to c-Si PV technology (which typically uses $\sim 20\text{g}$ per standard panel and accounts for $\sim 90\%$ of the PV market). Efficiencies over 5% have been demonstrated

with the n-type AZTSe absorber material using a Schottky-type device configuration where a high work function MoO_3 contact is used for junction formation[24]. While the previous study provided a proof-of-concept device implementation, it did not delve into the dependence of the PV performance and material properties on the chemical composition of AZTSe.

In this investigation, the composition-dependence of AZTSe material properties and device performance is studied. It is shown that the grain size scales with the Ag/Sn ratio in the absorber and that insufficient Ag results in non-radiative recombination and device shunting. Additionally, samples with low Ag are found to luminesce at lower photon energies, indicating either deeper bulk defects or a band gap narrowing effect which could be caused by a larger density of bulk defects. Both scenarios could be detrimental to device performance. Finally, nanoscale compositional analysis of the AZTSe surfaces via Auger nanoprobe microscopy (NanoAuger) demonstrates evidence of surface decomposition into Ag-rich and Zn-rich phases during the annealing process. KCN etch is found to selectively remove potentially harmful Ag-rich secondary phases, improving the overall PV performance. In addition, KCN etch resulted in both top surface and grain boundary oxidation leaving grain boundaries terminated by SnO_x . While the formation of SnO_x along grain boundaries is beneficial in CZTSSe technology[25], in AZTSe there may be a trade-off between helping (e.g. with grain boundary passivation) and hindering (e.g. by obstructing Schottky barrier formation with high-work function materials such as MoO_3).

2. Experimental

Photovoltaic devices based on AZTSe absorbers were fabricated on commercial SnO:F (FTO)-coated glass cleaned by etching in a NoChromix / Sulfuric acid solution. Substrates were loaded into an ultra-high-vacuum (UHV) system held at a base pressure of 10^{-9} Torr. High purity (> 99.999%) Ag, Zn, Sn,

and Se were co-evaporated onto the substrates held at $\sim 150^{\circ}\text{C}$ until the absorber thickness reached $\sim 1.5\text{-}2\text{ }\mu\text{m}$. Then, samples were annealed in an N_2 -filled glove box on a hot plate at $\sim 450\text{-}500^{\circ}\text{C}$ in an excess Se ambient to coarsen the grains, as described previously[26]. Following the anneal, the samples were subjected to a 3-minute etch in 1M KCN solution to remove secondary phases from the surface. Photovoltaic (PV) devices utilizing these films were then fabricated by deposition of $\sim 20\text{ nm}$ thick MoO_3 layer followed by $\sim 100\text{ nm}$ of $\text{In}_2\text{O}_3\text{:Sn}$ (ITO) to produce a Schottky-type contact for the n-type AZTSe absorber. The device characteristics were measured in a solar simulator calibrated to 1 sun at room temperature after at least 60 seconds of light soaking. Following the device fabrication and characterization, the samples were cross-sectioned and energy-dispersive x-ray spectroscopy (EDX) measurements were performed in a scanning electron microscope (SEM) using a beam voltage of 10 kV. At least three line-scans taken over several microns were averaged to produce an approximate composition measurement for the absorber. Room-temperature photoluminescence (PL) measurements were recorded using a Hamamatsu single-photon counting system equipped with a 532-nm pulsed laser with a 1ns pulse width and a 15-kHz pulse rate. The spot size of this laser was $\sim 1\text{mm}$.

Elemental analysis was performed using a Physical Electronics PHI-700 Auger Nanoprobe microscope (NanoAuger) which enables both Auger elemental mapping and spectroscopy with about 10 nm lateral resolution. Details of the NanoAuger operation are given elsewhere[27]. For elemental mapping, incident electron beam of 20 kV and 1.0 nA was rastered over the sample surfaces with 256 points per line and 256 lines per frame (256 x 256 data points). During the measurements, chamber pressure was kept within 6×10^{-10} - 3×10^{-9} Torr. Intensities used for the composition measurements were normalized to the relative sensitivity factors of the elements' primary Auger peaks.

