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Journal of Vacuum Science & Technology B

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al ba ie ha ac ed ce h le ec mbina i n. S ch c m i i nal and elec a ic a ia i n be een g ain b nda ie and g ain in e i in C In

$_{1-x}$Ga$_x$Se$_2$ la cell ab be la e ma im e he e all h laic ef cienc . The high deg ee f in e g an la inh m genei em ha ize he im ance f de ailed g ain-b -g ain anal i . The e e l h ha ca ef l ecimen e a a i n and l ahigh ac m c ndi i n , c led i h nan cale in men al e l i n, a e i al f ch anal i .

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I. INTRODUCTION

C In$_{1-x}$Ga$_x$Se$_2$ (CIGS) i an im an h laic mate-ial. N abl , ec d c n e i n ef ciencie f nea l 20% (Ref. 1) a e b e ed f l c alline CIGS de ice , which e f m he ingle c alline c n e a .[2] Thi

Gi en ch a a ie f ed m del , a e f echni e i needed be CIGS ichi me and elec - a ic i h nan cale en i i i in de e al a e he different mechani m . N me die ha e been e f med n CIGS and ela ed em add e ing g ain chemi and m h l g .[14–17] In ecen a e [18] e e ed n he di ec mea emen f elemen al c m i i n f he indi id al g ain and hei b nda ie . We h ed ha c e c m i i n a CIGS GB dec ea e , me ime b alm a fac f 2, and ha he k f nc i n dec ea e b e e al h nd ed meV. In hi a icle, e ide addi i nal e l ing nding . We in e iga e chemical c m i i n, en ial di ib i n, and elec nic fea e f GI and GB n l a high ac m (UHV) clea ed CIGS c - ec i n face . B em l ing A ge elec n ec c (AES), ec nda elec n h e h ld (SET) mea emen , ca h d l mine cence ec c (CLS), and ec nda i n ma ec c (SIMS) e c n m he he e ical edic i n f he h le ba ie a GB d e C de cienc and e n he c m le m h l gical e ie f hi ma e ial.

II. EXPERIMENTAL DETAILS

The am le died in hi k e e g n n a da lime gla b a e i h a M back c n ac ing a ee e ce de c ibed el e he e.[1] The la e hickne e e e 1.5 2.0 m f CIGS and ∼0.7 m f M . The am le had f diffe en n minal C /(In+Ga) a i f 0.78, 0.85, 0.93, and 0.99, and a Ga/(In+Ga) a i f 0.30, a de e mined b ind c i el c led la ma ec c . In de b ain high- ali clea ed c ec i n , he f ll ing ced e a im lemen ed. Fi , he gla backide f a am le a hinned b g inding b ing he am le hickne ∼1 mm. The back ide e e hen n ched i h a diam nd a a de h f ∼500 m. An ∼300 hick Ni la e a de i ed n he back ide c ea e an elec ical c n ac ed ce cha ging d e elec n-beam b mba dmen . The am le e e clea ed in ac m i mea emen in an ambien e e f ∼10 9 T and hen immedia el an fe ed he main chambe i h e e f ∼10 10 T . The *in situ* mea emen e e e f med eml ing a JEOL 7800F canning elec n mic be e i ed i h a hemi he ical elec n analm338. heef9.978 f-272.1a-27

