Cu depletion at the CuInSe$_2$ surface

Dongxiang Liao$^a$ and Angus Rockett

Department of Materials Science and Engineering, University of Illinois, Illinois 61801

(Received 16 December 2002; accepted 4 March 2003)

The chemical composition of the (112)B surface of epitaxial CuInSe$_2$ thin films is investigated by angle resolved x-ray photoelectron spectroscopy. Results show that a severe Cu depletion exists in the top 1–2 atomic layers. No bulk second phase is found at the surface. The source of this depletion and its relation to the Cd doping at the CdS/CuInSe$_2$ interface are discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1570516]

Polycrystalline Cu(In,Ga)$_2$Se$_2$ (CIGS)-based heterojunction diodes are promising candidates for photovoltaic applications. Currently, the conversion efficiency is approaching 20%. However, there are still unresolved fundamental issues about the interface of the CIGS/CdS junction, whose properties largely decide the performance of the device. For example, device characteristics indicate that there is a large band bending in the p-type CIGS absorber, and its surface (the region that contacts the CdS) is inverted to n type. This favorable quality cannot be accounted for with a device structure in which a CdS buffer layer mates with a perfect CIGS surface—CdS is a weakly n-type material and cannot cause the band bending by itself. The understanding and further improvement of the devices demand characterization of the structure and the chemical composition of the interface.

Our recent work$^1$ indicated that in the device the first couple of atomic layers of CuInSe$_2$ (CIS) are heavily doped by Cd. The results also suggest Cu depletion with respect to In in the doped region. Since the rate of Cd diffusion in near-stoichiometric CuInSe$_2$ is negligible at the processing temperature,$^2$ it is likely that Cd atoms simply occupy the vacant cation sites near the surface. This implies that there is a very shallow Cu depletion in the CIS surface during the CdS deposition.

Cu depletion at the CIS surface exists prior to the deposition of CdS. It has been known that the free surface of the Cu-poor CIGS absorber has a different stoichiometry from the bulk.$^3$ As the compositions measured were close to those of the ordered defects compounds$^4$ (ODC), it was interpreted that these compounds exist at the free surface of Cu-poor CIGS surfaces as a second phase. However, to date no such bulk phases near the CIS surface have been observed and it is now thought by some to be a surface phase instead.$^5$ A recent electron microscopic study$^6$ specifically looked at the top 0.2 $\mu$m of the quality CIGS films. They found the surface layer structurally similar to the bulk and no signs of an ODC were observed, although a slight Cu depletion near the surface was detected. Currently, no information about the thickness of the Cu-depletion layer or its effect on the device performances is available.

This work set out to determine the composition depth profile (CDP) of the free CIS surface. Using angle resolved x-ray photoelectron spectroscopy (ARXPS), we show that the Cu depletion is limited to the top layer of the CIS surface. We propose that this depletion is essential to the Cd doping of the CIS surface in the CIS/CdS heterojunction. The source of this depletion is discussed from the viewpoint of polar surface reconstruction.

The (112)B surface of epitaxial CIS films was studied. It is extremely difficult to accurately determine the CDP of polycrystalline films due to the surface roughness. The (112)B surface, while not the equivalent of the polycrystal surface, is a good substitute for the study since polycrystalline device absorber layers are thought to facet to {112} type planes.$^7$ Slightly In-rich CIS epitaxial films were deposited on GaAs (111)B substrates using a hybrid sputtering and evaporation technique.$^8$ The surfaces are very smooth$^9$ with atomically flat terrace widths up to 100 nm, which allows composition depth profiling of the first several nanometers under the surface by ARXPS.

To prevent surface contamination during transport from the growth environment to the XPS instrument, we capped the free surface of CIS with about 1-$\mu$m-thick Se by evaporation at the end of the growth. In the XPS load lock chamber, the Se cap layers were removed by heating the films in vacuum to about 300 °C for 3 min. The temperature is sufficient to evaporate elemental Se, but not high enough to cause the decomposition of CIS. Then the samples were quickly transfered to the UHV analysis chamber. The x-ray source was Mg $K\alpha$ (1253.6 eV). Surveys indicated that samples were generally free of carbon and oxygen contamination. In rare cases, trace amounts of oxygen could be detected from the O 1$s$ signal at the background noise level. Ultraviolet photoelectron spectroscopy was also carried out using He I (21.2 eV) and He II (40.8 eV) light sources. Figure 1 gives the resulting spectra. The distance between valence maximum and the Fermi energy was about 0.6 eV, suggesting that the surface band structure was not affected by oxygen exposure.$^5$ There was also no signature peak of oxygen in the spectra. We believe that the oxygen contamination we might have encountered is not sufficient to cause a large composition change in the CIS surface.