3. Results

A series of AZTSe samples were studied with compositions ranging from Ag-poor to nearly stoichiometric. Figure 1 summarizes the relationship between the Ag/Sn ratio (measured by cross-sectional EDX line scans) and each of the important PV performance metrics. As shown, there is a strong correlation between Ag content and each performance metric, with the best results coming from samples closest to stoichiometry (i.e. Ag/Sn = 2). This is in contrast to what has been observed in the sister technology, CZTSSe, where samples with a Cu-rich stoichiometry always yield poor PV performance and a Cu-poor and Zn-rich composition is essential for high conversion efficiency[1, 2, 5]. Samples prepared with Ag/Sn ratios significantly above 2 were found to be badly shunted, likely due to inclusions of highly conductive Ag-Se and Ag-Sn-Se phases. It is noted that, similar to CZTSSe, Zn-rich compositions are still beneficial (see supplemental info).

Figure 1: PV performance parameters of AZTSe solar cells including (a) V_{OC} , (b) J_{SC} , (c) fill factor (FF), (d) power conversion efficiency, and (e) R-Jsc as functions of Ag/Sn ratio measured by cross-sectional EDX linescans of completed devices.

Figure 2 demonstrates one of the mechanisms whereby higher Ag/Sn ratios result in better performance metrics. Ag-poor samples tend to have smaller grains than those with more Ag. Large grains are readily observed in the near-stoichiometric AZTSe films, whereas they are not observed in CZTSSe in the absence of sodium. In CZTSSe, Na-rich species segregate to the grain boundaries and aid in grain boundary motion through a surfactant-type effect[28-30]. In this study, no sodium was intentionally added to the films. Therefore, it is believed that Ag-Se secondary phases may be acting as a flux agent in this system, similar to the role of Cu_2Se in the CIGS system[31].

Figure 2: SEM cross-sections of samples with varying compositions: (a) Ag/Sn = 1.50, Zn/Sn = 1.03, (b) Ag/Sn = 1.72, Zn/Sn = 1.07, (c) Ag/Sn = 1.85, Zn/Sn = 1.15

To further examine the effect of Ag excess on grain growth, a series of samples was prepared with larger variations in the Ag content. Figure 3(a-c) displays top-down SEM images of the samples where the Zn and Sn fluxes remained roughly constant during the deposition while the Ag flux was increased by $\sim 30\%$ (Fig. 3b) and $\sim 60\%$ (Fig. 3c) relative to a control (Fig. 3a). The samples were annealed and treated with a KCN etch prior to examination in SEM and x-ray diffraction (XRD). There were several key observations. First, there is a clear trend between grain size and Ag concentration (Fig. 3d). By

increasing the Ag flux during the deposition by 60%, the average grain size after annealing more than doubled. This large excess of Ag also, predictably, produced secondary phases as can be seen in the XRD patterns despite the KCN etch. The main AZTSe peaks are identified by the black reference pattern, and all peaks not associated with AZTSe or the underlying FTO-coated substrate can be attributed to ZnSe (same magnitude across all three samples), Ag_2Se , and Ag_8SnSe_6 secondary phases (determined from comparison with JCPDS standards, which scale with Ag content). Ag-Se compounds are well-known superionic conductors displaying fast ion diffusion,[32-36] and their presence along grain boundaries would be consistent with accelerated grain boundary motion and the creation of larger AZTSe grains. Notably, the KCN etch appears to selectively remove these Ag-rich secondary phases. Additionally, voids or grooves are observed in the SEM images along the grain boundaries in the samples with excess Ag after the KCN etch. These grooves offer further evidence to support that Ag-Se compounds segregate along the grain boundaries and play an important role in the AZTSe grain growth.

Figure 3: (a-c) Top-down SEM images of AZTSe samples prepared with various Ag fluxes during deposition (after annealing and KCN etching): (a) Ag/Sn ~ 1.5 , (b) Ag/Sn ~ 2.0 , (c) Ag/Sn ~ 2.4 . (d) Comparison of grain size of AZTSe samples as a function of Ag/Sn ratio. (e) XRD patterns from the above samples after KCN etch, indicating incomplete removal of secondary phases.