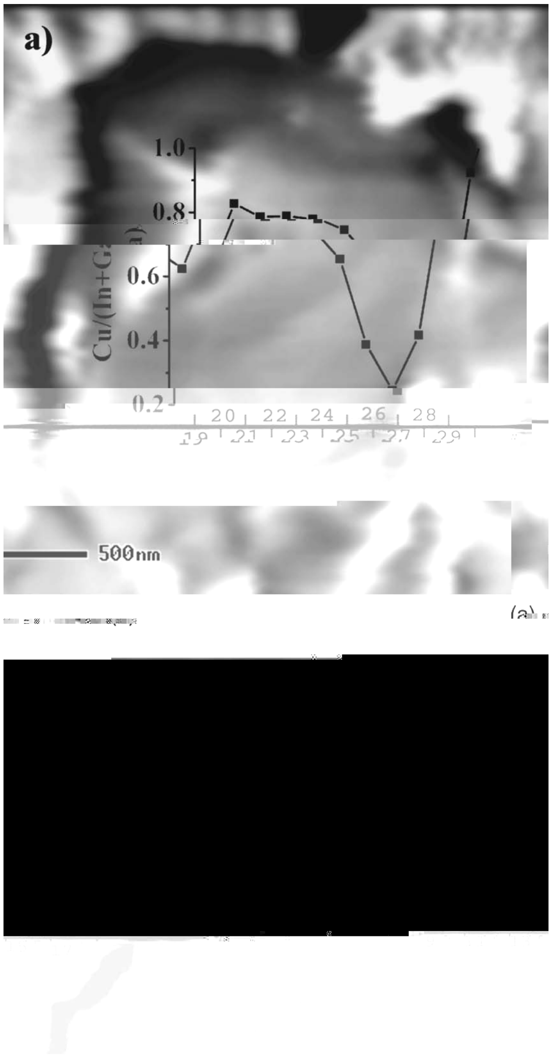

FIG. 1. (a) AES Cu/(In+Ga) ratio vs position, shown in SEM image. A decrease occurs at the GB (point 27). The data points were taken along the line shown in the figure at the labeled points. The Cu/(In+Ga) ratio at each point is overlaid. (b) AES Cu/(In+Ga) ratio vs position, shown in SEM image. A decrease occurs at the GBs (points 10 and 17). The data points were taken along the line shown in the figure at the labeled points. The Cu/(In+Ga) ratio at each point is overlaid.

statistical analysis for all of the AES data taken. Data points were classified as either GI or GB as determined from the secondary electron (SE) image taken for each scan. Over 100 GBs, with significantly more GI points, were studied and analyzed from the AES data to compile these statistics. The data collected for each sample showed a predominance of Cu/(In+Ga) ratios that decrease at the GB. For each sample, the average Cu to group III ratio was calculated at the GI and at the GB. For the sample with a nominal Cu/(In+Ga) ratio of 0.78, the value of this ratio was 0.085 lower at the GB compared to the GI. The other three samples with Cu/(In+Ga) ratios of 0.85, 0.93, and 0.99 showed decreases of 0.024, 0.071, and 0.041, respectively. The sample with the largest number of scans performed also showed the largest average difference from GB to GI. The standard deviations in the statistics for the GI values of the 0.78, 0.85, 0.93, and 0.99 composition samples were 0.011, 0.016, 0.011, and 0.014, respectively. The standard deviations of the GB statistics were 0.022, 0.028, 0.029, and 0.022, respectively. Thus, in all but the 0.85 concentration sample the average differences are outside the statistical errors. In general, the observed Cu/(In+Ga) ratios were on the average approximately 30% lower than expected from the nominal values. This effect may be explained by the fact that some grains cleave along their boundaries rather than through the bulk of the grain. Our cleaves can expose both grain interiors and grain boundaries since cleaving can break apart grains as well as separate whole grains from each other. AES measurements across exposed grains would therefore not show significant change between grain "interiors" and grain boundaries since both are actually boundaries. This is consistent with some of the minor AES variations already mentioned and the high surface sensitivity of the AES technique. However, many grains studied did show values close to the expected stoichiometries. From the statistical data, it is therefore possible to conclude that both types of grains were present after a cleave, with boundary-cleaved grains more common than bulk-cleaved grains. The average values listed above include all grains. In cases for which it appeared that the grain cleaved through its interior, the compositional changes are much larger than these averages, as shown in Fig. 1. Despite this, even grains with the low Cu/(In+Ga) ratios still displayed Cu deficiency at GBs. This is likely because the electron beam incident on the grain boundary probes proportionally more boundary versus interior volume. Similar analysis was performed for the O and Se species to test the prediction of Cahen and Noufi.[6] The resulting data revealed no clear indication of increased O or decreased Se at GBs.

B. Surface work function measurements

SET data from several samples showed pronounced work function decreases at GBs. Values of the work function difference between the semiconductor and the electron analyzer were determined from the onset energy of the SE emission, obtained from a linear extrapolation to the base line. We found that the accuracy of SET as a probe of gauging the work function is strongly dependent on both the level of surface contamination and the quality of the cleave. High amounts of contamination and a rough surface seem to suppress the SET onset from the CIGS layer in favor of one from contamination species and/or the Mo back contact. In order to determine the effect of a rough surface morphology on the SET measurements, the angular dependence of the SET peak was measured on a piece of gold foil, presputtered to remove contamination. We observed a relatively weak (less than 20 meV) dependence of the onset position for small (□5) angular changes relative to the surface normal. Somewhat larger (up to 200 meV) changes occurred as the angular variation reached 15 and rapidly grew with change in by both the onset energy and intensity for angle ≈20°. To avoid spurious onset changes due to uneven grain interfaces, care was taken to examine a GB with an interface at normal incidence.