XPS is a surface sensitive technique due to the short inelastic mean free path (IMFP) of photoelectrons in solids. The probability $p$ of photoelectrons escaping from an amorphous (or finely polycrystalline) sample without losing energy decreases exponentially with the length of the path $l$, i.e., $p = \exp(-l/\lambda_p)$, where $\lambda_p$ is the photoelectron’s IMFP.

$^a$Electronic mail: d-liao@uiuc.edu
For XPS experiments on a flat specimen surface, the path length is given by \( l = z / \cos \theta \), where \( z \) is the depth of the photoelectron source and \( \theta \) is the emission angle (defined as the angle between surface normal and the photoelectron direction). We can see that 95% of the information obtained by XPS comes from the volume within \( 3 \lambda \cos \theta \) of the surface.

By varying the emission angle, we obtain information at different sampling depths. The approximate composition depth profile can then be reconstructed by numerical modeling.

For single crystal samples like ours, the electron scattering process demands more careful treatment that includes the structural information, i.e., \( \lambda_1 \) becomes a function of the emission direction. Secondary effects such as elastic scattering also must be taken into consideration. Nevertheless, assuming a constant signal attenuation length \( \lambda_1 \) in place of the IMFP, we can obtain a first order approximation of the angle dependence of the XPS signal intensity. Let \( q = \exp(\frac{d}{dcos \theta}) \), where \( d \) is the interlayer spacing and \( \lambda \) is the AL. The intensity \( I \) can then be written as function of the composition of each atomic layer \((c_1, c_2, c_3, \ldots)\):

\[
I(\theta) \approx c_1 + qc_2 + q^2 c_3 + \ldots
\] (1)

Photoemission angles from 0° to 61° were used in experiments here. Figure 2(a) shows the intensity of Cu 2p_{3/2}, In 3d_{5/2}, and Se 3d peaks of a CIS sample at different angles. The bulk composition of this CIS sample was determined by energy dispersive x-ray spectroscopy to be 23% Cu, 25.5% In, and 51.5% Se. By applying the relative sensitivity factors to the respective photoelectron peak intensities and then normalizing to 100%, we can get the “composition” at a certain angle. At 61°, the largest emission angle, hence the shallowest sampling depth, Cu/In/Se = 14/35/51. Apparently the surface of the CIS is Cu depleted. However, at smaller emission angles, the Cu/In ratio steadily increases toward the bulk value, reaching 20/28 at 0°. This change indicates that the composition at slightly larger depth (comparable to the attenuation length) is very different from the that of the top layer.

A more quantitative composition depth profile is obtained by fitting the peak intensities at different emission angles according to Equation (1). The intensity versus emission angle relationship suggests that the In concentration is approximately constant throughout the XPS detection depth. The variations of In peak intensity are likely due to geometric factors from the experimental setup and orientation of the single crystal. There were also errors in focusing the electron detector to the sample surface. (The sample surface rotated off-axis on the special heating stage and the focus had to be adjusted manually at each angle.) However, since Cu and In occupy almost identical cation sites, we expected the systematic errors for them to be similar. To cancel out the errors from the geometric factors, the Cu/In peak intensity ratio was used to calculate the Cu composition depth profile.

Figure 2(b) shows the experimental Cu/In ratio and the fitting curves as a function of the emission angle. Since the AL of the IMFP of electrons in CIS is not known experimentally, we estimated the AL using the IMFP\(^{10}\) of electrons in similar materials such as InAs\(^{11}\) and GaAs.\(^{12}\) The AL of the Cu 2p_{3/2} (\(KE=316.3\) eV) photoelectron falls between 0.6 and 1.0 nm, or 1.8 and 3.0 \(112\) atomic layer spacings. The models corresponding to these two AL values are given in Table I. The corresponding fit curves are fit1 and fit2 in Fig. 2.