AZTSe is weakly n-type. AC field Hall measurement using rotating parallel dipole line system[37] yields a carrier density of $\sim 10^{12}/\text{cm}^3$ and electron mobility ($\sim 100 \text{ cm}^2/\text{Vs}$)[22]. The sign of the Hall signal and the high mobility value confirm that the system's majority carrier is electron. It has previously been shown that the Fermi level moves away from the valence band (towards the conduction band, CB) with increasing Sn content[24]. The dominant defect in this material is predicted to be the Sn_{Zn} donor defect[21], which may explain the observation that increasing the relative Sn content in the film shifts the Fermi level towards the conduction band, making the material appear more n-type. Increasing the carrier density by increasing Sn should correlate with an increased V_{oc} in the devices. However, the data shows the opposite trend as can be seen in Fig. 1. As discussed above, one explanation is the effect of composition on grain size. Another potential explanation is a change in bulk defect properties in the absorber layer.

As seen in Fig. 4(a, b), increasing Sn (decreasing the Ag/Sn ratio) results in a reduction of the PL intensity. This loss in PL indicates increasing activation of a non-radiative recombination pathway, which could include recombination at Sn-rich secondary phases in the absorber or Sn-related deep defects. In general, non-radiative recombination is frequently correlated with poor device performance, consistent with the findings of this study. Furthermore, the PL shifts towards lower photon energies at high Sn content (Fig. 4(c,d)). This indicates an increase in the bulk defect density, leading to a narrowing of the band gap and/or the presence of deep bulk defects. The better-performing samples in this study were correlated with the samples with higher PL intensity and photon energy (i.e. higher Ag/Sn).

Figure 4: Room-temperature PL characteristics of AZTSe samples with Ag/Sn ratios between 1.36 and 1.78: (a) raw PL spectra, (b) PL intensity as a function of Ag/Sn ratio, (c) normalized PL spectra, (d) PL peak position as a function of Ag/Sn ratio.

Although more reproducible PV performance was observed for films treated by KCN etch before device fabrication, the etching mechanism is yet to be understood. To better understand the mechanism of KCN reaction with the AZTSe surface, Nano-Auger spectroscopy mapping was employed. Figure 5 shows elemental maps of the Ag, Zn, Sn, and O on different pieces of an un-etched (Fig 5a) and KCN-etched (Fig 5b) AZTSe film. Several types of phase segregation are evident.

First, the bright spots are observed in the SEM image are correlated with local enrichment of Zn and Se (Se map not shown). Thus, these bright spots are attributed to ZnSe. It is also notable that the O signal from the ZnSe secondary phases is stronger after KCN etch, indicating partial oxidation of these

particles. The ZnSe precipitates are also present in the un-etched sample (Fig. 5a); in addition, in the unetched sample the Ag and Sn signals are locally enriched outside of the ZnSe regions. The KCN-etched sample (Fig. 5b) shows more uniform Ag and Sn distributions in those regions, indicating the removal of these potentially harmful compounds condition with KCN improving device performance.

Second, the KCN etched sample is found to have local Sn and O enrichment along the grain boundaries (Fig. 5c). Grain boundaries in CZTSSe also exhibit enrichment of Sn and O[25, 38], and this Sn-O is believed to be important for CZTSSe grain boundary passivation in that system[25, 38, 39]. While SnO_x may also passivate grain boundaries in AZTSe, the presence of this low work function layer may hinder the formation of a Schottky barrier with MoO₃, which would thereby limit device performance. It is also notable that the O signal from the ZnSe secondary phases is stronger after KCN etch, indicating partial oxidation of these particles.

Figure 5: NanoAuger secondary electron and elemental maps for Ag, Zn, Sn, O on (a) as-is and (b) KCN-etched AZTSe thin films. (c) Auger intensity linescan across grain boundaries in a KCN-etched AZTSe sample. The line scan was taken from a region with minimal ZnSe coverage (denoted by the red dotted frame).

In conclusion, the Ag/Sn ratio is found to be a critical compositional parameter in determining the efficiency of AZTSe-based thin film photovoltaics. High, near-stoichiometry, Ag/Sn ratios are found to (1) increase average grain size, (2) minimize non-radiative recombination, and (3) prevent band gap narrowing or the formation of deep defects. KCN etch is also found to be important in achieving high conversion efficiencies. XRD and NanoAuger experiments show that following annealing of the absorber, ZnSe and AgSnSe secondary phases are present on the surface. KCN etch selectively removed the Ag-rich secondary phases, leaving the Zn-rich secondary phases behind mostly in the oxidized state. KCN etch also induces enrichment of Sn and O along the grain boundaries and surface which may passivate the surface but leave a surface layer which inhibits contact efficiency.

