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Dear Bolko,

This is the first quarterly report of our second year in the Thin Film Partnership Program (Subcontract No. XXL-5-44205-12 to University of Nevada, Las Vegas: Characterization of the electronic and chemical structure at thin film solar cell interfaces). A brief summary and details of our activities are given below. This report is in fulfillment of the deliverable schedule of the subcontract statement of work (SOW).

Summary

This project is devoted to deriving the electronic structure of interfaces in Cu(In,Ga)(S,Se)_2 and CdTe thin film solar cells. By using a unique combination of spectroscopic methods (photoelectron spectroscopy, inverse photoemission, and X-ray absorption and emission) a comprehensive picture of the electronic (i.e., band alignment in the valence and conduction band) as well as chemical structure can be painted. The work focuses on (a) deriving the bench mark picture for world-record cells, (b) analyze state-of-the-art cells from industrial processes, and (c) aid in the troubleshooting of cells with substandard performance.

In the last months, we could gather first results for Cu(In,Ga)Se_2 ("CIGSe") and Cu(In,Ga)(S,Se)_2 ("CIGSSe") samples prepared by the group of W. Shafarman (Institute of Energy Conversion, University of Delaware). The aim of the conducted experiments is to shed light on the deeply buried absorber/back contact interface in terms of its chemical and electronic properties.

Detailed Description of the Activities:

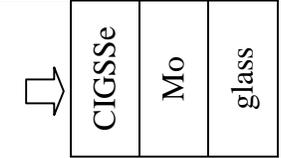
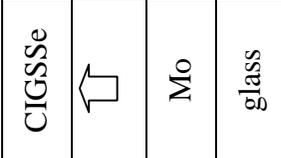
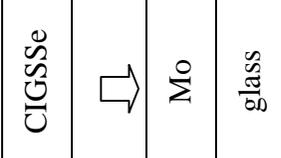
In the past months we have focused on the characterization of the deeply buried interface between absorber and Mo back contact in chalcopyrite thin film solar cells. These investigations were based on two different types of samples, namely CIGSe/Mo/glass and CIGSSe/Mo/glass. Both sample types were provided by the group of W. Shafarman (IEC, U Delaware). In order to make the interface between absorber and Mo accessible for characterization by photoelectron spectroscopy (PES), we had to develop a suitable lift-off (or cleavage) technique, which allowed us to cleave the absorber/Mo/glass samples at the desired interface. It turned out that gluing the front side of the absorber/Mo/glass thin

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film stack to a stainless a steel plate using a conductive (Ag-containing) epoxy allows a subsequent division of the stack in two parts and provides the necessary conductivity for the PES measurements. In all cases the thin film stack cleaved at the absorber/Mo interface. However, there were differences in terms of the area exposed after lift-off. Comparing the CIGSe/Mo/glass and CIGSSe/Mo/glass samples with respect to their cleavage behavior, it seems that for the latter it is rather easy to lift off large areas (in the range of cm^2). This is favorable with respect to the characterization by PES but even more important for the planned inverse photoemission (IPES) measurements, since the IPES detector is not able to “artificially” reduce the spot size of the e-gun on the sample (which is approx. 1 cm^2) as it can easily be done in the PES case, probing differently sized areas by using different lens modes of the electron analyzer. Thus, even when only a small sample area is cleaved properly, the PES setup still allows a reasonable characterization, which might not be the case for the IPES measurements.

Due to the better cleavage behavior, in the following we will focus on our results stemming from (cleaved) CIGSSe/Mo/glass samples. We looked at three different samples for each lift-off process (the arrows show the direction of measurement):

Table I

Sample	Name in the following text	Sketch
CIGSSe/Mo/glass	CIGSSe Front	
CIGSSe/Mo/glass cleaved, top part	CIGSSe Back	
CIGSSe/Mo/glass cleaved, bottom part	Mo Front	

