



Direct observation of copper depletion and potential changes at copper indium gallium diselenide grain boundaries

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Di`V`]g\YX`VmiH`Y`5`Đ`Di`V`]g\]b[

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Direct observation of copper depletion and potential changes at copper indium gallium diselenide grain boundaries

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been no direct measurements of elemental composition of the individual grains and their boundaries. Here we present results of micro-Auger electron spectroscopy (AES), CLS, and work function extracted from secondary electron threshold (SET) measurements of individual CIGS GBs and GIs cleaved in UHV. These show that copper composition at CIGS GBs decreases, sometimes by almost a factor of two, work function decreases by several hundred meV, and that no radiative recombination centers appear at the GBs. These results confirm the prediction of strongly reduced Cu composition at CIGS surfaces, an energy barrier of several hundred meV to majority carrier (hole) GB diffusion, and the absence of new deep level radiative recombination centers at the GBs within ~ 0.4 eV of either band edge.

Specimens consist of CIGS layers nominally $1-2 \mu\text{m}$ thick grown by evaporation at the National Renewable Energy Laboratory (Golden, Co) (NREL) on Mo-coated soda-lime glass. These samples had nominal Cu/(In+Ga) compositions of 0.78, 0.85, 0.93, and 0.99 and Ga/(In+Ga) ~ 0.30 determined by inductively coupled plasma spectroscopy. The glass substrate was coated with Ni prior to cleaving to minimize charging and grooved with a diamond saw to promote relatively flat cleavage faces. Specimens were cleaved in a low 10^{-9} Torr prechamber and immediately (<1 min) transferred under vacuum to the 10^{-10} Torr base pressure analysis chamber. The JEOL 7800F operated with ~ 15 nm spot size at 5, 10 keV for CLS, 10 nA for AES, 1 nA for work function, and 100 pA for SET. AES spectra and SET measurements were taken with sample oriented 45° to incident electron beam and normal to hemispherical electron energy analyzer. Electron beam was normal to the CIGS surface for CLS. We took care to select relatively flat CIGS cleaved surfaces to avoid any angular dependent artifacts. We obtained both wide energy spectra at closely spaced individual spots as well as continuous line profiles of specific AES feature intensities versus position. [-357.4(mSn-)]

level E_{vac} relative to Fermi level E_{F}) measurements of CIGS with nominal composition $\text{Cu}/(\text{In}+\text{Ga})=0.99$ obtained from the linear extrapolated onset of secondary electron emission. Negative distances indicate initial measurements in one grain, origin at the GB, and positive distances from the boundary into an adjacent grain. SET energies decrease at the GB and rise in both directions into the GI. For both scans, work function decreases at GBs relative to GIs by an average of 0.48 eV. Work function decreases of this magnitude are observed in GBs of both $\text{Cu}/(\text{In}+\text{Ga})=0.99$ and 0.78 samples.¹² Calculated³ 0.2 – 0.4 eV band offset with the GB valence band maximum being *below* the GI valence band maximum, means that the valence band bends down from the bulk to the boundary and that holes are repelled from the GB. In turn, this means that electrons at the GB do not have holes to recombine with—thereby reducing the recombination rate. Our SET results to gauge work function energy decrease vary for individual GBs but they are in general several hundred meV, extending as high as 480 meV. Such a lowering of E_{vac} at the GB can arise both from positive charges and from a charge-neutral band offset. However, only the latter is likely to be effective in reducing recombination. The fact that the work function at the GB decreases agrees with earlier work function studies of related material using scanning probe techniques⁹ but the effect was smaller (~150 meV) presumably due to air exposure. However, the authors of Ref. 10 note that additional potential changes due to GBs below the surface could contribute as well. Similarly, band bending at the free CIGS surface due to air exposure can reduce the contrast of potential between the grain and its boundary.

Emission from GB: Figure 3 illustrates CLS spectra for $\text{Cu}/(\text{In}+\text{Ga})=0.99$ CIGS measured at 12 K for two adjoining grains and their common boundary. We see almost the same three-peak spectra at the GB and the GI, indicating no deterioration of the emission at the GB despite its many defects. No obvious changes are evident. CLS spectra obtained for 0.78 CIGS measured at room temperature (not shown) exhibit only one dominant peak at 1.12 eV and a shoulder at 1.17 eV. There is no emission present below the 1.12 eV peak. In general, the 0.99 CIGS exhibits a three-peak structure throughout the 1–2 μm thick film. However, the relative intensities of these peaks vary on a micron scale with depth along the growth direction, with the 1.2 eV peak dominating in CIGS near the Mo substrate and the 1.06 eV peak showing a relative increase in CIGS near the opposite bound-

ary. Such variations emphasize the importance of individual GB measurements.

The significant reduction of Cu content at the GB (Fig. 1) would increase the band gap as observed experimentally in CIGS thin films,¹³ and as predicted theoretically earlier.¹⁴ (This represents a reduction in Cu-induced *p-d* repulsion which reduces band gaps.) A band gap increases at the GB mostly due to a depression of the valence band maximum, which was indeed predicted by Persson and Zunger.³ The constancy of CLS emission observed in Fig. 3 may thus suggest that free carriers diffuse away from higher gap regions into the lower band gap GI before recombining. This requires further investigation.

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