4. Acknowledgements

TG and KS were equal contributors to this work. Stanford Nano Shared Facilities (SNSF) are acknowledged for NanoAuger measurements. K.S. thanks Chuck Hitzman for assistance with the NanoAuger measurements. The information, data, or work presented herein was funded in part by the U.S. Department of Energy, Energy Efficiency and Renewable Energy Program, under Award Number DE- EE0006334. The information, data, or work presented herein was funded in part by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express

or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Supplemental:

While the Ag/Sn ratio clearly plays a strong role in determining the performance of AZTSe-based photovoltaic devices, the Zn/Sn ratio is also found to play a role. Figure S1 shows a scatterplot of the performance of devices with varying Zn/Sn ratios. For most of the compositional range ($\text{Zn/Sn} \sim 1.1\text{-}1.5$) there is significant scatter in the data and no clear trend is observed. However, samples prepared with $\text{Zn/Sn} < 1.1$ in the absorber tend to have lower Voc and shunt resistance values. Therefore, similar to what is observed in CZTSSe, a slightly Zn-rich absorber is found to be important for preparing higher-performing AZTSe devices.

Figure S1: (a) V_{oc} and (b) R_{-Jsc} as a function of Zn/Sn ratio.

Figure S2: Se maps, complimentary to Fig. 5a and 5b from before (a) and after (b) the KCN etch.

References

- [1] D.B. Mitzi, O. Gunawan, T.K. Todorov, K. Wang, S. Guha, The path towards a high-performance solution-processed kesterite solar cell, *Solar Energy Materials and Solar Cells* 95(6) (2011) 1421-1436.
- [2] D.B. Mitzi, O. Gunawan, T.K. Todorov, D.A.R. Barkhouse, Prospects and performance limitations for Cu–Zn–Sn–S–Se photovoltaic technology, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 371(1996) (2013) 20110432.
- [3] H. Katagiri, Cu₂ZnSnS₄ thin film solar cells, *Thin Solid Films* 480 (2005) 426-432.
- [4] H. Katagiri, K. Jimbo, W.S. Maw, K. Oishi, M. Yamazaki, H. Araki, A. Takeuchi, Development of CZTS-based thin film solar cells, *Thin Solid Films* 517(7) (2009) 2455-2460.
- [5] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, D.B. Mitzi, Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency, *Advanced Energy Materials* 4(7) (2014).
- [6] X. Liu, Y. Feng, H. Cui, F. Liu, X. Hao, G. Conibeer, D.B. Mitzi, M. Green, The current status and future prospects of kesterite solar cells: a brief review, *Progress in Photovoltaics: Research and Applications* (2016).
- [7] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, Solar cell efficiency tables (Version 45), *Progress in photovoltaics: research and applications* 23(1) (2015) 1-9.
- [8] T. Gershon, T. Gokmen, O. Gunawan, R. Haight, S. Guha, B. Shin, Understanding the relationship between Cu₂ZnSn (S, Se) ₄ material properties and device performance, *MRS Communications* 4(04) (2014) 159-170.
- [9] S. Schorr, H.-J. Hoebler, M. Tovar, A neutron diffraction study of the stannite-kesterite solid solution series, *European Journal of Mineralogy* 19(1) (2007) 65-73.
- [10] D.M. Többsens, G. Gurieva, S. Levchenko, T. Unold, S. Schorr, Temperature dependency of Cu/Zn ordering in CZTSe kesterites determined by anomalous diffraction, *physica status solidi (b)* (2016).
- [11] S. Bourdais, C. Choné, B. Delatouche, A. Jacob, G. Larramona, C. Moisan, A. Lafond, F. Donatini, G. Rey, S. Siebentritt, Is the Cu/Zn Disorder the Main Culprit for the Voltage Deficit in Kesterite Solar Cells?, *Advanced Energy Materials* (2016).
- [12] M. Paris, L. Choubac, A. Lafond, C. Guillot-Deudon, S. Jobic, Solid-State NMR and Raman spectroscopy to address the local structure of defects and the tricky issue of the Cu/Zn disorder in Cu-poor, Zn-rich CZTS materials, *Inorganic chemistry* 53(16) (2014) 8646-8653.
- [13] J.J. Scragg, L. Choubac, A. Lafond, T. Ericson, C. Platzer-Björkman, A low-temperature order-disorder transition in Cu₂ZnSnS₄ thin films, *Applied Physics Letters* 104(4) (2014) 041911.
- [14] J.J. Scragg, J.K. Larsen, M. Kumar, C. Persson, J. Sandler, S. Siebentritt, C. Platzer Björkman, Cu–Zn disorder and band gap fluctuations in Cu₂ZnSn (S, Se) ₄: Theoretical and experimental investigations, *physica status solidi (b)* 253(2) (2016) 247-254.
- [15] C. Krämer, C. Huber, T. Schnabel, C. Zimmermann, M. Lang, E. Ahlswede, H. Kalt, M. Hetterich, Order-disorder related band gap changes in Cu₂ZnSn (S, Se) ₄: Impact on solar cell performance, *Photovoltaic Specialist Conference (PVSC), 2015 IEEE 42nd, IEEE, 2015*, pp. 1-4.
- [16] C. Krämer, C. Huber, C. Zimmermann, M. Lang, T. Schnabel, T. Abzieher, E. Ahlswede, H. Kalt, M. Hetterich, Reversible order-disorder related band gap changes in Cu₂ZnSn (S, Se) ₄ via post-annealing of solar cells measured by electroluminescence, *Applied Physics Letters* 105(26) (2014) 262104.
- [17] B.G. Mendis, M.D. Shannon, M.C. Goodman, J.D. Major, R. Claridge, D.P. Halliday, K. Durose, Direct observation of Cu, Zn cation disorder in Cu₂ZnSnS₄ solar cell absorber material using aberration corrected scanning transmission electron microscopy, *Progress in Photovoltaics: Research and Applications* 22(1) (2014) 24-34.

