DEFECT CHALCOPYRITE $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ MATERIALS AND HIGH-Ga-CONTENT $\text{Cu}(\text{In,Ga})\text{Se}_2$ -BASED SOLAR CELLS

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ABSTRACT

Crystallographic, optical, and electrical properties of defect chalcopyrite $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ ($0 < x < 1$) materials in polycrystalline thin-film form are reported. Also, an energy band alignment between such materials and CdS has been calculated from X-ray photoelectron spectroscopy data. A comparison of some properties against published data on similarly prepared chalcopyrite $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ absorber materials is presented. Considering the chalcopyrite/defect chalcopyrite junction model, we postulate that the traditionally poor device performance of *uniform* high-Ga-content absorbers ($x > 0.3$) is due to a relatively inferior character—both structural and electrical—at the very chalcopyrite/defect chalcopyrite interface. We demonstrate that this situation can be circumvented (for absorbers with $x > 0.3$) by properly engineering such an interface by reducing Ga content in the region near the surface of the absorber.

INTRODUCTION

High-efficiency $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) solar cells have been shown to contain a thin layer of a "defect chalcopyrite" material—identified as $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ —at the surface of the absorber [1]. This thin surface layer seems to play an essential role in the operation of the CIGS-based solar cell and has led to the development of a chalcopyrite/defect chalcopyrite junction model for such devices. This very significant finding gives much support to earlier observations of a "buried" junction [2] elucidated by electron-beam induced current (EBIC) methods. In that work, the mapping of the space-charge region (by EBIC) showed consistently that the electronic junction did not appear to be at the metallurgical junction between CIGS and CdS but rather somewhere *within* the CIGS absorber. The ramifications of this proposed junction model are numerous, and its concept must be put to a test in structures incorporating Ga. In essence, the chalcopyrite/defect chalcopyrite model tells us that in state-of-the-art devices, ZnO plays no active role in junction formation; rather, ZnO can be viewed merely as an efficient medium to extract current from a given device.

Materials characterization of CIGS absorber materials is quite extensive and can be found in the literature. On the other hand, data on the defect chalcopyrites is rather minimal. Because knowledge of some physical properties of defect chalcopyrite materials may help us better understand the junction phenomena in CIGS-based devices, we present crystallographic data obtained by X-ray diffraction (XRD) methods, an optical characterization, and electrical properties as determined

by Hall measurements. An experimentally determined band alignment between CdS and the defect chalcopyrites (as a function of Ga content) is also presented. To elucidate and confirm the findings of electrical properties in the defect chalcopyrites, we perform an EBIC mapping of junction position in solar cells incorporating different Ga contents.

The knowledge gained from the fundamental characterization of defect chalcopyrite materials is put to a test in solar cells incorporating a modified high-Ga-content absorber.

DEFECT CHALCOPYRITE AND ABSORBER MATERIALS

Structural Analysis

First, we must distinguish the crystallographic differences between the "absorber" $\text{Cu}(\text{In,Ga})\text{Se}_2$ and the defect chalcopyrite $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ materials. The unit cell of the absorber has been related to an atomic arrangement described by space group $I\bar{4}2d$, whereas experimental XRD data for the defect chalcopyrite [3] have been associated with space group $P\bar{4}2c$. This group belongs to the tetragonal system, but there are reports [4,5] about the existence of a cubic phase in $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ materials. Our experimental XRD data on such samples show a spectra characteristic only of the tetragonal phase, as indicated by the presence of a 101 diffraction peak at 2θ -17.2°-18.1° (depending on Ga content) that should be absent in a cubic structure.

Polycrystalline $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ thin films (~0.5 μm thick) have been grown on 7059 Corning glass by coevaporation from the elemental sources and at a fixed substrate temperature of 550°C. After the 10 min. deposition of Cu-In-Ga-Se, a selenization step followed (at 15 Å/s of Se vapor), in which the sample was cooled from 550°C to 350°C in 20 min.

We have calculated lattice parameters for such materials with near-stoichiometry compositions, that is, atomic compositions close to the ideal given by $\text{Cu}:(\text{In,Ga}): \text{Se}=11.1:33.3:55.6$. XRD spectra have been obtained using Cu $K\alpha$ radiation (unfiltered). The XRD system has been calibrated with an external standard (Si powder SRM 640) and doublets due to $K\alpha_2$ radiation are removed from a given spectrum via software. Peak positions have been determined by a Split Pearson curve-fitting routine (at constant $K\alpha_1$ and $K\alpha_2$), and lattice parameter calculations for all films have been done using a least-squares refinement of the calculated 2θ values. No corrections of the lattice parameters have been done due to stress or thermal effects. Fig. 1 shows our calculated

lattice parameters for the defect chalcopyrite materials, along with published lattice parameter values for CIGS [6] absorber materials with near-stoichiometry compositions.

