Synthesis and Characterization of Solution Processed Silver Indium Diselenide Thin Films

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***Abstract*—Silver indium diselenide ($AgInSe_2$) is a promising but under-investigated absorber material. In this work, we present a solution processing route to fabricate $AgIn(S,Se)_2$ thin films and characterize basic electronic properties. We present Hall Effect, Kelvin Probe Force Microscopy (KPFM), and Photoluminescence (PL) results that demonstrate promising characteristics, including high carrier mobilities and benign grain boundaries. We propose that weakly *n*-type $AgInSe_2$ should be applied in *p-i-n* type solar cells, contrary to prior attempts at making *p-n* $AgInSe_2$ devices. This will necessitate a careful selection of suitable electron and hole transporting layers.**

Keywords—Chalcogenide, Thin Film, Silver Indium Diselenide, ACIGS

I. Introduction

Recent research efforts have investigated the effects of adding silver to the $Cu(In,Ga)(S,Se)_2$ (**CIGS)** material system to create $(Ag,Cu)(In,Ga)(S,Se)_2$ (**ACIGS**). In addition to adjusting the bandgap, this also affords benefits in the electronic characteristics of the resulting material. A lower melting point translates to improved structural order and reduced defect concentrations compared to Ag-free chalcopyrites [1]. Furthermore, slight Ag addition has been found to reduce the carrier concentration in solution-processed CIGSe devices which allowed for the expansion of the depletion region deeper into the absorber layer, improving charge carrier collection [2]. Despite demonstrable benefits of silver alloying in CIGS, we anticipate that the addition of another cation will aggravate problems with compositional fluctuations across the surface of ACIGS devices, leading to worsened film uniformity. Indeed, some reports have already discussed the phase-separation challenges observed in ACIGS [3]. We anticipate that this will be a hurdle in large-scale manufacturing of ACIGS devices.

In this work, we propose that the benefits of Ag incorporation in chalcopyrite absorber layers might be better utilized by studying $AgInSe_2$, which maximizes the improvements in structural order via the dissimilar ionic sizes of Ag^+ and In^{3+} and circumvents the expected compositional uniformity challenges of ACIGS by reducing the number of constituent elements. $AgInSe_2$ possesses a bandgap in the ideal range for single-junction PV absorbers and has previously demonstrated high carrier mobilities in bulk crystal samples [4]. It is worth mentioning that while concern has been expressed over Ag abundance and its effect on device scalability, it has been reported that Ag usage in Ag-based thin film PVs will be less than Ag consumption in contacts for c-Si solar cells [5].

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II. Experimental Details

A. Materials and Methods

$AgInS_2$ inks were created by separately dissolving silver sulfide (Ag_2S, 99.998%) and indium metal (In, 99.999%) in solutions of butylamine (99.5%) and 1,2-ethanedithiol (98%). The two solutions were then mixed together at a 1:1 Ag:In mole ratio and diluted with butylamine to a total metals concentration of 0.4M. Inks were coated on to molybdenum-coated alkali-free Eagle XG substrates using a 3D printer modified to perform doctor blading. Each layer of the coated films was dried at ambient temperature for 60s before being transferred to a hot plate set to 300°C for 90s. The coating and annealing procedure was repeated 6 times for each sample, creating a film of orthorhombic $AgInS_2$. Solutions and films were synthesized in an N_2-filled glovebox.

The $AgInS_2$ films were placed in a graphite box with ~350mg selenium pellets (≥99.999%) and treated in a tubular furnace at 475-500°C for 15-20 minutes in an argon atmosphere to form ~700-900nm thick selenized films.

Films were exfoliated from their substrates to expose the flat, clean bottom interface as needed for electrical characterization. This was done by applying fast-curing epoxy to the top surface of the film and affixing it to a 2mm thick glass support. The Eagle XG substrate was similarly glued to a glass support. The epoxy was allowed to cure and the two supports were then mechanically torn apart, cleaving the film from the molybdenum substrate.

Chromium/gold contacts were deposited via thermal evaporation on exfoliated samples in the van der Pauw configuration for Hall Effect Measurements. Kelvin Probe Force Microscopy (KPFM) was conducted on samples soon after exfoliation. Care was taken to minimize sample exposure to air.

III. Results and Discussion

A. Solution Chemistry

An advantage of the amine-thiol solvent system is its ability to dissolve pure metals and metal chalcogenides, eliminating the need for metal salts that may introduce anionic contaminants into the film. These impurities could complicate attempts to study the electronic properties of the material. The behavior of silver sulfide in amine-thiol solutions was not previously studied, although the reaction pathway that leads to the dissolution of indium metal has already been elucidated by our group [6]. Analysis of silver sulfide amine-thiol solutions through Electrospray Ionization Mass Spectrometry showed

