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

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We have used micro-Auger electron spectroscopy, cathodoluminescence spectroscopy, and work function measurements in copper indium gallium diselenide polycrystalline solar cell films cleaved in ultrahigh vacuum. We establish that, relative to the grain interior, the grain boundary shows (1) a Cu composition decrease, as large as a factor of two, (2) a work function decrease of up to 480 meV, and (3) no additional radiative recombination centers despite a high concentration of grain boundary (GB) defects. These results confirm theoretical predictions that (i) polar GB interfaces are stabilized by massive ($\sim 50\%$) removal of Cu atoms, leading to (ii) a valence band offset between GB and grain interiors that (iii) repels holes from the GB, thus likely reducing GB electron-hole recombination and improving photovoltaic (and other photonic) device operation. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1906331]

Copper indium gallium diselenide (CIGS) thin films are a leading candidate for solar cells due to factors such as its record high energy conversion efficiency (19.5%) along with the reproducibility and flexibility of the many growth process used to fabricate them.[1] This is surprising because grain boundaries (GBs) are known to have high concentrations of defects and impurities that normally enhance recombination and thus adversely affect cell performance. Remarkably, experimental studies have shown that CIGS polycrystalline thin films grown on Mo on soda-lime glass exhibit higher internal quantum efficiencies than single crystal CIGS films grown epitaxially on GaAs.[2] Theoretical studies[3] have proposed an explanation in terms of the unusual composition at the GB: Unlike the surface of III-V materials, which are most stable for a nonpolar orientation[4] (having equal numbers of cations and anions), chalcopyrite surfaces are most stable for polar orientations.[5] Such orientations require a massive (up to 50%) removal of Cu atoms to cancel the otherwise energetically costly electrostatic dipole. Viewing a GB as a surface-like dipolar structure, calculations predict that the interface between the (Cu-normal) grain interior (GI) and the (Cu-deficient) GB would lower the valence band maximum at the GB by ~ 400 meV. Significantly, these electronic changes are predicted to produce only charge neutral band bending. This chemically induced (nonelectrostatic) band offset is predicted to repel holes from the GB, depriving the electrons of recombination partners despite a large, expected density of recombination centers. Note that since only the valence band bends downward in this nonelectrostatic mechanism, this

will repel holes without attracting electrons, thus electron-hole recombination must be diminished. This is achieved without the mobility-reducing charge defects at the GB. This theory predicts reduced band–to–band recombination of the photogenerated free carriers in polycrystalline CIGS. Persson and Zunger[3] have pointed out that such behavior has wider significance for polycrystalline materials in general and could usher in a more extensive range of applications for polycrystalline films.[6] Alternatively, generic surface donors have been suggested that could produce *n*-type band bending.[7] However, such downward band bending would repel holes while attracting electrons so it is not obvious that electron-hole recombination would be diminished.

There have been numerous solar cell studies of CIGS to explore the polycrystalline GB properties and establish optimal conditions of grain size and composition.[8] A number of studies have attempted to measure the potential changes between GI and GB.[9,10] These have typically involved scanning probe measurements after growth and subsequent air exposure. These studies have shown potential decreases (downward band bending) at CIGS GBs that are less than one-third those reported here, emphasizing the significance of the presently used ultrahigh vacuum (UHV) to avoid complications due to air exposure, namely, potential changes due to adventitious adsorbed species and band bending normal to all the grain surfaces. Furthermore, these air-exposed measurements are limited by the resolution of the scanning probe technique, typically tens of nanometers or more. Micro-cathodoluminescence spectroscopy (CLS) measurements of air-exposed CIGS grains in plan view reveal spatially localized variations in near band edge emission both above and below the nominal band edge energy.[11] To date, there have

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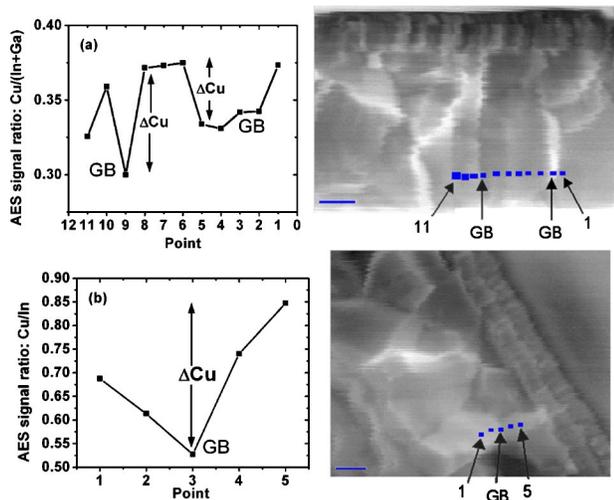
FIG. 1. (Color online) (a) AES Cu/(In+Ga) ratios vs position across GBs for nominal 0.85 CIGS. Points 1–11 increase from right to left, crossing two GBs. (b). AES Cu/In ratios vs position across GB for nominal 0.93 CIGS. Points 1–5 increase from left to right. Scale bar is 500 nm in both figures.

