

Semi-statistical Atom Probe Tomography Analysis of Thin Film Grain Boundaries

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In thin film photovoltaics, a large leap in lab level record efficiency has recently taken place. Perovskites and chalcopyrite structures are garnering the most attention due to their strong efficiencies and recent advances [1]. Yet most of the gains have been empirical and a fundamental understanding is still lacking. The most marketable thin films to date are the chalcopyrites and their spinoffs, i.e CdTe, Cu(In,Ga)Se₂, CZTS, etc., due to both their high efficiencies and reliabilities. Interestingly, a monocrystalline Cu(In,Ga)Se₂ is less efficient than its poly-crystalline counterpart. This goes against intuition, which assumes a single crystal contains fewer defects and therefore has larger diffusion lengths and less recombination, which lead to a higher cell efficiency. Perhaps the reason poly-Cu(In,Ga)Se₂ works so well is that the grain boundaries (GBs) are either benign or beneficial. One theory that has been around for over two decades is that the grain boundaries are Cu-poor, which leads to a lower valence band maximum (VBM). Since Cu(In,Ga)Se₂ is a p-type semiconductor, a lowered VBM would be a hole-barrier and thereby block the holes from recombining at defect rich GBs. During the technology's infancy (mid 1990s), the incorporation of Na was correlated with large gains in efficiency and theorized to assistance in a Cu-poor stoichiometry at GBs. Since then Na has been introduced either naturally by the soda-lime glass substrate via diffusion or by a post-deposition treatment of NaF after growth. Over the last few years, gains in efficiency have been attributed to the addition of K along with Na. However, the reasons why K incorporation increases efficiency are still unknown. A clear picture of the chemical profiles of impurities (K and Na) and matrix elements (Cu, In, Ga and Se) at the grain boundaries is needed. In this study, atom probe tomography (APT) provides insights into the complexities of GB chemistry in Cu(In,Ga)Se₂.

For thin film materials APT is a great tool to capture chemistry at interfaces and GBs as it uniquely combines high spatial resolution (sub nm) with high chemical sensitivity (10s of ppm). Some previous studies have used APT to characterize grain boundaries in Cu(In,Ga)Se₂, which have shown both Cu-poor and Cu-rich grain boundaries [2]–[4]. However, only a couple of grain boundaries have been analyzed and a more thorough statistical picture is needed.

This study includes a semi-statistical analysis of 13 grain boundaries from an 18.2% efficient cell intentionally grown to possess enhanced Na and K incorporation. The samples were prepared for APT and transmission electron microscopy (TEM) analysis using an FEI Helios 600i DualBeam focused ion beam/scanning electron microscope similar to Ref [5]. APT data were collected using a CAMECA LEAP 4000X Si instrument using a laser energy of 5 pJ, a base temperature of 40K, a detection rate of 1.5%, and a laser pulse rate of 500kHz, conditions optimized to get an accurate composition profile of stoichiometric Cu(In,Ga)Se₂. A Philips CM200 TEM was used to image the specimen dimensions before and after APT using the hardware described in Ref [6] for more accurate 3D reconstructions.

Figure 1 shows a TEM image (bottom) of an atom probe specimen before analysis and the APT reconstruction (top). Parameters such as image compression factor, ionic volume, detection efficiency, and sphere-to-cone ratios were adjusted so the GB in both the reconstruction and the TEM image are

well correlated. Chemical profiles perpendicular to the grain boundaries were measured. Figure 2 shows the chemical change in atomic percent from the bulk to the GB for all elements. Cd segregation into the grain boundaries was a result of diffusion from the n-type emitter layer (CdS), which appears to only happen when the CIGS grain boundary intersects the junction. All the GBs analyzed were Cu-poor and (In+Ga)-rich, which would support the theory of a decrease in the VBM. However, there is a wide-degree of “off-stoichiometry” leading to a wide-degree of possible energy barriers. From these data there is a good overall picture of how the stoichiometry changes at the grain boundaries and the amount of segregation of impurity atoms.

References:

- [1] M. A. Green et al. *Progress in Photovoltaics* pp. 1–9, 2015.
- [2] P.-P. Choi et al. *J. Appl. Phys.*, vol. **110**, no. 12, p. 124513, 2011.
- [3] O. Cojocaru-mir et al. *IEEE J. Photovoltaics*, vol. **1**, no. 2, pp. 207–212, 2011.
- [4] J. Keller et al. *Sol. Energy Mater. Sol. Cells*, vol. **117**, pp. 592–598, Oct. 2013.
- [5] K. Thompson et al. *Ultramicroscopy*, vol. **107**, no. 2–3, pp. 131–9, 2007.
- [6] B. P. Gorman et al. *Microscopy Today* **16**, pp. 42–48, 2008.

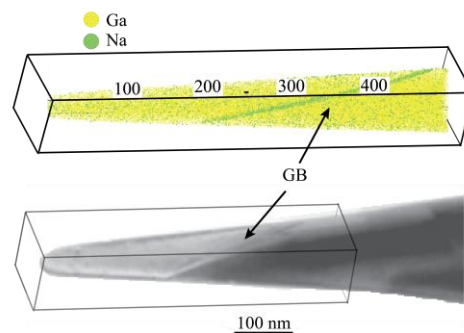


Figure 1. TEM (bottom) and APT (top) correlative microscopy of a grain boundary (GB) in Cu(In,Ga)Se₂. TEM imaging before APT analysis was used to improve the accuracy of reconstruction.

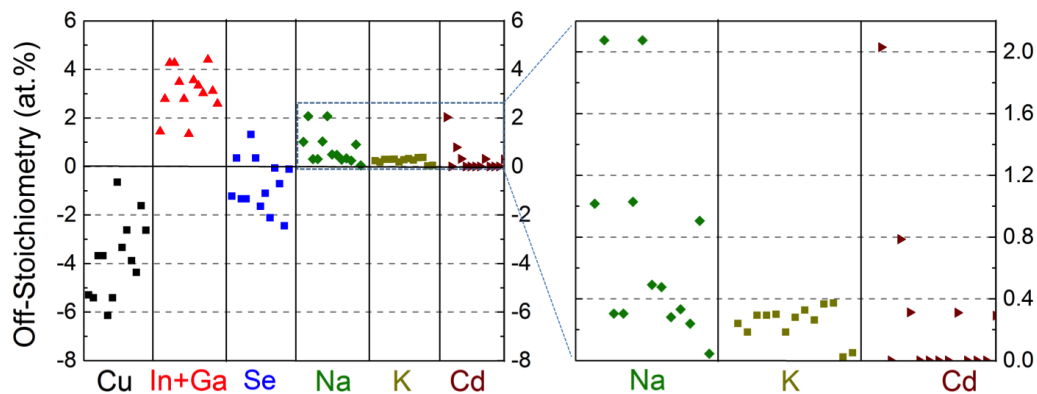


Figure 2. The change in composition relative to the bulk for each element at thirteen different grain boundaries. The figure on the right shows finer resolution for Na, K, and Cd.