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Compositional effects in Ag₂ZnSnSe₄ thin films and photovoltaic devices

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A R T I C L E I N F O

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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 Agrich secondary phases, therefore improving the MoO₃/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.

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1. Introduction

For over a decade, Cu₂ZnSn(S,Se)₄ (CZTSSe) thin-film photovoltaic absorbers have been studied as earth-abundant alternatives to more conventional materials such as Cu(In,Ga)Se₂ (CIGS) and CdTe [1–4]. However, the performance of CZTSSe-based devices lags behind CIGS due to its limited open-circuit voltage (Voc) [5–8]. Materials analysis (neutron diffraction, Raman spectroscopy, photoluminescence measurements, scanning tunneling microscopy, etc.) has revealed that the CZTSSe bulk contains a large density (>10²⁰ 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

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a low formation enthalpy for defects due to the small strain resulting from Cu^{+1}/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 Ag₂ZnSnSe₄ (AZTSe) and the (Ag,Cu)₂ZnSnSe₄ 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- μ m film) compared to c-Si PV technology (which typically uses ~ 20 g per standard panel and accounts for ~ 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 MoO₃ contact is used for junction formation [24]. While the previous study provided a proof-ofconcept 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

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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 SnOx. While the formation of SnOx 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 MoO₃).

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 coevaporated onto the substrates held at ~ 150 °C until the absorber thickness reached ~ 1.5–2 µm. Then, samples were annealed in an N₂-filled glove box on a hot plate at ~450–500 °C in an excess Se ambient to coarsen the grains, as described previously [26]. Following the anneal, the samples were subjected to a 3-min etch in 1 M KCN solution to remove secondary phases from the surface. Photovoltaic (PV) devices utilizing these films were then fabricated by deposition of ~20 nm thick MoO₃ layer followed by ~ 100 nm of In₂O₃: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 s 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 ~ 1 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 × 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. Fig. 1 summarizes the relationship between the Ag/Sn ratio (measured by cross-



Fig. 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.



Fig. 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.

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).

Fig. 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].

To further examine the effect of Ag excess on grain growth, a series of samples was prepared with larger variations in the Ag content. Fig. 3a-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 ~ 30% (Fig. 3b) and ~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. 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.

(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), Ag₂Se, and Ag₈SnSe₆ 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.

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 Voc 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. 4a, 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. 4c,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).

Although more reproducible PV performance was observed for films treated by KCN ecth before device fabrication, the etching



Fig. 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 f, (d) PL peak position as a function of Ag/Sn ratio.



Fig. 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). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mechanism is yet to be understood. To better understand the mechanism of KCN reaction with the AZTSe surface, Nano-Auger spectroscopy mapping was employed. Fig. 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 SnOx 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.

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 Znrich 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.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.actamat.2017.01.003.

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