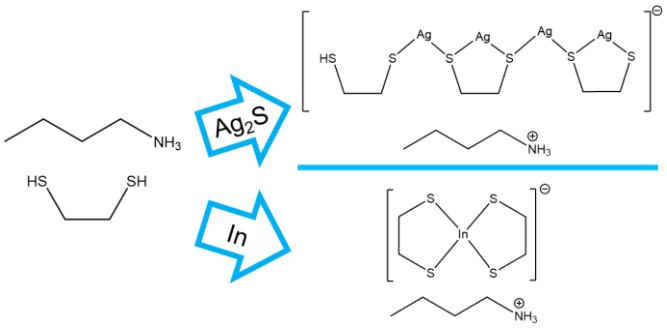

Fig. 1. Reaction overview for Ag_2S and In dissolution in amine-thiol solution. Shown is one example of the oligomeric silver thiolate structures that form during dissolution in amine-thiol.

that oligomeric silver sulfide species were formed in solution analogous to those formed by copper in amine-thiol solutions [6]. An example of such a structure is presented in Figure 1.

B. Thin Film Characterization

X-Ray Diffraction results showed that the annealed as-coated films were orthorhombic $AgInS_2$ while the selenized films were chalcopyrite $AgIn(S,Se)_2$ (sulfur is not completely eliminated during the selenization process). XRD results did not identify the presence of any secondary phases such as Ag_2Se and $AgIn_5Se_8$.

Raman Spectroscopy measurements showed C-C bonds on the surface of the selenized films, pointing to the presence of a carbonaceous layer on the surface of the films which may interfere with forming electrical contacts and hindering thorough characterization of the material. To remedy this, the $AgIn(S,Se)_2$ films were exfoliated as described above to facilitate electrical characterization.

Scanning Electron Microscopy demonstrated large-grain absorber layers had been obtained after selenization. Figure 2 shows crystalline domains that span nearly the full thickness of the selenized film, which will aid in carrier transport during device operation.

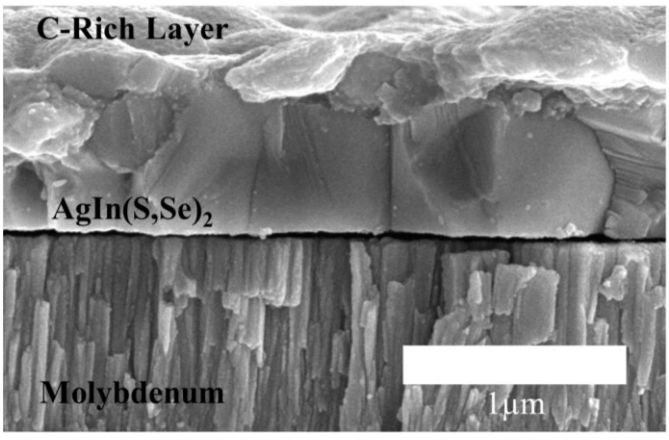

Fig. 2. Scanning Electron Microscopy cross-section of a $AgIn(S,Se)_2$ thin film. The molybdenum substrate is clearly visible below the coarsened grains, and the carbonaceous impurity layer can be seen as a thin coating over the top of the film.

C. Photoluminescence

Photoluminescence (PL) is a powerful tool for characterizing electronic properties of PV absorber layers. Width of steady-state PL spectra can be used to understand the structural order in different samples. PL measurements were conducted with a Horiba Jobin Yvon LabRAM HR equipped with a 632.8nm HeNe laser. Here, we find that $AgIn(S,Se)_2$ demonstrates a full-width half maximum of ~60meV in room-temperature photoluminescence as seen in Figure 3. This suggests good structural order within the film. Further work is being done to calibrate measurements for absolute photon counts to gain a deeper understanding into material physics.

D. Hall Effect

Hall Effect Measurements were carried out to determine the carrier concentration and mobility of the $AgIn(S,Se)_2$ thin films. Measurements were taken using a Lakeshore M91 FastHall controller with magnetic fields that were swept between -9T and 9T. Films were determined to be *n*-type with room temperature carrier concentrations in the range of $8 \times 10^{12} - 2 \times 10^{13}$ cm^{-3}, measured on three different samples from three distinct syntheses. These results are significantly lower than previous carrier concentration measurements for thin-film samples of $AgInSe_2$, and are approaching the values obtained for bulk crystals of $AgInSe_2$ grown from the melt [4]. This suggests that this synthesis technique avoids the incorporation of impurities or defects that raise the carrier concentration in other synthesis approaches. These results also imply that $AgInSe_2$ should not be employed in standard *p-n* junction device architectures as has been pursued in prior literature but instead should be used as the "intrinsic" layer in a *p-i-n* type device. Determining suitable electron and hole transport layers is an area of interest for future research.