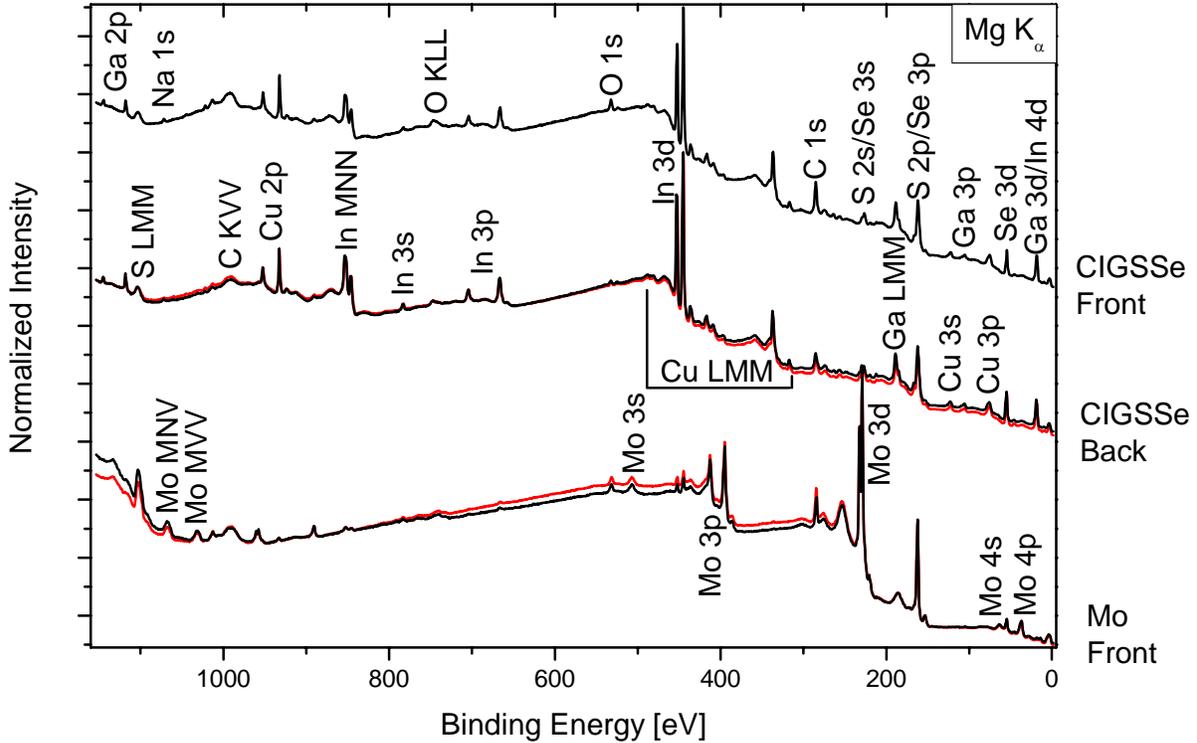


Fig. 1: XPS survey spectra of the CIGSSe front, the CIGSSe back, and the Mo front of a $\text{Cu}(\text{In,Ga})(\text{S,Se})_2/\text{Mo}/\text{glass}$ sample. The spectra in red represent a second set of cleaved samples.

The considered samples were investigated by X-ray photoelectron spectroscopy (XPS). Fig. 1 shows the XPS survey spectra of the CIGSSe front, the CIGSSe back, and the Mo front. Although the samples were handled and shipped under inert gas atmosphere and stored in ultra-high vacuum (UHV), one can observe distinct peaks which can be ascribed to C and O on the CIGSSe Front stemming from a contamination layer formed on the absorber surface. In contrast, we find only minor amounts of C and O on the CIGSSe Back. This shows that the applied cleavage process, which was done in a N_2 filled glovebag/glovebox together with the immediate transfer of the cleaved samples into the attached UHV characterization system is able to provide surfaces with minimized contamination. The intensity difference of all absorber features (e.g., Ga 2p, Cu 2p, and In 3d) between CIGSSe Front and CIGSSe Back can hence be explained by the different attenuation of the differently thick contamination layers. Note that the still significant C 1s signal observed on the CIGSSe Back points to a C incorporation into the absorber layer. The fact that no Mo can be found on the CIGSSe Back and only minor amounts of the absorber components (as indicated by the small In 3d peak - the most prominent absorber feature) can be observed on the Mo Front confirms the cleavage at the absorber/Mo interface with only some CIGSSe grains remaining on the back contact (this characteristic of the lift-off mechanism was already described in Ref. [1]). In consequence, the comparatively large intensities of the photoemission and Auger lines ascribed to S and Se, respectively, observed on the Mo Front point to the formation of a $\text{Mo}(\text{S,Se})_2$ layer at the back