FIG. 2. Work function vs position across two separate GBs for nominal 0.99 CIGS. Work function decreases by nearly 0.5 eV at the GB.

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 μm 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 CLS. 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.

Cu Composition: Figure 1 shows Cu/(In+Ga) ratio plotted versus position across GBs; the positions are indicated in the secondary electron images. The results exhibit Cu/(In+Ga) decreases at the GBs averaging 15% and 22% shown via the dips in Cu/(In+Ga) ratio located at the GBs. These
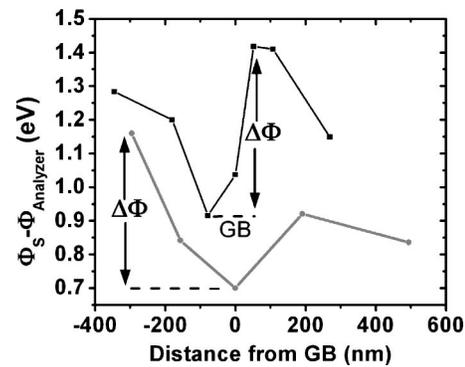
ratios are based on JEOL AES sensitivity factors for each element. If GI ratios are renormalized to the nominal bulk value of 0.85, the decreases at the GBs would more than double. On the other hand, the relatively low Cu/(In+Ga) ratios in Fig. 1(a) may reflect exposed grain surfaces rather than cleaved GIs for this particular case. Figure 1(b) illustrates AES spectra of CIGs with nominal composition Cu/(In+Ga)=0.93. The Ga/In ratio was comparable but the Ga signal was relatively noisy so that Cu/In ratios are plotted. Here the average Cu/In decrease at the GB is 47%. Furthermore, the GI Cu/In ratio ranges as high as 0.85, corresponding to a Cu/(In+Ga) ratio of 0.65, twice as large and closer to the nominal composition. This suggests that the JEOL AES sensitivity factors are reasonable and that the relatively low values measured in Fig. 1(a) are due to whole grain surfaces exposed during cleavage. Cu/(In+Ga) invariably decreases, and decreases of this magnitude are observed for many GBs and for all four specimens studied. The micro-AES measurements of Cu/(In+Ga) and Cu/In ratios obtained (Fig. 1) demonstrate unambiguously that the Cu concentration decreases dramatically at CIGS GBs. To our knowledge, there have been no previous measurements of elemental composition across GBs of atomically clean CIGS. These results provide strong support for first-principles calculations of Jaffe and Zunger[5] showing that, in order to stabilize the polar CIGS surface, one needs to remove 25%–50% of the Cu from the GB region. Our data indicate a spatial extent to the predicted Cu deficiency, extending into the grain. This is similar to the microphase formation at CIGS surfaces and Ref. 3 mentions such "ordered defect compounds" as an additional GB effect. *Remarkably, Cu/(In+Ga) decreases of this magnitude are in fact observed.* This can be regarded as an upper limit since smaller changes at other grains could be due to film cleavage that exposes the uncleaved surfaces, polar and nonpolar, of previously unexposed grains rather than the cleaved surfaces of such grains. Both will exhibit clean surfaces, although only minor compositional changes are expected for scans over intact CIGS grains. Angle-dependent images and AES spectra of >100 bounding grain surfaces are consistent with both types, displaying both flat cleavagelike versus irregular grain faces and $0.5 \leqslant$ Cu/(In+Ga)$_{AES}$/Cu/(In+Ga)$_{Nominal} <$ ~1 ratios. Based on AES escape depths, new facets with different orientation near the interface produce only small and random AES signal changes, compared with the predominant Cu decreases observed.

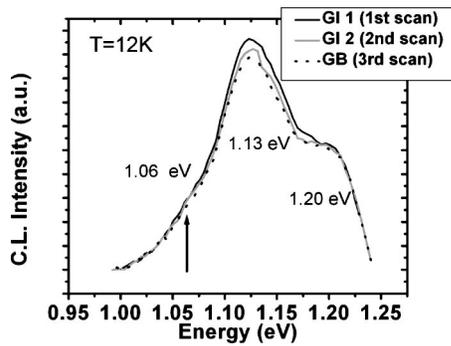*Work Function:* Figure 2 shows work function (vacuum

FIG. 3. CLS spectra for 0.99 CIGS at 12 K showing similar three-peak structure for two grains and their common boundary.

level E_{vac} relative to Fermi level E_F) measurements of CIGS with nominal composition Cu/(In+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 Cu/(In+Ga)=0.99 and 0.78 samples.[12] Calculated[3] 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 techniques[9] 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 Cu/(In+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.

Our AES and work function measurements confirm that the GB is abnormally Cu poor and hence the valence band maximum at the GB repels holes. These results emphasize the importance of defect energetics localized at GBs in altering recombination. The reduction of recombination rates by such changes opens new possibilities for polycrystalline films in transport devices.

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