Comparing the fit curve with the experimental data, we see that except for very small emission angles, the models fit the Cu/In ratio very well. The 0° data (both the raw peak intensities and the Cu/In ratio) do not fit the general trend, nor is it possible to explain the sudden jump in the data by any chemical composition effect. Since a control ARXPS experiment on a smooth, pure Au polycrystalline film gave approximately constant Au 4f_{7/2} peak intensities at all angles, we conclude that this aberration is not likely due to the geometric factors of the equipment setup, but the geometric factors of the single crystal sample instead. The change in the Cu concentration is likely due to geometric factors from the experimental setup and orientation of the single crystal. There were also errors in focusing the electron detector to the sample surface. (The sample surface rotated off-axis on the special heating stage and the focus had to be adjusted manually at each angle.) However, since Cu and In occupy almost identical cation sites, we expected the systematic errors for them to be similar. To cancel out the errors from the geometric factors, the Cu/In peak intensity ratio was used to calculate the Cu composition depth profile.

Figure 2(b) shows the experimental Cu/In ratio and the fitting curves as a function of the emission angle. Since the AL of the IMFP of electrons in CIS is not known experimentally, we estimated the AL using the IMFP\(^{10}\) of electrons in similar materials such as InAs\(^{11}\) and GaAs.\(^{12}\) The AL of the Cu 2p_{3/2} (\(KE=316.3\) eV) photoelectron falls between 0.6 and 1.0 nm, or 1.8 and 3.0 \(112\) atomic layer spacings. The models corresponding to these two AL values are given in Table I. The corresponding fit curves are fit1 and fit2 in Fig. 2.

Comparing the fit curve with the experimental data, we see that except for very small emission angles, the models fit the Cu/In ratio very well. The 0° data (both the raw peak intensities and the Cu/In ratio) do not fit the general trend, nor is it possible to explain the sudden jump in the data by any chemical composition effect. Since a control ARXPS experiment on a smooth, pure Au polycrystalline film gave approximately constant Au 4f_{7/2} peak intensities at all angles, we conclude that this aberration is not likely due to the geometric factors of the equipment setup, but the geometric factors of the single crystal sample instead. The change in the Cu concentration is likely due to geometric factors from the experimental setup and orientation of the single crystal. There were also errors in focusing the electron detector to the sample surface. (The sample surface rotated off-axis on the special heating stage and the focus had to be adjusted manually at each angle.) However, since Cu and In occupy almost identical cation sites, we expected the systematic errors for them to be similar. To cancel out the errors from the geometric factors, the Cu/In peak intensity ratio was used to calculate the Cu composition depth profile.

Figure 2(b) shows the experimental Cu/In ratio and the fitting curves as a function of the emission angle. Since the AL of the IMFP of electrons in CIS is not known experimentally, we estimated the AL using the IMFP\(^{10}\) of electrons in similar materials such as InAs\(^{11}\) and GaAs.\(^{12}\) The AL of the Cu 2p_{3/2} (\(KE=316.3\) eV) photoelectron falls between 0.6 and 1.0 nm, or 1.8 and 3.0 \(112\) atomic layer spacings. The models corresponding to these two AL values are given in Table I. The corresponding fit curves are fit1 and fit2 in Fig. 2.

Comparing the fit curve with the experimental data, we see that except for very small emission angles, the models fit the Cu/In ratio very well. The 0° data (both the raw peak intensities and the Cu/In ratio) do not fit the general trend, nor is it possible to explain the sudden jump in the data by any chemical composition effect. Since a control ARXPS experiment on a smooth, pure Au polycrystalline film gave approximately constant Au 4f_{7/2} peak intensities at all angles, we conclude that this aberration is not likely due to the geometric factors of the equipment setup, but the geometric factors of the single crystal sample instead. The changes in the Cu concentration is likely due to geometric factors from the experimental setup and orientation of the single crystal. There were also errors in focusing the electron detector to the sample surface. (The sample surface rotated off-axis on the special heating stage and the focus had to be adjusted manually at each angle.) However, since Cu and In occupy almost identical cation sites, we expected the systematic errors for them to be similar. To cancel out the errors from the geometric factors, the Cu/In peak intensity ratio was used to calculate the Cu composition depth profile.