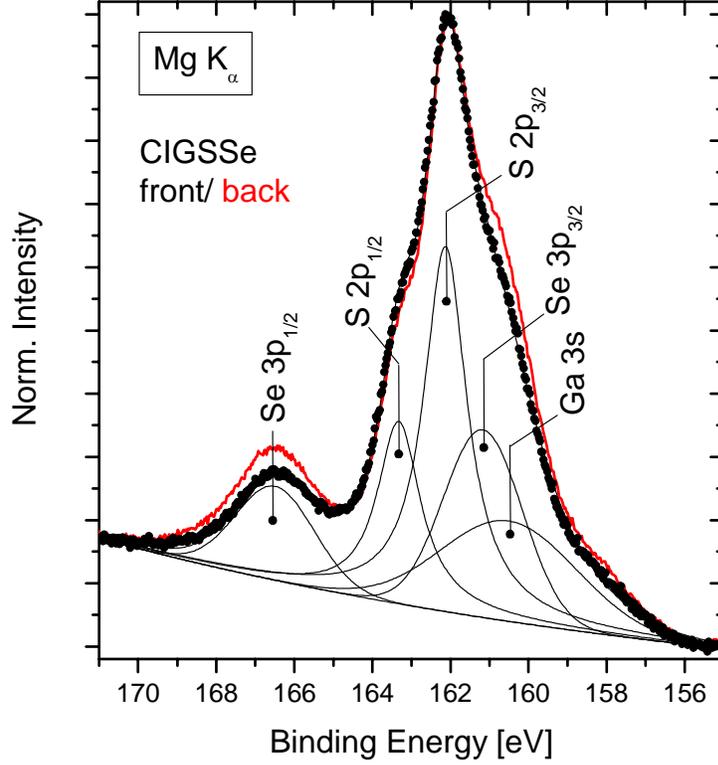


Fig. 2: Region of the S 2p, Se3p and Ga 3s photoemission lines of the cleaved samples CIGSSe Front (black dots) and CIGSSe Back (red line). For the CIGSSe Front spectrum also the corresponding fits (black lines) are shown.

contact, which was similarly reported/suggested in the past [1-7]. The red spectra in Fig.1 represent a second set of cleaved samples. Their similarity to the corresponding black spectra demonstrates the reproducibility of the lift-off process and the associated measurement results. In the following we will focus on the comparison of the CIGSSe Front and CIGSSe Back in terms of their composition. In order to determine the $\text{Ga}/(\text{Ga}+\text{In}) = X$ and the $\text{S}/(\text{S}+\text{Se}) = Y$ composition of the front and back side of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)(\text{S}_y\text{Se}_{1-y})_2$ absorber, the S 2p/Se 3p (Fig. 2) and the Ga 3d/In 4d detail spectra (Fig. 3) are evaluated. For direct comparison of CIGSSe Front and CIGSSe Back, the spectra are normalized to their maximum. In addition, the spectra of the latter have been shifted to lower binding energies by 0.1 eV for maximal overlap. The discovered higher binding energies for both, the S 2p/Se3p and the Ga 3d/In4d spectra for the CIGSSe Back point to an increased surface band bending compared to the CIGSSe Front. Fig. 2 shows the region of the S 2p, Se 3p, and Ga 3s photoemission lines of the cleaved samples CIGSSe Front (black dots) and CIGSSe Back (red line). For the CIGSSe Front spectrum also the corresponding fits (black lines) are shown. The comparison of the spectra clearly shows that the S/(S+Se) ratio at the CIGSSe Front is higher than that of the CIGSSe Back. For quantification of the S/(S+Se) ratio we have used the intensity of the S 2p_{3/2} and the Se 3p_{3/2} photoemission lines, which were determined by fitting the corresponding contributions of the spectra with Voigt area functions (exemplary shown in Fig. 2). Due to the