Figure 2 shows scans through two different GBs of the sample with nominal Cu/(In+Ga) ratio of 0.99. The work function difference between the sample and the analyzer (ΔE) is plotted for several measurements versus distance from each GB. Negative distance indicates initial measurements in one grain, origin at the GB, and positive distance from the boundary in an adjacent grain. This figure shows decrease in the work function from 250 to almost 500 meV for grain boundaries 1 and 2, respectively. Other grain boundaries show similar decreases although such decreases can vary widely from 0 to 500 meV. The errors in these measurements are typically tens of meV with outliers ~200 meV. These decreases in potential are qualitatively similar to the scanning Kelvin probe measurements of the band offsets at chalcopyrite GB reported in Refs. 15 and 16, where the authors found a potential decrease (downward band bending) at the GB of 100–200 meV, which is significantly less than the changes reported here. This indicates the importance of UHV in avoiding contamination not only for chemical composition analysis but also to correctly gauge potential changes.

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CLS results were obtained from the sample with the nominal bulk Cu/(In+Ga) ratio of 0.99. This particular sample was cleaved *ex situ* and then immediately loaded into the vacuum chamber. The data was acquired through imaging of emission at particular wavelength and through spectra collected from spots and rastered areas. Location-specific variations in CLS data were observed as well. Practically all the spectra exhibited multiple peaks, the positions of which vary from grain to grain. Figure 3 shows an example of several spectra taken from different regions of the sample: three distinct peaks with emission energies of 1.12, 1.16, and 1.19 eV are present in the spectra. These features change in intensity at different locations on the sample. The low energy tail on the spectra likely arises from defects and disorder within the film.[21]

CLS imaging at different selected emission energies further illustrates this lack of uniformity. Figure 4 shows several CLS images superimposed on a corresponding SE image. The higher energy peaks are localized consistently near the

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A SIMS depth profile from the sample with Cu/(In+Ga) equal to 0.99 is shown in Fig. 6. The data indicate a Ga gradient through the sample consistent with standard growth conditions[1] and the spatial dependence of the CLS result. The Ga signal drops by approximately 50% from its maximum value near the front surface of the film. A Na increase of over an order of magnitude (from approximately 10 to 200 counts ±10 counts) near the Mo back contact is typical and may be due to microstructure changes in the Mo surface. It is consistent with results previously reported.[22] The depth profile also shows diffusion of In and Ga into the Mo layer, broadening the back interface. Imaging of the In and Ga signals within this broadened interface shows inhomogeneity in both the In and Ga signal layers all on a scale of tens of microns, much larger than the measurement resolution (120 nm), the typical grain size (∼1 μm), or the Mo layer roughness (90). No lateral spatial localization of the Na signal was discernable either within the bulk CIGS layer or within the Mo layer.

IV. DISCUSSION

The AES results found for the CIGS specimens measured are consistent with theoretical predictions of Cu deficiency at CIGS GBs.[3] Indeed, the 25%–50% decrease of Cu content we observe experimentally are in good quantitative agreement with those predicted by Jaffe and Zunger.[10] While the exact interfacial characteristics of the chemical bonding at GBs are not known, models that assume GBs to be similar to free surfaces are reasonable since neighboring grains may not form chemical bonds between them. GBs are commonly modeled as back-to-back Schottky barriers, and this is consistent with an approach assuming the GB to be

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relevant statistics on the CIGS layer properties were [illegible] at a larger number of measurements across various regions of the samples.

The observed SET inhomogeneities were stronger than those exhibited in the AES and CLS measurements. Sometimes grain-to-grain potential changes were so significant that they obscured any changes of potential at the GBs. We attributed the observation to several factors: (i) variation in grain-to-grain stoichiometry, (ii) potential difference between grain faces with dissimilar crystallographic orientation (consistent with the reported Kelvin probe results[23] depleted GB interface can inhibit hole recombination, generating higher short circuit currents. Our results also show that the vacuum level relative to the Fermi level decreases substantially near the GBs, consistent with either a band offset due to Cu vacancy formation or p-type band bending. In either case, the hole barriers that form serve to inhibit majority carrier movement away from the GB and therefore reduced recombination. We also find major nonuniform grain-to-grain stoichiometry, which can account for the well known difficulty maintaining CIGS uniformity in device structures. Our results emphasize the importance of studying such complex systems as polycrystalline CIGS employing nanoscale resolution, UHV environment, and careful sample preparation procedures.

ACKNOWLEDGMENTS

This work was supported by DOE Grant No. DE-FG02-97ER45666 (localized AES and CLS, Jane Zhu). Two of the authors (M.A.C. and A.Z.) are supported by DOE-EERE under NREL Grant No. DEAC36-98-G010337. The authors would like to thank Mark Gloeckler for useful discussions.

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