- [18] G. Rey, A. Redinger, J. Sendler, T.P. Weiss, M. Thevenin, M. Guennou, B. El Adib, S. Siebentritt, The band gap of Cu₂ZnSnSe₄: Effect of order-disorder, *Applied Physics Letters* 105(11) (2014) 112106.
- [19] S. Chen, X. Gong, A. Walsh, S.-H. Wei, Crystal and electronic band structure of Cu₂ZnSnX₄ (X= S and Se) photovoltaic absorbers: first-principles insights, *Applied Physics Letters* 94(4) (2009) 41903.
- [20] E. Chagarov, K. Sardashti, A.C. Kummel, Y.S. Lee, R. Haight, T. Gershon, Ag₂ZnSn(S,Se)₄: A highly-promising absorber for thin film photovoltaics, *Journal of Chemical Physics* 144(104704) (2016) 1-5.
- [21] Z.K. Yuan, S. Chen, H. Xiang, X.G. Gong, A. Walsh, J.S. Park, I. Repins, S.H. Wei, Engineering Solar Cell Absorbers by Exploring the Band Alignment and Defect Disparity: The Case of Cu- and Ag-Based Kesterite Compounds, *Advanced Functional Materials* 25(43) (2015) 6733-6743.
- [22] T. Gershon, Y.S. Lee, P. Antunez, R. Mankad, S. Singh, D. Bishop, O. Gunawan, M. Hopstaken, R. Haight, Photovoltaic Materials and Devices Based on the Alloyed Kesterite Absorber (Ag_xCu_{1-x})₂ZnSnSe₄, *Advanced Energy Materials* (2016).
- [23] C.J. Hages, M.J. Koeper, R. Agrawal, Optoelectronic and material properties of nanocrystal-based CZTSe absorbers with Ag-alloying, *Solar Energy Materials and Solar Cells* 145 (2016) 342-348.
- [24] T. Gershon, K. Sardashti, O. Gunawan, R. Mankad, S. Singh, Y.S. Lee, J.A. Ott, A. Kummel, R. Haight, Photovoltaic Device with over 5% Efficiency Based on an n-Type Ag₂ZnSnSe₄ Absorber, *Advanced Energy Materials* (2016).
- [25] K. Sardashti, R. Haight, T. Gokmen, W. Wang, L.Y. Chang, D.B. Mitzi, A.C. Kummel, Impact of Nanoscale Elemental Distribution in High-Performance Kesterite Solar Cells, *Advanced Energy Materials* 5(10) (2015).
- [26] B. Shin, Y. Zhu, N.A. Bojarczuk, S.J. Chey, S. Guha, Control of an interfacial MoSe₂ layer in Cu₂ZnSnSe₄ thin film solar cells: 8.9% power conversion efficiency with a TiN diffusion barrier, *Applied Physics Letters* 101(5) (2012) 053903.
- [27] K. Sardashti, R. Haight, R. Anderson, M. Contreras, B. Fruhberger, A.C. Kummel, Grazing Incidence Cross-sectioning of Thin-Film Solar Cells via Cryogenic Focused Ion Beam: A case study on CIGSe, Manuscript submitted for publication (2016).
- [28] T. Gershon, B. Shin, N. Bojarczuk, M. Hopstaken, D.B. Mitzi, S. Guha, The Role Of Sodium As A Surfactant And Suppressor Of Non-Radiative Recombination At Internal Surfaces In Cu₂ZnSnS₄, *Advanced Energy Materials* 5(2) (2014).