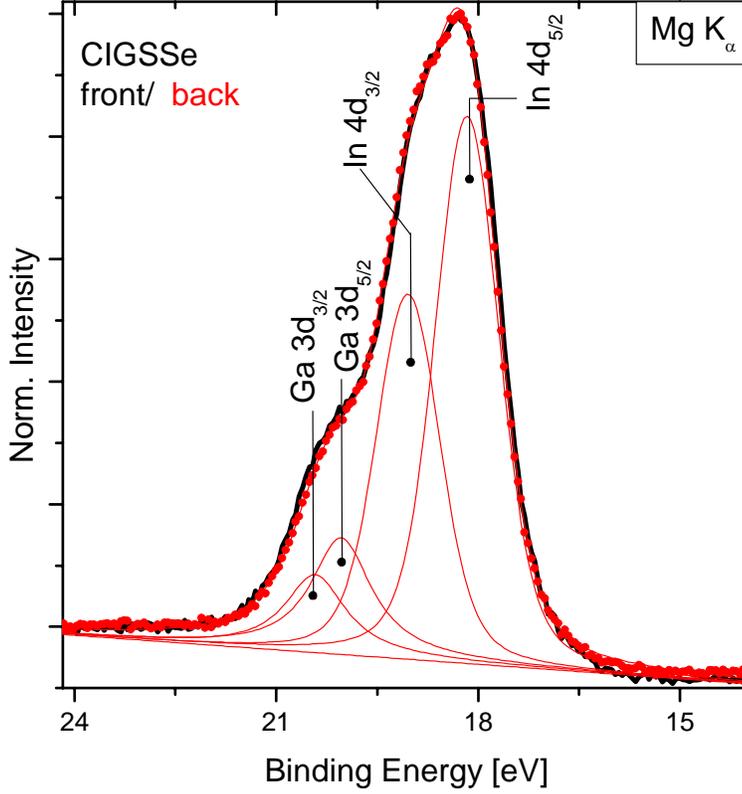


Fig. 3: Ga 3d and In 4d spectra of the cleaved samples CIGSSe Front (black line) and CIGSSe Back (red dots). For the CIGSSe Back spectrum also the corresponding fits (red lines) are shown.

similar binding energies for the S 2p and the Se 3p peaks, it was legitimately assumed that the inelastic mean free paths and the analyzer characteristics are the same for the corresponding photoelectrons. Thus, for the calculation of the S/(S+Se) ratio the corresponding peak intensities were only corrected by the respective cross-sections (from Ref. [8]). In consequence, Y (the S/(S+Se) ratio) of the absorber front and back side was determined to 0.79 and 0.65, respectively, as shown in Table II. For the determination of X (the Ga/(Ga+In) ratio) of the CIGSSe Front and CIGSSe Back, we again have used adjacent photoemission lines (as shown in Fig. 3). The direct comparison of the Ga 3d/In 4d spectra of the cleaved samples CIGSSe Front (black line) and CIGSSe Back (red dots) reveals that both sample surfaces are quite similar. The quantification of the Ga 3d_{5/2} and the In 4d_{5/2} photoemission lines for the calculation of the Ga/(Ga+In) ratio was done similarly to the one described above. The determined Y values (0.36 and 0.33, see Table II) are, within the error margins, identical for the CIGSSe Front and CIGSSe Back, confirming the result of the direct comparison of the spectra.

Table II

sample	X Ga/(Ga+In)	Y S/(S+Se)	E _g [eV]
CIGSSe Front	0.36	0.79	1.68
CIGSSe Back	0.33	0.65	1.58

Assuming a stoichiometric absorber composition (e.g., no Cu deficiency towards the absorber surface) the X and Y compositions should allow a direct (“theoretical”) estimate of the absorber band gap (E_g). Using equation (1) (Ref. [9]) we have determined E_g for the CIGSSe Front to 1.68 eV and for the CIGSSe Back to 1.58 eV (see Table II).

$$E_g = 1 + 0.13X^2 + 0.08X^2Y + 0.13XY + 0.55X + 0.54Y \quad (1)$$

It is planned to continue the investigations described above and extend them by investigating corresponding sets of cleaved samples with UPS and IPES. This will allow us to derive direct experimental information for the electronic surface band gaps and to compare them with “bulk” band gaps derived from the stoichiometric composition at the surface (as was done above). Furthermore, these experiments will allow us to gain insights into the electronic properties of the absorber/back contact *interface*. Of special interest are the valence and conduction band alignment at this interface, and whether they change significantly when going from CIGSSe to CIGSe and thus from a Mo(S,Se)₂ to a MoSe₂ interlayer between the absorber and the Mo back contact.

If you have any questions, please do not hesitate to call me at (702) 895-2694.

Sincerely,

C. Heske
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CC: C. Lopez

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