Hall mobilities from 10-16 cm^2/Vs were obtained, a high value for solution-processed chalcogenide thin films. It should be noted that Hall Effect measurements characterize the in-

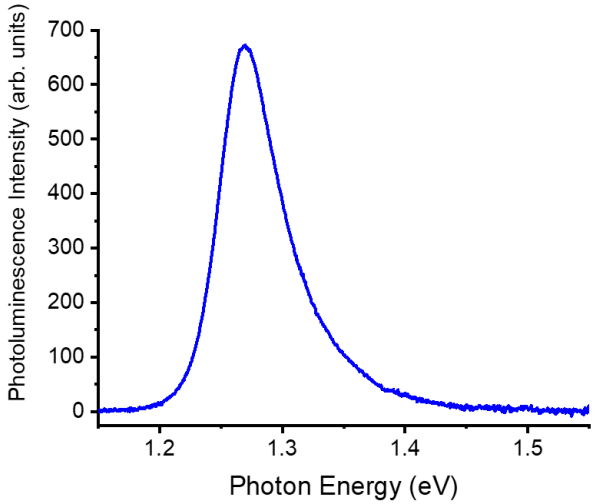

Fig. 3. Steady-state photoluminescence of $AgIn(S,Se)_2$ conducted at room temperature. PL maximum is approximately 1.27eV

plane carrier mobility over a length scale of millimeters, often giving values less than the out-of-plane mobility relevant to device operation [7].

E. Kelvin Probe Force Microscopy

Freshly exfoliated films were analyzed in Kelvin Probe Force Microscopy using a Pt/Ir cantilever tip to understand the band bending present at grain boundaries. These $AgIn(S,Se)_2$ films were synthesized on alkali-free substrates, enabling characterization of grain boundaries unaffected by alkali metals, which are known to play a significant role in CIGS grain boundary characteristics [8]. Gaining an early understanding of grain boundary behavior in $AgInSe_2$ is crucial as large fluctuations could present a significant hindrance to material development.

KPFM results suggested that there is minimal band bending at grain boundaries as shown in Figure 4. An impurity, thought to be residual carbon from the decomposition of the silver thiolates and indium thiolate complexes, can be seen at some of the grain boundaries. Band bending going from the grain interior to the contaminated grain boundaries in the given line scan shows a decrease in measured potential of ~50meV, suggesting a small barrier to minority-carriers (holes) is present. Other non-contaminated grain boundaries (indicated by blue arrows) exhibit almost no band bending. It should be noted that the magnitude of measured potential values can differ depending on KPFM measurement conditions [8]. However, these results suggest that band bending, where observed, would create only minority carrier barriers, and no upward band bending (which blocks majority carriers) is seen. This suggests favorable grain boundary characteristics in $AgIn(S,Se)_2$, even without post-deposition treatments.

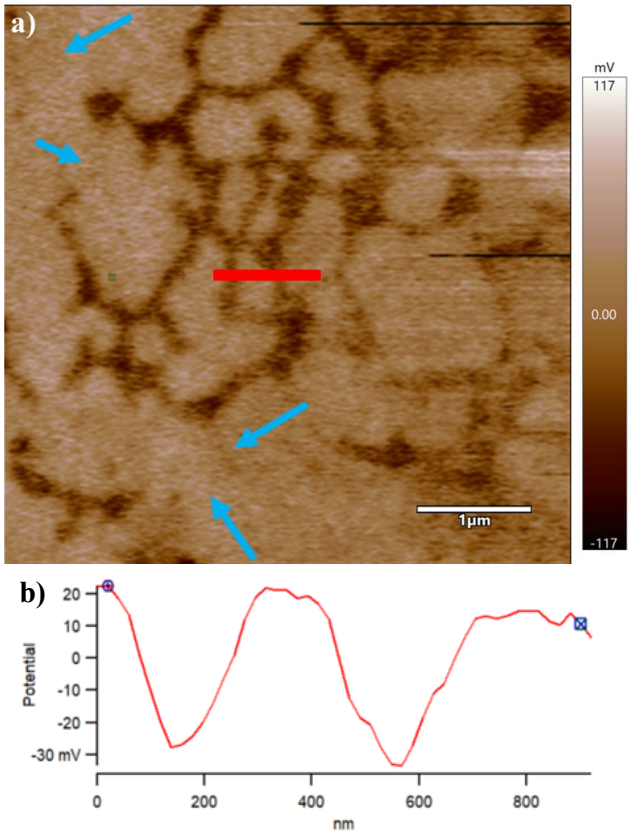

Fig. 4. KPFM results from a $AgIn(S,Se)_2$ film. a) potential map over the surface of the film. Blue arrows indicate some locations of passive grain boundaries. b) Surface potential scan across the line denoted by the red marker in the center of the map in a).

IV. Conclusion

$AgInSe_2$ has only briefly been studied by the PV community, and represents an opportunity to not only gain a better understanding of the electronic characteristics of one end of the compositional space explored in ACIGS research, but also exhibits promising electrical properties as an absorber material in its own right. In this work an effective solution-processing approach to the fabrication of chalcopyrite $AgIn(S,Se)_2$ thin films was presented. Characterization results demonstrated exciting charge transport metrics and superior electronic properties to other chalcogenide absorber materials. The carrier concentration is low enough to guide future research towards applications of $AgInSe_2$ in *p-i-n* device architectures, and determination of effective electron and hole transport layers will be an area of future research. These results suggest that $AgInSe_2$ may be a fruitful area of investigation not only in the solution-processed chalcogenide community, but in the broader thin film PV community.

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