![FIG. 1. Valence band photoemission spectra of the (112)Se surface of a CuInSe\(_2\) film.](image)

![FIG. 2. (a) The photoemission intensity (after the application of sensitivity factors) of Cu 2p_{3/2}, In 3d_{5/2}, and Se 3d from a CuInSe\(_2\) sample as a function of emission angle \(\theta\). (b) The Cu/In peak intensity ratios and fit curves from two models. The bulk composition of the CuInSe\(_2\) is 22.5% Cu, 25.5% In, and 52% Se.](image)

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>Layer 1</th>
<th>Layer 2</th>
<th>Layer 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>5.4</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>1.0</td>
<td>3.8</td>
<td>12.1</td>
<td>23</td>
</tr>
</tbody>
</table>

TABLE I. Layer-by-layer breakdown of the Cu composition of a CuInSe\(_2\) (112) surface. Fitting results are given for the lower and upper limit of the attenuation length \(\lambda\) for Cu 2p_{3/2} photoelectrons.
neling or focusing of the photoelectrons along the crystallographic direction (221) is probably the major factor. This could possibly account for the sharp increase of Cu/In ratio around 0°, given the Cu/In ratio of the second atomic layer is significantly higher than that of the first layer as described in our CDP models.

It is interesting to compare our results with those of by Schmid and co-workers. Their surface Cu/In ratios for samples with similar bulk composition are about 1/3. In comparison with our “compositions,” this seems to indicate that the Cu depletion in their samples is much more severe. Certainly, large differences could exist simply because the deposition processes are quite different: in their bilayer process, In$_x$Se$_y$ is deposited on top of CIS as the finishing step. However, if the surface morphologies of the samples are taken into consideration, the actual difference in the surface composition is possibly smaller. Polycrystal samples usually have rough, faceted surfaces (we estimate an average facetting angle of about 30° for several device layers from National Renewable Energy Laboratory). This leads to a larger effective emission angle and reduces the sampling depth of XPS.

Our calculations strongly suggest that the Cu depletion is limited to the first atomic layer or the first two layers of CIS. There is apparently no bulk CuIn$_x$Se$_y$ phase near the surface of our samples. The implication for the device modeling and characterization is significant: there is no need to introduce an ODC layer as the n-type partner in the device model. The answer for the questions about the heterojunction lies in the characterization is significant: there is no need to introduce an ODC layer as the n-type partner in the device model. The answer for the questions about the heterojunction lies in the case of the ternary compound CuInSe$_2$, the two types of cations have different valences, so changing the Cu/In ratio of the surface can effectively increase or reduce the number of electrons on the surface. Zhang and Wei suggested several possible reconstruction models for 112 surfaces of CIS and calculated that these reconstructions significantly lower the surface energy. While the actual reconstruction of 112 is yet to be determined experimentally, the compositional data obtained from our experiments favor the Cu-poor varieties among Zhang and Wei’s models.

The composition depth profiles obtained in this study also agree very well with the result of our recent study of the CIS/Cds interface, where the first one or two layers of the CIS (112)Se surface were found heavily doped with about 6 x 10$^{14}$/cm$^2$ of Cd. Since the Cd diffusion in CIS is very limited at the processing temperature ($\sim$70°C), it is very likely that when Cds is deposited on CIS, the Cd mostly occupies the large number of vacant Cu sites (3–6 x 10$^{12}$/cm$^2$ according to the models). If this is indeed the case, the donor defect Cd$_x$Cu will contribute a large number of free electrons to the surface. The result would be a type-inversion of the CIS absorber.

This work is supported by the U.S. Department of Energy through the division of Basic Energy Sciences (Contract No. DEFG02-91ER45439) and the National Renewable Energy Laboratory (Contract Nos. AA-1-30620-05 and ACQ-1-30619-07). The authors thank Rick Haasch for his assistance in the photoelectron spectroscopy experiments, which was carried out in the Center for Microanalysis of Materials at the University of Illinois.