Fig. 1. Lattice parameters comparison between tetragonal near-stoichiometry defect chalcopyrite and near-stoichiometry absorber materials.

From Fig. 1 we see that there is a significant difference in the basal lattice parameters between both crystal structures. Indeed, the lattice mismatch at $x \sim 0.3$ has been calculated to be near 1% and becomes worse for higher values of x . The lattice parameter "c", on the other hand, shows a maximum mismatch of about 0.7% at $x=0$. The consequences of lattice mismatch are well understood in other semiconductor systems, and for a p-n junction, mismatch results in an increased density of recombination centers due to point, line, and/or plane defects induced by the mismatch. The question becomes: is the $\text{Cu}(\text{In,Ga})\text{Se}_2/\text{Cu}(\text{In,Ga})_3\text{Se}_5$ interface an abrupt interface or a naturally occurring, smooth-graded transition that accommodates and diffuses strains? First, there is the fact that we were able to grow defect chalcopyrite materials in a wide range of deviations from stoichiometry (Cu-rich to Cu-poor) [7]. Second, compositional depth profiles done by X-ray photoemission spectroscopy (XPS) and other methods [8,9] on absorber

materials show a smooth decrease in Cu content in the region near the surface of *low-Ga-content* CIGS absorbers. These findings suggest that—at least in the low-Ga-content end, i.e., $x < 0.3$ —the interface might accommodate a graded transition from one phase to the other. But this situation may be more difficult to accomplish as Ga is increased ($x > 0.3$) because the lattice mismatch becomes more significant.

Optical and Electrical Analysis

Absorption coefficients have been determined from reflection and transmission data obtained using a Cary 2000 spectrophotometer and applying the approximations given by Pankove [10]. Bandgap calculations on near-stoichiometry samples have been done by extrapolation of $(\alpha)^2$ vs. photon energy, and their relationship to Ga content is shown in Fig. 2. The figure includes a second-degree polynomial curve fit of the calculated bandgap values.

Fig. 2. Optical bandgap for near-stoichiometry defect chalcopyrite and near-stoichiometry absorber materials. Data for $\text{Cu}(\text{In,Ga})\text{Se}_2$ after Ref. [6]

Fig. 2 also includes the bandgap values for absorber materials (solid line) as reported in Ref. 6. In general, the defect chalcopyrite materials show a bandgap ~ 180 meV higher than their absorber counterparts with similar Ga contents.

Hall measurements reveal highly resistive materials with rather low mobility and carrier concentrations. There is also an apparent change in conductivity type as Ga is increased. Materials with low Ga content show n-type conductivity, and for high Ga content they turn to p-type conductivity. This change in conductivity type was also observed by testing similar samples with a thermoelectric probe. Table 1 summarizes Hall measurements obtained with a system in compliance to the ASTM F76-1985 standard for obtaining Hall data. Results presented in Table 1 were consistent in the conductivity type; however, mobility and carrier concentrations calculated by the *software* varied as much as one order of magnitude when remeasured.

Fig. 3. EBIC scan of ZnO/CdS/CuIn_{1-x}Ga_xSe₂/Mo/glass devices with x~0.3 (left), x~0.5 (center), and x~1 (right).

Even though the table shows a conductivity type, we must emphasize that the low values of carrier concentrations combined with a high resistivity are more indicative of intrinsic-type materials. However, the electrical implications of such weak conductivity types may have a significant influence on the space-charge distribution (and band alignment) at the very junction when these materials form an interface with the absorber. In effect, EBIC studies done on solar cells with different Ga contents [11] reveal a systematic shift of the junction position with increased Ga content. This situation can be seen in Fig. 3, where the EBIC mapping is shown for three of these cases, namely, uniform CuIn_{1-x}Ga_xSe₂ with x~0.3, x~0.5, and x~1.0. Because EBIC maps the junction position, we see that as Ga is increased the structure becomes more and more a true heterojunction, where the CdS/ZnO layers begin to play an influential role in junction formation. This situation agrees with the electrical characterization presented above. If indeed the chalcopyrite/defect chalcopyrite interface loses its p-n character (becoming more a p-p' type of junction with increased Ga), the junction position can be expected to shift toward the metallurgical junction.