- [29] H. Zhou, T.-B. Song, W.-C. Hsu, S. Luo, S. Ye, H.-S. Duan, C.-J. Hsu, W. Yang, Y. Yang, Rational defect passivation of Cu₂ZnSn (S, Se)₄ photovoltaics with solution-processed Cu₂ZnSnS₄: Na nanocrystals, *Journal of the American Chemical Society* 135(43) (2013) 15998-16001.
- [30] C.M. Sutter-Fella, J.A. Stückelberger, H. Hagendorfer, F. La Mattina, L. Kranz, S. Nishiwaki, A.R. Uhl, Y.E. Romanyuk, A.N. Tiwari, Sodium Assisted Sintering of Chalcogenides and Its Application to Solution Processed Cu₂ZnSn (S, Se)₄ Thin Film Solar Cells, *Chemistry of Materials* 26(3) (2014) 1420-1425.
- [31] A.M. Gabor, J.R. Tuttle, D.S. Albin, M.A. Contreras, R. Noufi, A.M. Hermann, High-efficiency CuIn_xGa_{1-x}Se₂ solar cells made from (In_x, Ga_{1-x})₂Se₃ precursor films, *Applied Physics Letters* 65(2) (1994) 198-200.
- [32] M. Urena, M. Fontana, B. Arcondo, M. Clavaguera-Mora, Crystallization processes of Ag-Ge-Se superionic glasses, *Journal of non-crystalline solids* 320(1) (2003) 151-167.
- [33] M. Rice, W. Roth, Ionic transport in super ionic conductors: a theoretical model, *Journal of Solid State Chemistry* 4(2) (1972) 294-310.
- [34] F. Kirchhoff, J. Holender, M. Gillan, Structure, dynamics, and electronic structure of liquid Ag-Se alloys investigated by ab initio simulation, *Physical Review B* 54(1) (1996) 190.
- [35] K. Honma, K. Iida, Specific heat of superionic conductor Ag₂S, Ag₂Se and Ag₂Te in α-phase, *Journal of the Physical Society of Japan* 56(5) (1987) 1828-1836.
- [36] F. Shimojo, H. Okazaki, Phase Transition in Superionic Conductor Ag₂Se: A Molecular Dynamics Study, *Journal of the Physical Society of Japan* 60(11) (1991) 3745-3753.

- [37] O. Gunawan, Y. Virgus, K.F. Tai, A parallel dipole line system, *Applied Physics Letters* 106(6) (2015) 062407.
- [38] R. Haight, X. Shao, W. Wang, D.B. Mitzi, Electronic and elemental properties of the $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ surface and grain boundaries, *Applied Physics Letters* 104(3) (2014) 033902.
- [39] J.H. Kim, S.Y. Choi, M. Choi, T. Gershon, Y.S. Lee, W. Wang, B. Shin, S.Y. Chung, Atomic-Scale Observation of Oxygen Substitution and Its Correlation with Hole-Transport Barriers in $\text{Cu}_2\text{ZnSnSe}_4$ Thin-Film Solar Cells, *Advanced Energy Materials* (2016).