Table 1. Room-temperature Hall Measurements for Cu(In_{1-x}Ga_x)₃Se₅ (0<x<1) Materials.

x=Ga/(Ga+In)	R (Ω-cm)	Hall mobility (cm ² /V-s)	Carrier density (cm ⁻³)	cond. type
0.00	2.7x10 ⁶	~10	~10 ¹¹	n
0.29	3.9x10 ⁶	~3	~10 ¹²	n
0.59	6.9x10 ⁵	~2	~10 ¹²	p
0.88	7.8x10 ⁵	~6	~10 ¹²	p
1.00	8.0x10 ⁶	~13	~10 ¹¹	p

On another subject, we have experimentally determined a band alignment between the defect chalcopyrites and CdS using X-ray photoelectron spectroscopy (XPS). Details of this measurement technique can be found in Ref. 12. The ~500 Å CdS layer has been deposited over the defect chalcopyrite thin films by the standard chemical bath deposition (CBD) technique used in solar-cell fabrication. We find that the valence-band offset (VBO) between CdS and the defect chalcopyrite is rather independent of Ga content and is in

the order of ~1.0 eV (see Fig. 4). To calculate the conduction-band offset (CBO) we use the relationship:

$$\text{CBO} = E_g(\text{CdS}) - E_g(\text{def. chalcop.}) - \text{VBO} \quad (1)$$

In general, the addition of Ga proves beneficial because the larger bandgaps (for x<0.3) in the defect chalcopyrite help reduce the CBO and, furthermore, for x>0.3, the CBO becomes negative. In other words, the band offset at the CdS/defect chalcopyrite interface does not seem to present adverse consequences for optimum PV performance.

Fig. 4. Band alignment for CdS/Cu(In_{1-x}Ga_x)₃Se₅ (0<x<1). CBM and VBM are conduction-band minimum and valence-band maximum, respectively. 135CIGS refers to Cu(In_{1-x}Ga_x)₃Se₅ materials.

HIGH-Ga-CONTENT DEVICES

As seen from the data presented above, there seems to be (at least) two detrimental factors in the chalcopyrite/defect chalcopyrite junction of *uniform* high-Ga-content absorbers (x>0.3); namely, the structural and electrical differences between both kind of materials. It follows that both factors could be circumvented by

tailoring the very surface of such high-Ga absorber materials ($x > 0.3$) to produce a low-Ga-content ($x < 0.3$) defect chalcopyrite. Because these defect chalcopyrites have been reported to be thin ($< 500 \text{ \AA}$), such proposed grading does not necessarily have to be over a long portion of the absorber; rather, a short and somewhat abrupt transition could suffice. This situation in actuality may be difficult to accomplish considering the high processing temperatures associated with absorber fabrication. We have nevertheless attempted to obtain some grading, but so far this grading is rather coarse and perhaps covers more absorber thickness than it needs to. The compositional depth profile—by Auger electron spectroscopy (AES)—of one such absorber is shown in Fig. 5. The graph clearly shows the intentional low Ga content at the surface and the high Ga content in the bulk of the absorber. Current-Voltage (I-V) data for selected devices made from similar absorber structures are shown in Table 2. These structures are the first we have made and further optimization is needed to increase efficiency.

Figure 5. Semi-quantitative AES depth profile of high-Ga absorber with low-Ga $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ surface layer.

Table 2. Summary of I-V data for CIGS devices made from absorbers with modified surface (low-Ga-content surface).

V_{oc} (mV)	J_{sc} (mA/cm ²)	Fill Factor	Efficiency
687	23.7	75	12.2*
674	28.0	74	14.0*
684	29.3	72.9	14.6

* No anti-reflection coating

On annealing these kind solar cells (high-Ga-content absorber with low-Ga-content surface) we find that they are rather insensitive to the heat treatment done at 200°C in air. Indeed, most of these devices did not change significantly their I-V characteristics—under light—even after 180 min. anneals.

CONCLUSIONS

We have shown that there are significant crystallographic differences between the absorber

$\text{Cu}(\text{In,Ga})\text{Se}_2$ and the defect chalcopyrite $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ materials. Lattice mismatch in the basal plane becomes $> 1\%$ for Ga contents of $> 30\%$ (relative to In). Also, the n-type conductivity of defect chalcopyrites is found to exist up to $x \sim 0.3$, and for higher Ga contents it shifts to p-type. Uniform high-Ga-content absorbers are observed to behave more like true heterostructures, where the CdS/ZnO layers begin to play a more active role in junction formation.

Considering the chalcopyrite/defect chalcopyrite junction model, we postulate that the traditionally poor device performance of *uniform* high-Ga-content absorbers ($x > 0.3$) is due to a relatively poorer character—both structural and electrical—at the very chalcopyrite/defect chalcopyrite interface. We have demonstrated that improved efficiencies are attainable in high-Ga-content absorbers by properly grading the very surface of such materials.

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